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BACKGROUND AND HISTORICAL EVOLUTION OF THE EURO-SOIL PROJECT

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Introduction

Environmental effects of chemicals can only be fully understood if studied in their fate, metabolisms as well as synergetic and systematic relations with the environmental compartments. Basically this requires a long-term ecosystem research providing for a comprehensive insight into structures, functions and absorptive capacities or stability and resilience of ecosystem compartments, respectively.
In the near future, however, other ecologically-related approaches appear necessary to tackle these problems in compliance with scientific, political and commercial requirements.

In order to enable realistic hazard predictions to be made for new chemicals, OECD working groups developed numerous test guidelines to evaluate the environmental behaviour and potential ecotoxicity of a chemical substance through laboratory experiments. Contrary to those guidelines designed e.g. for the determination of physical-chemical properties and dealing solely with the pure substance, other more ecologically orientated guidelines require environmental samples as test material. In this context the problem of selecting representative specimens always becomes evident, because the properties of the samples used should reflect those of a whole set of cases with a measurable amount of accuracy.

Soil testing in the context of chemicals control in the European Union

Directive 79/831/EEC is the sixth amendment to Directive 67/548/EEC on the classification, packaging and labelling of dangerous substances. Annex V to the Directive contains a series of methods for the safety testing of chemicals and on the basis of the results generated in these tests, chemicals are classified and labelled according to the criteria also laid down in the Directive. The test methods described in Annex V are referred to in other European Union legislatia dealing for example with chemical preparations and pesticides and these methods are therefore considered as being standard testing procedures for the evaluation of all chemicals.

Annex V to the Directive is constantly being updated and modified and in 1986 an anomaly which became apparent to the Commission was the absence of a standard test procedure for assessing adsorption/desorption in soils. While the Directive currently foresees that this information may sometimes be appropriate in the evaluation of a chemical no test procedure had been introduced into the Annex and chemical manufacturers were referred to appropriate international methods, in this instance OECD Test Guideline 106.

In 1986 the Commission was therefore considering the transposition of the OECD test guideline into Annex V when it became aware of an initiative taken by the German Federal Environmental Agency (UBA) to evaluate the utility of Guideline 106. Subsequently the UBA, the Commission (DG XI), the University of Kiel and the Commissions Joint Research Centre at Ispra collaborated in an extensive investigation many of the elements of which are described in this report.

Mobility testing in soils

The OECD Test Guideline 106 "Adsorption/Desorption" belongs to those guidelines requiring environmental specimens. It has been developed for determining the potential mobility of chemicals in soil. The adsorption/desorption behaviour indicate the tendency of a substance either to be bound in the topsoil, making it potentially bioavailable, or to be transported down-ward, which increases the risk of groundwater pollution.

The fate of a chemical in soil can be investigated directly by complex and expensive migration experiments or indirectly by using equilibrium adsorption/desorption data for subsequent mobility modeling. The latter approach requires less effort in obtaining the adsorption/desorption data, is more flexible in being adaptable to different soils and in addition gives a sufficient basis for extra and interpolations. Although the data obtained are not directly transferable to natural conditions, the method offers a practical first step in gaining insight on a chemicals' likely impact on soil, plants or groundwater. The OECD Test Guideline 106 contains precise instructions on the respective laboratory testing procedures. With regard to the technical side of testing the guideline in its present form generally satisfies the practical requirements. However, equivalent attention has not been paid to the selection of soil samples for testing purposes.
According to the relevant recommendation in the latest version of OECD Test Guideline 106 three different soils - Spodosol, Alfisol and Entisol - are considered to give satisfactory results for the interpretation of chemicals mobility in soils. The soils are classified in terms of the US Soil Taxonomy and the locations where the samples can be taken are described. When adapting the OECD Test Guideline 106 to the situation in the European Union it is however open the question whether the soil types described in the OECD guideline represent an adequate basis upon which to make extrapolations of the potential impact of a chemical on European soils.
Furthermore the EEC-Directive 79/831/EEC asks for a stepwise testing and assessment approach (Annex VII and VIII). It is the basic assumption that data which were measured and submitted to one competent authority in one Member Country are valid and should fulfil the requirements for all other EEC Member States.
Most properties which have to be measured are inherent data of the chemical (e.g. vapor pressure, melting point) or their test media (e.g. water, air or solvents) are available in equal or comparable quality in all Member States. This holds not true - by principle - for the soil as test substrate. Because of genetic reasons, closely related to climate, geology, topography, vegetation etc., there is a variety of more than 300 principally different kinds of soil within the EC realm.

Obviously, chemicals cannot be tested on 300 soil types and European reference soils, being of maximum representativity for the whole Community could instead be identified.
On the background of this situation, in 1984 the German Federal Environmental Agency in cooperation with the Commission of the European Communities launched a research project to solve the problems mentioned above.
The overall concept for estimating the exposure of chemicals in soils comprises four elements to be worked out and implemented:

- the **Adsorption/Desorption** test method,
- the **Standard Operating Procedure** for the selection of sampling sites, treatment and characterization of soil samples,
- the selection of **Representative Soils** which reflect either the major properties or wide areas of the total soil cover,
- **Distribution Models** which take into account adsorption/desorption data, the soil constituency and specific local conditions in order to simulate and predict the portions of adsorption/desorption in quantitative terms.

Requirements with respect to the EEC-Directive 79/831/EEC

Annex VIII of the EEC-Directive 79/831/EEC asks for mobility testing in soils, including adsorption/desorption and biodegradation, if previous environmental hazard assessments which are based on Annex VII tests (baseset and level 1) indicate that chemicals are exposed to soils.

In carrying out testing on soils, some direction has to be given regarding the character of the soil samples to be used; this is particularly true in the case of adsorption/desorption testing. In order to achieve an acceptable degree of harmonization these possible options were considered:

Option 1

Standardized test soils are selected, stored and supplied by a central "soil bank" for all test laboratories within the European Community.
The advantage of such a central supply body is that representative test soils can be selected, sampled, worked up and analyzed in a harmonized way, which will lead to a quick and efficient provision of notifiers with homogeneous material, forming the basis for highly comparable test results.
The disadvantage on the other hand is that a consensus about the location, size and framework of such a centralized EEC-institution is difficult to achieve and problems with regard to practicability might occur.
An additional disadvantage would be the fact that denaturalized soil samples from a central supply body would lose their biological activity so that further testing on biodegradation and metabolism cannot be performed in an appropriate way.

Option 2

A minimum set of reference soils, representative for the EC territory, could be determined, sampled and analyzed and a certain portion of homogenized material from these soils are stored for comparison reasons. On this basis, corresponding nationally available test soils can be identified in the various Member States of the European Union.

The advantage of such a moderately decentralized system is that most of the test soils are available under the responsibility of the respective EU-Member Countries and that comparability of the test results is given over the reference soil system. Furthermore this approach facilitates a practical compromise, because in respect to soil selection and mobility assessments the regional/local requirements are met in a more sufficient way. As a matter of fact, however, the sorption controlling properties of the various test soils vary within specified limits and so, to a certain extent, the reproducibility of the mobility tests is reduced.

During an ad-hoc meeting of soil experts organized by the European Commission at Brussels in June, 1986 the implementation of Option 2 was considered more realistic and feasible.

Selection of soils and sorption testing

The scientific basis of the above meeting was formed by the first results of a research program, the German Federal Environmental Agency launched in 1984 together with the Department of Soil Science and the Department of Geography of the University of Kiel (BRÜMMER et al. 1987). In view of the fact that the soils recommended in the OECD Test Guideline 106 were deemed not indicative for European soils, one of the major tasks of the research project was the selection of European reference soils for adsorption/desorption testing and the identification of regionally representative sampling sites. To reach this goal the Working Group on Regional Planning and Environmental Assessment at the Department of Geography developed a method on the basis of computational map interpretation techniques in order to identify representative soils within the EU territory. It makes appropriate allowance for the fact that the limited number of soils best suited for testing procedures ought to represent both a maximum area of the whole EU territory and the wide variability of the relevant parameters responsible for sorption processes in soils. Furthermore, the requirement of a minimum set of soils had to be considered due to economic reasons.

By applying various geostatistical procedures to soil maps and evaluating metric soil profile data, followed by intensive field work at regionally representative areas, five topsoils have been identified which were considered to meet the above requirements in a satisfactory way. The soils are typical representatives of the most widespread soil associations of the European Union, they are developed on different parent material as well as under several vegetational covers and the sampling sites are scattered throughout the EU realm which leads to an adequate consideration of the main climatic zones.

From detailed pedological analyses of the samples taken at representative locations it was found, that the soils vary significantly with respect to sorption controlling properties and that the ranges of the relevant parameters in most cases even extent those suggested by the OECD, but in general they fit within the frame of OECD-selected soils so that there is no disharmonization expected. The following soil types, showing completely different sorption controlling properties, were selected to form reference material.

E 1 - Vertic Cambisol	Sicily	Italy
E 2 - Rendzina	Peloponnesos	Greece
E 3 - Dystric Cambisol	Wales	Great Britain
E 4 - Orthic Luvisol	Normandy	France
E 5 - Orthic Podzol	Schleswig-Holstein	F.R. Germany.

Under these circumstances, different sorption capacities had to be expected. To prove this, adsorption/desorption experiments with environmentally relevant test chemicals and the soil samples were performed. It could be demonstrated that the soils selected have in fact quite different sorption capacities.

The results of sorption experiments with Lindane, Atrazine and 2,4-Dichlorophenoxyacetic acid, described in terms of K' values, display a strong relationship between the sorption behaviour of the chemicals and individual soil properties. Depending on the specific and distinctly different combinations of sorption controlling parameters the K' values range from almost zero to about fifty. It also ensues from the figure that the variability of the sorption processes not only covariates with the wide spectrum of the soil properties. The influence of the different physical-chemical properties of the individual substances on the sorption behaviour is also clearly observable. While Atrazine and 2,4-D, for instance, are strongly adsorbed in the Podzol which is characterized by a low pH value and high amounts of organic matter, Lindane shows the highest K' value in the Vertic Cambisol which is poor in organic carbon but contains outstanding amounts of clay minerals.

It follows from this brief compilation that the soil samples selected are highly representative and that the range of parameters controlling the sorption behaviour is such that the recommendations of the latest version of the Test Guideline 106 are complemented in compliance with the basic precautionary principles of EU policy. In addition spatial representativity, as defined by means of the comprehensive geostatistical approach developed, ensures maximum comparability or optimum suitability for extrapolation purposes, respectively. Regarding the fact that soils being similar to the reference soils are assigned for use in testing newly developed chemicals with unknown environmental behaviour, a comparison of the test results from various soil samples is indicative for the mobility of a substance under different environmental boundary conditions.

Further developments and present state of the project

In June 1987 the results summarized above were presented during the first meeting of the expert sub-group on soils held in Brussels. It was decided to establish an EEC-wide intercomparison test to compare the behaviour of test substances in the soil types selected and to find out if the OECD Guideline 106 in its modified form is a suitable tool for a standardized testing system. Since various delegations referred to the necessity to incorporate also soil samples with a very low organic carbon content, additional sub-soils had to be considered for use in the ring-test exercise.

To provide sufficient soil material for the intercomparison test and for long-term storage experiments, members from the working group at the Department of Geography, Kiel in cooperation with the Commission Research Centre in Ispra/Italy organized a second sampling campaign which was carried out in spring 1988. The material obtained from five different topsoils and one additional sub-soil was subsequently analyzed and prepared for use in the ring-test. Parallel to the work on soil sampling and treatment the German Federal Environmental Agency prepared the intercomparison test by contacting numerous laboratories from the various EU Member States. During an 'ad- hoc' meeting of soil experts in June, 1988 it was decided that three substances with different physical-chemical properties (Lindane, Atrazine and 2,4-D) should be used in the ring-test. According to the prerequisites of the OECD Guideline 106 the soil samples had to be air-dried, sieved to less than two millimeters and homogenized, the latter to minimize alteration in soil structure and sorption capacities both within and between the aliquotes bottled. To avoid possible problems related to biodegradation in the course of the ring-test, the material finally has been gamma irradiated. During the meeting mentioned the test guideline has been improved by the participating experts and the first draft of a standard operating procedure for soil selection and characterization has been presented.

To establish a common basis for the intercomparison test, a preparatory meeting of representatives of the participating laboratories was held in September 1988. At present nearly all of the laboratories have finished the work and the data obtained have to be evaluated with respect to several questions concerning the feasibility of the test protocol, the selection of soils and the differences between the sorption capacities for the various test chemicals. The results of this evaluation can form the basis for a definite decision on the soils to be used, a step-wise testing scheme and - in general - the feasibility of the modified OECD Test Guideline 106 for soil protection within the European Union.

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FUNDAMENTALS OF REPRESENTATIVE SOIL SAMPLING

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1. Selection of representative soil samples

The selection of area-specific and ecosystem-specific sets of soil specimens has emerged as one of the most complex and challenging problems facing the inauguration of ecosystem research programs, real-time monitoring of the environment and environmental specimen banks. Soils are deemed to be of particular importance since they form essential regulative compartments of terrestrial and freshwater ecosystems, and their chemical and physical properties and the related microbial activity make them sensitive indicators of a very wide range of environmental pollutants.

1.1 Methodology of statistical design

Like many other spatially differentiated phenomena soils exhibit such a variability that only a careful and systematic primary study of their particular distribution functions can ascertain that a specimen selected is representative. In this connection the term "representative" (i) means reproducing faithfully the properties of sets of phenomena in terms of characteristic frequency distributions, and (ii) it relates to specific spatial patterns.

The latter aspect merits special attention since soils, like many other things, are not discrete independent and unambiguously identifiable objects or entities; the habitual and well-known statistical procedures cannot be applied to them as a consequence. The particular problems relating to areal data such as mapping units on soil maps "concern (i) the arbitrariness involved in defining a geographical individual, (ii) the effects of variation in size and shape of the individual areal units, (iii) the nature and measurement of location" (MATHER 1972). Difficulties encountered in separating individual areal units from a continuum like soil cover are most frequently, and at least partially, overcome by the selection of grid squares as the basic units, geographical characteristics being averaged out for each grid square. Since grid squares are all of the same shape and size their use eliminates variability in these properties and thus solves the second problem. The most common solution of the third problem, which is peculiar to geography, is to make relative location as measured by spatial continuity the dominant variable of analysis. It can be accomplished by means of spatial diversity analyses or regionalization procedures which are based on comprehensive geographical data matrices whose elements are derived from the digital evaluation of soil an related maps, i.e. maps of geology, national land capacity, land use, and pore space of soils. The scale varies according to the size of the area investigated, i.e. normally between the 1:1 000 000 and 1:25 000 scales.

The first step in selecting representative soils is the determination of their acreages, i.e. a simple frequency analysis in terms of descriptive statistics. The next step is to define the characteristic spatial patterns of soil distribution by means of neighbourhood analysis. The methodology basically consists in determining the individual nearest-neighbourhood relationships of each grid point, i.e. the positive or negative spatial autocorrelation which is a distance-weighted measure for each point in relation to 80 neighbours (FRÄNZLE & KUHNT 1983). The resultant data matrix permits to define average association frequencies of all the soil units of the original maps, which, in turn is the basis for a comparison of each individual grid point as defined by positive or negative autocorrelation with these average frequencies. The vectorial distance of each grid point from the corresponding soil average is a measure of similarity or representativeness. In terms of spatial structure it ensures that those soil units are most representative which differ least in their neighbourhood relationships from the average association pattern of the respective soil type. The sampling sites of these representative soil units are more precisely determined by subsequent application of the above analytical techniques to large-scale maps the results of which are eventually corroborated by inspection in the field, including larger-scale mapping and variogram-analytical verification of experimental samples taken to ultimately define the provably representative soil specimens (FRÄNZLE 1984, FRÄNZLE & KUHNT 1983).

1.2 Determination of regionally representative soils in Germany by means of crosstabulation and neighbourhood analysis.

As a result of the primary digital evaluation of the base maps the data are nominally scaled in terms of descriptive statistics. Thus the distributional characteristics of the variable soil and the genetically related other variables considered may be defined in terms of frequency distributions and by means of crosstabulation procedures.

The following Table 1 shows the relative acreages of the ten most frequent soils of the Federal Republic of Germany, which corresponds to a pre-evaluation indicating a first trend but not allowing more precise statements about the regional representativeness or the location of sampling sites.

TABLE 1: The relative acreages of the 10 most frequent soils of the Federal Republic of Germany

1	Albic Luvisols in association with Dystric Planosols and Gleysols	7.4%
2	Orthic to Calcic Luvisols	7.4%
3	Dystric Cambisols, Dystric Planosols	6.7%
4	Renzinas, locally Chromic Luvisols	6.4%
5	Orthic and Calcic Luvisols, locally Calcaric Regosols and Planosols	5.2%
6	Dystric Cambisols, locally Planosols	4.7%
7	Eutric Gleysols, Gleyic and Eutric Cambisols	4.4%
8	Orthic and Gleyic Podzols	3.9%
9	Dystric Cambisols, frequently in association with Rankers	3.7%
10	Orthic Podzols	3.5%

After defining the relative importance of soil types in terms of acreage contingency table analysis or crosstabulation (NIE et al. 1975) relationships with associated variables, e.g. parent material, land use, etc. Table 2 summarizes the results of crosstabulation, indicating, for example, that an Orthic Luvisol on loess comprises an optimum of representative qualities.

On the basis of the above statistical pre-evaluations regionally representative sampling sites are defined by means of specific spatial statistics among which nearest-neighbourhood analysis is particularly useful. It is specifically designed for measuring patterns in terms of their arrangement in two or more dimensions (EBDON 1977). It involves calculations of the nearest neighbour of all points and their scores defining how many per cent of the cases have a neighbour of the same type, which would mean a positive spatial autocorrelation, or how many per cent of the cases have a neighbour of another type, which would indicate a negative spatial autocorrelation.

In Figure 1, the soil neighbourhood matrix is a summary reflection of these facts and shows how often one great soil group is associated with itself or with different ones, limiting the spatial relationships to the 4 most frequent neighbours of each great soil group. Such a matrix is not necessarily symmetric since the acreage of the various soil groups differs considerably. For example, the Orthic Luvisols have the most marked neighbourhood relationship to Chernozems but these, in turn, are not among the 4 most frequent neighbours of the Orthic Luvisols.

The final step of spatial analysis then involves searching for the areas which correspond in their actual soil patterns most closely to the average association pattern of the respective dominant soil types of Figure 1. After determining the regionally representative sampling sites for each soil the corresponding occurrences primarily identified on the small-scale soil map have to be localized more precisely on maps of the 1:25 000 scale and the findings finally corroborated in the field. Table 3 summarizes the locations of regionally representative soils in the Federal Republic of Germany.

	Rendzinas	Chernozems	Cambisols	Orthic Luvisols	Planozols	Podzols	Highly variable soils	Fluvial Fluvisols	Marine Fluvisols	Dystric & Eutric Histosols	Others	Lithosols
Lithosols												**8,3**
Others											**0,0**	
Dystric & Eutric Histosols						7,8			10,7	**20,2**		2,1
Marine Fluvisols									**34,4**	5,7		
Fluvial Fluvisols		17,0	4,5	6,7				**16,6**			12,5	18.7
Highly variable soils							**23,3**					18,7
Podzols			6,1	9,0		**38,0**		11,4	15,2	25,9		
Planozols	11,5				**24,2**							
Orthic Luvisols	17,0	34,1	12,0	**50,7**	19,9	18,1	16,6	30,2	7,4	28,2	60,0	2,1
Cambisols	11,0		**59,8**	10,2	15,9	10,5	21,6	17,2			10,0	
Chernozems		**15,9**										
Rendzinas	**44,4**	11.4			15,1		7,4					

FIGURE 1 Soil neighbourhood matrix

TABLE 2 : Representative soils of the Federal Republic of Germany (arranged in decreasing order of acreages)

Great soil group	Relative acreage*	Parent material	Land use	Land capacity	Drainable pore volume of rooty horizon
Orthic Luvisols	28.1 %	Loess	Grain production	50	medium
Cambisol	23.9 %	Middle Bunter Sandstone	Foresty	38	medium
Podzols	14.0 %	Glacifluvial or Saalian deposits	Root crop production	30	high
Rendzinas and associated soils	8.2 %	Upper Jurassic Limestone	Grain production	45	high
Planosols, Gleysols p.p.	6.3 %	Gypsum (Keuper formation)	Grain production	38	high
Fluvial Fluvisols	6.2 %	Various fluvial deposits	Root crop production	57	medium
Dystric & Eutric Histosols	4.2 %	Peat (> 2 m thick)	Grassland	30	high
Marine Fluvisols	2.3 %	Marine silty deposits	Grassland	58	high
Chernozems	0.4 %	Loess	Root crop production	72	medium
Lithosols	0.2 %	Alpine carbonate rocks	Grassland	32	medium

* Total 93.8 %; the remaining 6.2% comprise other soil groups, settlements, rivers and lakes.

TABLE 3: Locations of representative soil in the Federal Republic of Germany (arranged in decreasing order of acreages)

Soil Type	Geographical coordinates
Albic Luvisol	13° 10' E, 48° 23' N
Dystric Cambisol	9° 10' E, 50° 19' N
Orthic Podzol	8° 13' E, 51° 54' N
Rendzina	12° 00' E, 49° 07' N
Dystric Histosol	8° 09', 53° 07' N
Eutric Fluvisol	9° 04' E, 54° 24' N

In terms of acreage these soils represent more than 75% of the total German soil inventory with a correspondingly wide span of pedophysical and chemical properties. On the regional level, finally, i.e. related to the Federal Land Schleswig-Holstein a combination of following soils exhibits a maximum spatial representativity: Gleyic Luvisol, Ferric-humic Podzol, Dystric Cambisol, Histic Gleysol and Eutric Hortisol. They represent about 80% of the Schleswig-Holstein soil cover in terms of acreage, and no less than 70% of the German soil inventory.

1.3 Large-scale soil variability in the light of variogram analysis.

Clearly the quality of soil maps constitues the crucial point in the application of this type of diversity analysis for preselection purposes. Also official surveying instructions for larger-scale soil maps may dismiss the subject of soil variability by stating that one auger sample for depth and horizon determinaitons for 50 or even 200 running meters gave a reasonable estimate of soil properties and boundaries (ARBEITSGEMEIN SCHAFT BODENKUNDE 1971). REYNOLDS (1971) has shown, however, that to estimate soil depth, pH, moisture and organic matter populations with an accuracy of 1% might require from 10 - 689 individuals and 0.2% 196 - 17,227 individuals.

These figures show that the determination of representative soil property-topography relationships requires a considerable number of random samples in order to comply with the demands of frequency statistics. Even if REYNOLDS' (1975) assumption vary within certain broad variability classes, so that the data presented here probably relate to areas of at least 1000 m^2 in size, the demand for a more practical method than random sampling remains imperative. Regionalized variables appear to adequately characterize the spatially distributed and stuctured phenomena under consideration, and consequently variogram analysis is the appropriate method.

1.3.1 Variogram analysis

Values of a measured variable, e.g., a diagnostic soil property, are ususally punctiform but are to be indicative of spatial interrelations. Therefore a random sample has to be considered as the measured value of an assumed distribution function Y(x) of a characteristic two- or three-dimensional vector x.

Customary mathematical functions are insufficient to give an adequate representation of a regionalized variable because of its

- high degree of complexity,
- high degree of not infrequently small-scale variability
- various correlations between neighbouring points.

A useful statistical method would therefore have to inform about the following problems:

(i) Is it possible to decide upon the existence of a spatial distribution function on the basis of the available random samples?

(ii) If such a function exists: How is a difference vector h related to the mean variance of all vectors x_i, y_i for which $x_i - y_i = h$?

(iii) To which (spatial) extent is a random sample representative within the limits of the imputed distribution function?

The most powerful statistical tool available to this end is variogram analysis (MATHERON 1963, DELFINER 1975).

The mathematical concept

A regionalized variable can be considered as the realisation of a random function Y. Usually this function is assumed to be stationary; this implies

(i) the expectation (m) of Y at any point x is constant and independent of x.

$$E [Y (x)] = m \tag{1}$$

(ii) the covariance function of any pair of points x and x+h depends exclusively on the vector h and is independent of x.

$$E [Y (x) Y (x+h)] - m^2 = k (h) \tag{2}$$

In many cases merely the increments of the functions are supposed to be stationary. The instrinsic hypothesis for a vector h concerning expected value and variance is:

$$E [Y (x+h) - Y (x)] = 0 \tag{3}$$

$$\mathrm{Var} [Y (x+h) - Y (x)] = 2 \gamma (h) \tag{4}$$

The so-called semi-variogram (further on designated as variogram), i.e., the function of the vector h is defined as:

$$\gamma(h) = 1/2 \text{ Var } [Y (x+h) - Y (x)] \qquad (5)$$

From (3) and (4) ensues that

$$\gamma(h) = 1/2 \text{ E } [Y (x+h) - Y (x)]^2 \qquad (6)$$

In the case of discontinuous data expected value $\gamma(h)$ can be estimated by the formula:

$$(h) = \frac{1}{2n} \sum_{i=1}^{n} [Y (x_i+h) - Y (x_i)]^2 \qquad (7)$$

(n= number of pairs of points)

The points are situated in either a one-, two- or three-dimensional space. In a two-dimensional space, as dealt with here, the coordinates h_1 and h_2 determine the vector h. Hence the variance of measured values is dependent on the distance and the direction of the difference vector h.

In practice the variogram is usually computed for 4 main axes in order to account for possible directional effects. Distinctions of the range in different directions (anisotropy) then enable a more detailed interpretation.

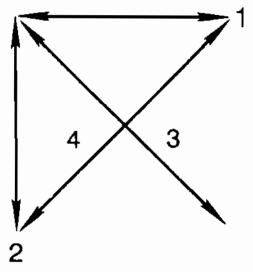

FIGURE 2: Main variogram axes

A mean variogram that is independent of such directional effects is usually computed on the basis of four directional variograms. A variogram is geometrically characterized by two boundary criteria which are called "still" and "range". The latter denotes the maximum extent of influence, while sill is the analogous limiting value of influence as measured on the ordinate.

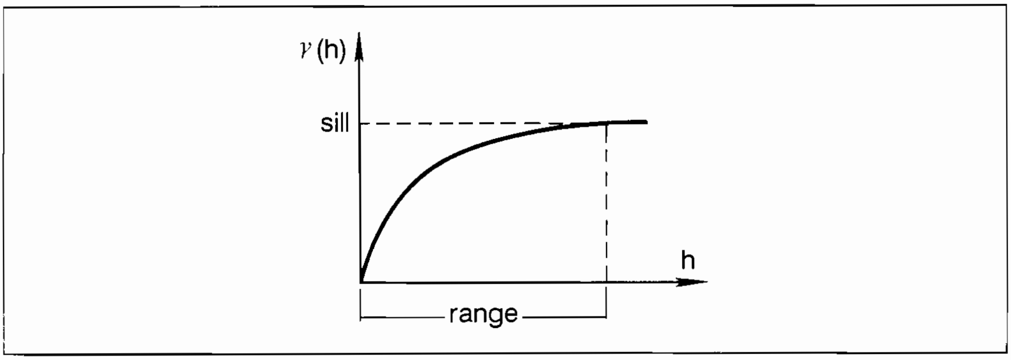

FIGURE 3: Sill and range of a variogram

The interpretation of the variogram

The zone of influence

It follows from the foregoing that a variogram does not necessarily have a maximum or a level of stabilization. Due to this criterion two basic types of variograms are distinguished.

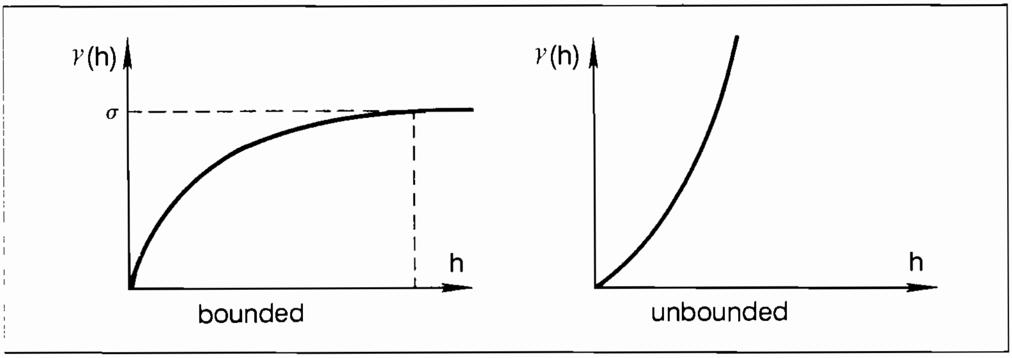

FIGURE 4: Bounded and unbounded variogram

In the case of a) the maximum range is reached when the correlation between Y(x) and Y(x+h) becomes nil.

$$\gamma(h) = 1/2 \, \mathrm{Var} \, [\, Y(x+h) - Y(x) \,] \tag{8.1}$$

$$= 1/2 \, \{ \mathrm{Var} \, [\, Y(x+h) \,] + \mathrm{Var} \, [\, Y(x) \,] \, \} \tag{8.2}$$

$$= \frac{2\sigma^2}{2} = \sigma^2 \tag{8.3}$$

In the case of b) the zone of influence extends beyond the area examinated.

Mathematical models of the curve

In order to best fit the curve of the variogram under construction to the sequence of points primarily obtained as a result of the computation of the variance function, various mathematical models are used, the most important of which are briefly described.

a) Power functions:

$$\gamma(h) = C\,|h|^{\lambda} \text{ with } 0<\lambda< 2 \qquad (9)$$

$$\gamma(h) = C\,|h| \text{ is the special case of a linar model.}$$

b) Spherical model:

$$\gamma(h) = \begin{cases} C\,[\,3/2\,\frac{h}{a} - 1/2\,\frac{|h|^3}{a^3}\,] & \text{for } |h| \leqq a \\ c & \text{for } |h| > a \end{cases} \qquad (10)$$

c) Exponential model:

$$\gamma(h) = C\,[\,1 - e\,\frac{-|h|}{a}\,] \;;\; a \cong 1/3 \text{ of range} \qquad (11)$$

d) Gaussian model:

$$\gamma(h) = C[\,1 - e\,\frac{-|h|^{2-}}{a^2}\,] \;;\; a \cong 0.58 \times \text{range} \qquad (12)$$

Often for a more exact fitting the models must be combined.

The variance of the sample is approximately the same as the value of the sill as far as bounded variograms are concerned. The model of the curve is primarily important for the determination of the "nugget-effect", a phenomenon that has to be dealt with when the curve's behaviour near the origin is considered.

The curve's behaviour near the origin

a) A parabolic shape shows a high degree of continuity of the regionalized variable. It is differentiable.

b) A linear shape shows continuity "in average" as MATHERON (1963) phrased it.

c) The curve does not intersect the abscissa at the origin. The "nugget-effect" reveals great irregularity and can be caused fundamentally by either an extremely discontinous distribution in the immediate neighbourhood of the sample taken or by observational errors. Supplementary information is consequently needed.

d) A straight line parallel to the abscissa indicates that there is nor correlation between any points Y(x+h) and Y(x) whatever their distance might be. The sample does not show any spatial structure.

Anisotropies

Distribution characterized by different variabilities in different directions are reflected in the resulting variogram and called anisotropy.

a) Geometrical or affine anisotropy exists whenever elliptical zones of influence can be deduced in a 2-dimensional space.

b) In a 3-dimensional space variations might also appear in the vertical direction; this is the case of stratified anisotropy.

Other structures

Some variograms display substructures as regards the limits of their maximum ranges. Typical ones are:

a) nested structures

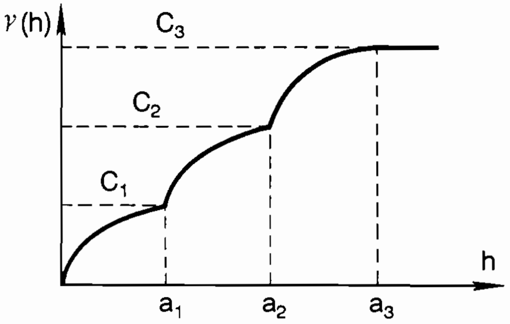

FIGURE 5: Nested variogram

b) periodical structures

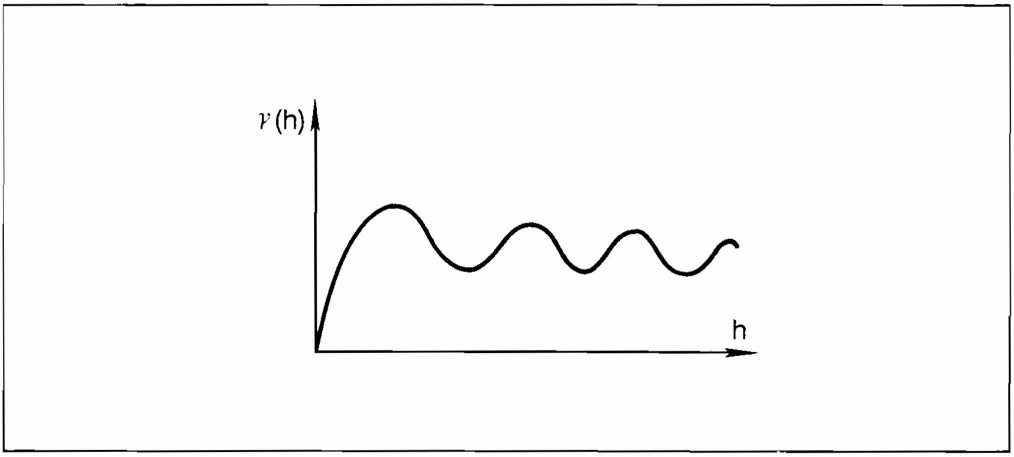

FIGURE 6: Periodical variogram

c) "hole-effect" structures

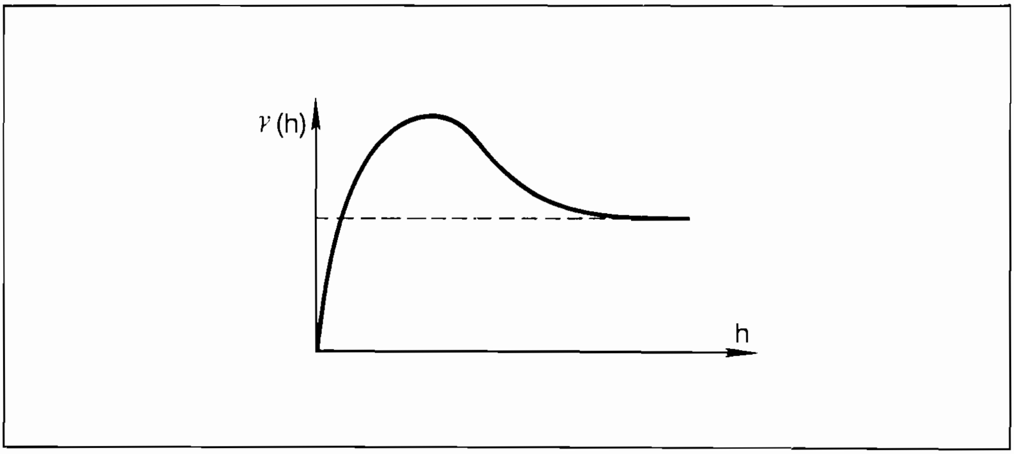

FIGURE 7: "Hole-effect" variogram

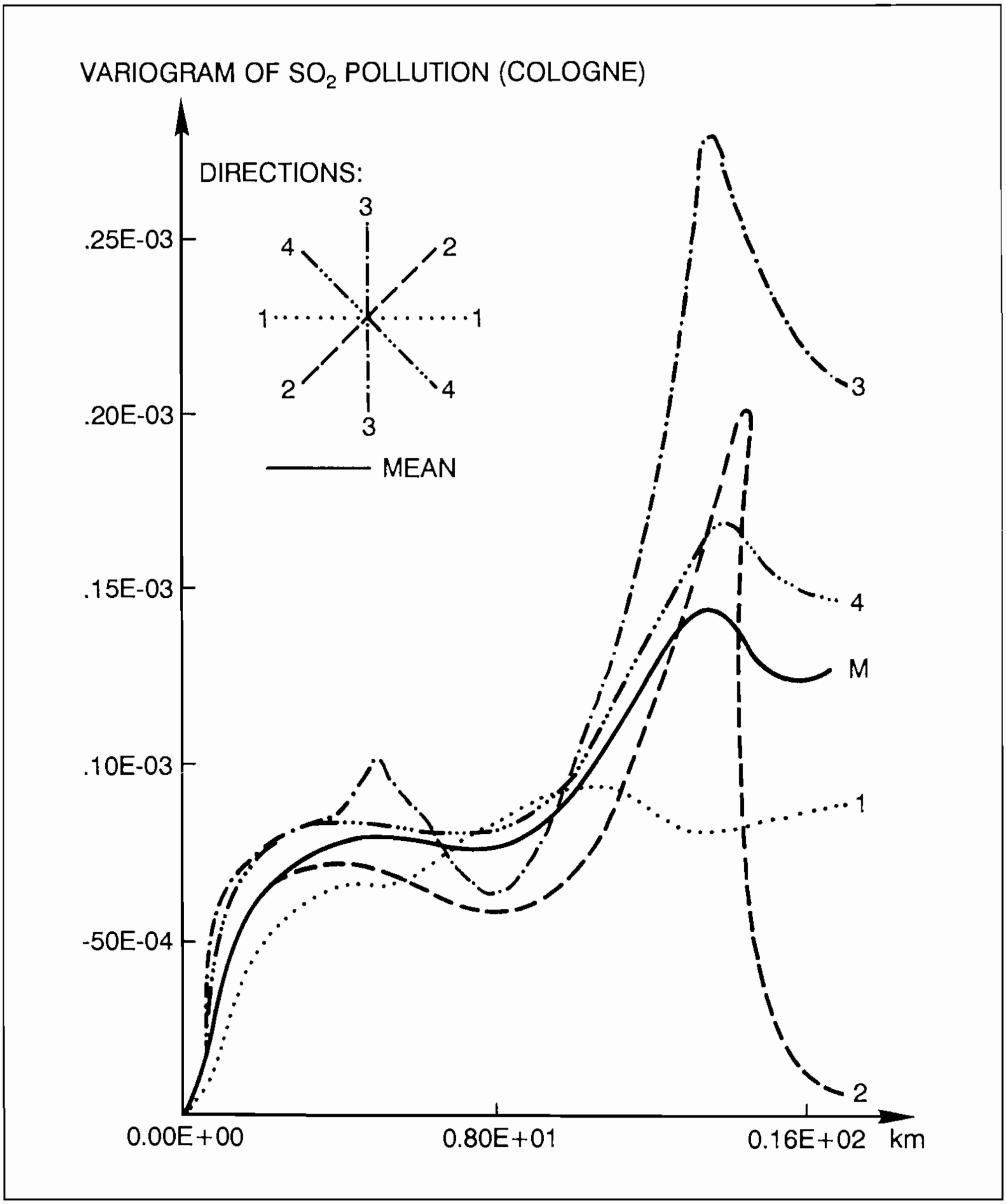

FIGURE 8:
Variogram of SO_2 pollution in the northern part of the Cologne industrial belt.

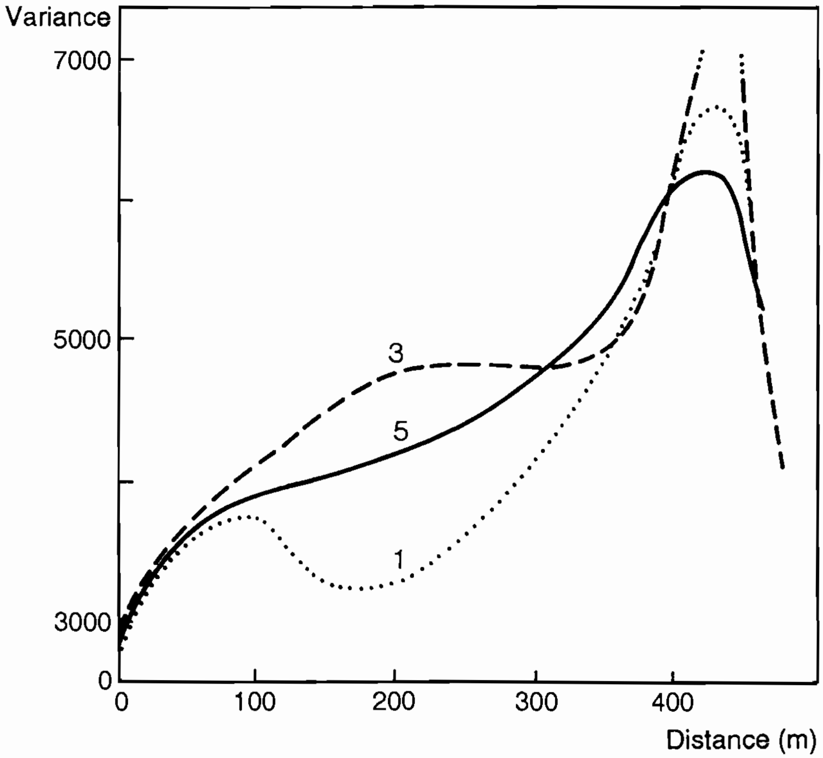

FIGURE 9:
Variograms of PO_4^{3-} distibution in soils near Bosau (Schleswig-Holstein, F.R.G.)
(After Zölitz, 1980).

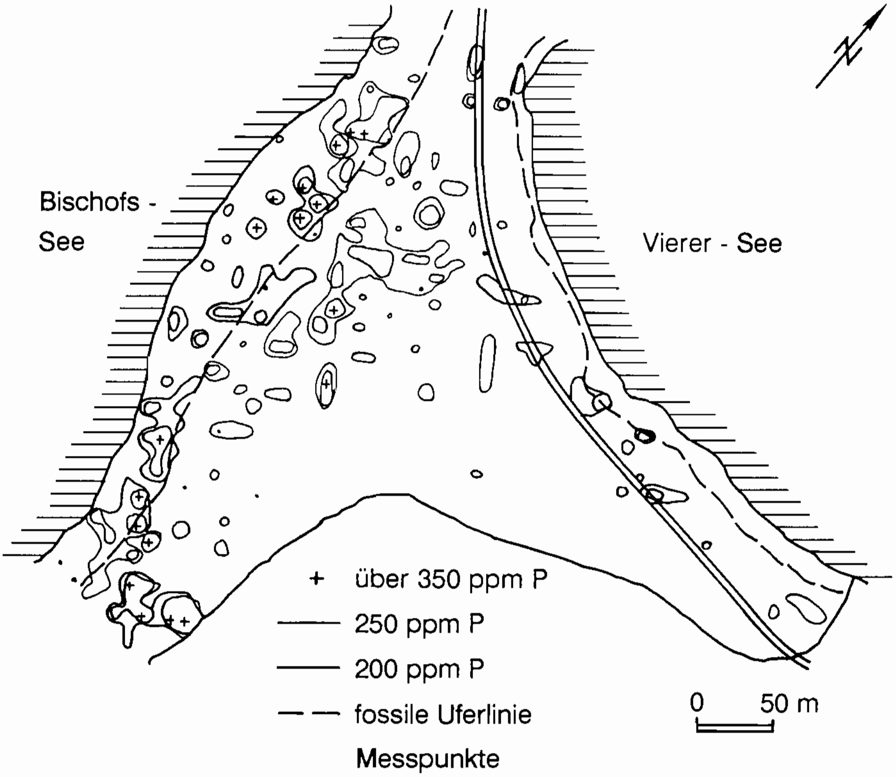

FIGURE 10:
Map of phosphorus contents in soils near Bosau (Schleswig-Holstein, F.R.G.)
(After Zölitz, 1980).

1.3.2. Model applications of variogram analysis

Two examples may finally illustrate the preceding theoretical considerations. The first is base on the spatial analysis of the 1975 data of the immission monitoring network of the Cologne industrial belt. The variogram shows the SO_2 distribution in the area north of the city, which is characterized by prominent industrial sites with remarkably high SO_2-emission rates at Merkenich, Weisdorf and Dormagen. The network consists of a 1 km^2 grid for which a mean value is derived from the measurements at the four grid points (Figure 8).

The variogram of the SO_2 distribution shows the following characteristics:

- two sills
- directional variation
- Gaussian model
- no "nugget-effect"

The sills at distances of 4 km and 13 km can be explained by two nested structures of which the inner one, with SO_2 immissions above average, covers the neighbourbood of the industrial plants.
Consequently the statistically appropriate maximum distance of SO_2 sampling is 3-4 km for the highly industrial core areas and 12-13 km for the adjacent peripheral parts of the industrial belt where immission concentrations are distinctly less.

Furthermore the variogram shows that the SO_2 distribution varies in different directions. The particularly marked immissions in directions 3 and 2 (N-S and NE-SW) are accounted for by the predominant winds which are canalized by the Rhine-valley. On the contrary only slight variations with growing distance can be noted in direction 1 (E-W).

The second example is derived from comprehensive soil investigations aiming at a detailed map of the anthropogenically induced PO_4^{3-} distibution in the A-horizons of Schleswig-Holstein soils. The variograms of Figure 9 are based on the following data (ZÖLITZ 1980).

Number of samples	1104
Distance	10 m
Mean	158.0 ppm P
Standard deviation	65.8
Minimum	11.0 ppm P
Maximum	570.0 ppm P
Direction 1	SW-NE
Direction 2	S-N
Direction 3	SE-NW
Direction 4	W-E

Variogram	sill	range	nugget effect?	bounded?
1	3680	100 m	yes	yes
2	4360	160 m	yes	yes
3	4800	240 m	yes	yes
4	5900	420 m	yes	yes
5 (mean)	6240	420 m	yes	yes

The relatively high "nugget effect" corresponding to a variance of 2800 is due to discontinuities in the immediate vicinity of the grid points sampled. Yet all variograms have well-defined sills and ranges much above the grid square dimensions. Hence the construction of a detailed P map is possible on the basis of the 10 m grid, and even distances up to at least 50 m (i.e. half the lowest range of the above variograms) would not essentially diminish the precision because metric interpolations between individual grid values remain valid.

Maps with a grid tested by variogram analysis (which in turn requires a minimum of 40-50 points evaluated) are indispensable for the planimetric deduction of valid areal mean values. As such or as elements of more comprehensive areal means they constitute regionally representative values. In view of this it may suffice to say that spatially oriented extrapolations of material and energetic fluxes from punctiform data are not only of lesser quality but simply erroneous if the appropriate dimensional structure of the underlying grid has not been ascertained by means of variogram analysis.

In the present case it served prospective archeological purposes by developing a soil-phosphate map whose isopleth structure was to be indicative of the outlines of an abandoned medieval Slavic village (in the meantime excavations have corroborated in detail the pertinent deductions). In view of the above marked "nugget effect", however, a far higher number of grid points or measurements, respectively, were necessary to derive reliable isopleth maps with a resolution appropriate for the distinction of individual houses, huts and stables.

1.4 Conclusions

An analysis of relevant literature (cf., e.g., the comprehensive review by REYNOLDS 1975) shows that studies relating the magnitude of soil or rock properties to topographical parameters like slope angle or aspect frequently neglect to indicate the limits of their statistical populations, and also fail to assess the degree of variability of the often undefined population. (An analogous statement would apply to numerous studies on vegetation or vegetation-soil relationships, or in the realm of geozoology). It should be clear that entirely spurious relationships can results if samples consist only of a few individuals and where sample means obtained are unrepresentative of population mean values.

Therefore the selection of soil samples for environmentally relevant analytical purposes should be based on the following five-level approach.

1.1 Frequency analysis,

1.2 Neighbourhood analysis,

1.3 Definition of representative structural units
on the basis of small-scale soil and related maps, satellite images, etc.

2.1 - 2.3 idem, on the basis of large-scale maps stereo couples, etc.

3.1 - 3.4 Visual inspection, high-resolution maping, sampling, chemical analysis.

4. Variogram analysis of samples

5. Definition of representative samples with regard to specific soil properties or test purposes, respectively.

Both the importance and costs of many environmental assessment projects urgently recommend such a sequential approach in order to obtain spatially valid data. These, however, are the essential pre-requisite for pertinent extrapolations, in particular in the wide fields of both pure and applied ecology, ecotoxicology or environmental chemistry.

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METHODOLOGICAL ASPECTS OF REFERENCE SOIL SAMPLING

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Introduction

The harmonization of testing procedures for new chemicals to be distributed on the EU market requires the identification of test media being representative for the respective territory. Especially the samples for laboratory experiments testing soil sorption according to the OECD Test Guideline 106 must be carefully selected from the points of view of both effective environmental protection and practicability. Therefore, complex map and data interpretation techniques were applied to identify EU-representative soils for testing the adsorption/desorption behaviour of new chemicals.

In this context, the term "representativity" reflects the following assumptions:

Scientific perception implies the transformation of real objectives into cognitive structures (ERDMANN & PETERSEN 1979). This involves the formulation of hypotheses and their operationalization. Hypotheses are formed on the basis of information. As correlates of objective structures they provide testable predicates of a defined section of reality. By means of verification hypotheses achieve the quality of theories that are (temporarily) valid as solutions.

Following these scientific principles, a method has been developed on various levels of complexity for identifying a minimum number of samples that are of maximum representativeness for the soil cover of the European Union.

Methodological aspects

From its very nature, the geographical analysis of spatial distribution implies that sampling procedures must always tackle the elementary problem of obtaining representative specimens. That is, samples must be representative in the sense that their properties reflect those of a whole set of cases with a measurable degree of accuracy. In the present context the two meanings of the term “representative” merit equal attention, because the word can either mean exactly reproducing the properties of a set of phenomena in the light of a characteristic frequency distribution or it can relate to spatial distribution. The latter case is particularly important wherever samples are considered that are taken from spatially differentiated objects such as soils. Because of their variability only a careful and systematic study of the particular distribution functions or associations can ascertain that a given sample is also representative from the regional point of view. The selection of representative soils therefore implies that the internal structural relationships within each group are the same, i.e. each member of the group must be a valid representative of this whole group, while the interstructural relationships between the defining characteristics of the various groups are disjunctive. Thus regionalization can be considered as the detection of latent spatial patterns by means of manifest phenomena or, to phrase it less stochastically, to make implicit objects explicit (VETTER, SCHRÖDER & FRÄNZLE 1986).

In the light of the above considerations, the EU reference soils for adsorption/ desorption testing must comply with three basic requirements:

(1) Representativity of soil characteristics

The selected soils must cover a wide range of sorption- controlling properties so that the basic parameters of the potential behaviour of a certain chemical in soil can be assessed by comparing the various test results.

(2) Representativity with respect to frequency distribution

If the reference soils are typical representatives of the soil associations that are most widespread within the EU, each test result is to a certain extent valid for a large area of the European Union.

(3) Regional representativity

Considering that in most cases the association patterns of different soil types reflect important factors of soil formation and development, such as geology, geomorphology, topography or climate (KUHNT 1989), the spatial distribution of the various soil units must be defined. Therefore, the soils sampled at the selected locations should be associated with other pedological units in such a manner that they are regionally representative of the EU Member States.

Since climatic conditions have both a direct and an indirect influence on important pedological factors, the selected sampling sites should be appropriately distributed, in order to adequately reflect the main climatic zones of the EU territory.

Soils and vegetational cover interact in manifold ways; therefore the main types of plant communities and of land use patterns in the EU territory must to be taken into account similarly.

In compliance with the above mentioned requirements the selection of soil samples is appropriately based on a five-level approach. The first step is the evaluation of small-scale maps in order to define the typical, i.e. the most frequent soils.
The second step is a nearest-neighbourhood analysis to determine regionally representative sampling sites. In a third step a study of the literature and the evaluation of large-scale maps, including metric soil profile data, are necessary to ascertain if the thus defined representative soil groups adequately reflect the wide variability of the whole soil inventory from an ecochemical point of view. The theoretical investigations must be verified by visual inspection in the field, including site exploration and geological and pedological mapping, to finally locate discrete soil profiles where samples are taken, analyzed and tested with various chemicals to determine the validity of the selection (fourth step). The last step consists in defining analogies or differences between the soils tested and those not further tested in order to make map-based extrapolations within or between the EU Member States possible.

Selection of representative test soils

Since only maps yield areal information on soils for the whole of Europe they form the basis for the following evaluation. Soils are not, however, discrete independent and unambiguously identifiable objects or entities. Consequently, the usual and well-known statistical procedures cannot be applied to them. The particular problems relating to areal data such as mapping units "concern (i) the arbitrariness involved in defining a geographical individual, (ii) the effects of variation in size and shape of the individual areal units, (iii) the nature and measurement of location" (MATHER 1972). Difficulties encountered in separating individual areal units from a continuum are most frequently overcome, with at least partial success, by selecting grid squares as the basic units, geographical characteristics being averaged out for each grid square. Since grid squares are all of the same shape and size their use eliminates variability in these properties and thus solves the second problem. The most common solution to the third problem, which is peculiar to geography, is to make relative location as measured by spatial contiguity the dominant variable in the analysis. This can be accomplished by means of special diversity analyses or regionalization procedures which are based on comprehensive geographical data matrices.

Map digitalization and statistical procedures

Digital evaluation of geoscientific maps forms the basis for the comparative selection of soil samples. In this context, the distribution of the relevant physical and chemical properties of soils, mostly indicated by the soil type, must be considered while locating regionally representative sampling sites.

The digitalization of the FAO Soil Map of Europe (1965), which due to its larger scale is better suited to the present purpose than the corresponding sheet V-1 of the FAO/UNESCO Soil Map of the World (1978), forms the basis for the following evaluations. The new Soil Map of the European Union (1985) has also been digitized and frequently used for detailed investigations of certain areas. For the first interpretational steps, however, it was found that the FAO Map of Europe fulfills the technical requirements for the application of mathematical procedures as described below most satisfactorily.

To assess the quality of the FAO map more precisely, a digital planimetric comparison was made with the 1:1,000,000 Soil Map of the Federal Republic of Germany (HOLLSTEIN 1963). By converting the different legends into the terms of the standard FAO classification it is possible to compare both distribution patterns and acreages of soil defined in terms of mapping units. In the following the results are shown, deliberately limiting the presentation to the three most important soil types or great soil groups, respectively.

Soil Groups	FAO-Map	HOLSTEIN-Map
Orthic Luvisols	29.2%	28.1%
Cambisols	24.3%	23.9%
Podzols	17.0%	14.0%

The soils of the Member States of the European Union constitute a heterogeneous three-dimensional space, which is imaged by the map as a two-dimensional relative representing a surface of 2,2 million square kilometers. In this context the polychotomous nominal character of the data aggregated is pertinent, because the relevant grouping algorithms depend on the scales of measurement adopted. This fact limits the evaluation of data, since the spectrum of grouping algorithms is restricted by the very nature of the underlying statistical approaches, for instance "nearest-neighbourhood analysis" or "entropy analysis".
As an inevitable consequence of this, metric soil profile data must be used to complement the nominal data.

The process of obtaining, handling and combining data from both map digitali is transformed into a reticulate 0.1x grid whose points are subsequently converted into nominal data (KUHNT et al, 1986). Each point of the digitized map can thus be identified on the basis of geographical coordinates.

Frequency distribution

The data used in the present study are primarily scaled nominally in terms of descriptive statistics, i.e. they are defined in the light of frequency distributions. Table shows the corresponding distributional characteristics on the variable "soil group".
They indicate a first evaluative trend but do not allow more precise statements about the regional representativity or the location of sampling sites. To obtain test results of maximum validity and to make extrapolations to larger areas of the EU realm possible, the reference soils should be typical representatives of the most widespread soil associations listed above.

Assuming that the first three soil groups were foreseen for the selection of representative soil samples, they would represent more than one fourth of the total soil acreage of the EU Member States. Clearly such a procedure is far from commendable since it would allow only quite a limited range of soil properties found within the territory of the EU to be documented. Instead, the wide variability of the entire catalogue of soils should be reflected as far as possible, from both the pedological and the ecochemical points of view. This clearly involves taking recourse to pertinent and consequently more complex geostatistical procedures. But defining the soil units that are to be considered solves only part of the problem. Another question is where the samples should be taken. Therefore a further requirement for reference soils is that the sampling locations be regionally representative.

Nearest-neighbourhood analysis - a geostatistical approach

Having examined the distribution of soil groups in terms of frequency statistics the next step is to investigate the spatial patterns of this variable. This involves a chorological analysis. An expert is able to approximately estimate relative frequencies of objects on a map, but he can hardly define complex spatial patterns, relationships or neighbourhoods without applying numerical assessment procedures. In processing qualitative data particular problems arise due to the relative scarcity of appropriate methods for defining "superdata" on distributions in the specific sense of spatial statistics. Because of the exceedingly large number of nominal data resulting from the initial digitalization procedure and the limited computing time, the nearest-neighbourhood analysis is the most appropriate geostatistical technique for providing pertinent solutions. This method is specifically designed for measuring patterns in terms of their arrangement in two or more dimensions (FRÄNZLE 1978, KUHNT & VETTER 1988, VETTER & SCHRÖDER 1988).

The nearest-neighbourhood analysis involves calculating the nearest neighbours of all points and their scores. The computer program applies the following tests:

- how high is the percentage of cases that have a neighbour of the same type; this indicates a positive spatial autocorrelation,
- how high is the percentage of cases that have a neighbour of a different type; this indicates a negative spatial autocorrelation,
- what is the composition of the negative spatial autocorrelation.

The function of the algorithm of representativity has been given earlier (KUHNT et al, 1986).

Based on an older approach (cf. KUHNT, FRÄNZLE & VETTER 1986), which involved only the direct neighbours, the present analysis uses a newly conceived index of neighbourhood (N) that is indicative of the individual nearest-neighbourhood relationships of each of the 26,603 reference squares into which the primary soil map is subdivided.

It has the particular advantage that it:

- is relatively independent of grid geometry,
- considers more than the immediate neighbours only,
- introduces a hierarchy of neighbours.

To this end the central point of a kind of quadratic "magnifier", which in fact constitutes the individual index N and which consists of 80 points, is superimposed onto every grid point of the computerized map. By means of the Euclidean distance the centre of the square is related to each of the 80 points (neighbours) (KUHNT & VETTER 1988).

The distance between the centre and point A is defined as:

$$\frac{1}{0^2 + 1^2} \quad \text{and for point D:} \quad \frac{1}{0^2 + 4^2}$$

To define neighbourhood or representativity relationships two n-dimensional vectors must be computed. To this end the neighbourhood relations defined by means of the moving 80 point reference grid (the "magnifier") are transferred into RN values, i.e. the real-neighbourhood vector. The following step involves a serial comparison of these individual RN values with the average RN values of each mapping unit designated EN, i.e. expected-neighbourhood vector.

The difference between the real-neighbourhood vector and the expected-neighbourhood vector defines the index of representativity (RI), a dimensionless figure which has the value 0 (zero) in the optimum case of identity.

A mathematical description of this approach is given as follows:

1. The basis of the neighbourhood coefficient is the neighbourhood index N, which is defined as the square of the Euclidean distance:

$$N_{\Delta x, \Delta y} = \frac{1}{\Delta x^2 + \Delta y^2}$$

2. Calculation of the real-neighbourhood vector RN for each point:

$$\begin{array}{lll} RN = \text{coordinate} \; (N_0 \cdot N_0) & \longrightarrow & R^n \\ (x,y) \longrightarrow \; (\Sigma N_{(x - x',\, y - y')}) & \ldots\ldots\ldots\ldots & (\Sigma N_{(x - x',\, y - y')}) \\ \qquad\qquad (x',y') \in N_0 \cdot N_0 & & (x',y') \in N_0 \cdot N_0 \\ \qquad\qquad \text{Bod } (x',y') = 1 & & \text{Bod } (x',y') = n \end{array}$$

3. Calculation of the expected-neighbourhood vector EN of one soil association (SI)

$$\text{EN: } 1\ldots n \text{ (code of the soil association)} \longrightarrow R^n$$

$$\text{SI} \longrightarrow \text{arithmetic mean of the real neighbourhoods of all points with soil (SI)}$$

$$\text{SI} \longrightarrow \; := \sum_{(x,y) \in N_0 \cdot N_0} RN_{(x,y)}$$

$$\frac{\text{SI } (x,y) = \text{SI}}{f_i \text{ SI}}$$

4. Construction of the neighbourhood matrix NNE

$$[NNE] := [EN_1 \ldots\ldots\ldots\ldots\ldots EN_n]$$

5. Calculation of the representativity index RI for one point

$$(x,y) \longrightarrow \| RN(x,y) - EN(SI(x,y)) \|$$

The results of this comparative procedure reproduce in a deliberately generalized way the distribution of the most representative soils of the European Union.

The neighbourhood matrix displays how often one soil group is associated with itself or with different ones. The Gray-brown Podzolic Soils, for example, have a positive spatial autocorrelation of 71.8 per cent. The series of negative spatial autocorrelations yields a typical chorosequence of **Gray-brown Podzolic Soils** consisting in Gray-brown Podzolic Soils and Brown Forest Soils (5.6%), Alluvial Soils (3.9%), Gray-brown Podzolic Soils and Podzolized Soils (3.8%), Podzolized Soils (2.6%) and Acid Brown Forest Soils (2.3%).

Results of the statistical analyses

The sampling sites are corroborated by the results of the frequency and nearest-neighbourhood analyses and by large-scale maps and soil data from the literature, always considering the wide variability of the physical and chemical properties of soils. In addition, climatic data and information on land use and vegetation were collected and evaluated in order to completely fulfill the requirements mentioned above. In this manner the soil groups and their sampling locations can be precisely determined.

By computer-aided evaluation of digitized soil maps it was found that

- Cambisols (Brown Forest Soils, Brown Mediterranean Soils)

- Luvisols (Gray-brown Podzolic Soils)

- Podzols (Podzolized Soils)

- Rendzinas (Rendzinas)

are the dominant soil units of the European Union.

Within the EU Member States the most common soils (in the sense of the mapping units of the FAO Soil Map) are the **Gray-brown Podzolic Soils**, covering 12.8 per cent of the whole area with a distinct maximum in the northern parts. The regionally representative sampling site is located near Caen (Normandy, France).

The **Brown Mediterranean Soils** are typical representatives of the soil cover in southern regions, reflecting 6.8 per cent of the European Union. The corresponding type locality is in Sicily.

In the light of frequency statistics the **Brown Forest Soils** cover nearly the same area (6.5 per cent) as the Brown Mediterranean Soils, but they differ in their physicochemical properties and in their specific distribution pattern. While the Brown Mediterranean Soils are concentrated mostly in coastal areas and on hills and plateaus in the southern parts of the EU, the Brown Forest Soils are typical of higher latitudes and altitudes. The sampling site is near Cardiff (Great Britain).

Rendzinas - covering 6.1 per cent of the area - reflect the group of moderately developed soils on calcareous material with the representative sampling site in Greece near Korinthos.

Podzolized Soils account for 4.2 per cent of the EU territory and occur mostly in the northern parts. The sampling site for the representative Podzol appears to be located in the Federal Republic of Germany near Lauenburg (Schleswig-Holstein).

From the statistical analysis it also ensues that Alluvial Soils, reflecting more than 7 per cent, are widely distributed throughout the EU area. These soils are, however, excluded from further consideration. Due to the great variety of parent materials and the resulting different combinations of soil horizons the sorption behaviour of these soils may vary within such a wide range that it appears impossible to define a typical representative of this soil group.

The five soil groups identified have an explicit chorological representativity of more than one third (36.4 per cent) of the entire catalogue of EU soils and reflect the wide variability of parameters responsible for the sorption behaviour of chemicals in soils. In the light of pedological considerations related to the legend of the FAO Soil Map and the results of spatial statistics an implicit chorological representativity of 62.0 percent is attained, because the legend indicates similarities and/or transitions between mapping units. In addition, nearest-neighbourhood analysis exactly verifies the legend from the standpoint of chorosequence. For instance, the mapping unit Luvisols and Podzols comprises the two pure soil types and the transitional forms.

Each Member State of the EU contains no fewer than two representative soil types, except for Luxembourg, for obvious reasons of size. The "most European" country with regard to its soil catalogue is France, which, due to its geographical setting and resultant pedogenetic variability, comprises the entire spectrum of representative soils.

With regard to implicit chorological representativity all of the Member States of the European Union have representative soils.

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FIELD WORK ON EURO-SOILS PROFILE ANALYSIS AND SAMPLING PROCEDURES

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Introduction

By means of complex map and data interpretation techniques five small areas scattered throughout the European Union were identified as sampling sites for reference soils to be used in adsorption/desorption testing. The areas are located near:

- Aliminusa in Sicily, Italy
- Krioneri on Peloponnesos, Greece
- Cardiff in Wales, Great Britain
- Caen in Normandy, France
- Lauenburg in Schleswig-Holstein, F.R. Germany.

As a matter of fact, however, even large-scale pedological or geological and geomorphological maps only reflect natural conditions in a more or less generalized way. Therefore a careful and systematic evaluation of the specific situation within the areas identified as being representative must be performed in the field in order to exactly determine the optimum location for the sampling of specimens.

The size of the areas taken into consideration varies according to the amount of material (maps, data, publications etc.) available for the preparation of the field trips. Since the soil cover and the geological and geomorphological situation of the respective regions in Great Britain, France and Germany are sufficiently documented by large-scale maps and/or profile analyses, the size of the areas to be explored could be limited to a few square kilometres. In the case of Italy and Greece only small-scale soil or geological maps are available and it was therefore necessary to study comparatively larger regions of up to 60 square kilometres intensively.

The first part of this report deals with the methods of site exploration applied to verify the preliminary selection and to find representative soil profiles during several field trips. In the second part, the five sampling areas are described with respect to their topographical, geological and geomorphological situation and a detailed presentation of the soil profiles from which the specimens were taken is given. The third part outlines the sampling procedures at the representative locations.

Site exploration

Since the formation and development of different soil types are highly dependent on topography as well as on geology and geomorphology, the first step in site exploration consists in a detailed survey of these parameters. Moreover, the spatial configuration and appearance of vegetation and land use patterns must be carefully analyzed in order to determine the degree of alteration in soil quality due to these factors.

With respect to the main task of the sampling campaigns, special attention was paid to adequately defining the optimum sampling point within the areas specified by computer analysis. This involved:

- a detailed analysis of numerous soil cores taken by drilling equipment,
- estimation or measurement of the main sorption controlling parameters, pH value, grain size distribution, organic matter and carbonates,
- a topographical, geomorphological, geological, and hydrological survey,
- evaluation and documentation of the land use situation.

To determine the appropriate site for sampling, the area taken into consideration was analyzed by means of grid sampling with an auger. The drill cores serve to determine the predominant soil types and the associated soils. Each drill core was scrutinized with respect to the above mentioned soil properties. The routine field methods for these parameters are important because a pedological evaluation of the area must be accomplished by finding the optimum profile, i.e. the profile must reflect the typical soil constituents of this soil type and the predominant spatial and pedological association patterns of the region. Sometimes the soil cover in the potential sampling area may be inhomogeneous, influenced by erosion, man, or other factors. To tackle this problem the drill core analyses were continuously compared.

With the help of routinely used field methods, the main sorption controlling parameters were determined or estimated for each core. To measure the pH value, sieved fine soil (grain size <2 mm) is brought into suspension in a soil solution ratio of 1:2.5. After 10-20 minutes the pH is measured using a glass electrode and a pH meter calibrated for the expected range of values. The approximate grain size distribution is determined by finger trial with plasticity, rollability, lubricity and asperity as relevant criteria. The content of organic matter is deduced from the colour of black, brown and/or grey coloured humus components and other coloured mineral particles according to the Munsell Soil Color Chart. The amount of free carbonates in the sample is estimated by the amount of carbon dioxide that forms in the reaction with hydrochloric acid.

After determining the final location of the sampling site, it is characterized according to the following criteria:

- topographical position (longitude, latitude)
- altitude,
- relief, inclination, exposition,
- climate,
- vegetation and land use.

For the pedological documentation of the profile, a pit including all genetic soil horizons down to the initial substratum was dug and prepared at the location. For documentation purposes general and detailed pictures of the profile were taken with a yardstick in position. The analysis of the profile, which resulted in the definition of diagnostic horizons, was made by estimating the relevant soil properties by means of the field methods briefly described above. The characteristics of the soil profile, as detected by visual inspection, measurements, or estimations were documented in the field book.

Beginning at the lower parts of the profile, samples were taken from typical sections of all different horizons of the key profile for subsequent analysis in the laboratory. Although only parts of the profiles (mainly top soil samples) are used to form reference material, a detailed analysis of all genetic horizons is necessary to characterize the soils and their specific properties definitively.

Table 1 summarizes the main results of soil selection by map interpretation and field research. This synopsis clearly shows the different features of the soils sampled. The dominant soil moisture regimes within the EU realm are udic and xeric, and the dominant temperature regimes are mesic and thermic. Cambisols are distributed all over the Union, therefore two representatives of this group under different climatic conditions are considered. Luvisols mostly occur in North and Central Europe, Rendzinas are frequent in the South, and Podzols are typical soils of the North. Accordingly, the sampling sites are located within the climatic zones where these soils predominantly occur.

From a detailed analysis of maps of the natural vegetation and land use in the European Union it was found that pasture and meadow, arable land, coniferous forest and broadleaved trees must be taken into account to assure representativity in this case as well. As a consequence, during field work special attention was also paid to these requirements.

Table 1: Main characteristics of EU representative soils and sampling sites

EU SOIL MAP 1:1 Mio	CAMBISOLS		LUVISOLS	PODZOLS	RENDZINAS
FAO SOIL MAP OF EUROPE	Brown Forest Soils p.p.	Brown Mediterranean Soils p.p.	Gray-brown Podzolic Soils	Podzolized Soils	Rendzinas
FREQUENCY (%)	44.7		15.7	6.7	5.0
SOIL CLIMATE					
Moisture Regime	udic	xeric	udic	udic	xeric
Temperature Regime	mesic	thermic	mesic	mesic	thermic
VEGETATION/ LAND USE	Pasture	Meadow	Arable Ground	Coniferous Forest	Broad-leaved Trees / Scrub
GEOLOGY/ PARENT MATERIAL	Till Glacial drift	Marine Deposits	Loess	Fluvioglacial Sediments	Lacustrine Deposits
FAO SOIL UNIT	Dystric Cambisol	Vertic Cambisol	Orthic Luvisol	Orthic Podzol	Orthic Rendzina
REPRESENTATIVE SAMPLING	Radyr	Aliminusa	Rots	Gudow	Souli
LOCATION	Wales	Sicily	Normandy	Schl.-Holst.	Peloponnesos
EC MEMBER STATE	Great Britain	Italy	France	F.R. Germany	Greece

The synopsis of the geological situation demonstrates that a reasonable diversity in the parent material of soil formation was also achieved.

All together, the combination of different soil types on alternate parent material under varying climatic conditions and numerous types of vegetation forms the best preconditions for obtaining reference material that is either representative for the EU territory or that differs with respect to its sorptive properties. In the following, the sampling sites and soil profiles will be described in detail.

Site description and profile analysis

EURO-SOIL 1

FAO SOIL UNIT	Vertic Cambisol
SOIL ASSOCIATION	Brown Mediterranean Soils
SAMPLING SITE	Aliminusa - Sicily
EU MEMBER STATE	Italy
VEGETATION / LAND USE	Grassland / Meadow
SAMPLING DATE	March 18, 1988

Topography

The sampling area for the Vertic Cambisol is located between 500 and 1000 meters a.s.l. It is characterized by moderate relief intensity with large-scale alternation of relatively steep slopes and flat or gently sloping areas, divided by small, mostly dry valleys. The combination of Mediterranean climate and relief leads to the acceleration of soil erosion processes on steeper slopes, resulting in the formation of colluvial soils on some terraces and valley floors.

Geology

Although the rocks exposed in the sampling region are almost entirely marine sediments from the Tertiary age, the petrography is rather inhomogenous. Greyish-brown clay stones and siltstones of varying degrees of compactness are associated with platy to massive limestone layers and light yellow sandstones poor in or free of carbonates. Intermittent outcrops of marine sandstones with a green shade due to glauconite also occur. Because of the alternating iron content of the parent material the weathering products of the sandstones appear in different colours.

Soil Properties

The Vertic Cambisol as sampled near the small village Aliminusa in Sicily, about 45 kilometers southeast of Palermo, is a typical representative of brown soils occurring in the Mediterranean region. Due to its high clay content of nearly 75 per cent, which is not untypical for soils of this kind, both the ochric A horizon and the cambic B horizon show vertic properties. During the hot and dry summer months shrinking of clay minerals results in the formation of deep cracks with a width of about 1-2 cm. In the relatively humid winter season the soil is usually very wet due to slow soil-water percolation. Alternating expansion and contraction appears to be responsible for a downward translocation of organic material from the A horizon and for some slickensided surfaces seen predominantly in the blocky to prismatic B horizon when dry. As a result of the soil properties mentioned the vegetation cover - mostly grass with some thistles and wild artichokes - is naturally thin, the surface of the soil has a sparse layer of litter and at some places the bare, yellow-brown, fine textured A horizon is exposed.

The Vertic Cambisols occur in small-scale association with Regosols and Vertisols, depending on the composition of the parent material exposed. The Ah-Bw-C profile under meadow is almost free of sand, the reaction is moderately acid and the organic carbon content does not exceed 1.6 per cent. The ratio of clay/organic matter indicates that the relatively high cation exchange capacity is based mainly on the sorptive qualities of the clay minerals. Within the complete set of EURO-Soils the latter is the outstanding feature of the soil sampled in Sicily, which stands for the soils rich in clay but relatively poor in organic carbon that are widely distributed in the Mediterranean region. Because the clay minerals might influence the sorptive properties of this sample in a lasting manner, the results of batch experiments indicate to a certain extent the affinity of chemicals to be bound at clay surfaces.

Soil Profile Description

Map:	Montemaggiore Belsito 1:25 000
Location:	2.2 kilometers east-northeast of the centre (church) of Aliminusa
Site:	gently sloping terrace with a northward exposure
Elevation:	approx. 650 meters a.s.l.
Weather:	cloudy, slight rain
Soil horizons:	Ah (0-30 cm) coarse granular to subangular blocky
	Bw (30-60 cm) angular blocky to prismatic
	BC (60- cm) coherent

The appearance of the soil profile is greatly influenced by a slight self-mulching effect caused by the periodical occurrence of wet and dry conditions. As mentioned above, a certain amount of organic material from the upper part of the soil is translocated into the Bw (BC) horizon. This effect is responsible for only weak changes in colour and wavy, gradual horizon boundaries. The A horizon, intersected by many long, small roots, is yellowish brown and slightly darker in the lower part due to a higher moisture content. The main difference between A and Bw horizon is that the latter is darker in colour, harder in consistency and that prismatic structures and some slickensides occur at the surfaces of the aggregates. The BC horizon is indicated by a complete lack of roots, an easily visible change of colour (light brown) and a coherent structure without any cracks.

During the wet season the soil profile looks completely different. Due to the high clay content the soil is poorly drained and below 60 centimeters from the surface the matrix is almost saturated with water, causing reducing conditions and grey to black colours. The dark brown Bw horizon shows predominantly aerobic conditions but since some parts are anaerobic, the matrix appears spotted. The structure of the soil is coherent and no aggregates or cracks exist.

EURO-SOIL 2

FAO SOIL UNIT	Rendzina
SOIL ASSOCIATION	Brown Forest Soils and Rendzinas
SAMPLING SITE	Souli - Peloponnesos
EU MEMBER STATE	Greece
VEGETATION / LAND USE	Broad-leaved trees
SAMPLING DATE	March 23, 1988

Topography

The sampling site for the Rendzina is situated on Peloponnesos/ Greece at about 600 m a. s. l., 12 kilometers south of the small port town of Kiato. The exact position is on the righthand side of the road to Krioneri, approx. 1000 m south of Souli. In general, the appearance of the relief is similar to the situation in Sicily (EURO-Soil 1), though flat or gently sloping plateaus on various levels are larger in extension. Deep valleys, opening to the north-northeast, are cut into the plateaus. Soil erosion processes occur mainly on the inclined parts of the area, accelerated by intensive agricultural use (viticulture, olives). On the broad (3.5 km) coastal plain in the north, fruit growing is the major land use.

Geology

As documented in the Nemea Sheet of the Geological Map of Greece 1:50,000, most of the exposed rocks are sediments of late Tertiary age. Specifically, for the sampling area taken into consideration, the parent material for soil formation is moderately consolidated Plio-Pleistocene sediment rich in clay and carbonates. More detailed petrographical analyses show that limnal and fluvial deposits are interbedded in small-scale alternation. Slightly dipping beds of compact siltstones and claystones containing large amounts of carbonates are interstratified with relatively unconsolidated layers of well-rounded pebbles with average diameters of 5 to 10 cm. The unweathered rock usually appears greyish white to light yellow.
Besides this, some thin dark brown to reddish brown stripes also occur due to selective accumulation of iron oxides.

Soil Properties

Since long-standing intensive agricultural use in large parts of the sampling area has led to soil profile degradation, the Rendzina in its typical form is found mainly under natural vegetation (scrubs, bushes, sclerophyllous woodland). The soil sampled at the location described here shows the characteristic features of a typical Rendzina. Loose leafy litter rests on a dark brown to black mollic A horizon that is speckled with white fragments of the parent material. The A horizon is characterized by a well-developed granular structure, a relatively low sand content and a considerable amount of free $CaCO_3$, resulting in a pH value above neutrality and complete base cation saturation. The dark colour is caused by a high content of organic matter.

Below the A horizon, at a depth of approx. 30 to 35 cm, there is a narrow light brown transitional horizon where weathering has softened the solid parent rock, followed by the white limestone forming the C horizon.

Soil Profile Description

Map:	Geological Map of Greece, Nemea Sheet 1:50 000
Location:	1.0 kilometer beyond the village of Souli on the road to Krioneri/ Nemea
Site:	moderate slope with eastward exposure
Elevation:	approx. 680 meters a.s.l.
Weather:	sunny, scattered clouds
Soil horizons:	Ahk (0-30 cm) granular ACk (30-35 cm) granular to fine subangular blocky Ck (35- cm) coherent

Rendzinas are very common soils in regions where limestones or other calcareous sediments are exposed. They are distributed throughout a wide range of climate and bear many different plant communities. Within the complete set of test soils the Rendzina from Greece represents soils with high pH values and a high organic carbon content.

EURO-SOIL 3	
FAO SOIL UNIT	Dystric Cambisol
SOIL ASSOCIATION	Acid Brown Forest Soils
SAMPLING SITE	Glamorgan Gwent - Wales
EU MEMBER STATE	Great Britain
VEGETATION / LAND USE	Grassland / Pasture
SAMPLING DATE	April 22, 1988

Topography

The Vale of Glamorgan, where the sampling area of the Dystric Cambisol is located, forms a low plateau rising gently inland from about 90 m to 120 m a.s.l.

The scarp is breached by several major rivers that drain the hills, some having cut spectacular gorges into the Carboniferous and Triassic strata. The downlands form a central rib of slightly higher ground. To the north extends the broad and undulating depression of Bro Miskin.

The gently rolling relief of the landscape in its present shape was formed predominantly by the Pleistocene glaciation.

Geology

The coastal belt is made up mainly of Lower Lias limestones. In the west sandstones become more predominant, as they do in the eastern part of the coast, where thick sandstone bands crop out near Cowbridge. In the southeast the Trias rocks are red and green mudstones with occasional calcareous intrusions. Also near Cowbridge limestone conglomerates appear.

East of Cardiff Devonian red mudstones crop out locally mixed with some sandstones. The latter are even more dominant north of Cardiff, near Dinas Powis and to the west on the inside of the anticlinal at Hensol Park and Stalling Down.

During the first phase of Pleistocene glaciation, ice from the Irish Sea entered the Vale from the west and crossed the coastal plateau, almost reaching Cardiff and leaving erratics while retreating. Ice-impounded lakes were formed in the major river valleys. Simultaneously local ice also crossed the plateau from the hills and abutted against the Irish Sea ice. During the second phase the Irish Sea ice did not reach as far as the plateau. Only local ice moved into the Bro Miskin Basin, where it deposited a hummocky terminal moraine, which has a kame and kettle topography.

Soil Properties

In the northeast of Glamorgan Gwent - about 5 kilometers north of the boundary of Cardiff - the Dystric Cambisol was sampled on the Richard farm. The location is characterized by a humid climate due to high annual rainfall, which is everywhere 1000 mm and more. The district is a typical mixed farming area where small and medium-sized holdings predominate. The land values vary between 100 and 200 pounds and 200 to 300 pounds per acre. First evidence of systematic agricultural land use dates back to the Roman Era. Extensive crop farming was practiced in the early 20th century on the well drained soils of the Vale, though it declined with the increasing demand for milk. Only recently a return to corn growing has taken place, particularly near the coast.

EURO-Soil 3, represented by the Radyr Series in the Vale of Glamorgan, comprises loamy well drained soils in drift largely from Carboniferous sandstones and shales. Generally the soils are less coarse in texture and mostly loams. The structure is usually fine crumb or very fine subangular blocky. The soils are naturally acid and lack phosphate. Organic matter is carried down in channels by earthworms to a considerable depth in the profile.

EURO-Soil 3 is associated on a small scale with Gleyic Cambisols, Calcic Cambisols and Calcaric Gleysols.

The Ap-Bw1-Bw2-Bw3/C profile of the soil sampled under pasture shows a well-visible Ap horizon resulting from the fact that until the early 70's the land was used for crop growing.

Soil Profile Description

Map:	Soils of the Vale of Glamorgan 1:63 360
Location:	200 m southeast of farmhouse
Site:	sloping moraine with westward exposure
Elevation:	approx. 60 meters a.s.l.
Weather:	foggy, overcast
Soil horizons:	Ap (0-30 cm) fine crumb to very fine subangular blocky
	Bw1 (30-60 cm) fine crumb to very fine subangular blocky
	Bw2 (60-150 cm) polyhedral
	Bw3/C (> 150 cm)

The solum is generally rather stony and has an overall brownish to reddish brown colour. As a typical result of intensive weathering under humid conditions the iron from primary silicates is transformed into oxides and hydroxides, coating quartz grains or forming coagulates. While the brown colour is caused by hydrated iron oxides from in-situ weathering, the reddish appearance of the profile is lithochromatic.

The pebbles and boulders scattered within the loamy moraine material are mostly of sandstone or glauconite sandstone. The gradient of weathering intensity clearly decreases with depth. The Ap horizon, which contains stones of up to 10 cm size, is characterized by a MUNSELL colour value of 5YR 3/3. Secondary pores, such as root channels, are sporadically found. A slight change to lighter colour (5YR 3/4) indicates the diffuse transition zone between the Ap and the Bw1 horizon. Characteristically, the boundaries of the horizons of Cambisols are blurred. In comparison with the Ap horizon, the Bw1 contains more and bigger stones but has a lower content of organic matter and clay. At a depth of approx. 60 cm, the boundary between the Bw1 and the Bw2 horizon is marked by a layer of about 5 cm width rich in medium to coarse grained sand with a MUNSELL colour value of 5YR 4/6. The Bw2 horizon is characterized by a polyhedral structure and a complete lack of roots. At a depth of >150 cm the Bw3/C horizon can be identified by a yellowish brown colour and a bulk density of about 1.5 to 1.8.

The profile description of the Cambisol sampled at the representative location in Wales indicates that this soil stands for widespread pedological associations developed on loamy, moderately consolidated parent material that are often found in the northern parts of the Union.

EURO-SOIL 4

FAO SOIL UNIT	Orthic Luvisol
SOIL ASSOCIATION	Gray-brown Podzolic Soils
SAMPLING SITE	Rots - Normandy
EU MEMBER STATE	France
VEGETATION / LAND USE	Wheat / Arable Land
SAMPLING DATE	April 26, 1988

Topography:

Normandy, a landscape in the Northwest of France, comprises the high plateaus of Cretaceous limestone at the mouth of the Seine and the peninsula of Cotentin.

Although Normandy consists of different individual landscapes, considered as a whole it is one of the characteristic regions of France. North of Caen near a small village named Rots, which is situated within an area of intensive agriculture, the sampling location of the Orthic Luvisol is situated on a gently sloping and westward exposed plateau at approx. 25 meters a.s.l..

Geology:

Geologically, Normandy is divided into two different regions: the western part belongs to the Armorican massif, whereas the eastern part is formed by the northern verge of the Paris Basin. During the Variscan Orogeny mountain ranges developed in the Carboniferous crystalline rocks. These ranges were subsequently leveled, leaving a peneplain. The marine transgressions of the Mesozoic and Tertiary Era deposited marine and terrestrial sediments into sedimentation troughs. The Paris Basin represents such a trough.

In the course of subsidence processes and the Alpidic Orogenesis during the Tertiary, the benchland landscape of the Paris Basin was formed. Since Normandy itself reaches into the Paris Basin, parts of it show benchland features. Accordingly, it is mainly the northern part that is built up of stratigraphic sequences from the Mesozoic and the Tertiary. In the west, flat plateaus (Contentin) and granite sandstone ridges (Bocage) predominate. The morphological processes that shaped the present day relief of Normandy can be traced back to the Oligocene. Under periglacial conditions during the Pleistocene, loess was deposited across wide areas.

Soil properties

The pedogenesis and the climate of this region are strongly influenced by its proximity to the open sea. The generally high precipitation values decline from west to east (1200 - 800 mm).

The mean annual temperature regime is quite constant with a low potential evaporation rate, the latter also being dependent on the latitude.

Vast areas of Normandy are covered by loess, an aeolian sediment of balanced grain size distribution that is rich in carbonates. The development of EURO-Soil 4 began during the late Pleistocene, when an arid and cold steppe and tundra climate was common, and continued under the temperate humid conditions of the Holocene. The typical brown colour of the Luvisols developed on the loess is the result of iron oxide formation. Intensive colouring can be observed in soils with pH values below 7 as a result of the washout of carbonates.

The weathering of mica results in the formation of clay minerals which, together with the primary clay minerals, are subjected to displacement if the soil pH is approx. 5 to 6.5. This leads to the formation of both eluvial and illuvial horizons. The argillic weathering residue can lead to an accumulation of water in the soil profile, adversely affecting the aeration of the soil. As a result of waterlogging, anaerobic conditions may partly cause a reduction of iron and manganese oxides.

The site of the EU-representative Orthic Luvisol near Caen in Rots (Normandy) is characterized by thick loess deposits of late Pleistocene age overlying compact Cretaceous limestone. Because of the soil's fertility and productivity most of the area best suited for sampling is under intensive agricultural use. This fact is responsible for some peculiar features of representative EURO-Soil 4. Due to the common practice of liming the pH value of the A horizon is 1 to 1.5 units higher than in untreated Orthic Luvisols. Another result of the intensive cultivation is that the tilled horizon is poor in organic matter. Apart from this the selected soil shows the typical attributes of downward translocation of clay-size material, including ferric oxides, from a loamy surface, forming a distinct brown, blocky to subpolyhedral structured Bt horizon with clay skins on ped surfaces and along channels.

The soils of all of Normandy represent a rather homogeneous area due to the geological and pedological situation. In this region, the Orthic Luvisol is associated with various Luvisols, such as especially Calcic and Gleyic Luvisols or with Cambisols and Gleysols.

Soil Profile Description

Map:	Cartes des formations superficielles et cartes gomorphologiques de Basse-Normandie (Feuille de Bayeux-Courseulles) 1:50 000
Location:	Rots, northern Caen
Site:	gently sloping plateau with a westward exposure approx. 25 meters a.s.l.
Weather:	sunny, cloudless
Soil horizons:	Ap (0-20 cm) fine crumb to subangular blocky
	E (20-55 cm) blocky to subpolyhedral
	Bt (55-90 cm) polyhedral
	Ck (> 90 cm)

The representative Orthic Luvisol shows a soil matrix with the typical horizon sequence Ap-E-Bt-BCk-Ck. The Ap is weakly intersected by roots. In accordance with the high productivity of this soil, the Ap horizon is highly influenced by anthropogenic treatment, such as ploughing and intensive application of fertilizers and pesticides. As a result of liming, some fine to coarse carbonate gravels are noticeable in this part of the soil body and the colour was determined as 10YR3/3. The eluvial horizon indicates isolated organic matter and its bulk density is negligibly higher than in the upper horizon. With a MUNSELL value of 10YR4/4, the E horizon is slightly paler due to clay translocation into the Bt. Occasional, but visible, clay cutanes and lightly sparkling peds are typical properties of an illuvial Bt horizon. The colour changes to 7.5YR4/4. The Ck horizon constitutes the transition from loess to the underlying limestone. Since the slightly weathered limestone does not represent the parent material of soil formation, it is to be called an R horizon.

EURO-SOIL 5

FAO SOIL UNIT	Orthic Podzol
SOIL ASSOCIATION	Podzolized Soils
SAMPLING SITE	Lauenburg - Schleswig-Holstein
EU MEMBER STATE	F.R. Germany
VEGETATION / LAND USE	Coniferous Forest
SAMPLING DATE	May 1, 1988

Topography

The representative sampling site of the Orthic Podzol was identified as being located about 23 kilometers (linear distance) northeast of Lauenburg in the southernmost part of Schleswig-Holstein, Federal Republic of Germany. The forest where the sample was taken is crossed by the highway from Hamburg to Berlin and the village of Gudow is located nearby. Due to the geological and geomorphological situation described in the following, the landscape appears to be a slightly undulating plain with some shallow, occasionally swampy depressions and a few elevations, seldom extending above 60 meters.

Geology

From the geological/geomorphological point of view the sampling area is characterized mainly by fluvioglacial sediments deposited during the late Pleistocene when the meltwaters of the Weichsel glaciation flowed from the north-northeast in the direction of the Elbe Marginal Streamway. During the late Pleistocene and early Holocene some modification of the landscape took place, but in general the region shows the typical features of a glacial outwash plain. Accordingly, the parent material of soil formation is almost entirely sand that is naturally acid and poor in nutrients.

Due to the short distance between the sampling location and the former ice margin in the north the coarse grain fraction dominates in the composition of the sediments.

Soil Properties

Orthic Podzols are associated mainly with coniferous vegetation and a cool humid climate, but they also occur under other conditions. The physicochemical properties of the reference soil sampled at the regionally representative location described here differ completely from those of the above soils. On the one hand, the clay content of the sandy soil substratum tends to zero and the pH value is extremely low. On the other hand, the organic carbon content of the Podzol is the highest of all the soils considered for testing purposes. Here it should be mentioned that due to inhibited microbial activity the organic matter in untreated Podzols under forest is usually poorly degraded and consists largely of fulvic acids. The Podzol sampled here is barely influenced by anthropogenic activities, making the soil representative of large regions of the Community in which coniferous woodlands are developed on acid soils from siliceous parent material.

Of the total recommended test soils, the Orthic Podzol and the Rendzina reflect, to a certain extent, the range of parameters that are largely responsible for the adsorption/desorption behaviour of chemicals in soils.

Soil Profile Description

Map: TK 25, 2430: Gudow 1:25 000
Location: approx. 1 000 m southwest of the highway station Gudow
Site: flat glacial outwash plain
Elevation: 30 m a.s.l.
Weather: sunny, cloudless
Soil horizons: O (-8- 0 cm) poorly degraded, loose and spongy surface litter
Ah (0-11 cm) single grain to fine granular
E (11-25 cm) single grain
Bhs (25-32 cm) loose subangular blocky
Bs (32-48cm) firm subangular blocky to coherent
BC (48-65 cm) bridge
C (65- cm) single grain

EURO-Soil 5 is a fully developed Orthic Podzol showing a sequence of horizons that are typical of soils of this kind. The loose and spongy surface litter, which is slightly fermented in the lower parts of the O horizon, consists of undegraded or poorly humified grass, moss and needles as well as branch and root residues or other plant fragments. With increasing depth the organic matter is in a more advanced state of decomposition and grades into the very dark grey mixture of organic matter and mineral material that forms the Ah horizon. This horizon is slightly intersected by small roots, and fragments of charcoal can be easily identified. Due to translocation of iron oxides from the Ah horizon into the deeper parts of the profile, the dark-coloured horizon is speckled with bleached quartz grains.

The pale grey E horizon, showing the characteristic single grain structure, consists almost completely of bleached quartz grains because either humic substances or iron oxide coatings and other metal ions (cf. aluminum) have been mobilized and subjected to translocation by percolating water. The substances washed out in the upper part of the profile are enriched in the following horizons. While in the very dark brown to black Bhs horizon, organic matter and iron and aluminum have accumulated, the deep brown colour of the Bs horizon and its coherent structure are the results of a selective accumulation of sesquioxides. The BC horizon indicates the transition zone between the typical horizon sequence of the Orthic Podzol and the parent material. Here, as a result of moderate weathering, the quartz grains are coated with iron oxides, resulting in the light brown colour of the BC horizon. At approx. 60 cm the soil profile slowly grades into the barely weathered fluvioglacial sediments forming the unconsolidated rock on which the Podzol is developed.

EURO-SOIL 6

SAMPLING SITE	Rots - Normandy
EU MEMBER STATE	France
VEGETATION / LAND USE	Wheat / Arable Land
SAMPLING DATE	April 26, 1988

"EURO-Soil 6" does not represent a EURO-Soil in the defined sense. The five reference soils described above were identified by means of various mathematical procedures and verified in the field by multiple site exploration techniques, in recognition of the fact that they should reflect wide areas of the Community, a maximum range of sorption controlling properties, typical soil horizon combinations and different vegetation covers. The so-called "EURO-Soil 6" does not fulfill these requirements at all. The sample is part of EURO-Soil 4, taken from the BC horizon to represent a subsoil that is poor in organic matter. From the technical point of view, it is not possible to identify representative subsoils by methods similar to those applied for EURO-Soils 1 to 5. Therefore, in order to reduce the expenditures for soil sampling and treatment, it was decided to take a subsoil sample from one of the existing reference soils. Material from the BC horizon of EURO-Soil 4 was considered to be best suited because it was easily obtainable in large quantities and the preparation and homogenization caused only slight problems. Apart from this, the sample is characterized by a relatively inhomogenous grain size distribution, and the organic carbon content does not exceed 0.5 per cent.

Sampling procedures

The fieldwork at the representative locations continued with the sampling of approx. 150 kg soil. The topsoil material was sampled from the A horizons, closely adjacent to the profile pit. Before that, numerous drill cores in the neighbourhood of the profile were taken to insure that changes in soil quality and structure do not occur and that the profiles described above are characteristic of the sampling area as a total. Before taking the specimens, litter and plants had to be removed carefully to guarantee proper sampling and maximum homogeneity. While the soil material was being filled into 50 kg boxes with a funnel it was sieved (mesh size approx. 6 mm), and cobbles, stones and rocks were sorted out. The specimens were immediately transported to the JRC Ispra/Italy for air-drying and further treatment.

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PEDOLOGICAL CHARACTERIZATION AND MAJOR ELEMENT COMPOSITION ANALYSIS

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Introduction

Five topsoils have been selected which are suggested to form reference soils for sorption testing of new chemicals in the European Union. In addition, one subsoil sample was collected to represent material that is very poor in organic carbon content. These six soil samples were dried, sieved, homogenized, sterilized, analyzed and bottled for use in an EU-wide ring-test exercise on adsorption/ desorption. The results of the intercomparison test shall enable the Commission of the European Union to decide, if

- the OECD Guideline 106 'Adsorption/Desorption' in its present form is a suitable tool for testing the sorption behaviour of new chemicals,
- the soils selected reflect the characteristics and variability of the EU soil cover in a convenient way, especially with respect to sorption controlling properties.

In the following the main results of a comprehensive pedological analysis of the reference soil samples will be presented and briefly interpreted. The analyses were performed by the LUFA (Muenster, Germany) according to the VDLUFA standard procedures for soil analysis, the EC Joint Research Centre (Ispra, Italy) and the Department of Geography (Kiel, Germany) using soil material being air-dried, sieved and homogenized at the JRC Ispra.

For better identification, the six soil samples have been named 'EURO-Soils' (abbreviation 'E') and numbered in chronological order of collection (cf. table 1).

Tab. 1: Designation of reference soil samples

FAO Soil Unit	Soil	Horizon	Sampling Site	EU Member State
EURO-Soil 1	Vertic Cambisol	A-horizon	Sicily	Italy
EURO-Soil 2	Rendzina	A-horizon	Peloponnesos	Greece
EURO-Soil 3	Dystric Cambisol	A-horizon	WalesGreat	Britain
EURO-Soil 4	Orthic Luvisol	A-horizon	Normandy	France
EURO-Soil 5	Orthic Podzol	A-horizon	Schleswig-Holstein	Germany
EURO-Soil 6	Orthic Luvisol	BC-horizon	Normandy	France

Grain size distribution

Figure 1 displays the percentage of clay, silt and sand in the mineralogical fraction of the EURO-Soils. While the soils 2 and 3 show a more or less balanced grain size

Tab. 2: Pedological characteristics of the EURO-Soils

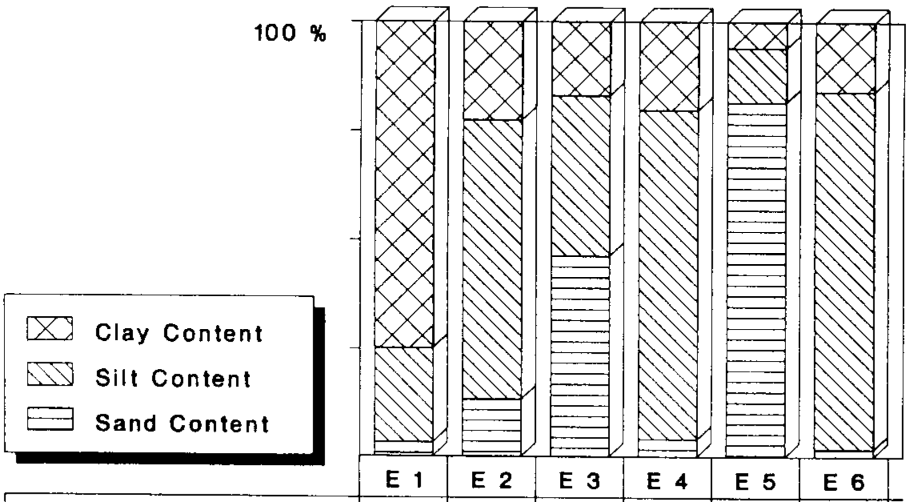
Pedologic. parameter	soil 1 clay soil	soil 2 silt loam	soil 3 loam	soil 4 silt	soil 5 loamy sand	soil 6 silt loam
SAND total[%]	3.31	13.4	46.4	4.1	81.6	1.7
coarse + medium[%]	2.0	4.4	23.1	1.1	64.8	0.3
fine[%]	1.3	9.0	23.3	3.01	6.8	1.4
SILT total[%]	21.9	64.1	36.8	75.7	12.6	82.4
coarse[%]	4.0	21.3	19.4	52.2	7.4	62.5
medium[%]	9.7	23.1	11.6	19.4	4.3	17.3
fine[%]	8.2	19.7	5.8	4.1	1.0	2.6
CLAY total[%]	75.0	22.6	17.0	20.3	6.0	16.0
pH values						
water	5.9	8.0	5.8	7.0	4.6	8.3
$CaCl_2$	5.1	7.4	5.2	6.5	3.2	7.2
NaCl	5.1	7.5	5.2	6.5	3.4	7.1
total carbon[%]	1.5	10.9	3.7	1.7	10.9	0.3
$CaCO_3$[%]	0.0	60.45	0.0	0.0	0.0	0.0
organic carbon[%]	1.30	3.70	3.45	1.55	9.25	0.25
organic matter[%]	2.65	6.4*	6.45	2.85	15.90	0.80
N[%]	0.17	0.20	0.26	0.16	0.30	0.02
C/N ratio	7.65	18.50	13.27	9.69	30.77	12.50
org. S[%]	0.05	0.028	0.06	0.03	0.078	0.012
P total[%]	0.15	0.15	0.38	0.29	0.21	0.15
SiO_2[%]	56.22	21.60	68.45	68.63	71.57	68.56
Al_2O_3[%]	23.92	8.66	11.92	12.07	3.85	12.64
CaO[%]	0.41	30.62	0.20	0.71	<0.02	0.59
K_2O[%]	1.85	1.27	1.59	1.84	0.63	1.71
Fe_2O_3[%]	10.76	1.66	4.14	2.71	<0.05	2.83
MgO[%]	1.12	1.82	1.19	1.11	0.65	1.16
TiO_2[%]	0.99	0.25	0.65	0.72	0.36	0.72
C.E.C.[mval/100 g]	29.9	28.3	18.3	17.5	32.7	11.4
Fe total[mg/kg]	37.05	9.85	14.37	11.50	1.04	12.44
Fe amorphous [%]	3.22	0.18	4.75	1.93	0.56	0.73
Fe HCl-sol.[mg/kg]	1.82	0.002	2.20	1.47	0.105	1.14
Al amorphous [%]	0.64	0.17	1.58	0.81	0.97	0.56
Al HCl-sol.[mg/kg]	0.83	traces	1.67	1.55	0.93	1.56

* = calculated from Corg by Corg = O.C. x 1.7

distribution the other samples are characterized by the dominance of certain particle sizes.

Induced by the composition of the parent material being marine clay-stone, the Vertic Cambisol of Sicily (E 1) contains exactly 75 per cent clay (cf. table 2), which is highest amongst the set of samples. This fact, however, is not untypical for soils of the Mediterranean region. In connection with the seasonal alternation of wet and dry climatic periods, rhythmical shrinking and expanding of the clay minerals is responsible for the vertic features of this Cambisol. In contrast, the Orthic Podzol contains only few clay-size particles but has a sand content of more than 80 per cent which is also induced by the parent material of soil formation being glacial outwash. Not only with respect to grain size distribution (see below) these two soils mark extreme positions within the set of EURO-Soils. The samples E 4 and E 6 also show a dominance of a certain grain fraction, in this case a total silt content of about 76 or

82 per cent, respectively. The similarity of the grain size distribution obviously results from the fact that these two samples were taken from the same soil, an Orthic Luvisol, at different depths. The relatively high silt content is typical for soils developed on Loess, an aeolian sediment which was deposited over vast areas of the sampling region (Normandy) during the last Ice Age. The parent material of the Dystric Cambisol from Wales (E 3) was also deposited during the Pleistocene glaciation, in this case as glacial drift. Since till usually is an unsorted mixture of different material, the balanced particle size distribution of soils developed on this sediment is a common appearance. EURO-Soil 3 reveals only a slight dominance of the sand fraction. Although the Rendzina (E 2) also shows a balanced grain size distribution an important factor has to be considered when comparing its particle size composition with those of the other soils. As common in soil science, the percentage of individual grain fractions is given related to the total of mineralogícal components. Accordingly, before measuring the particle size distribution humic substances as well as carbonates are destroyed. Normally this does not affect the comparability of the results in an undue way. In this case, however, and especially with respect to the interpretation of sorption experiments, it has to be carefully considered that the E 2 sample consists of more than 60 per cent calcium carbonate, reducing the content of minerals to nearly one third of the total. In general, the sample represents a typical A horizon of Rendzinas under natural vegetation in the Mediterranean region where the solution and downward



	E 1	E 2	E 3	E 4	E 5	E 6
Clay Content	75,0	22,6	17,0	20,3	6,0	16,0
Silt Content	21,9	64,1	36,8	75,7	12,5	82,4
Sand Content	3,3	13,4	46,4	4,1	81,6	1,7

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Fig. 1: Grain size distribution of the EURO-Soils

translocation of calcium carbonate is not as intensive as in regions with mesic soil moisture regimes.

The main features of the EURO-Soils' grain size composition as mentioned above are displayed in a more differenciated form in figure 2 (exact values see table 2). The antagonistic character of the EURO-Soils 1 and 5, the similarities between E 4 and E 6 as well as the balanced grain size distribution of the Rendzina on the one hand and the Dystric Cambisol on the other plainly become apparent.

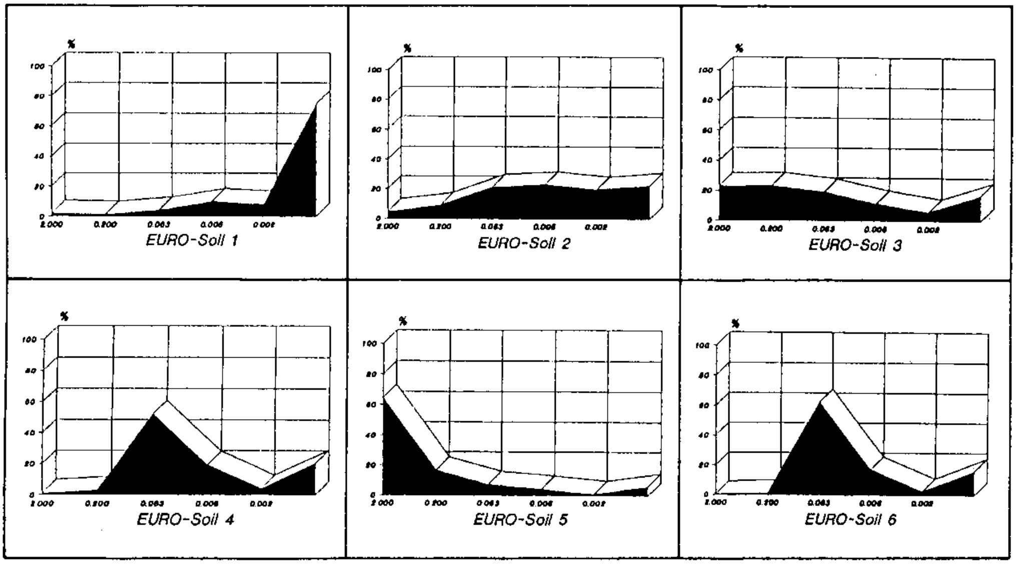


Fig. 2: Grain size profiles of the EURO-Soils

With respect to sorption controlling properties of the soil samples, however, the knowledge of the garin size distribution alone is not sufficiently indicative to interpret the tendency of a certain chemical to be bound at mineral surfaces. Since clay-size particles and, to a certain extent, the fine-silt fraction are mainly responsible for the sorption capacity of a soils' mineral body, a careful analysis of the mineralogical composition of these fractions has to be performed because the sorptive qualities depend on the nature of the minerals.

Clay-mineral composition and weathering trends

Samples from the A and the C or BC horizons, which are considered to be the parent material of the EURO-Soils, were analyzed regarding clay mineralogical composition following standard procedures (RICH & BARNHISEL 1977). Organic matter, calcium carbonate and secondary iron-oxides were removed from the fine earth and the clay fraction ($<2\,\mu m$) as well as the fine-silt fraction ($2\text{-}6.3\,\mu m$) were obtained gravimetrically. The clay and silt samples were sucked on micro filters, treated with specific cations (Mg^{2+}, K^{+}), and mounted on glass slides. Ethylene glycolated samples were subjected to semi-quantitative estimation following LAVES and JOHN (1972) using corrected peak area of diagnostic peaks. On the base of the relative proportion of each mineral group it is of course hard to tell if the differences in composition are due to degradation of the silica-clays or due to weathering of the primary minerals like feldspars or micas. So interpretation was done quite carefully by expressing only trends in weathering from the parent material to the upper soil. Table 3 summarizes the results of the mineralogical analysis.

Tab. 3: Mineralogical composition of the clay and fine-silt fraction

	Ml	Sm	Cl	Verm	Il	Kl	Q	F
Soil 1								
clay	--	15	--	--	25	55	++	--
fine silt	--	++	--	--	10	10	60	10
parent clay	++	15	--	--	25	55	++	10
SOIL 2								
clay	--	30	10	--	40	10	++	--
fine silt	--	--	10	--	30	10	++	--
parent clay	--	35	5	--	50	5	++	++
SOIL 3								
clay	--	--	20	10	40	20	++	--
fine silt	--	--	10	--	20	++	50	10
parent clay	--	--	10	10	65	10	++	++
SOIL 4								
clay	--	++	++	20	60	15	++	--
fine silt	--	--	--	10	20	--	55	15
parent clay	--	12	--	35	33	10	++	++
SOIL 5								
clay	--	++	--	--	20	10	70	--
fine silt	--	--	--	--	10	--	80	10
parent clay	--	9	43	--	35	13	++	++
SOIL 6								
clay	++	++	--	30	40	< 20	++	--
fine silt	--	--	--	15	25	--	40	20

Abbreviations

F= Feldspars
++ = traces
Verm = Vermiculites
Cl =Chlorites and minerals pedological chlorites
Q =QuartzK = Kaolinites
Sm= mineral Smectites
-- = not detected
Il =Illites
Ml= mixel layer

The Vertic Cambisol (E 1), derived from marine clay-stones and shales, has a dominantly kaolinitic mineralogy, which is completely inherited from the parent material. Soil development does not seem to affect weathering of silica-clays, which is considered to be quite low.

In the Rendzina (E 2) the clay mineral composition of the soil only slightly differs from the composition of the limestone residuum. The decrease in smectites and illites and the increase in chlorites and kaolinites from the parent material to the soil indicates some weathering, although the pedogenetic environment of the A horizon (i.e. high base saturation and presence of calcium carbonates) unlikely promotes the formation of kaolinites. Because the composition of the intermedial horizon is unknown and no information on i.e. clay translocation is available, weathering of illites and smectites seems to be a questionable process in this soil. With respect to the two soils mentioned it has to be considered that both are located on sloping areas which, in combination with the alternation of long dry periods and heavy rainfalls typical for the Mediterranean climate, may cause a considerable amount of soil erosion. Although the soils are well developed, a certain balance between soil erosion and formation may occur which could explain the relatively similar composition of topsoil and parent material.

Concerning the Dystric Cambisol (E 3) weathering of illites and vermiculites to pedogenic chlorites (hydroxy interlayered vermiculites) is likely. Formation of kaolinites although indicated by the data is questionable under temperate climate and limited time. Most of the kaolinites are inherited from the parent material, which also contains appreciable amounts of hematite. The latter is indicative for the fact that the material being eroded, transported and deposited through glacier action were formed under climatic conditions also appropriate for the formation of larger amounts of kaolinites (TAVERNIER, R. & MARECHAL, R., 1962).

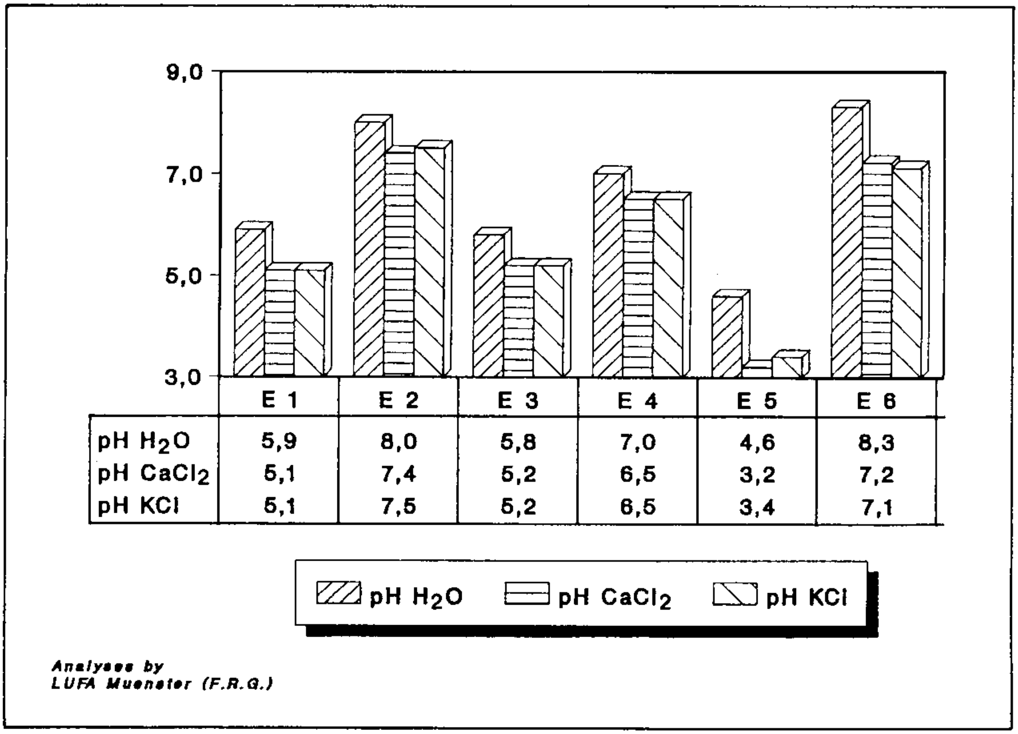
In the Luvisol (E 4/6), the formation of illites probably due to mica weathering leads to a dominantly illitic mineralogy. The smectites as well as the vermiculites seem to take up Al-hydroxy-polymers to form pedogenic chlorites. Especially the vermiculites in the topsoil do not completely contract on potassium saturation and heating and show properties of pedogenic chlorites.

The clay content of the sandy parent material (glacial outwash) of the Orthic Podzol (E 5) is quite low and even decreases in the A horizon. So clay decomposition as well as eluviation of the clay minerals seem to be the dominant soil forming processes affecting the clay minerals. Smectites are obviously more stable than chlorites.

With respect to the sorptive qualities of the various minerals it has to be pointed out that the exchange capacity significantly varies due to the different sheet structure. In general, vermiculites and smectites have the highest sorption capacity which decreases in the order illites > chlorites > kaolinites. Since kaolinites are poorly expandable two-layer minerals their exchange capacity does not exceed 15 mval per 100 grams while vermiculites may adsorb up to 200 mval. The different sorption capacities of the clay minerals have to be considered while interpreting data from sorption experiments. For example, regarding the whole set of EURO-Soils, the outstanding feature of the Vertic Cambisol is its high clay content. As a matter of fact, however, more than one half of the clay fraction consists of poorly sorbing kaolinite.

pH values

Figure 3 shows the completely different character of the six EURO-Soils with respect to their pH values. The two outstanding topsoils, defining the maximum range of pH values represented, are the Rendzina (E 2) on the one hand and the Podzol (E 5) on the other. As already expected from the appearance of the soil profile in the field, the Rendzina in all cases and independent on the solution the pH was measured in, shows values above neutrality. Considering the fact, however, that the sample contains no less than 60 per cent free calcium carbonate (which in this case is evidently of lithogenic nature), such a high pH value had to be expected. Although Rendzinas in general need not necessarily contain this much of free calcium carbonate within their a horizons, the common feature of these soils, being also responsible for the respective classification, is the high pH value of the topsoil.



	E 1	E 2	E 3	E 4	E 5	E 6
pH H_2O	5,9	8,0	5,8	7,0	4,6	8,3
pH $CaCl_2$	5,1	7,4	5,2	6,5	3,2	7,2
pH KCl	5,1	7,5	5,2	6,5	3,4	7,1

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Fig. 3: pH values of the EURO-Soils

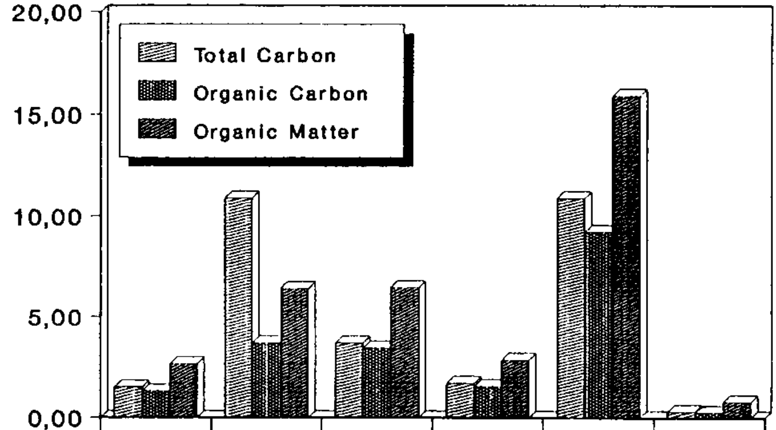
The pH value of EURO-Soil 6 is also very high and with regard to this specific property the subsoil sample is directly comparable to the topsoil sample of the

Rendzina. In this context, however, it has to be considered that because of the different genesis and physicochemical properties of the subsoil sample the high pH value is not caused by free calcium carbonate (see table 2) but by a complete base saturation of exchange surfaces. In contrast, the Orthic Podzol (E 5) shows the highest acidity amongst all the EURO-Soils which finds its direct explication in exteremely low pH values. This also can be explained by the specific combination of parent material and soil forming processes. The coarse-grained siliceous material Podzols are normally developed on is naturally acid and the intensive washout processes during soil formation under cool humid conditions additionally increased the deficiency of alkaline cations in the A horizon. As a consequence of inhibited microbial activity a more or less thick layer of partly degraded litter and a huge amount of organic matter that is rich in fulvo-acids developed under natural vegetation. These factors are all together responsible for the low pH values measured in the Orthic Podzol. The pH values of the two Cambisols (E 1, E 3) are almost identical and typical for this soil type. Under natural conditions, the A horizon of the Orthic Luvisol (E 4) should also have a pH value around five because otherwise no clay translocation would have taken place during soil development. In this case, however, a higher pH value was measured which is undoubtly caused by liming in connection with the intensive agricultural use of the soil. Some carbonate gravels found in the Ap horizon clearly indicate this anthropogenic influence.

Summarizing this point it can be underlined that the wide range of pH values possible in European soils is adequately covered by the reference material. Moderately acid topsoils with pH values around five are very common for both natural and agriculturally used soils and pH values up to seven often occur in Ap horizons of several different soil types when they are intensively used for crop production. These fact were also taken into consideration by choosing two reference samples with comparable or even identical pH values in each case. Apart from the adequate documentation of the European soil situation this constellation has another very important advantage: For the assessment of the behaviour of a new chemical in soil it is important to determine the influence of other sorption controlling properties at similar pH values.

Organic matter

In Figure 4 the total carbon content, the organic carbon content and the amount of organic matter are synoptically displayed for the six EURO-Soils. Regarding the organic carbon clearly shows that a wide span, ranging from 0.25% in EURO-Soil 6 to 9.23% in the Orthic Podzol (E 5), is covered. Within this range, Rendzina and Dystric Cambisol on the one hand as well as Vertic Cambisol and Orthic Luvisol on the other form two pairs of soils, one of them with low the other with average contents of organic matter. This constellation is of particular importance since especially the organic carbon content in many cases is highly responsible for the sorption behaviour of chemicals in soil.



	E 1	E 2	E 3	E 4	E 5	E 6
Total Carbon	1,50	10,90	3,70	1,70	10,90	0,30
Organic Carbon	1,30	3,70	3,45	1,55	9,23	0,25
Organic Matter	2,65	6,40	6,44	2,86	15,92	0,78

Analyses by
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Fig. 4: Carbon and organic matter content of the EURO-Soils

Regarding the top soils (1-5) first, the Vertic Cambisol for some reasons is characterized by the lowest humus content of all soils sampled. In general, the sparce vegetation provides the soil with only few litter which, in addition, is subjected to a relatively effective microbial degradation especially during the warm and moist months between summer and winter season. Moreover, the organic matter which usually accumulates in the top soil is translocated into lower parts of the profile through vertisol dynamics. Probably some soil erosion effects occuring on the inclined surface of this very dense soil also lead to an output of loose litter or slightly humified material. The occurence of colluvial soils in the depressions and valleys of the sampling area may confirm this statement. All together, the various reasons mentioned fully explain the lack of organic matter in this non-agricultural soil. On the contrary, the low organic matter content of EURO-Soil 4 clearly is a consequence of intensive agricultural use. The high microbial activity of a soil sufficiently equiped with nutrients and characterized by good temperature- and moisture conditions promotes a rapid degradation of the organic material, worked into the soil by ploughing. The uptake of nutrients by plants and the subsequent reduction by harvesting result in low values for the organic carbon content. The EURO-Soils 2 and 3 contain nearly identical amounts of organic carbon (around 3.5). In both soils accumulation of organic material took place over longer periods of extensive use (E 3) or natural development (E 2). However, some rough estimations in the field led to the conclusion that the degree of humification is comparably higher for the Rendzina. The highest amount of organic material, already indicated by the dark black appearance of the sample, was detected in the Orthic Podzol. Due to the inhibited microbial activity and the acid character of the litter under coniferous vegetation an enrichment of poorly degraded organic matter takes place in the topsoil. Although podzolization processes cause the translocation of certain amounts of humic acids into deeper layers of the profile, an accumulation of organic material in the topsil is clearly detectable. However, some parts of the organic matter can not be called humus since they consist of only physically grinded residues of roots and branches or pieces of bark being worked into the topsoil by animals. This phenomenon being typical for forest soils should be taken into consideration in the same way as the fact, that the major part of the organic matter consists of poorly polymerized molecules.

Regarding the fact that EURO-Soil 6 as a subsoil was introduced into the set of topsoils to reflect a sample being poor in organic matter the low value of 0.25 per cent organic carbon is quite understandable. There is no need for further interpretation because for the BC horizon of an Orthic Luvisol nothing other had to be expected.

Also with respect to this important factor influencing sorption quality and quantity it once again can be stated that the reference soils selected cover a wide range of different amounts and compositions of organic matter. Therefore the role of organic matter for the adsorption/desorption behaviour of a certain chemical substance can be estimated by comparing the results of shaking experiments from different soils.

Iron and aluminum oxides

The role of amorphous oxides and hydoxides of iron and aluminum for the sorption of chemical substances is often underestimated. Not only the direct pH dependent sorption especially of anions on protonized surfaces but also the chemicals' ability to form complexes often depends on the amount and composition of Fe- and Al-oxides and hydroxides. Consequently, also with respect to these sorption controlling components the EURO-Soils cover the wide range of different amounts typical for European soils. The remarkably high amount of amorphous iron in the Dystric Cambisol from Wales (see figure 5) was already visible in the field because the lower parts of the profile appear in intensive red-brown colors. This is mainly due to the origin of the till from Carboniferous Old-Red sediments containing high amounts of hematite and other iron oxides/-hydroxides. Also the Vertic Cambisol show relatively high values for amorphous iron whereas the aluminum content is relatively low. The marine sediments this Cambisol is developed on usually contain considerable amounts of iron. In addition, stagnating water in spring leads to a reduction and therefore mobilization of iron which is transported upward by capillary rise. Since the redox potential in the upper parts of the profile is higher, iron is immobilized by oxidation. This process may aditionally cause a certain enrichment of amorphous iron in the A horizon of the Vertic Cambisol. An interesting fact concerning EURO-Soil 4 and its subsoil (E 6) is the inverse relationship of amorphous and

HCl-soluble iron: while the topsoil contains more amorphous iron the subsoils' content of HCl-soluble iron is comparably higher. This is obviously due to the different intensities of weathering. Under the direct influence of climatic parameters and cultivation at the soils' surface, larger quantities of iron are released from the primary minerals mostly forming amorphous iron hydroxides. With respect to the aluminum content a distinct similarity of the two samples from one soil can be stated.

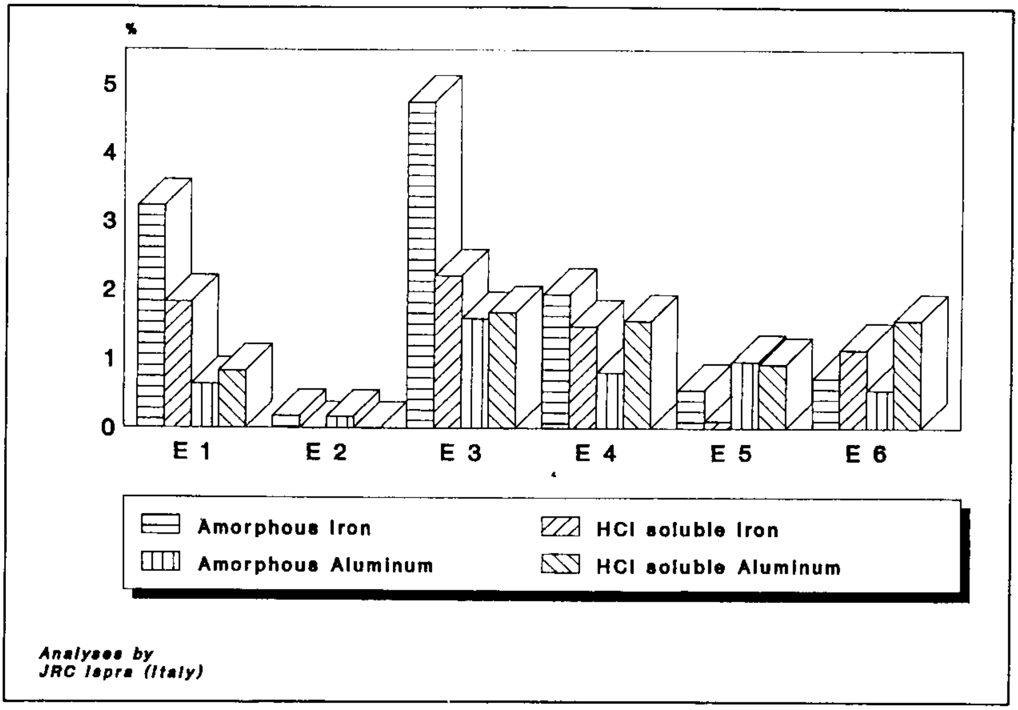

Fig. 5: Iron and aluminum contents of the EURO-Soils

Especially the iron content in the topsoil of the Orthic Podzol is very low. Due to the process of podzolization iron and aluminum oxides are, together with fulvo-acids, subjected to translocation into deeper parts of the profile which is clearly visible in the brown-colored Bs horizon. The slightly higher content of aluminum confirms the above statement that in the A horizon clay minerals are continously degraded because these minerals predominantly consist of silica and aluminum.

The Rendzina (E 2) is almost free of iron and aluminum which has already been expected from the appearance of the profile in the field. The parent material of soil formation is white limestone which consists in relatively pure calcium carbonate. Although in the nearer neighbourhood of the profils also limestones of less purity are found, the sampling spot is characterized by a nearly complete absence of free iron and aluminum.

With respect to the interpretation of sorption experiment results the Dystric Cambisol seems to be of particular importance to assess the affinity of chemicals to be bound to iron oxide surfaces. With a balanced grain size distribution and an average content of organic matter at slightly acid pH values, the amorphous iron oxides could largely affect adsorption/desorption, especially for anionic substances.

Other pedological characteristics of the EURO-Soils

In the following, for each of the EURO-Soils some other striking properties which are of less importance for the sorptive quality of the samples are briefly mentioned.

Although the Vertic Cambisol (E 1) is characterized by a low organic matter content and the clay minerals consist mainly in low-sorbing kaolinite, the CEC is remarkably high. Especially the content of expandable smectites and illites seem to be responsible for this phenomenon. Probably just a small amount of the organic matter forms complexes with clay minerals which in total exceeds the sorption capacity of the soil. Another striking aspect are the high values of SiO_2, Al_2O_3 and Fe_2O_3 (Hematite), the latter indicating intensive weathering at high temperatures under dry conditions. The values for calcium and potassium lie within the normal ranges for Cambisols under natural vegetation. The detected amount of nutrients in generally low which can be regarded as a proof for the fact that this soil is more or less natural and not agriculturally treated by liming or fertilizing (MADSEN, H., 1983).

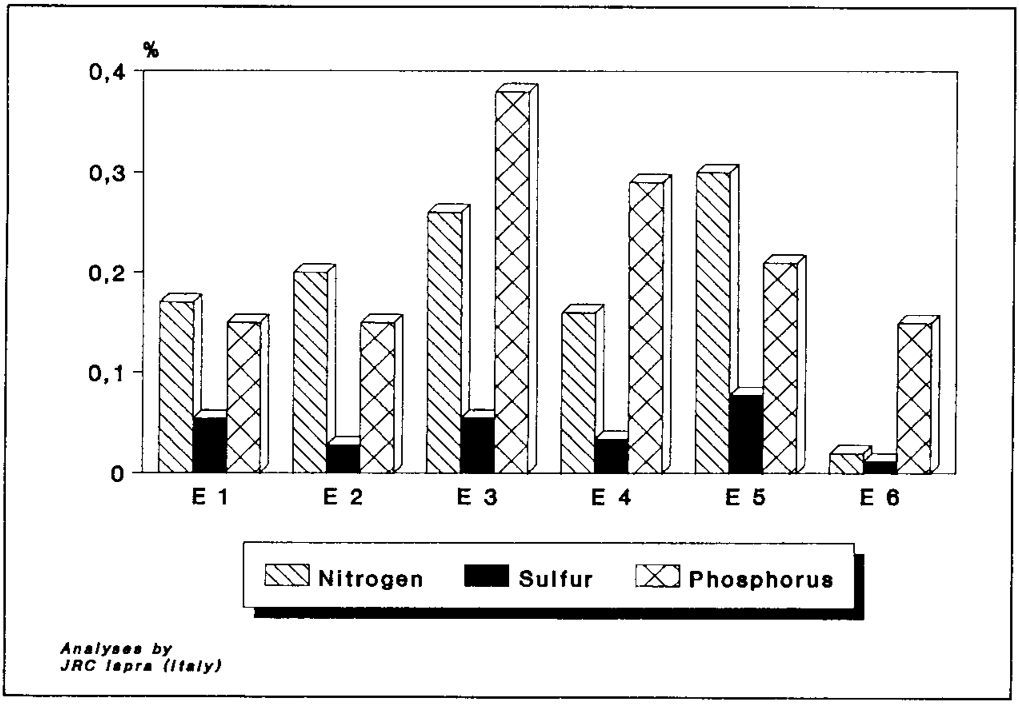

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Fig. 6: Composition of main nutrients in the EURO-Soils

Also the Rendzina (E 2) shows a relatively high cation exchange capacity which is caused by the combination of well humified organic matter and highly sorptive clay minerals. The extremely low SiO_2-content confirms the above mentioned fact that the parent material of this soil is calcium carbonate of high purity. Accordingly, the calcium content of this soil is more than sufficient. This also counts for phosphor and sulfur, because due to the high microbial activity in this soil litter and plant residues are continously degraded and nutrients are released.

It has already been mentioned that the Dystric Cambisol (E 3) in most cases shows average values with respect to its pedological parameters. This holds true also for the points not yet mentioned. Besides the high hematite content also the amount of about 68 per cent SiO_2 confirms the origin of the material. The Old-Red-Sandstone being eroded, transported and deposited by glacier action has an average SiO_2-content of 70 per cent. The relatively high phosphor content is clearly induced by fertilizing the grassland because under natural conditions Dystric Cambisols usually contain 0.02 - 0.08 per cent of this essential nutrient. Also the nitrogen content is higher than in agriculturally untreated soils of this kind while sulfur lies within the normal range.

The Orthic Luvisol (E 4) is characterized by a low cation exchange capacity which is not untypical for soils of this kind because either the organic matter or the clay content is relatively low. In addition, a considerable amount of clay-humus complexes might also reduce the CEC. Sufficient amounts of calcium, magnesium and potassium were detected which clearly is a consequence of liming and fertilizing. There are also enough phosphor and nitrogen in the topsoil whereas organic sulfur lies at a very low level.

The Orthic Podzol shows the highest cation exchange capacity amongst the complete set of EURO-Soils. Regarding the extremely low pH value, the low clay mineral content and the poor humification of the organic substance, the latter being indicated by a very high C/N-ratio, this fact seems to be unintelligible at first sight. However, the value is just slightly above those of the EURO-Soils 1 and 2 which does not contain this much of organic carbon. Apart from that the EURO-Soil 5 sample show the typical features of a soil being poor in nutrients and other components due to either an inhibited provision by weathering of primary particles and microbial transformation of organic matter or a translocation into deeper layers of the profile.

Assessment of the pedological data

Regarding the different pedological parameters of the EURO-Soils presented and interpreted above it can be underlined that the demand for considering wide ranges of pedological, particularly sorption-controlling properties can be regarded as being fully satisfied. Moreover, each individual soil sample represents typical properties of a broad set of European soils not only related to pedology but also to vegetation, climate, land-use and more. Very often the two extremes of the ranges are marked by EURO-Soil 5 on the hand and EURO-Soil 6 on the other but except EURO-Soil 4, which more or less marks the average in sorption capacities of all soils, at least once the other samples show highest or lowest values. For example, the Vertic Cambisol is characterized by the highest clay content and the best C/N-ratio, the outstanding features of the Rendzina are the high pH value and the low iron and aluminum content, the latter being highest in the Dystric Cambisol. The Orthic Podzol shows the lowest pH value but the highest content of sand and organic matter within the total set and the subsoil contains more silt but less organic carbon than any other EURO-Soil. Furthermore it has to be underlined that within the complete set of EURO-Soils there are often different pairs which show identical values for important sorption controlling properties (E 1 and E 3 for pH, E 3 and E 6 for clay, E 1 and E 4 as well as E 2 and E 3 for organic carbon, E 1 and E 2 as well as E 3 and E 4 for CEC), but sometimes totally differ with respect to other parameters. Apart from the fact that the reference soils selected are highly representative for the EC soil cover they perfectly meet the requirements for testing and interpreting the behaviour of new chemicals in the soil environment. A comparison of the results from shaking experiments with the various soil samples allows clear statements on the relevance of certain soil components for the quality and quantity of the chemicals' adsorption/desorption.

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DETERMINATION OF ORGANOCHLORINE COMPOUNDS

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Introduction

Trace contamination at remote sites by wide-range transported organochlorine (OC) pollutants is a very well documentated phenomenon.

Therefore, it was decided to analyse the concentrations of chlorinated pesticides, chlorobenzenes (CBz) and polychlorinated biphenyls (PCB) in the six European standard soils. Since the level of contamination was expected to be very low it was necessary to develop an efficient extraction method and trace enrichment procedure. The chemical clean-up of the extracts was optimized in order to eliminate interference from co-extracted non-target compounds. The resulting analytical method facilitated the study of the following compounds (abbrevation and analytical recovery in brackets):

Lindane (γ-HCH=86%, β-HCH=88%; α-HCH=93%; δ-HCH=88%), 4,4'-DDT (DDT=81%), 4,4'-DDD (DDD=89%), 4,4'-DDE (DDE=93%), Heptachlor (=95%), Dichlorobenzene (1,2-DBz=79%; 1,3-DBz=81%; 1,4-DBz=83%), Trichlorobenzene (1,2,3-TCBz=89%; 1,2,4-TCBz=91%; 1,3,5-TCBz=95%), Pentachlorobenzene (QCBz=92%), Hexachlorobenzene (HCBz=93%). Polychlorinated biphenyls (PCB-20=90%; PCB-28=90%; PCB-52=91%; PCB-101=89%; PCB-118=103%; PCB-138=91%; PCB-153=89%; PCB-180=92%).

Extraction and trace enrichment

All solvents were pesticide grade from Merck Ltd (Milano). Adsorbents were p.a. grade, rinsed in hexane and stored at 200 °C until used. Glasswere was cleaned according to EPA standards for dioxin analysis. Immediately before use glasswere was rinsed three times with acetone and once with petroleum ether.

The ground soil material was homogenized by 2 min hand-shaking and 30 g were weighed into a 50 ml centrifuge tube. Ca. 30 ml hexane-acetone (1+1) were added, stirred with a glass spatula, given ultrasound for 10 min and allowed to soak overnight (18 hrs). The ultrasonic treatment was repeated and the slurry was centrifuged at 4200 rpm for 10 min. The centrifugate was carefully removed by aspiration and transferred to a separatory funnel. This extraction step was repeated twice (without the intermediate 18 hrs soaking). The extracts were combined and acetone was removed by partitioning (three times) with equal amounts of distilled water. In order to ensure quantitative yields the water-acetone phase was re-extracted with hexane. The combined hexane phases were reduced to ca. 5 mL under vacuum (40 °C, 40psi) and cleaned-up on activated silica.

A glass column (25 cm x 1 cm, 60 ml solvent reservoir) was packed from the bottom with in turn: silanized glass-wool, 1 cm anhydrous sodium sulphate, 4 g silica (60-120 mesh), 4 g acidic silica (prepared by mixing 4 parts w/w of concentrated

(60-120 mesh), 4 g acidic silica (prepared by mixing 4 parts w/w of concentrated sulphuric acid with 6 parts of silica) and 1 cm anhydrous sodium sulphate. Before use this column was conditioned with 50 ml hexane.

The soil extract was transferred to the top of the column and eluted with 50 ml hexane (fraction 1) and 50 ml (1+1) hexane+dichloromethane (fraction 2). The second fraction contained Lindane with its metabolites, DDD and parts of DDT. The first fraction contained the other OC compounds mentioned in the introduction. Dodecane (1 μl) as keeper was added and the eluates were reduced separartely to ca. 10 ml under vacuum (40 °C,-40psi) and blown in to nearly dryness with a mild flow of nitrogen. The residues were taken up with 200 μl iso-octane including PCB imbracketing internal standards (Wells et al., 1985) shaken with 100 μl mercury for sulphur removal and analysed by gaschromatography (GC).

Analysis

Aliquots (0.5 μl) were split-less injected into a Dani 8520 GC equipped with an SPB-5 (60 m, 0.25 mm ID, 0.25 μm film) capillary colums and a ^{63}Ni ECD- The injector was temperature-programmed ballistically from 60 to 280 °C. The oven temperature was programmed at 90-180 °C with a 10 °C/min rise and then to 270 °C with a 1.5 C/min rise (for the analysis of fraction 2 the rise was 20 °C/min and 3.0 °C/min, respectively); the detector temperature was kept at 300 °C; helium was used as carrier gas (24 cm/s) and argon/methane (90/10) as make-up gas. The OC compounds were automatically identified and quantified by comparison to standards using a Chromstation-2 software (Spectra Physics, Milano, Italy) running on an IBM PS/2 personal computer. Calibrants were obtained from Supelco Ltd., Milano, Italy (pesticides and CBz) and from BCR, Bureau Communitaire de Reference-Bruxelles, (PCB).

The quality of analysis was controlled by analysis in parallel a blank (hexane rinsed silica) and a sludge sample certified for PCB contents (obtained from BCR). The analytical results were all clearly within the certified 95% confidential range.

Major peaks in the chromatograms of fraction 1 and 2 not matching standard were investigated by GC-MS analysis on a HP-MSD instrument (Hewlett Packard, Milano, Italy). The mass spectrometer was operated in the total ion mode. The sensitivity of this type of analysis (ng level) allowed the identification of only a few additional compounds, all long chain non-OC alifats (data not shown).

Data on soil organic carbon obtained from H. Muntau (personal communication) derived from measurements of the differential weight loss of water free samples at 550 °C and 1000 °C. These data compare favourably with soil organic carbon measurements presented in chapter 2, this issue.

Results and discussion

This method produced lean chromatograms with stable baselines free of interface (Fig. 1). The general concentration level of OC compounds was very low (ppt to ppb) indicating the lack of any major pollution sources (Table 1). Pesticide residues in agriculturally contaminated soils as well as CBz and PCB residues in surroundings of incinerators may easily reach hundred or thousand fold higher levels (Waid, 1986). Thus the six Eurosoils seem to represent regional background contamination levels with possible contributions from minor local sources).

Despite the very low each Eurosoil has its own contamination pattern reflecting the origin of the soil, as will be discussed in the following.

Apart from the source, the factors determining the soil residue of any compound are many such as chemical and biological persistency, water solubility, volability and ability of sorption to soil. For Eurosoil 1 and 2 coming from the Southern Italy and Greece a low precipitation and a strong sun may stress the importance of evaporation and chemical (photo-chemical) degradation, where as leaching with rain water may be an important parameter in the three northern soils. For the OC compounds in regard, taking their proved persistency into account the dominating parameter seems to be sorption to soil.

A linear relationship between soil sorption and soil organic matter/organic carbon has been demonstrated for a broad range of hydrophobic pollutants (Karichkhoff, 1981). This relationship has recently been confirmed for CBz and PCB (Paya-Perez et al., 1989). The relationship breaks down in soil with very little organic matter (Eurosoil 6) and other factors become decisive such as specific surface area, amorphous iron oxides and alumina oxides (Cortés et al., 1989). In order to evaluate the degree of exposure of different soils the concentration of OC pollutants normalized to soil organic carbon may be a better parameter than the absolute concentrations.

The concentration of OC pollutants in Eurosoil 1-5 calculated on organic carbon basis is shown in Table 2 together with the concentrations of organic carbon.

The data in Table 1 may indicated a higher DDT load to Eurosoil 2 and 3. However, the higher concentrations may also be explained by a stronger soil sorption as it appears from Table 2. The use of DDT in Europe was severly restricted in 1973 and totally banned in 1978). Nevertheless, the use may have been continued illegally as indicated by recent findings e.g. Greece (Larsen and Fytianos, 1988). The environmental half life-time of DDT from its degradation to DDD and DDE is estimated to be in the order of 10 years (Oliver et al., 1989). Thus, the ration of DDT/DDD+DDE today is expected to be in the order of 15-25%. None of the Eurosoils significantly exceed this ratio. Hence, the residue of -DDT in the Eurosoils must be concluded to represent regional background levels.

The use of Lindane is also severely restricted today. In its latest use Lindane was purchased as formulations with more than 90% of the active γ-isomer. Due to its higher water solubility and lower octanol-water partition coefficient γ-HCH is adsorbed to soil to a lesser degree than α-HCH and with the leapse of time the γ/α ratio is expected to decrease due to preferential wash-out of the γ-isomer. The concentration data of Table 1 supported by sorption data of Table 2 indicate a use of Lindane in the regions of Eurosoil 1 (Sicily) and Eurosoil 4 (Normandy). Based on the γ/α ratio the Italian use may be of older date, where as the French use seems to be recent. The sampling site of Eurosoil 4 in an agricultural area with heavy pesticide treatment of the fields (personal communication from local farmers) support this findings.

As opposed to DDT and Lindane which represent agricultural activity PCB and CBz derive from industrial sources (HCBz and QCBz has been used in very limited amounts as fungicides and TCBz may occur a minor by products in agricultural chemicals). A major source of wind-spread CBz and PCB is incinerators working at inadequately low temperatures. CBz are used in the industry as solvents and reactants from synthesis of a broad range of chemicals. PCB is mainly used as transformer liquids. From the latter half of the 1950s PCB production in European countries increased drastically and its peak was a the end of the 1960s (De Voogt, P. and Brinkman, U, 1989). After the discovery of a widespread environmental contamination in the 1970s, PCB production decreased, but significant quantities are still in use, primarily in older electric equipment. PCBs have been purchased as mixtures with variable chlorine content ranging from 20-60% by weight. In all European countries PCBs are used in pure forms under different names (Aroclors, Fenclors, Chlorphenes) except for Italy where PCBs are diluted with 50% of CBz with 1,2,4-TCBz as the dominating isomer. PCBs consist of 209 theoretically possible isomers and congeners with more than 100 represented in the commercial mixtures. Until recently no method existed for the isomer specific analysis of PCBs and scientists were obliged to compare bulks of non-separated compounds to commercial PCB mixtures. Since, the isomer pattern in the environment is very different from the pattern of commercial mixtures, analysis became inaccurate and difficult to reproduce. With the development of fused silica column capillary GC has become a routine method, and all the virtually impossible task of including all 209 PCBs in routine analysis, another strategy focusing on 6-9 selected PCBs has been recommended by the legislation in many countries. The 6-9 PCBs have been selected based on their toxicity and occurrence in the environment, animals and man. In the present study we have measured this group of PCBs. There is no correct way of extrapolating from the concentrations of these 6-9 PCBs to the total concentration of all 209 PCBs. The assumption used here that they account for 40% w/w of all PCBs gives a conservative estimate of the total PCB content.

In Tables 1 and 2 it appears that Eurosoils 1 has experienced a higher PCB and CBz exposure. The ration of Σ-CBz to total PCB of 40/60 in this italian soil compares favourably with the same ration in the Italian commercial PCB mixture, Askarel.

Eurosoil 2-4 seem to be equally exposed. Their level nmay be taken as a European background level in industrialized zones. Eurosoil 5 contains more CBz than Eurosoil 2-4, but this fact may be explained by the stronger adsorption in this forest soil rich in organic carbon.

Conclusion

All six European soils are contaminated at trace levels (ppt-ppb) with organochlorine pollutants coming probably from long-range air transport. Some soils show signs of the presence of local sources. The Italian Eurosoil 1 indicates exposure to Lindane and the commercial transformer liquid, Askarel. The Greek and British Eurosoil 2 and 3 may have elevated -DDT concentrations. The French Eurosoil 4 seems to have been exposed recently to Lindane. The German Eurosoil 5 with its strong sorption ability have slightly increased CBz concentrations. The French Eurosoil 6 coming from a deeper horizon of the same sampling site as Eurosoil 4 has the lowest concentration of all studied OC pollutants.

Acknowledgments

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TABLE 1

Concentrations* (μg/kg d.m.) of organochlorine pesticides, chlorobenzenes and PCB congeners in six european soils.

	EUsoil 1	EUsoil 2	EUsoil 3	EUsoil 4	EUsoil 5	EUsoil 6
p,p'-DDT	0.11	0.13	0.08	0.03	0.05	0.05
p,p'-DDD	0.06	0.09	0.12	0.02	0.06	0.01
p,p'-DDE	0.25	1.36	0.98	0.10	0.24	0.04
Σ-DDT	**0.41**	**1.58**	**1.18**	**0.15**	**0.35**	**0.10**
pp-HCH	1.25	0.17	0.32	2.24	0.23	0.08
pp-HCH	1.59	0.13	0.16	0.12	0.14	0.09
Σ-Lindane	**2.84**	**0.30**	**0.48**	**2.36**	**0.37**	**0.17**
1,2,3-TCBz	0.78	0.30	0.07	0.05	0.32	0.01
1,2,4-TCBz	2.04	0.44	0.27	0.24	1.04	0.02
1,3,5-TCBz	0.19	0.03	0.02	0.14	0.05	0.01
QCBz	0.73	0.15	0.23	0.05	0.25	0.03
HCBz	0.68	0.07	0.15	0.09	0.15	0.02
Σ-CBz	**4.42**	**0.99**	**0.74**	**0.57**	**1.81**	**0.09**
PCB-20	0.19	0.17	0.10	0.09	0.13	0.07
PCB-28	0.30	0.42	0.21	0.13	0.18	0.06
PCB-52	0.53	0.23	0.26	0.10	0.20	0.08
PCB-101	0.39	0.22	0.26	0.13	0.18	0.07
PCB-118	0.28	0.18	0.26	0.16	0.18	0.11
PCB-138	0.37	0.24	0.47	0.26	0.22	0.14
PCB-153	0.40	0.26	0.44	0.25	0.24	0.12
PCB-180	0.12	0.07	0.20	0.08	0.07	0.04
TOTAL-PCB	**6.5**	**4.5**	**5.5**	**3.0**	**3.5**	**1.7**

* One replicate only. CV at this trace level normally 10-20%

** Estimation based on the conservative assumption that the measured PCBs account for 40% of all occuring congeners

TABLE 2

Concentrations (μg/kg organic carbon) or organochlorine pesticides, chlorobenzenes and PCB congeners in five european soils.

	EUsoil 1	EUsoil 2	EUsoil 3	EUsoil 4	EUsoil 5
Organic carbon	1.3%	3.7%	3.5%	1.6%	10.3%
Σ-DDT	32	43	34	10	3
Σ-Lindane	218	8	14	152	4
Σ-CBz	340	27	21	36	18
TOTAL-PCB	500	122	159	194	34

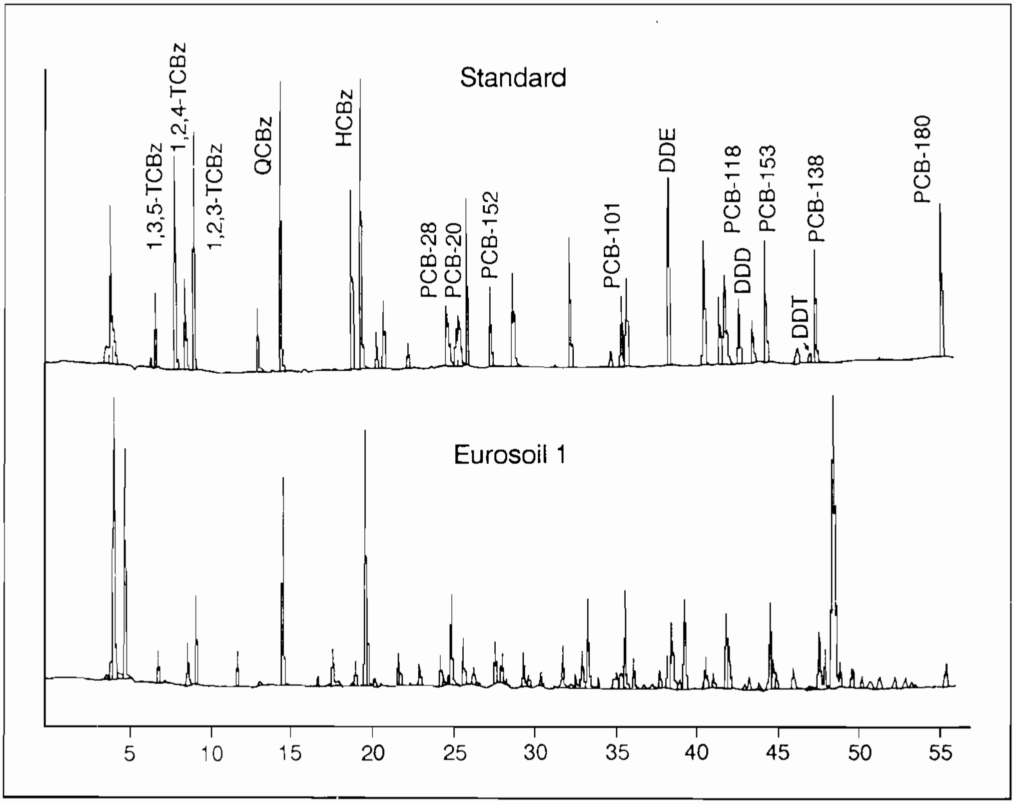

Fig. 1 Chromatograms of a standard mixture and 1st fraction of the cleaned-up extract from Eurosoil 1.

EVALUATION OF THE EEC LABORATORY RINGTEST "ADSORPTION/DESORPTION OF CHEMICALS IN SOIL"

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1. Abstract

This intercomparison-test of the revised guideline on adsorption/ desorption was initiated by the Commission revising the OECD-Guideline 106. For purposes of ring-testing a modified version of the Guideline on adsorption/desorption was checked with respect to its feasibility.

27 laboratories from EC member countries performed the test with all or a part of the offered soils and substances. The results and first conclusions concerning the reproducibility and validity of the adsorption/desorption studies were discussed between the participants on 3.-4.12.1991 at JRC Ispra. The results are reported.

2. Introduction

Adsorption/desorption data are necessary for the evaluation of the mobility of chemicals within soils or sediments and their migratory tendency e.g. to air or water. They are necessary to estimate e.g. leaching from soil to groundwater, concentration in seepage waters or run-off from land surface to natural water bodies. Besides their influence on transport processes within soils (mass flow) adsorption processes also affect bioavailability by reducing the concentration of chemicals in aqueous solution.

Soils have varying adsorption capacities in relation to their content of organic matter, clay and metal oxides as well as pH and redox potential. The very complex interactions of all these parameters with a chemical in soil solution cannot be completely defined by a simple testing scheme. Nevertheless the pedologic properties of test soil(s) are to be varied broadly enough to reveal their influence on sorption behaviour of the chemical. Furthermore the resulting distribution between the adsorbed and solution phase depends upon environmental parameters such as temperature, the ratio of soil to water and ionic strength.

The present test method starts with a simple screening step on the sorption behaviour of the chemical. When warranted, more extensive testing can be performed to more accurately define the effect of a specific soil or one single environmental parameter.

The experimental procedure measures the decrease in concentration when aqueous solutions of a test chemical are in contact with various types of soil samples at room temperature.

A $CaCl_2$-solution (0,01 m) is used as the aqueous solvent phase to improve separation during centrifugation and simulate ionic strength of soil water - but in some cases adsorption will be influenced. This is the case especially for polar or ionic chemicals like 2,4-D.

3. Test Sequence

The ring-testing was performed according to the flow chart (Fig. 1) and includes the following steps.

3.1 Set up of a suitable analytical method

The method first establishes that a suitable analytical procedure is available (preliminary test) as a prerequisite for proceeding to the following steps of the test flow scheme.

3.2 Measurement of Adsorption Kinetics

For measuring adsorption kinetics three topsoils were used. As the sorption behaviour of Gray-brown Podzolic Soils and Rendzinas as well as that of Acid Brown Forest Soils and Brown Mediterranean Soils are quite similar, it was proposed to use one out of each of the above described soil pairs optionally and the Podzolic soil mandatorily.

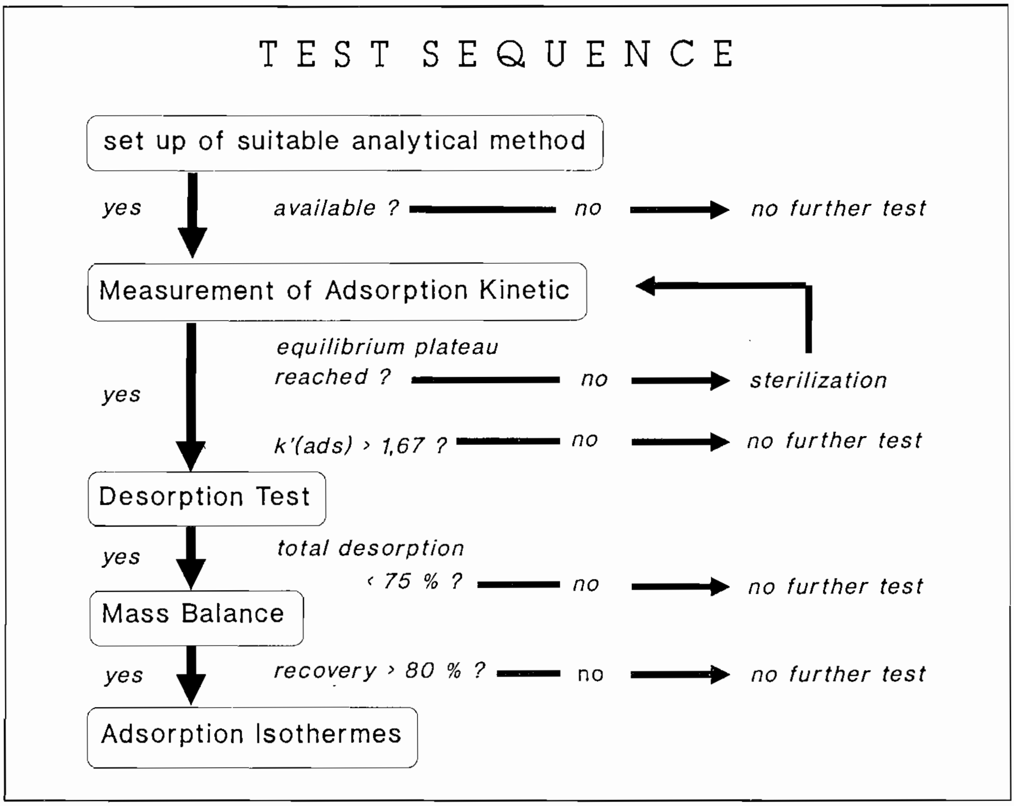


Fig. 1. Flow chart of ring-testing

If no adsorption equilibrium was obtained, that means no plateau value was reached in plotting concentration of the test chemical in solution versus equilibration time, the soil sample should be tested again after sterilization. Testing proceeds only with that (those) soil sample(s) which have reached a plateau value for equilibrium.

3.3 Desorption Test

If a K'-value of > 1,67 will be observed (corresponding to > 25 % ob adsorbed test chemical at a soil/solution ration of 1/5) a two step desorption test will be performed in order to check, if the chemical is reversibly or irreversibly fixed by the soil sample.

If the test substance is readily desorbed (a total of > 75 % from the two step desorption) no further tests are necessary. Otherwise the flow scheme proceeds to determination of the mass balance.

3.4 Mass Balance

It will be tested by extraction with a suitable organic solvent (preferably one which is completely miscible with water), if the used test substance can be recovered to a minimum of 80 % (amount of extracted test substance + amount in equilibrium solution).

3.5 Adsorption Isotherms

For those test substances which:-show K' (Adsorption) > 1.67 (25 % adsorbed at soil/solution 1/5)

-show a total desorption of < 75 %

-can be recovered to > 80 % in the mass balance study

further testing is required by varying the concentration range of the test chemical solution at a larger scale. It will be checked if a logarithmic plot of soil equilibrium concentration [g/g] versus aqueous phase concentration yields a straight line (= fits FREUNDLICH isotherm).

An extended description of the test performance is given in the Guideline for testing of Chemicals 'Adsorption/Desorption'.

4. Material and methods

4.1 Soil selection

For this ringtest 6 soils including one sub-soil were selected by Dr. Kuhnt, University Kiel from different soil types which vary considerably in their sorption relevant physico-chemical properties, e.g. organic carbon content, pH, clay content and content of metal oxides.

Soil 1: VERTIC CAMBISOL
Soil 2: RENDZINA
Soil 3: DYSTRIC CAMBISOL
Soil 4: ORTHIC LUVISOL
Soil 5: ORTHIC PODZOL
Soil 6: Sub-horizon from soil 4.

All selected soil samples are common in temperate zones, but are not representative for arid or tropical regions. The may also be used for further testing designed to study behaviour in sediments.

Tab. 1a-c contain the results of the soil characterization of the soils included in the ring-test (see next pages).

Table 1a: Pedological characterization of soil samples

Pedologic.parameter	soil 1	soil 2	soil 3	soil 4	soil 5	soil 6
SAND total[%]	3.31	3.4	46.4	4.1	81.6	1.7
coarse + medium[%]	2.0	4.4	23.1	1.1	64.8	0.3
fine[%]	1.3	9.0	23.3	3.01	6.8	1.4
SILT total[%]	21.9	64.1	36.8	75.7	12.6	82.4
coarse[%]	4.0	21.3	19.4	52.2	7.4	62.5
medium[%]	9.7	23.1	11.6	19.4	4.3	17.3
fine[%]	8.2	19.7	5.8	4.1	1.0	2.6
CLAY total[%]	75.0	22.6	17.0	20.3	6.0	16.0
pH values						
water	5.9	8.0	5.8	7.0	4.6	8.3
$CaCl_2$	5.1	7.4	5.2	6.5	3.2	7.2
NaCl	5.1	7.5	5.2	6.5	3.4	7.1
total carbon[%]	1.5	10.9	3.7	1.7	10.9	0.3
$CaCO_3$[%]	0.0	60.45	0.0	0.0	0.0	0.0
organic carbon[%]	1.30	3.70	3.45	1.55	9.25	0.25
organic matter[%]	2.65	6.4*	6.45	2.85	15.90	0.80
N[%]	0.17	0.20	0.26	0.16	0.30	0.02
C/N ratio	7.65	18.50	13.27	9.69	30.77	12.50
org. S[%]	0.05	0.028	0.06	0.03	0.078	0.012
P total[%]	0.15	0.15	0.38	0.29	0.21	0.15
SiO_2[%]	56.22	21.60	68.45	68.63	71.57	68.56
Al_2O_3[%]	23.92	8.66	11.92	12.07	3.85	12.64
CaO[%]	0.41	30.62	0.20	0.71	<0.02	0.59
K_2O[%]	1.85	1.27	1.59	1.84	0.63	1.71
Fe_2O_3[%]	10.76	1.66	4.14	2.71	<0.05	2.83
MgO[%]	1.12	1.82	1.19	1.11	0.65	1.16
TiO_2[%]	0.99	0.25	0.65	0.72	0.36	0.72
C E C [mval/100 g]	29.9	28.3	18.3	17.5	32.7	11.4
Fe total[mg/kg]	37.05	9.85	14.37	11.50	1.04	12.44
Fe amorphous [mg/kg]	3.22	0.18	4.75	1.93	0.56	0.73
Fe HCl-sol.[mg/kg]	1.82	0.002	2.20	1.47	0.105	1.14
Al amorphous[mg/kg]	0.64	0.17	1.58	0.81	0.97	0.56
Al HCl-sol.[mg/kg]	0.83	traces	1.67	1.55	0.93	1.56

* = calculated from Corg by Corg = O.C. x 1.7

Table 1b: Mineralogical composition of soil samples and parent material (values in [%])

	MI	Sm	Cl	Verm	Il	K	Q	F
Soil 1								
clay	--	15	--	--	25	55	++	--
fine silt	--	++	--	--	10	10	60	10
parent clay	++	15	--	--	25	55	++	10
SOIL 2								
clay	--	30	10	--	40	10	++	--
fine silt	--	--	10	--	30	10	++	--
parent clay	--	35	5	--	50	5	++	++
SOIL 3								
clay	--	--	20	10	40	20	++	--
fine silt	--	--	10	--	20	++	50	10
parent clay	--	--	10	10	65	10	++	++
SOIL 4								
clay	--	++	++	20	60	15	++	--
fine silt	--	--	--	10	20	--	55	15
parent clay	--	12	--	35	33	10	++	++
SOIL 5								
clay	--	++	--	--	20	10	70	--
fine silt	--	--	--	--	10	--	80	10
parent clay	--	9	43	--	35	13	++	++
SOIL 6								
clay	++	++	--	30	40	< 20	++	--
fine silt	--	--	--	15	25	--	40	20

Abbreviations

F= Feldspars
++ = traces
Verm = Vermiculites
Q =Quartz
Sm= mineral Smectites
-- = not detected
K = Kaolinites
Il =Illites
MI= mixel layer
Cl =Chlorites and minerals pedological chlorites

Table 1c: Major element composition of reference soil samples (values in [ppm])

ELEMENT	soil 1	soil 2	soil 3	soil 4	soil 5	soil 6
Mn	286.8	541.4	981.7	578.5	39.6	408.7
Cu	23.0	21.2	20.9	14.5	8.0	10.9
Ca	2590.0	87180.0	1860.0	4670.0	410.0	4040.0
K	13990.0	6220.0	6790.0	5580.0	380.0	5450.0
Na	400.0	490.0	320.0	300.0	130.0	180.0
Mg	5300.0	3550.0	2650.0	2290.0	120.0	2640.0
Zn	132.9	38.5	128.6	48.1	14.8	41.0
Cd	2.7	0.4	0.8	0.5	0.0	0.5
Pb	31.7	28.5	61.6	30.7	34.7	19.1
Ni	41.6	50.6	21.6	40.1	1.9	23.0
Cr	118.7	64.4	51.1	71.9	7.4	75.9
Sn	19.7	19.9	18.0	19.0	17.5	18.7
Ti	118.4	159.9	210.5	205.0	188.9	301.1
B	1700.9	1699.2	1128.8	1593.5	1728.6	1433.4
Sr	92.4	349.9	30.0	33.2	6.4	33.2
Mo	5.7	4.0	4.8	5.2	4.8	3.5
Co	22.0	12.9	12.4	12.1	6.3	10.8
Be	3.0	1.1	1.2	1.2	0.7	1.2
Ba	80.4	65.5	73.7	69.0	46.9	58.7
Li	51.0	13.1	18.1	16.9	0.0	18.0

4.2 Soil preparation

The OECD Guideline 106 gives a recommendation of running the tests using sieved soil to be less than or equal to 2 [mm]. No further comment is given for the procedure of providing these material, e.g. on the intensity of shearing lumps through sieving meshs.

Following the request for representing the wide spectrum of different soil types within the Community the test soils however show marked differences in their particle size distribution pattern as well as in their tendency for generating aggregates during the preparation steps (e.g. drying). Thus the preparation technique of the soil samples is of critical importance for several reasons.

Inhomogenous material in different bottles (inter bottle variance) on one side and inhomogenous portioning from weighing several sub-samples out of one bottle (intra bottle variance) may cause high variances in respect to sorption sites.

By crushing the aggregates to powder problems of inhomogenous sampling can be avoided. On the other side particullary intensive grinding modes provide an artificial material which no longer resembles the properties of the original soil.

The conflict between these two contrary aspects cannot be resolved but has to be balanced carefully. For purposes of the ring test the "inter"- and "intra-bottle" variances were investigated on the full set of test soils which had been prepared by different techniques ("no grinding", "slight grinding" and homogenization"). The adsorption properties were quantified respectively by determining the k'-values of Atrazine of each of the samples. The results are summarized in the table 2a, 2b, 2c :

Table 2a: Comparison of soil preparation techniques (k'values for ATRAZINE)

	ground		homogen.	sieved	
	intra-bottle	inter-bottle		intra-bottle	inter-bottle
SOIL 1	8.23	8.40	7.70	7.75	7.49
SOIL 2	2.55	2.33	2.33	2.89	2.98
SOIL 3	2.69	2.66	3.00	2.93	3.10
SOIL 4	1.02	0.92	0.61	0.73	0.75
SOIL 5	45.8	45.1	59.6	37.1	37.4
SOIL 6	0.09	0.22	0.11	0.26	0.28

soil 1 = Vertic Cambisol
soil 2 = Rendzina
soil 3 = Dystric Cambisol
soil 4 = Orthic Luvisol
soil 5 = Orthic Podzol
soil 6 = soil 4 sub-horizon

Table 2b: Soil samples sieved [2 mm] “without grinding”

Soil - Type	Intra-bottle		Inter-bottle	
	k’	s [%]	k’	s [%]
Vertic Cambisol	7.75	1.96	7.49	2.16
Rendzina	2.89	3.34	2.98	5.75
Dystric Cambisol	2.93	2.38	3.10	1.75
Orthic Luvisol	0.73	7.32	0.75	6.00
Orthic Podzol	37.1	3.35	37.4	2.03
Sub soil	0.26	10.8	0.28	28.1

TEST CONDITIONS:

5 [g] soil per 25 [ml] test solution
test substance ATRAZINE / conc. 5 [mg/l]
agitation period: 16 [h]; re-equilibration: 6 [h]

Table 2c: Soil samples sieved [2 mm] "with slight grinding"

Soil-Type	Intra-bottle		Inter-bottle	
	k’	s [%]	k’	s [%]
Vertic Cambisol	8.23	2.07	8.40	1.75
Rendzina	2.55	2.73	2.33	5.07
Dystric Cambisol	2.69	4.70	2.66	8.04
Orthic Luvisol	1.02	3.15	0.92	6.89
Orthic Podzol	45.77	5.16	45.09	4.29
Sub soil	0.09	65.2	0.22	47.4

TEST CONDITIONS:

5 [g] soil per 25 [ml] test solution
test substance ATRAZINE / conc. 5 [mg/l]
agitation period: 16 [h] / re-equilibration: 6 [h]

The results show that there is actually no difference between the sorption capacities of grinded soil samples and non-grinded ones. On the other hand the application of strong crushing forces (e.g. hammer mills) to provide "homogenized" samples results at least for some soil types in a marked change of sorption capacity (e.g. soil 5, soil 6).

For purposes of the ring test all participating laboratories were provided with slightly grounded soil samples from one common source, respectively. The preparation of the 6 soils selected for the test was performed by Dr. Muntau, Ispra. The air dried soils were grounded and sieved to obtain a fraction < 2 mm. The soil were sterilized by means of Gamma-Radiation.

The interspecific variance (in respect to sorption sites) between material from different bottles as well as the intraspecific variance due to inhomogenity from weighing several sub-samples out one bottle are verified (Tab. 2a, 2b, 2c).

So it was guaranteed that all participants of the test were provided with the same quality of soil samples. Differences in the measured values only results from the variation in the test performance by the laboratories.

4.3 Substances used in the test

For purposes of ring-testing the revised version of the guideline on adsorption/desorption the following three chemicals had been selected as test substances:

- Gamma-hexachlorocyclo hexane ("LINDANE")
- 2-Chloro-4-ethylamino-6-methylethylamin-s-triazine ("ATRAZINE")
- 2,4-Dichlorophenoxy acetic acid ("2,4-D")

for the following reasons:

- the properties (incl. information on the adsorption/desorption behaviour) are well documented in the literature.
- the selected compounds are considered as sufficiently stable to biotic or hydrolytical degradation during the testing period.
- the physical and chemical properties of the test compounds cover a range of parameters which are looked upon as the most relevant for adsorption/desorption behaviour. Lindane exhibits a high affinity to the organic matter of the soil matrix ($\log P_{ow} = 3.7$). Atrazine with its two secondary amine moieties represents a moderate pH-dependancy, while 2,4-D stands for anionic structures ($pK_a = 3.6$) with considerable water solubility.
- for the selected test chemicals suitable and highly sensitive analytical procedures for detection of even small amounts are documented (e.g. GLC with ECD detection). They can be commercially purchased in their ^{14}C-radiolabelled form.

Table 3: Physical and chemical data of the test compounds

PROPERTY	LINDANE	ATRAZINE	2,4-D
molec. mass [g/Mol]	290.8	215.7	221.0
water solub. [mg/l]	8	70	600
log P_{ow}	3.7	2.3	0.1
vapour pressure [Pa]	$1.3 \quad 10^{-3}$	$4.0 \cdot 10^{-5}$	$<1.0 \cdot 10^{-5}$

The selected test compounds are not very volatile and are soluble in water to at least ~ 10 mg/l. Therefore detection limits from solubility problems were not expected.

Biotic and abiotic degradation processes were considered as negligible for duration of the testing period.

5. Evaluation of the test adsorption/desorption

5.1 Adsorption

Adsorption in the present method does not distinguish between different adsorption processes (physical and chemical adsorption) and such processes as surface catalysed degradation, bulk adsorption or chemical reaction.

Adsorption (A) is defined as the percentage of the quantity of the substance adsorbed on the soil related to the quantity present at the beginning of the test, under the test conditions.

$$\boxed{A = \frac{G_{ASoil} \cdot 100}{Go} \quad (\%)} \qquad \text{(equ. 1)}$$

where:

G_{ASoil} = mass of the test substance adsorbed on the soil after the adsorption test (g)

G_o = mass of the test substance in the test tube, at the beginning of the adsorption test (g)

The adsorption coefficient K' is the ratio between the concentration of the substance in the soil phase and the concentration of the substance in the aqueous solution, under the test conditions, when adsorption equilibrium is reached.

$$K' = \frac{G_{ASoil}}{C_{AW}} \qquad \text{(equ. 2)}$$

where:

C_{ASoil} = concentration of the substance in the soil, at the end of the adsorption test ($g_{substance} \cdot g_{soil}^{-1}$)

C_{AW} = concentration of the substance in the aqueous phase, after the adsorption test ($g_{substance} \cdot ml_{solution}^{-1}$)

The relation between A and K' is given by:

$$K' = \frac{A}{100 - A} \cdot \frac{V_W}{E} \qquad \text{(equ. 3)}$$

where:

V_W = volume of the aqueous phase (ml) (volume of added solution + volume of water in the soil)

E = quantity of the soil phase (g) (expressed in dry weight at 105 °C)

$\frac{E}{V_W}$ = soil / solution ratio V_W

The adsorption coefficient K'_{oc} relates the adsorption coefficient K' to the content of organic carbon of the soil sample:

$$K'_{oc} = K' \cdot \frac{100}{\%\ OC} \qquad \text{(equ. 4)}$$

where: % OC = percentage of organic carbon in the soil sample

$$K'_{oc} \text{ is expressed in } \frac{\text{g adsorbed/g organic carbon}}{\text{g/ml solution}}$$

K'_{oc} is not a useful parameter for very polar or ionic compounds. It also depends on the specific characteristics of the humic fractions which differ considerably in their sorption capacity, due to differences in origin, genesis etc.

5.2 Desorption

Desorption D is defined as the percentage of test substance which is desorbed, related to the quantity of substance previously adsorbed, under the test conditions.

$$\boxed{D = \frac{G_{DSoil}}{G_{ASoil}} \cdot 100(\%)} \qquad \text{(equ. 5)}$$

where:

G_{DSoil} = mass of the test substance desorbed from soil after the desorption test (g)

5.3 Mass balance

The mass balance MB is defined as the percentage of substance which can be analytically recovered after an adsorption and desorption test including desorption with a suitable organic solvent versus the nominal amount of substance at the beginning of the test.

$$\boxed{MB = \frac{\text{substance in the aqueous phase} + \text{substance extracted}}{\text{substance at the beginning of the test}} \times 100}$$

5.4 Adsorption isotherms

The Freundlich adsorption isotherms equation relates the amount of the test substance adsorbed to the concentration of the test substance in solution at equilibrium:

$$\boxed{y/m = K_F \cdot C^{1/n}} \qquad \text{(equ. 6)}$$

where:

y/m = g of adsorbed substance per g of soil ($g_{substance} \cdot g_{soil}^{-1}$)
C = equilibrium concentration in the aqueous phase ($g_{substance} \cdot ml_{solution}^{-1}$)
$1/n$ = constant
K_F = constant

6. Performed investigations

27 laboratories participated in the ring-test. The detailed addresses are given in appendix I. The following investigations were carried out concerning sorption test from the laboratories.

Table 4a: Adsorption Kinetics

	Lindane		Atrazine		2,4-D	
	labelled	non-lab.	labelled	non-lab.	labelled	non-lab.
Soil 1	4	4	7	9	5	3
Soil 2	4	3	6	5	5	2
Soil 3	5	5	7	8	5	3
Soil 4	6	6	12	9	7	2
Soil 5	7	6	14	10	9	3
Soil 6	6	3	8	7	5	2

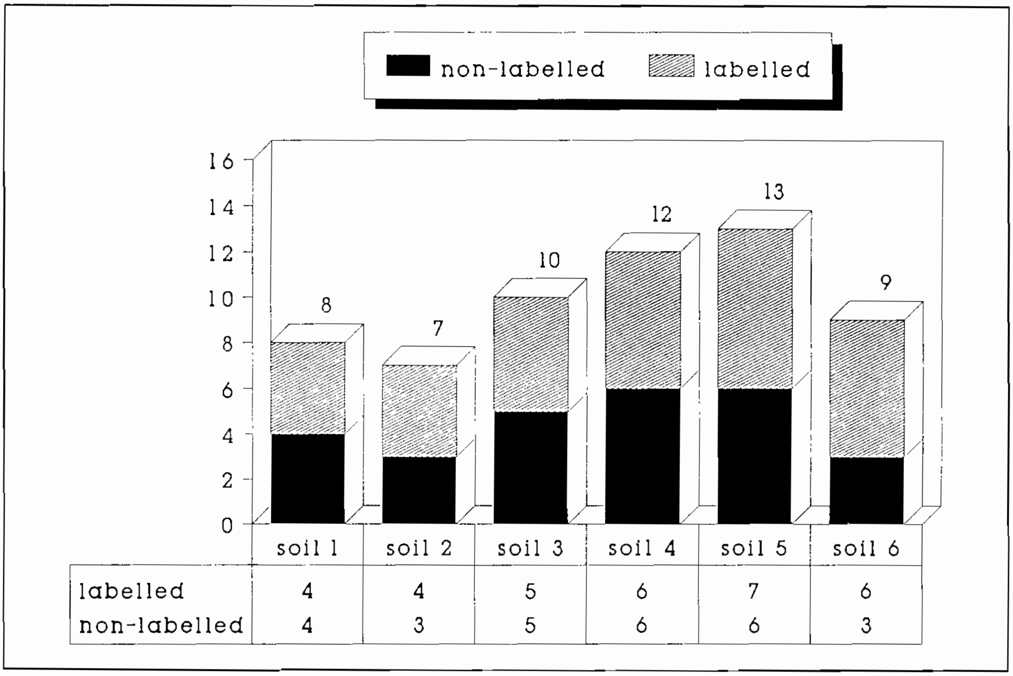
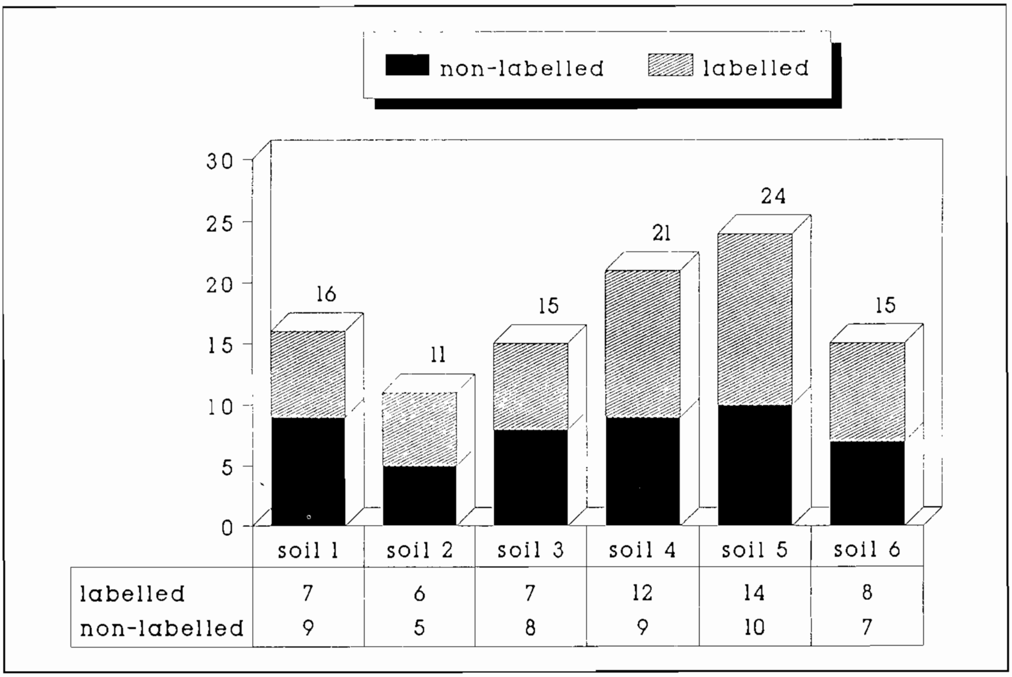
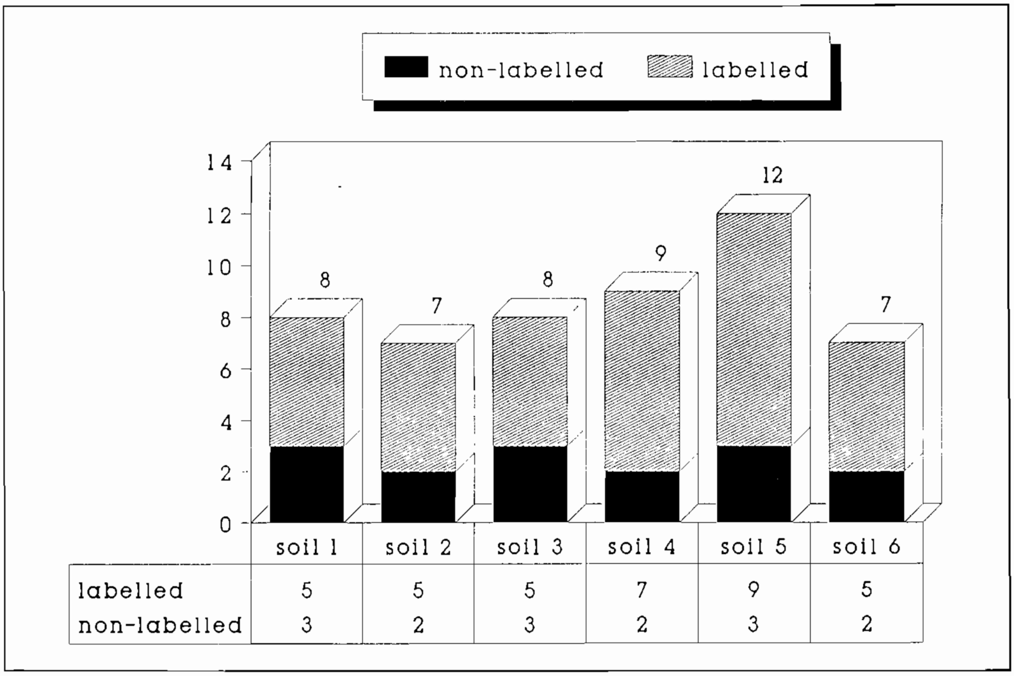


Fig. 2a: Adsorption Kinetics for LINDANE



	soil 1	soil 2	soil 3	soil 4	soil 5	soil 6
labelled	7	6	7	12	14	8
non-labelled	9	5	8	9	10	7

Fig 2b: Adsorption Kinetics for ATRAZINE



	soil 1	soil 2	soil 3	soil 4	soil 5	soil 6
labelled	5	5	5	7	9	5
non-labelled	3	2	3	2	3	2

Fig 2c: Adsorption Kinetics for 2,4 - D

Table 4b: Adsorption Isotherms

	Lindane		Atrazine		2,4-D	
	labelled	non-lab.	labelled	non-lab.	labelled	non-lab.
Soil 1	1	2	5	6	2	2
Soil 2	2	1	2	3	1	1
Soil 3	3	3	5	6	1	2
Soil 4	3	4	2	4	2	1
Soil 5	4	4	9	6	5	2
Soil 6	1	1	3	2	2	1

Table 4c: Mass Balance

	Lindane		Atrazine		2,4-D	
	labelled	non-lab.	labelled	non-lab.	labelled	non-lab.
Soil 1	1	3	6	6	2	1
Soil 2	2	2	1	1	0	0
Soil 3	4	4	5	4	0	1
Soil 4	5	4	1	1	1	0
Soil 5	5	4	11	6	6	1
Soil 6	0	2	0	0	0	0

Table 4d: Desorption

	Lindane		Atrazine		2,4-D	
	labelled	non-lab.	labelled	non-lab.	labelled	non-lab.
Soil 1	1	3	6	8	4	1
Soil 2	2	2	4	2	1	0
Soil 3	4	4	9	6	1	2
Soil 4	5	5	2	2	2	0
Soil 5	5	5	11	9	6	2
Soil 6	1	2	2	1	1	0

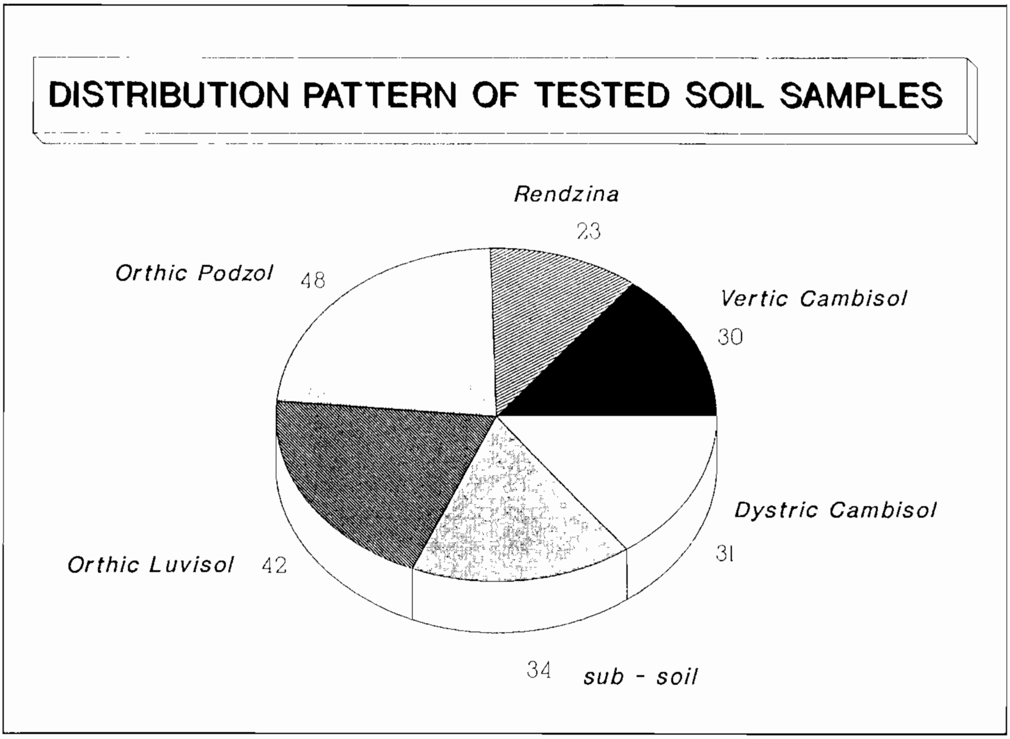


Fig 3: Numbers of soils tested for k'

Only a minority of participating laboratories performed the whole test programme including all soils, substances and steps of the protocol. No distinctive preference for any of the soil types could be observed (Fig. 3)

7. Results and Discussion

Most of the sorption coefficients (given in table 3-5 and 9) are taken from the original data of the participants. The data were checked and some sorption coefficients had to be calculated. Outliers not included in the calculation of the mean values were identified using the Dixon test (1953).

7.1 Sorption Kinetics

7.1.1 Lindane

Table 5: Comparison of the distribution coefficients of Lindane after 16 hours. The results of each participant performing the test are compared for soil 1 - 6 as well labelled and non-labelled.

		Soil 1	**Lindane**		
labelled			non-labelled		
No.	c	K'(16h)	No.	c	K'(16h)
2	5.01	33.4	1	5.45	38.1
6	5	37.28	8	4.39	35.53
12	3.5	35.251	10	5	21.9
27	5.0	41.3	17	3.8	41.1
mean:		36.81	mean:		34.16
standard deviation:	3.39		standard deviation:	8.48	
% S.D. of mean:		9.2	% S.D. of mean:		24.8

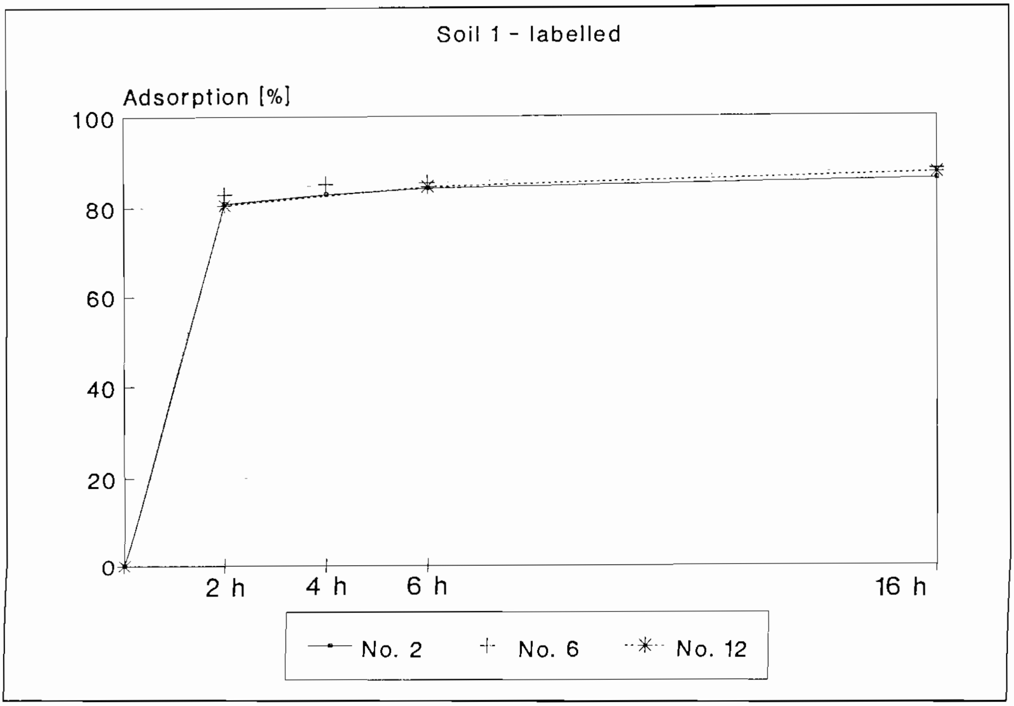
		Soil 2	**Lindane**		
labelled			non-labelled		
No.	c	K'(16h)	No.	c	K'(16h)
2	5.01	39.8	1	5.45	41.6
6	5	42.12	10	5	1.615
12	3.5	41.711	17	3.8	43.6
27	5.0	37.8			
mean:		40.36	mean:		
standard deviation:	1.98		standard deviation:		
% S.D. of mean:		4.9	% S.D. of mean:		

		Soil 3	**Lindane**		
labelled			non-labelled		
No.	c	K'(16h)	No.	c	K'(16h)
6	5	47.18	1	5.45	45.5
9	4.98	43.6	8	4.39	45.8
12	3.5	37.372	10	5	5.15
13	4.97	41.6	17	3.796	36.6
27	5.0	42.8	22	4.6	18.2
mean:		42.51	mean:		30.25
standard deviation:	3.55		standard deviation:	17.96	
% S.D. of mean:		8.4	% S.D. of mean:		59.4

Soil 4 Lindane					
labelled			non-labelled		
No.	c	K'(16h)	No.	c	K'(16h)
6	5	11.75	1	5.45	12.9
9	4.98	11.9	8	4.39	11.19
12	3.5	9.115	10	5	14.85
13	4.97	10.7	15	4.667	11.5
16	5	12.05	17	3.796	9.3
19	5	11	22	4.5	3.7 *
mean:		11.09	mean:		11.95
standard deviation:	1.10		standard deviation:	2.07	
% S.D. of mean:		9.9	% S.D. of mean:		17.3

Soil 5 Lindane					
labelled			non-labelled		
No.	c	K'(16h)	No.	c	K'(16h)
2	5.01	39.8	1	5.45	231
6	5	42.12	8	4.39	98.08
9	4.98		10	5	3.56
12	3.5	248.036	15	4.667	293.5
13	4.95	280	17	3.796	297
16	5	223.2	22	4.6	83.3
19	5	257			
mean:		234.57	mean:		167.74
standard deviation:	27.80		standard deviation:	122.85	
% S.D. of mean:		11	% S.D. of mean:		73.2

Soil 6 Lindane					
labelled			non-labelled		
No.	c	K'(16h)	No.	c	K'(16h)
6	5	0.45	8	4.39	0.52
12	3.5	0.617			
13	4.97	0.39	15	4.667	0.5
16	5	0.4			
19	5	0.34	22	4.4	0.48
mean:		0.44	mean:		0.52
standard deviation:	0.11		standard deviation:	0.02	
% S.D. of mean:		25.0	% S.D. of mean:		4.0



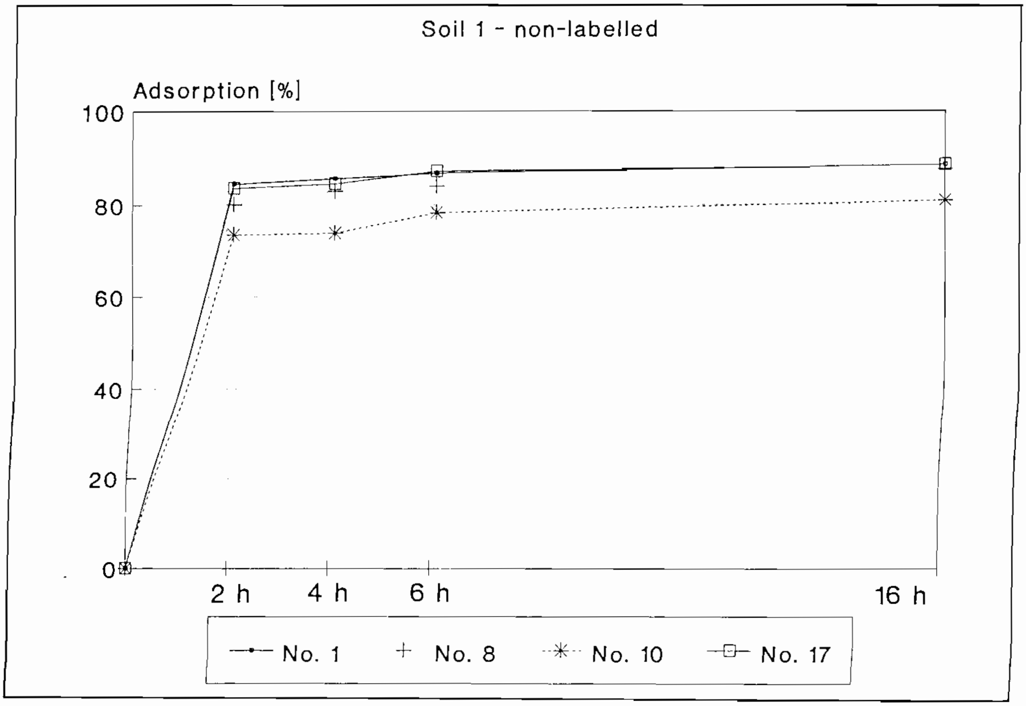
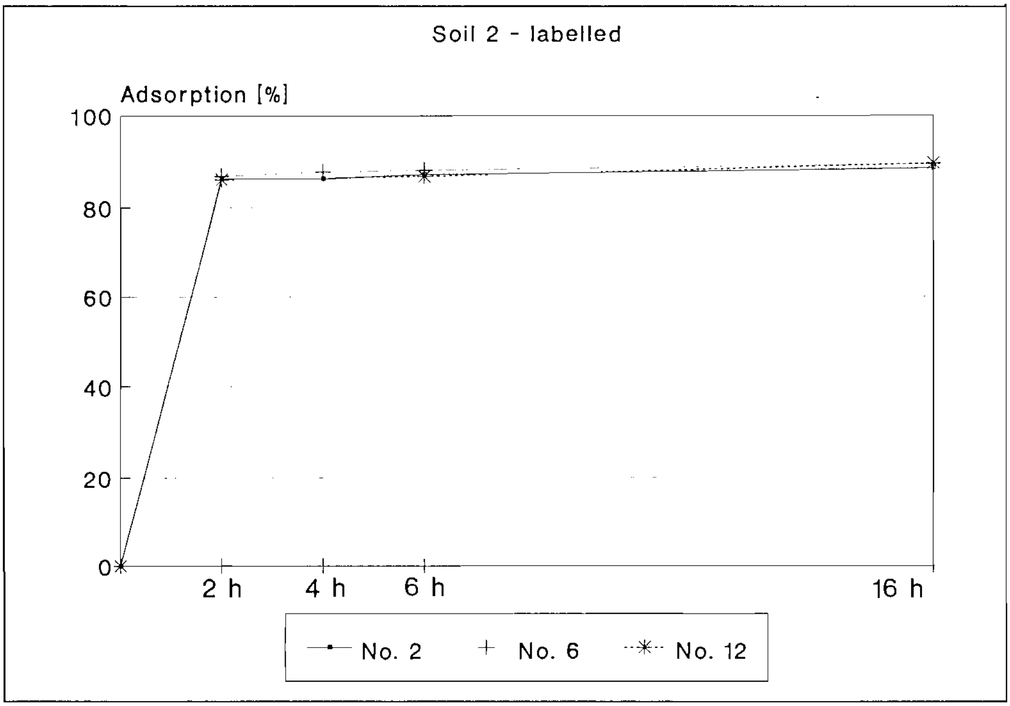


Fig. 4a: Sorption Kinetic of Lindane for Soil 1 (only representative data)



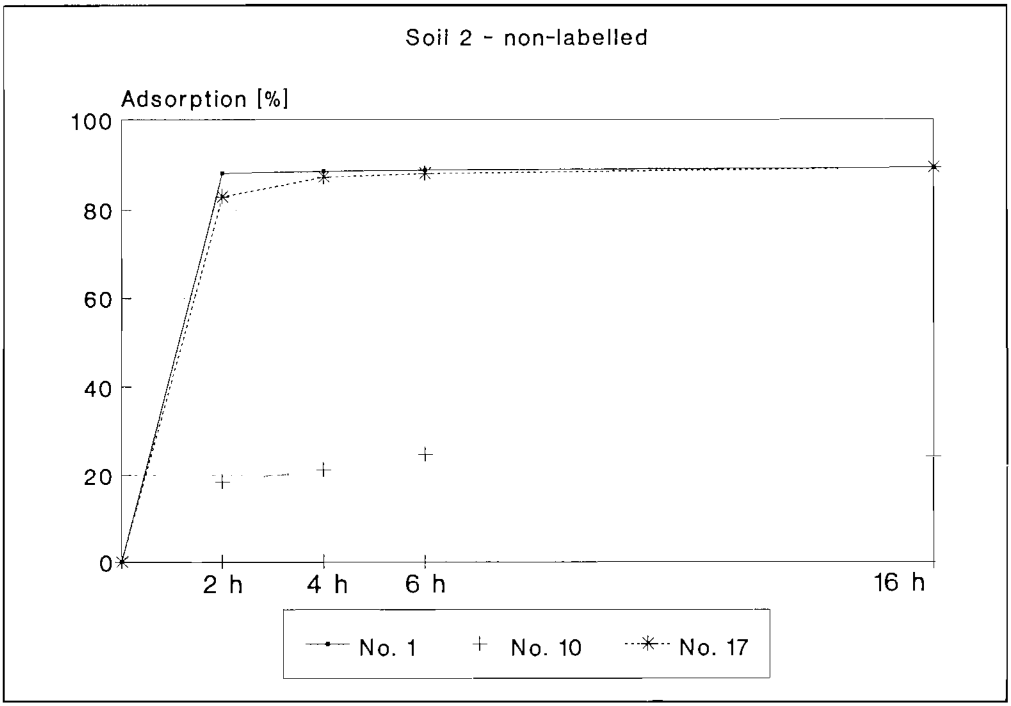
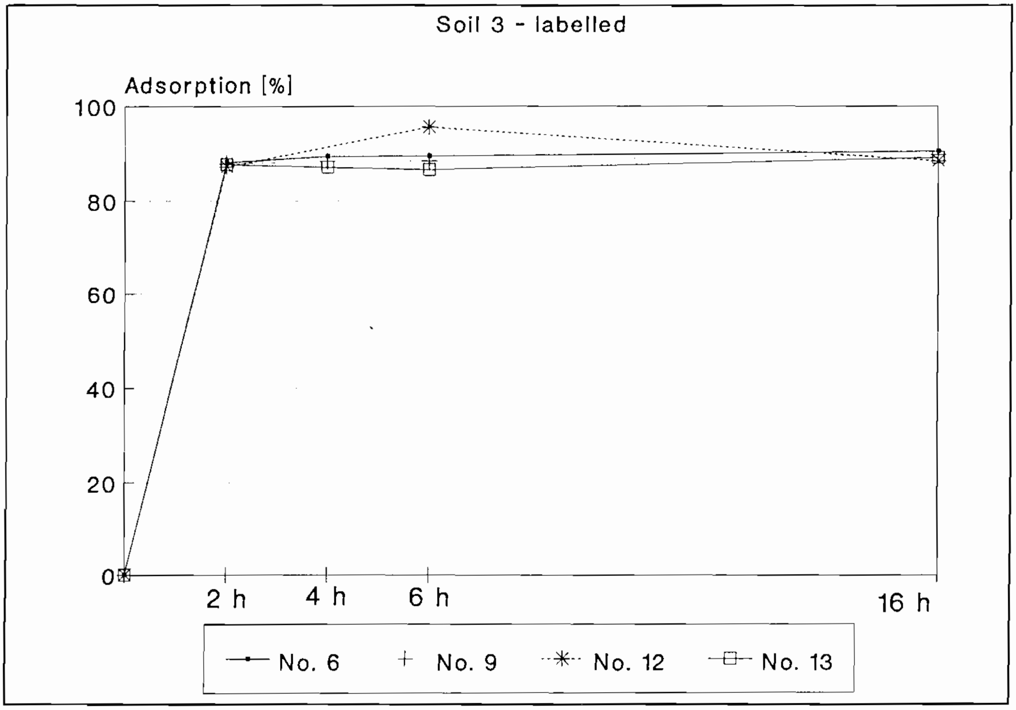


Fig. 4b: Sorption Kinetic of Lindane for Soil 2 (only representative data)



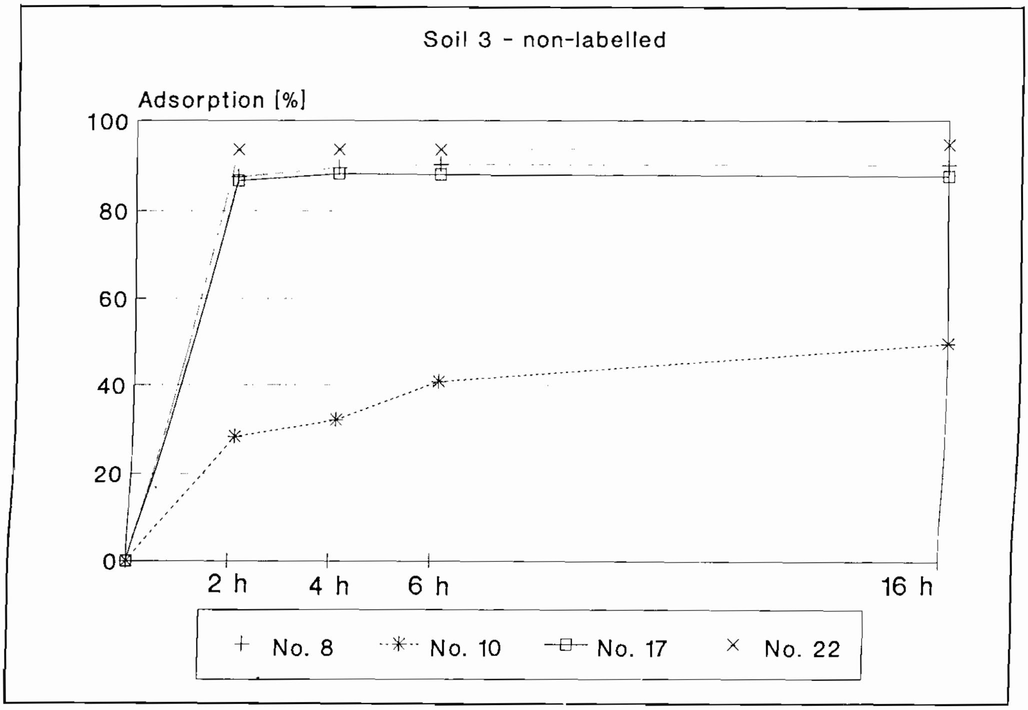


Fig. 4c: Sorption Kinetic of Lindane for Soil 3 (only representative data)

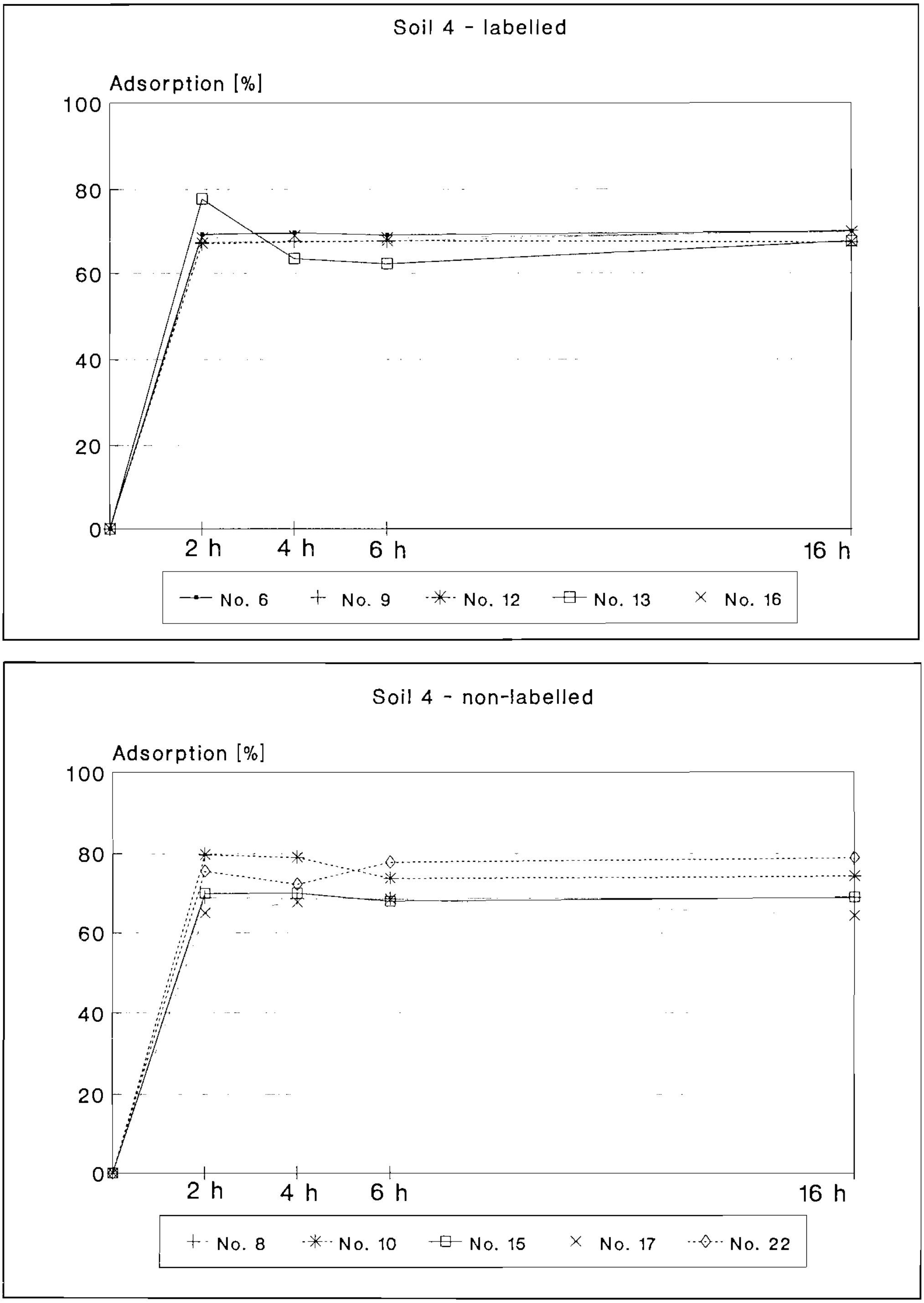


Fig. 4d: Sorption Kinetic of Lindane for Soil 4 (only representative data)

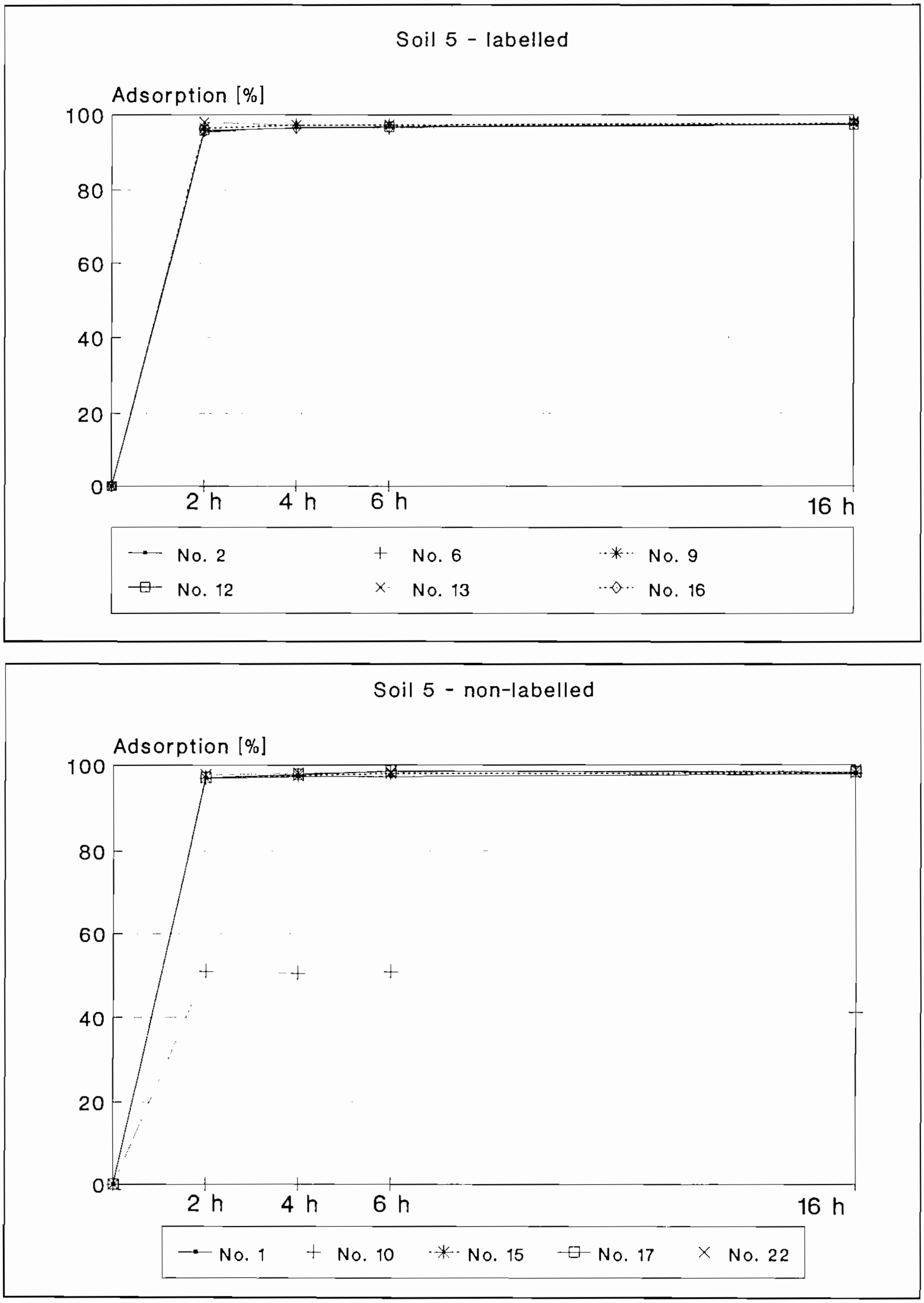
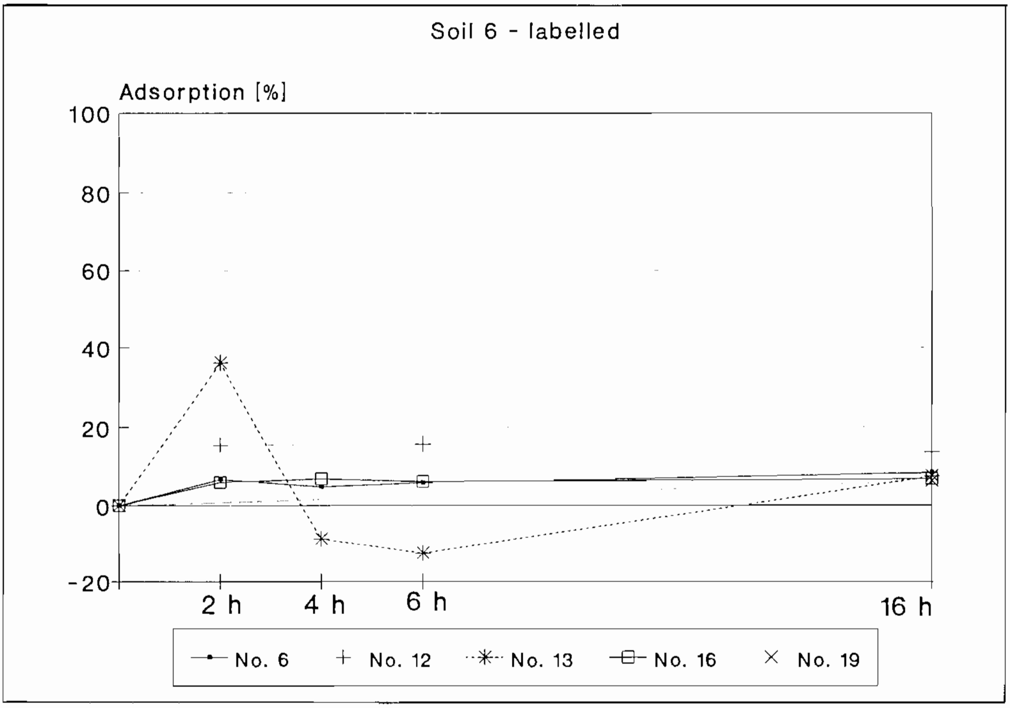


Fig. 4e: Sorption Kinetic of Lindane for Soil 5 (only representative data)



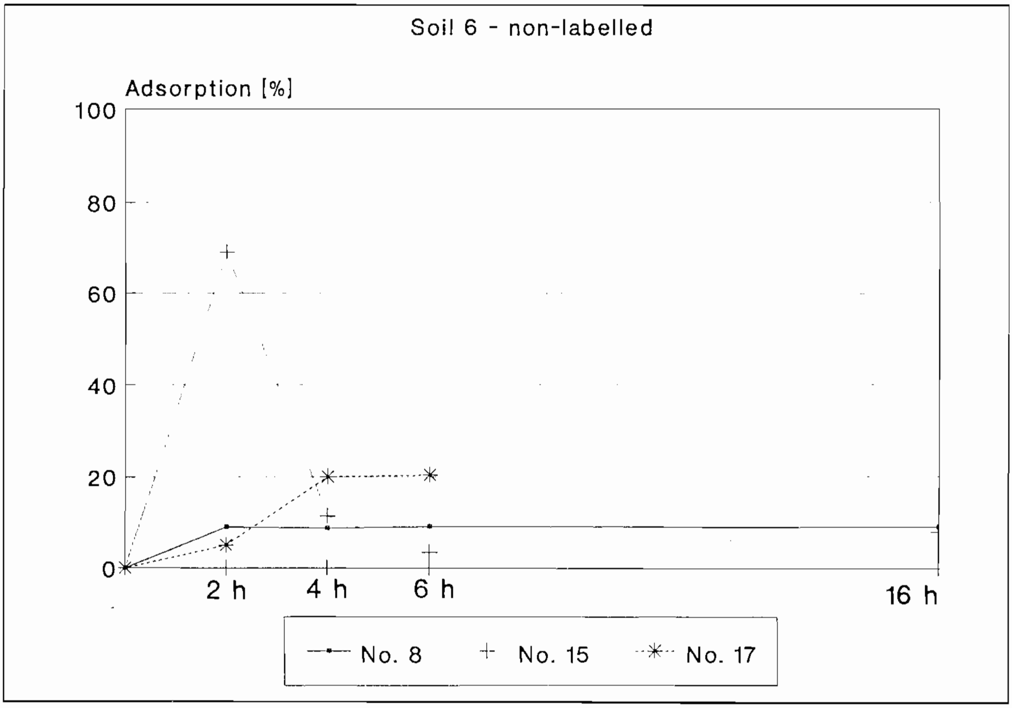


Fig. 4f: Sorption Kinetic of Lindane for Soil 6 (only representative data)

Sorption equilibrium is attained rapidly, after two hours the plateau was reached to a large extent (90%) (see Fig. 4a - f). A comparison of the distribution coefficients determined after 16 hours show that the results are in good agreement. A standard deviation not exceeding 12 % for ^{14}C labelled substances (soil 1-5) is acceptable for studies on soil related properties. Furthermore it has to be taken into account that the experiments were carried out with different initial concentrations. The results of the sub-soil (soil 6) with a low organic carbon content show a high variation (25%). This fact is conditioned by the low adsorption (K' < 1) where small errors in analytical measurement lead to enormous standard deviations. The results of the tests with non-labelled substances generally show a much higher variation of up to 73 %. Some results with strong deviations were not included in the calculation of the mean value (Outlier test, Dixon 1953). The large deviation is assumed to depend on analytical errors. The results of the distribution coefficients determined either with ^{14}C Lindane or with non-labelled Lindane are in good agreement for distribution coefficients with standard deviations up to 20 %.

7.1.2 Atrazine

Table 6: Comparison of the distribution coefficients of Atrazine after 16 hours. The results of each participant performing the test are compared for soil 1 - 6 as well labelled and non-labelled.

Soil 1 Atrazine					
labelled			non-labelled		
No.	c	K'(16h)	No.	c	K'(16h)
2	5	8.7	4	5.0496	7.94 (20h)
6	5	10.74	7	4.947	8.26
11	5	8.71	8	5	8.29
12	4.602	7.641	10	5	3.66
18	5	8.94	12	4.602	7.586
20	5.1	9	23	5	7.54
27	5	7.6	24	5	9.75
			26	5.039	8.5
			25	5.23	6.82 (23h)
mean:		8.76	mean:		7.59
standard deviation:	1.05		standard deviation:	1.68	
% S.D. of mean:		12.0	% S.D. of mean:		22.13

Soil 2 Atrazine					
labelled			non-labelled		
No.	c	K‘(16h)	No.	c	K‘(16h)
2	5	2.2	10	5	1.46
6	5	3.04	12	4.602	2.611
11	5	2.5	23	5	1.95
12	4.602	2.474	26	5.039	2.19
21	5	2.25	25	5.23	2.48 (16.33h)
27	5	2.38			
mean:		2.47	mean:		2.14
standard deviation:	0.30		standard deviation:	0.46	
% S.D. of mean:		12.1	% S.D. of mean:		21.5

Soil 3 Atrazine					
labelled			non-labelled		
No.	c	K‘(16h)	No.	c	K‘(16h)
6	5	3.68	5	5	2.87
9	5.06	2.7	8	5	4.94
12	4.602	2.310	10	5	1.57
13	4.97	2.85	12	4.602	1.994
14	5	2.24	23	5	0.7
21	5	2.91	24	5	2.92
27	5	3.17	26	5.039	2.62
			25	5.23	3.265 (16.33h)
mean:		2.84	mean:		2.61
standard deviation:	0.50		standard deviation:	1.26	
% S.D. of mean:		17.6	% S.D. of mean:		48.32

Soil 4 Atrazine					
labelled			non-labelled		
No.	c	K‘(16h)	No.	c	K‘(16h)
3	5	0.78	5	5	1.11
6	5	1.02	7	4.974	1.005
9	5.06	0.86	8	5	2.33
12	4.602	0.635	10	5	0.33
13	4.97	0.834	12	4.602	0.54
14	5	0.75	15	7.12	1.7
15	?	0.85	23	5	0.64
16	5	0.8	26	5.039	0.78
18	5	0.92	25	5.23	0.8155 (20.55h)
19	5.2	0.91			
20	5.1	0.9			
27	5	0.94			
mean:		0.85	mean:		1.03
standard deviation:	0.10 %		standard deviation:	0.63	
S.D. of mean:		11.8	% S.D. of mean:		60.92

Soil 5 Atrazine					
labelled			non-labelled		
No.	c	K‘(16h)	No.	c	K‘(16h)
2	5	36.5	4	5.0496	43.0 (20h)
3	5	40.87	7	4.962	25.43
6	5	56.19	8	5	72.3
9	5.06	40.2	10	5	18.05
11	5	43.5	15	7.12	52.8
12	4.602	43.879	12	4.602	42.662
13	4.95	45.6	23	5	48.2
15	?	38.85	24	5	50.585
16	5	37.4	25	5.23	32.665 (20.55h)
18	5	56.52	26	5.039	43.12
19	5.2	45			
20	5.1	45.4			
21	5	40.1			
27	5	40.3			
mean:		43.59	mean:		42.88
standard deviation:	6.13		standard deviation:	15.19	
% S.D. of mean:		14.1	% S.D. of mean:		35.42

Soil 6 Atrazine					
labelled			non-labelled		
No.	c	K‘(16h)	No.	c	K‘(16h)
5	5	0.15	5	5	0.23
12	4.602	0.15 (24h)	8	5	0.48
13	4.98	0.03	12	4.602	0.345
14	5	0.18	15	7.12	0.2
15	?	0.105	23	5	0
16	5	0.0 (24h)	25	5.23	0.1675 (20.83h)
19	5.2	0.26	26	5.039	0.02
27	5	0.10			
mean:		0.122	mean:		0.21
standard deviation:	0.08		standard deviation:	0.17	
% S.D. of mean:		65.6	% S.D. of mean:		81.0

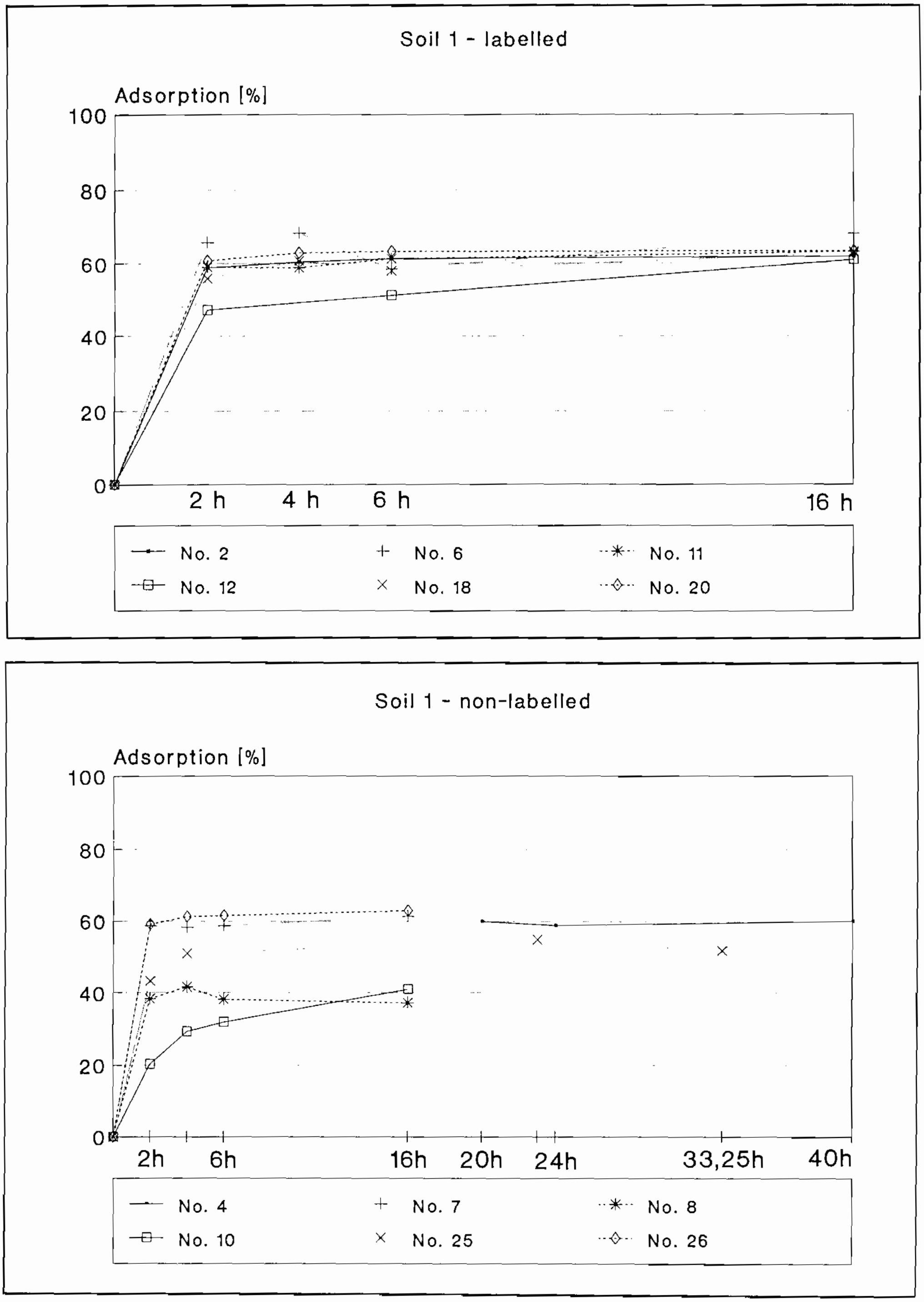
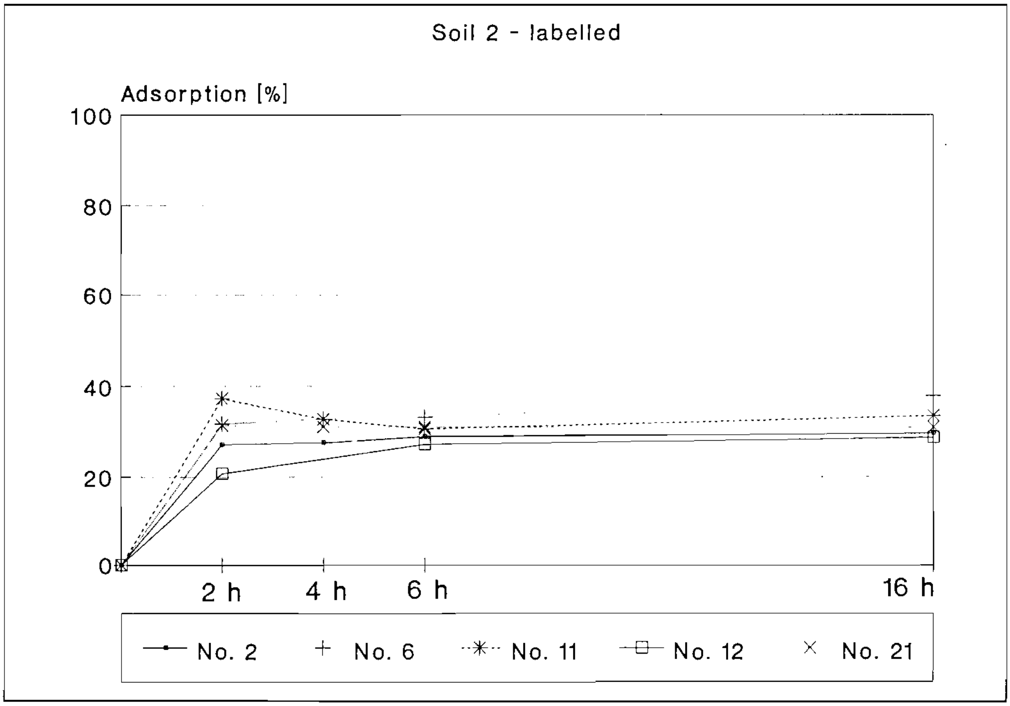


Fig. 5a: Sorption Kinetic of Atrazine for Soil 1 (only representative data)



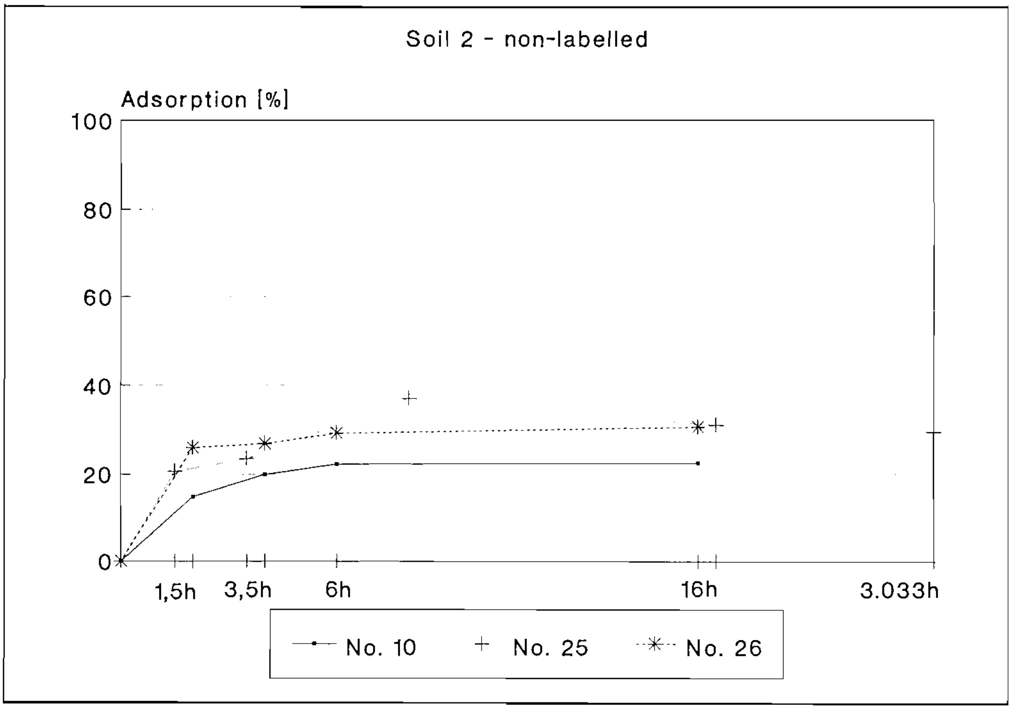
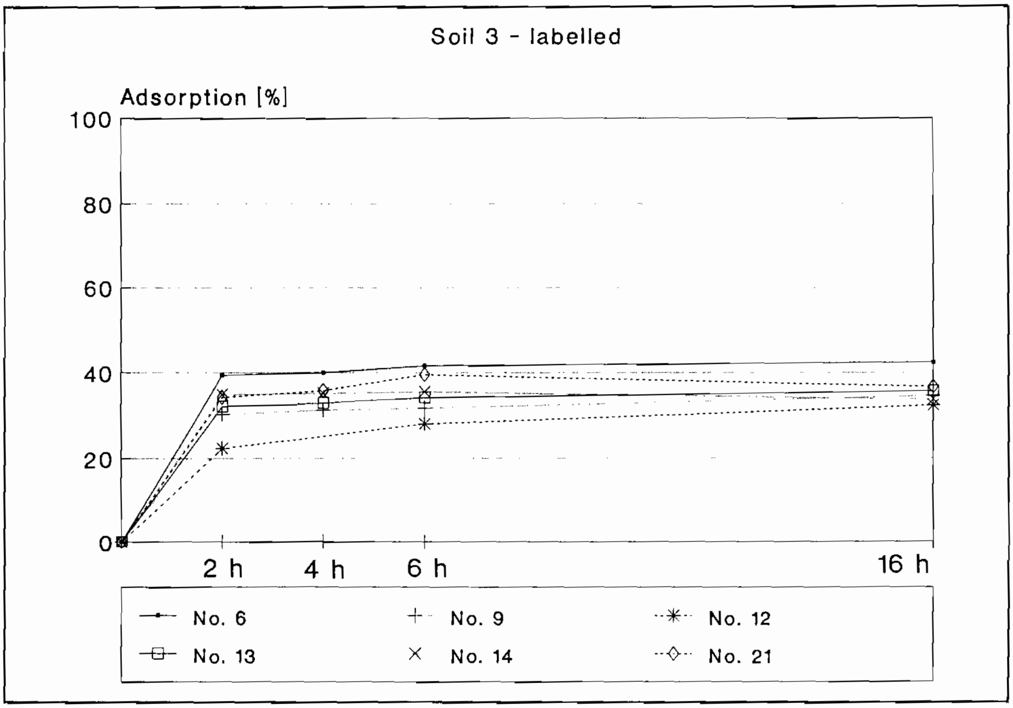


Fig. 5b: Sorption Kinetic of Atrazine for Soil 2 (only representative data)



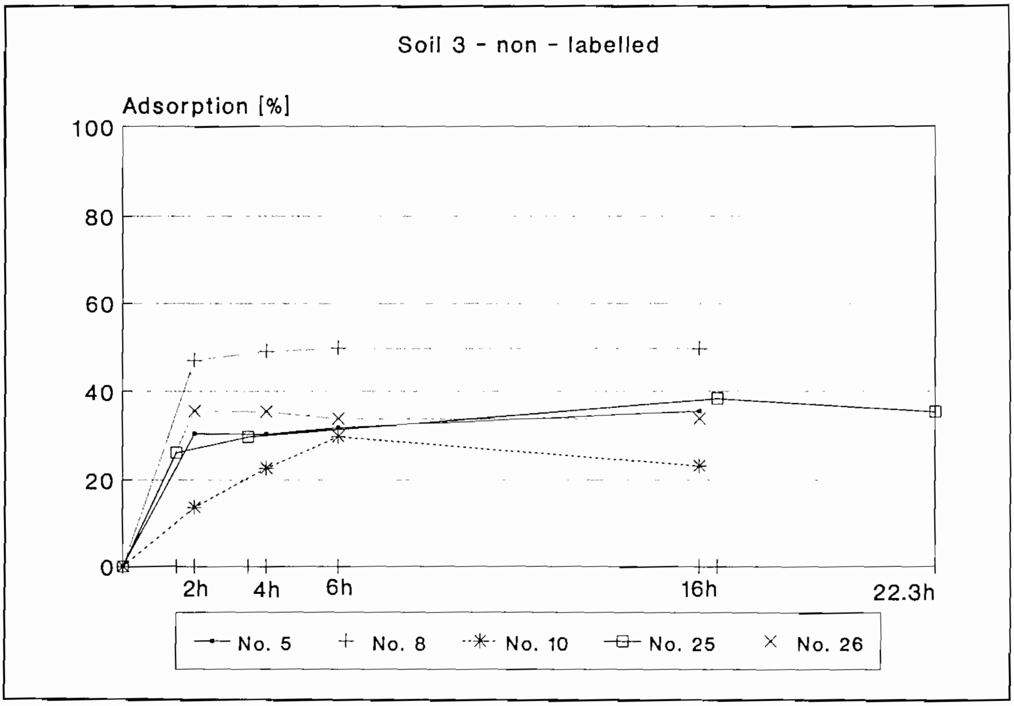


Fig. 5c: Sorption Kinetic of Atrazine for Soil 3 (only representative data)

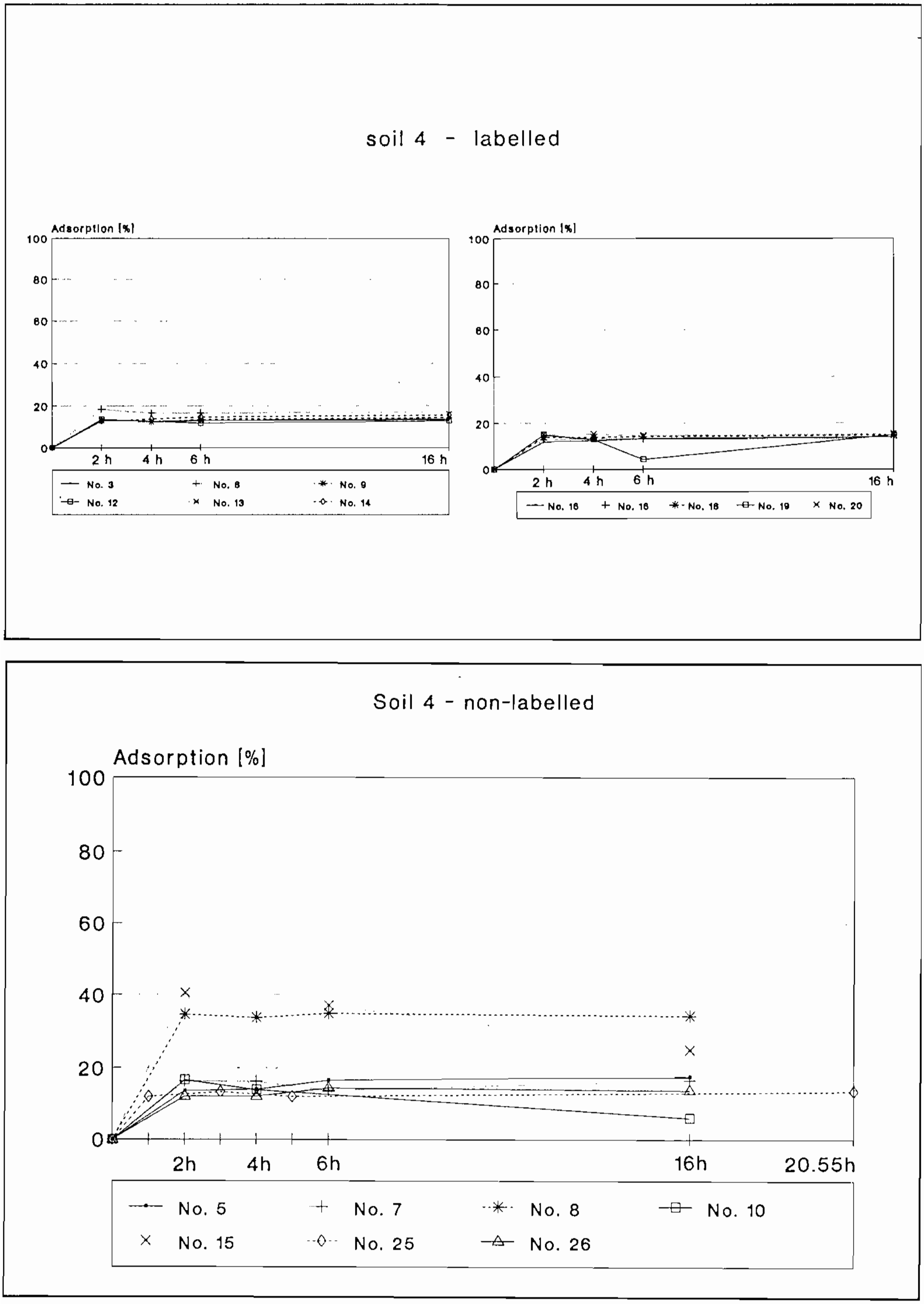
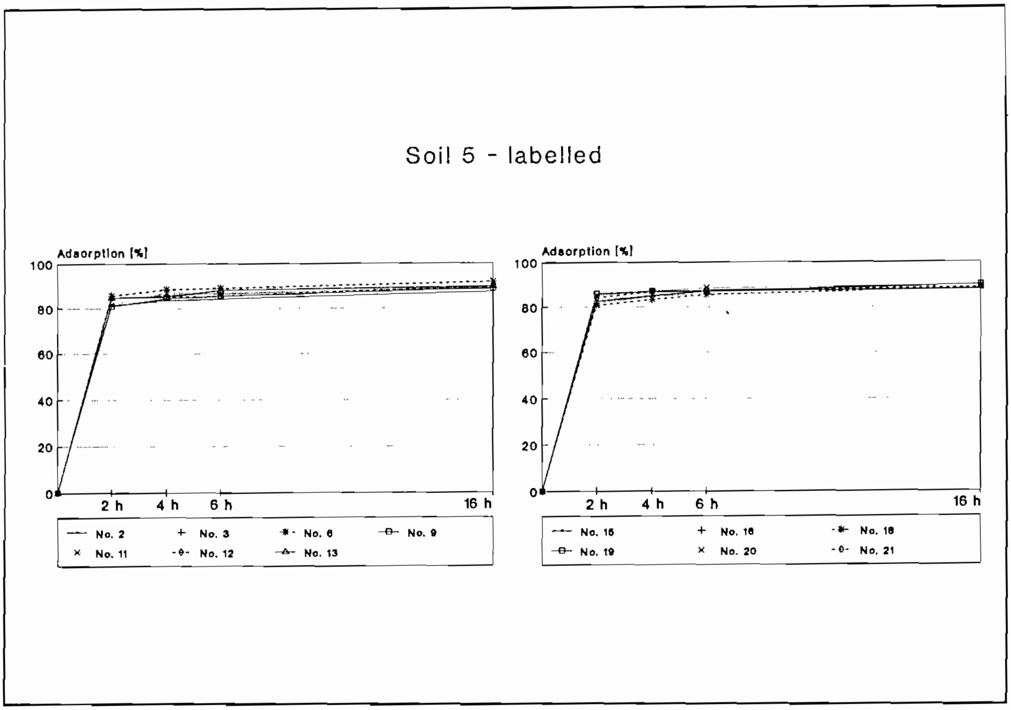


Fig. 5d: Sorption Kinetic of Atrazine for Soil 4 (only representative data)


Soil 5 - labelled

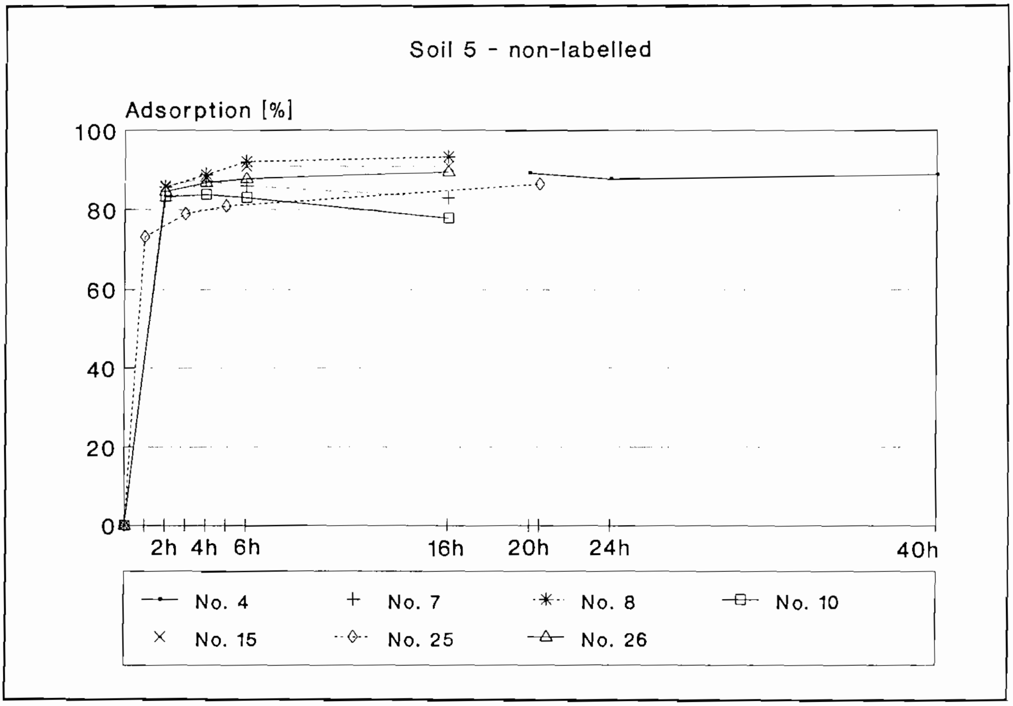
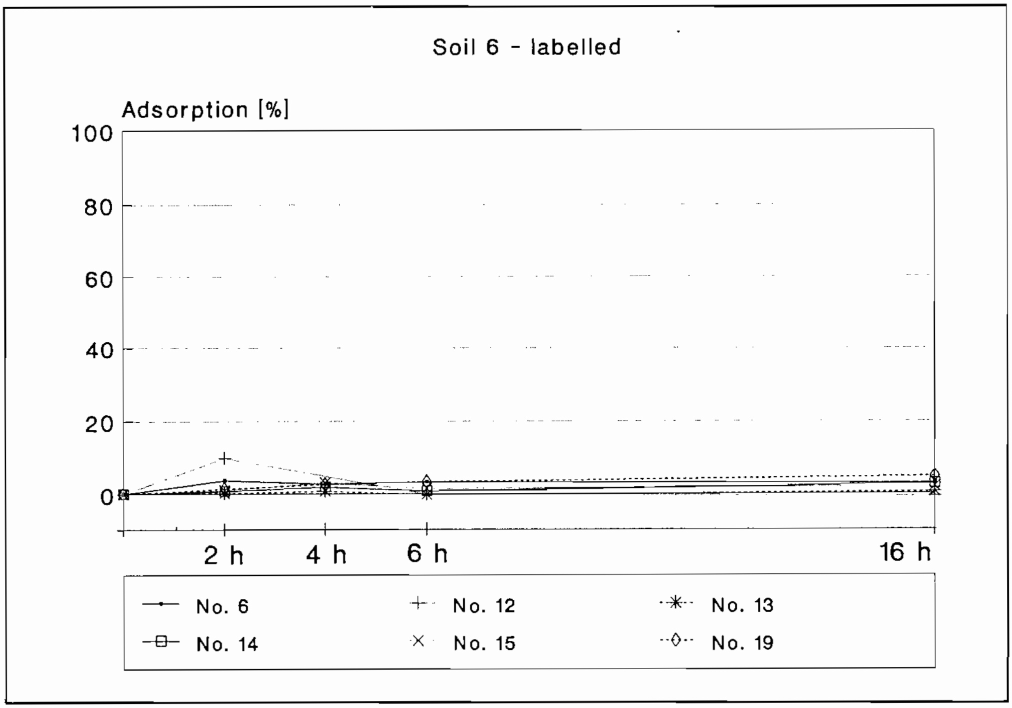

Soil 5 - non-labelled

Fig. 5e: Sorption Kinetic of Atrazine for Soil 5 (only representative data)



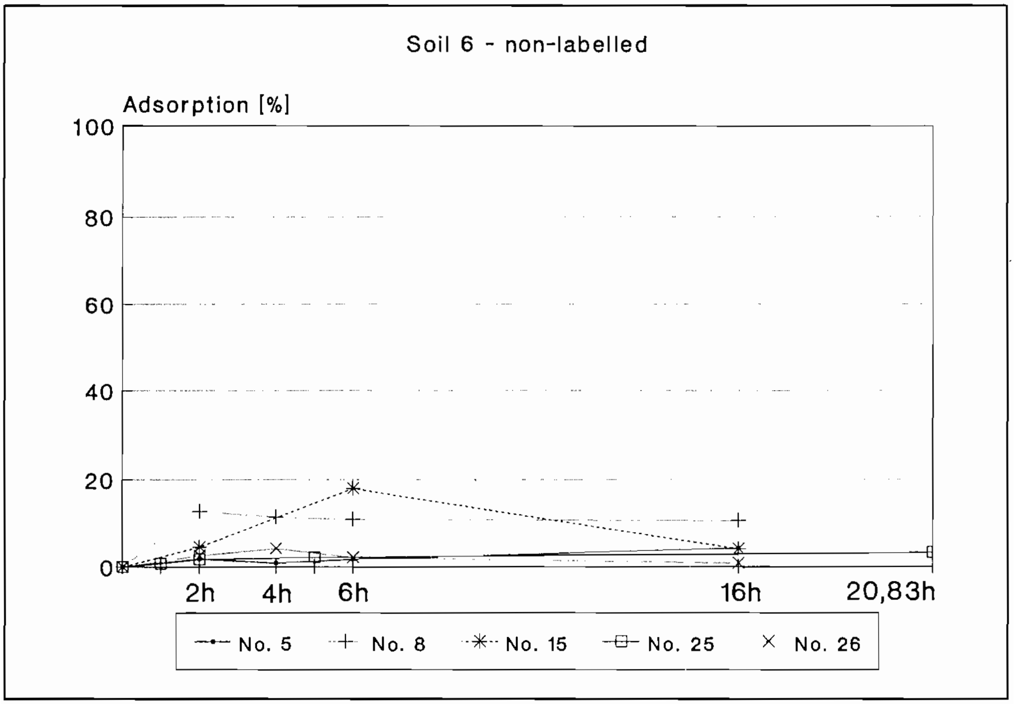


Fig. 5f: Sorption Kinetic of Atrazine for Soil 6 (only representative data)

Sorption equilibrium was reached after two hours to a great extent (see Fig 6a - d). With the exception of soil 6 (sub-soil) the standard deviation of ^{14}C-Atrazine is up to 19 %. The sorption coefficients determined with non-labelled substances show a higher variation (standard deviation up to 65 %, soil 6: 81 %). Furthermore it has to be taken into account that the experiments were carried out with different initial concentrations. A comparison of the distribution coefficients show that the measured k'-values (^{14}C-Atrazine and non-labelled Atrazine) are in good agreement. Due to the scattering of the distribution coefficients the same arguments (mentioned above for Lindane) can be applied.

7.1.3 2,4-D

2,4-D was only tested by a few participants. Therefore the results and their interpretation have to be regarded with reservations.

Table 7: Comparison of the distribution coefficients of 2,4-D after 16 hours. The results of each participant performing the test are compared for soil 1 - 6 as well labelled and non-labelled.

Soil 1	**2,4-D**				
labelled			non-labelled		
No.	c	K'(16h)	No.	c	K'(16h)
2	5.01	2.11	23	5.1	0
6	5	1.7	24	5	1.23
11	5	2.33	25	5.28	1.47
12	5	3.032			
27	5	1.9			
mean:		2.21	mean:		0.90
standard deviation:	0.51		standard deviation:	0.79	
% S.D. of mean:		23.1	% S.D. of mean:		87.8

Soil 2	**2,4-D**				
labelled			non-labelled		
No.	c	K‘(16h)	No.	c	K‘(16h)
2	5.01	0.75	23	5	0
6	5	0.82	25	5.28	0.7925 (19h)
11	5	0.6			
12	5	0.781			
27	5	0.8			
mean:		0.75	mean:		
standard deviation:	0.09		standard deviation:		
% S.D. of mean:		12.0	% S.D. of mean:		

Soil 3	**2,4-D**				
labelled			non-labelled		
No.	c	K‘(16h)	No.	c	K‘(16h)
6	5	1.86	23	5	1.13
9	5.05	1.5	24	5	0.925
12	5	1.417	25	5.28	1.4115 (19h)
13	4.97	1.46			
27	5	1.7			
mean:		1.59	mean:		1.16
standard deviation:	0.19		standard deviation:	0.244	
% S.D. of mean:		11.9	% S.D. of mean:		40.94

Soil 4	**2,4-D**				
labelled			non-labelled		
No.	c	K‘(16h)	No.	c	K‘(16h)
3	5	0.3	23	5	0.595
6	5	0.49	25	5.39	0.1625 (20.67h)
9	5.05	0.39			
12	5	0.639			
13	4.97	0.344			
19	5	0.385			
27	5	0.6			
mean:		0.45	mean:		
standard deviation:	0.13		standard deviation:		
% S.D. of mean:		28.9	%S.D. of mean:		

Soil 5	2,4-D				
labelled			non-labelled		
No.	c	K‘(16h)	No.	c	K‘(16h)
2	5.01	44.7	23	5	43.05
3	5	47.18	24	5	661.5
6	5	51.73	25	5.39	45.67 (20.67h)
9	5.05	48.6			
11	5	48.2			
12	5	61.03 (6h)			
13	4.95	45.5			
19	5	42			
27	5	46.5			
mean:		48.38	mean:		250.73
standard deviation:	5.46		standard deviation:	356.31	
% S.D. of mean:		11.3	% S.D. of mean:		142.48

Soil 6	2,4-D				
labelled			non-labelled		
No.	c	K‘(16h)	No.	c	K‘(16h)
6	5	0.28	5	5	0.84
12	5	0.169	25	5.39	0.002
13	4.97	0.005			
19	5	0.16			
27	5	0.2			
mean:		0.16	mean:		
standard deviation:	0.10		standard deviation:		
% S.D. of mean:		62.5	% S.D. of mean:		

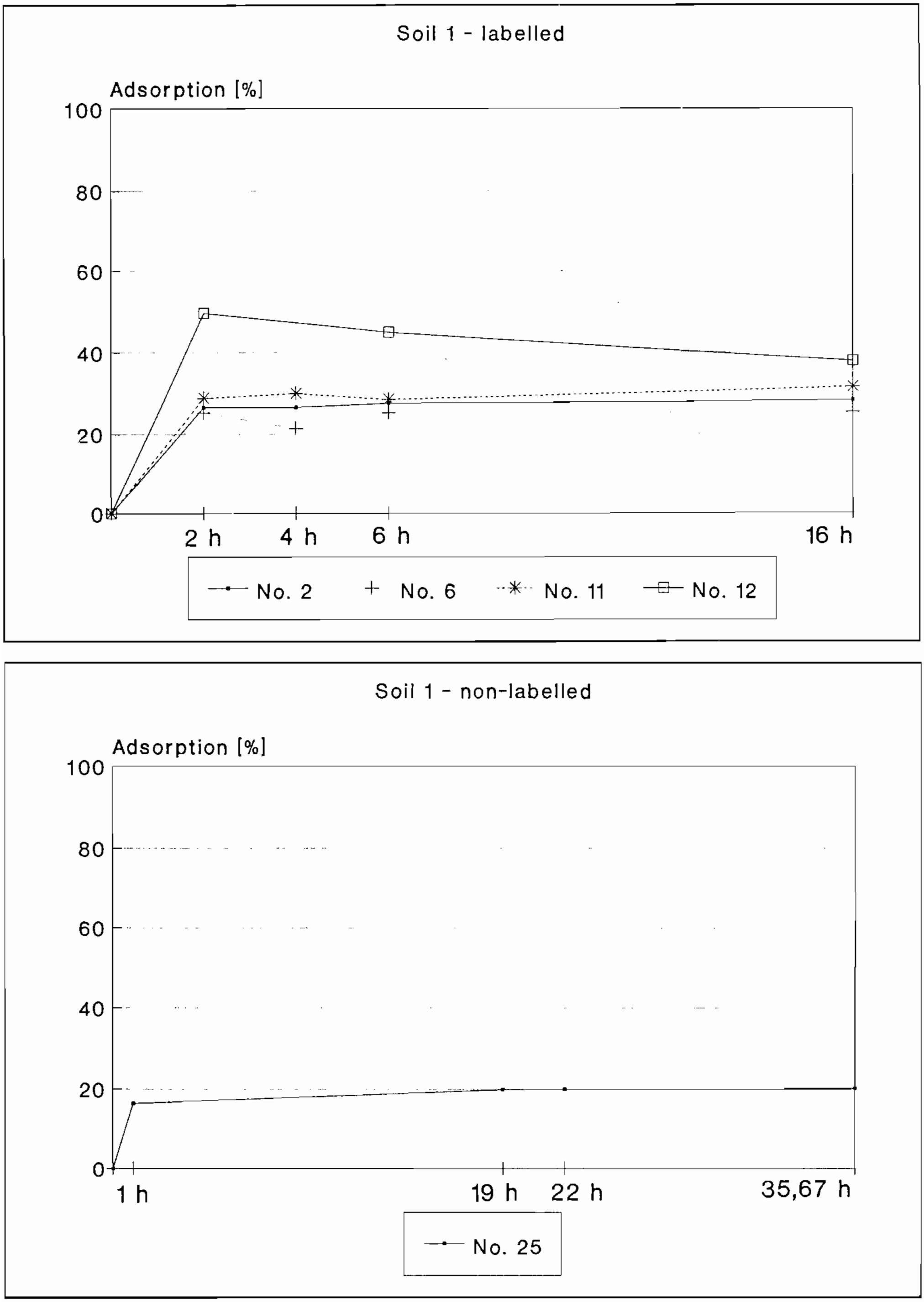
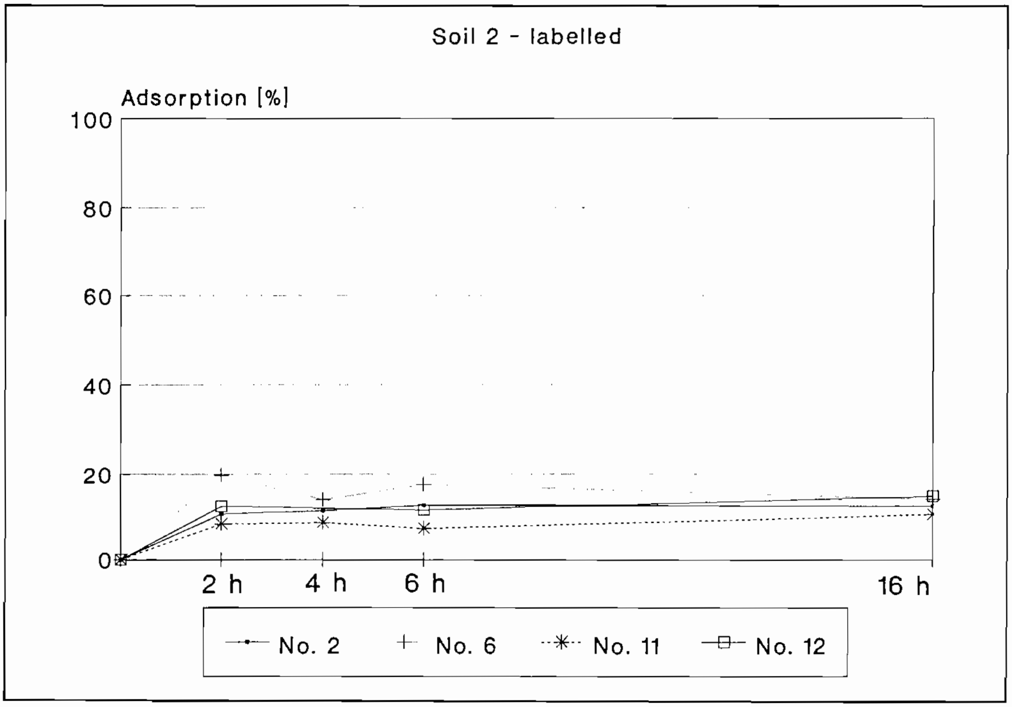


Fig. 6a: Sorption Kinetic of 2,4-D for Soil 1 (only representative data)



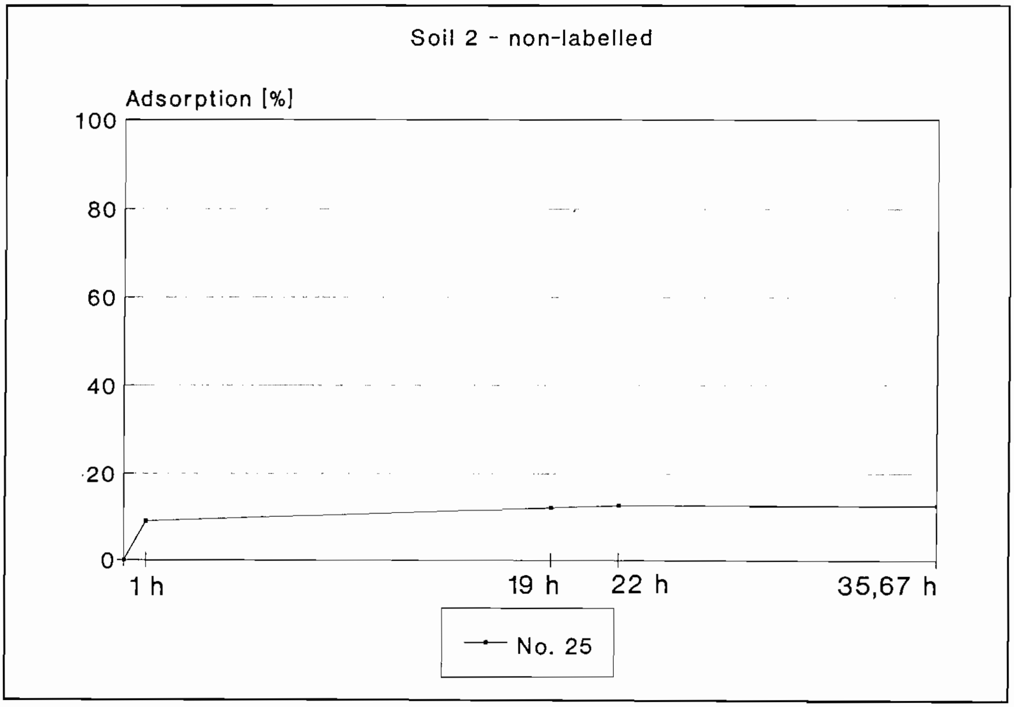
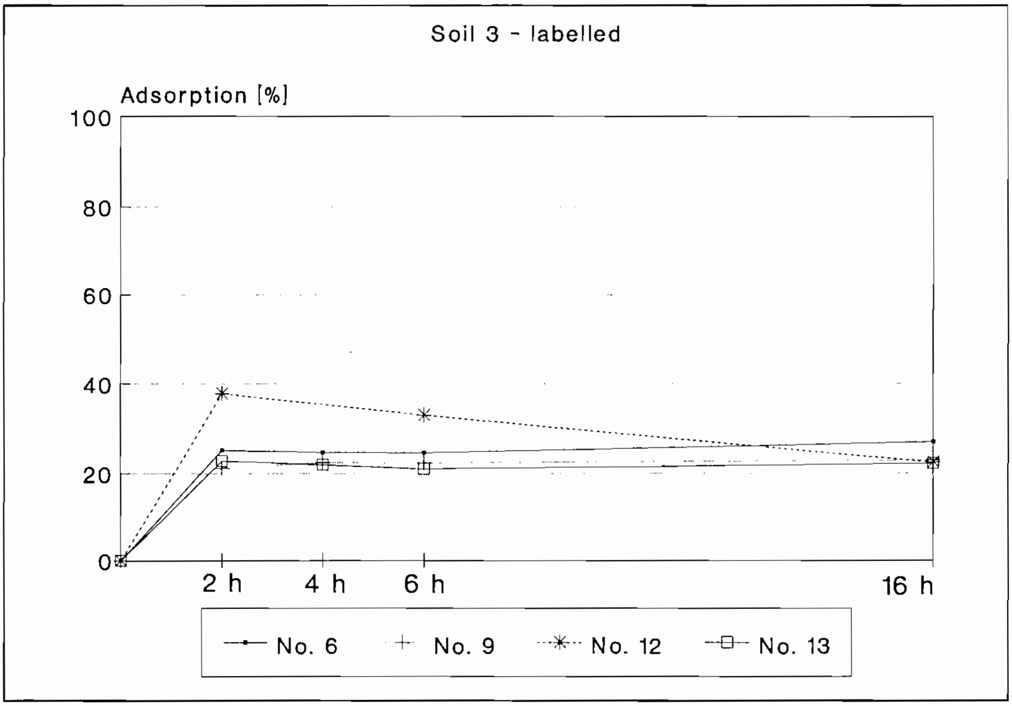


Fig. 6b: Sorption Kinetic of 2,4-D for Soil 2 (only representative data)



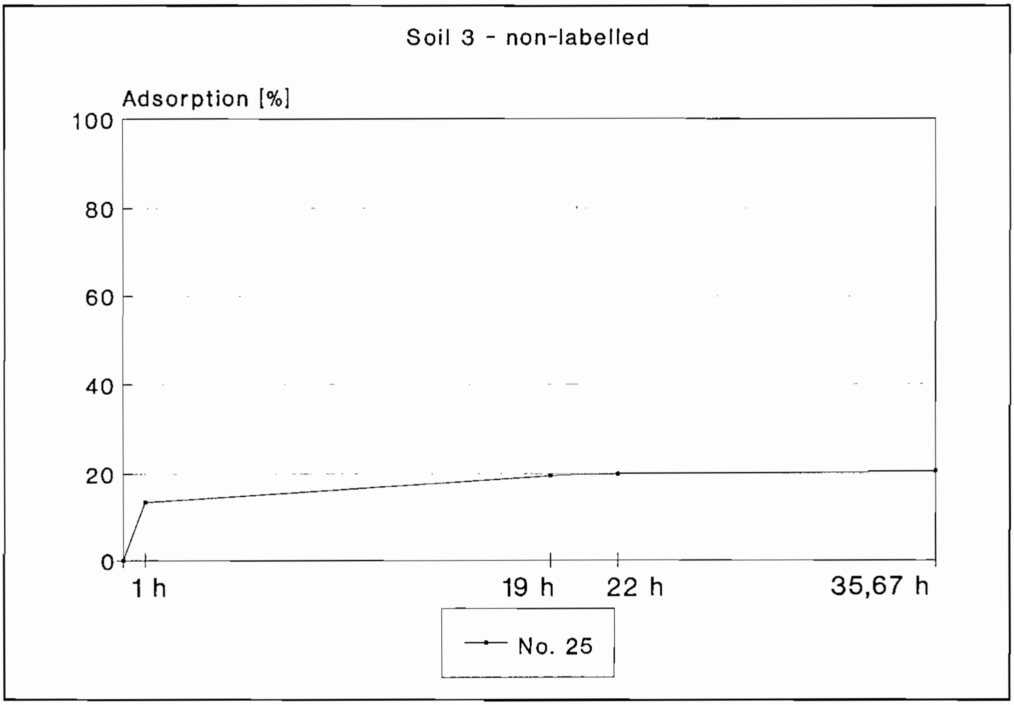
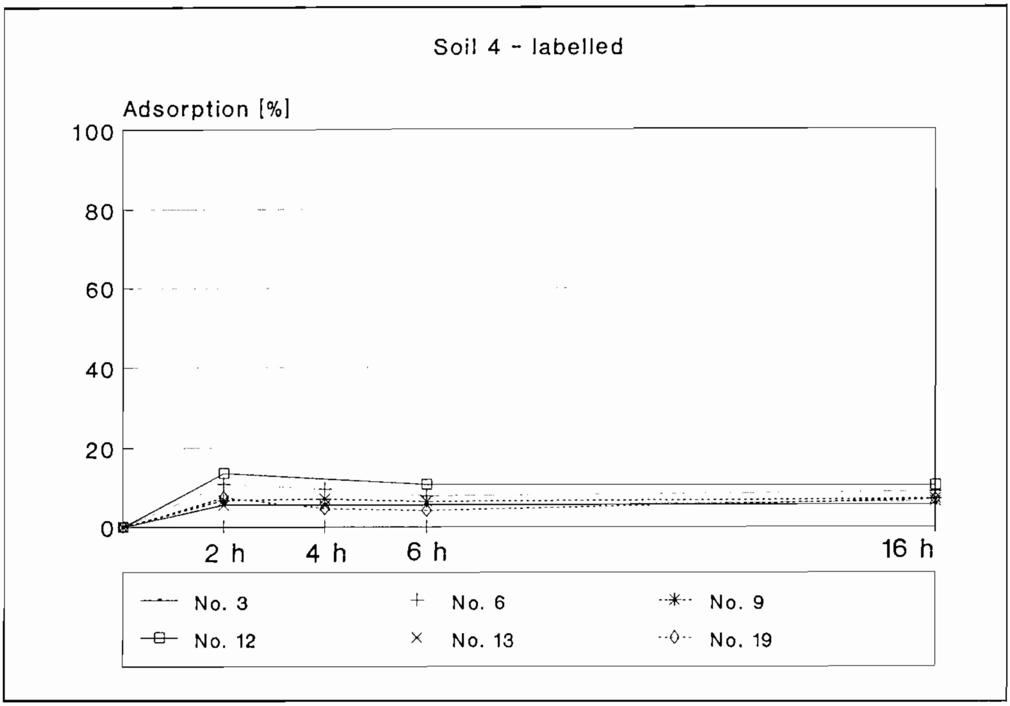


Fig. 6c: Sorption Kinetic of 2,4-D for Soil 3 (only representative data)



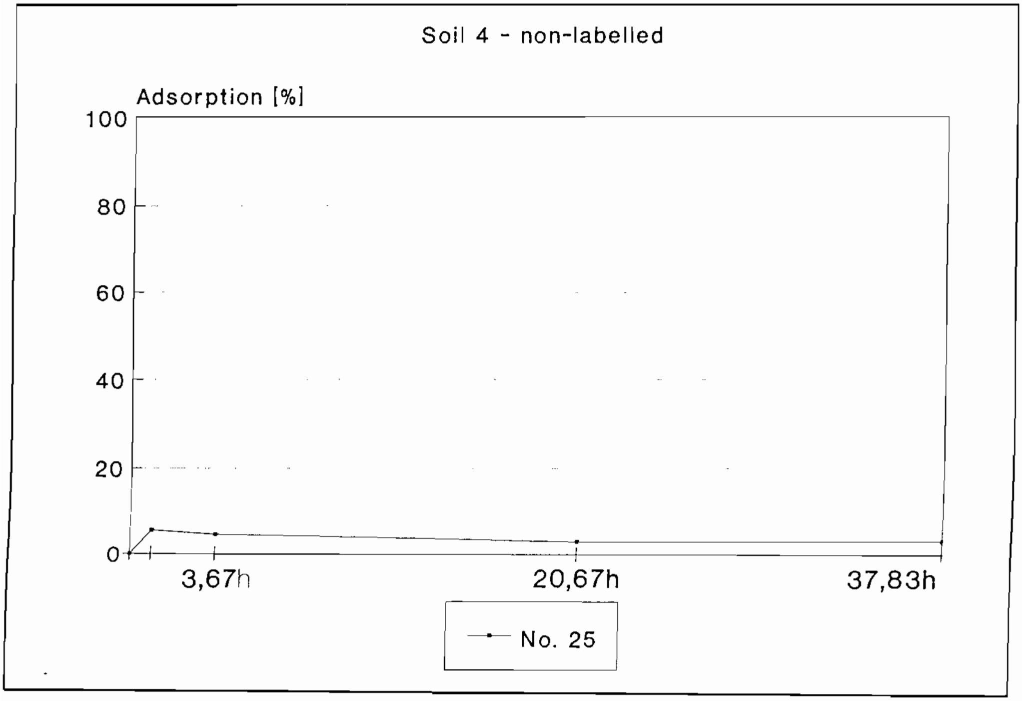
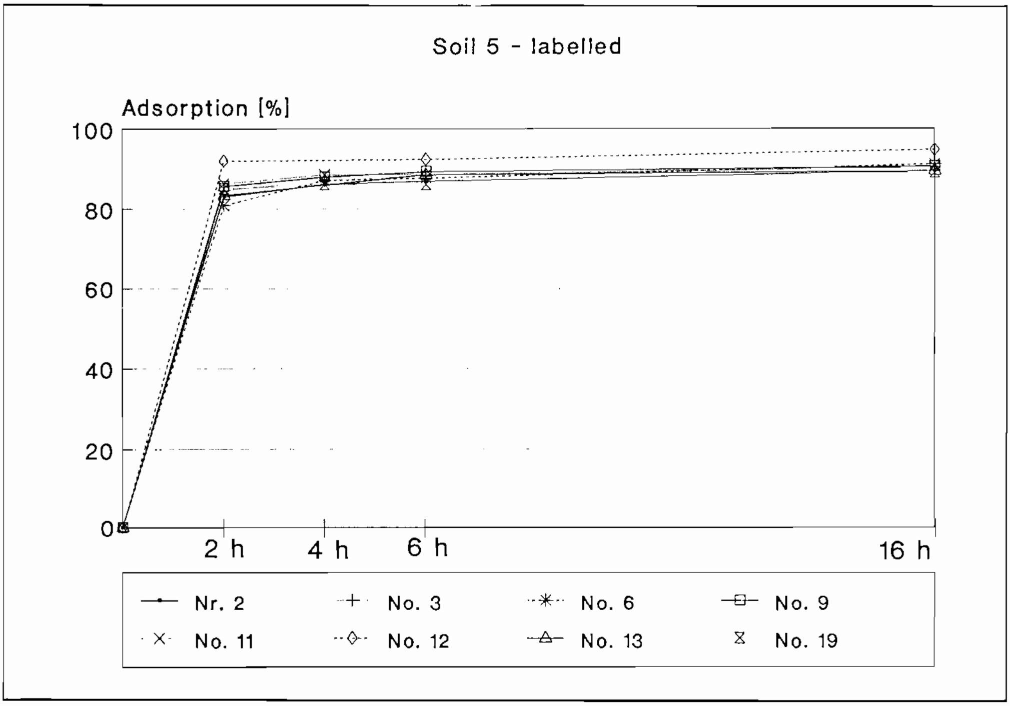


Fig. 6d: Sorption Kinetic of 2,4-D for Soil 4 (only representative data)



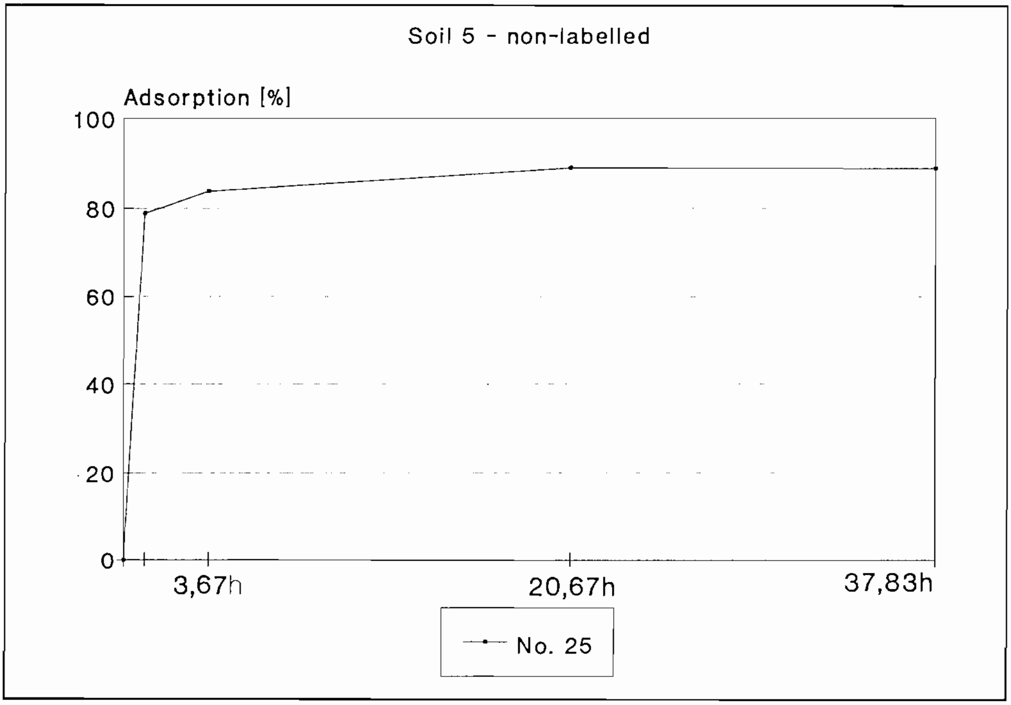


Fig. 6e: Sorption Kinetic of 2,4-D for Soil 5 (only representative data)

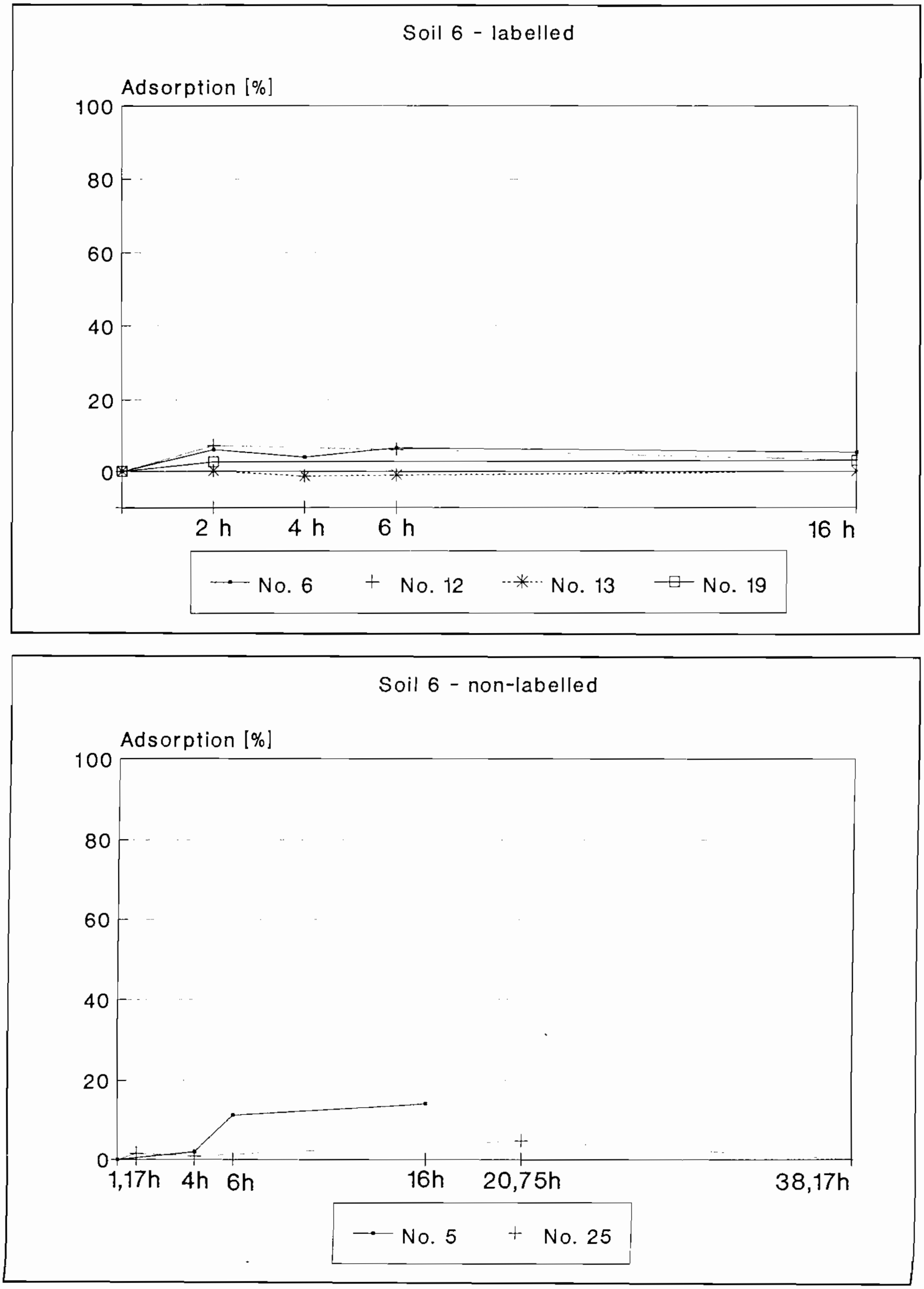
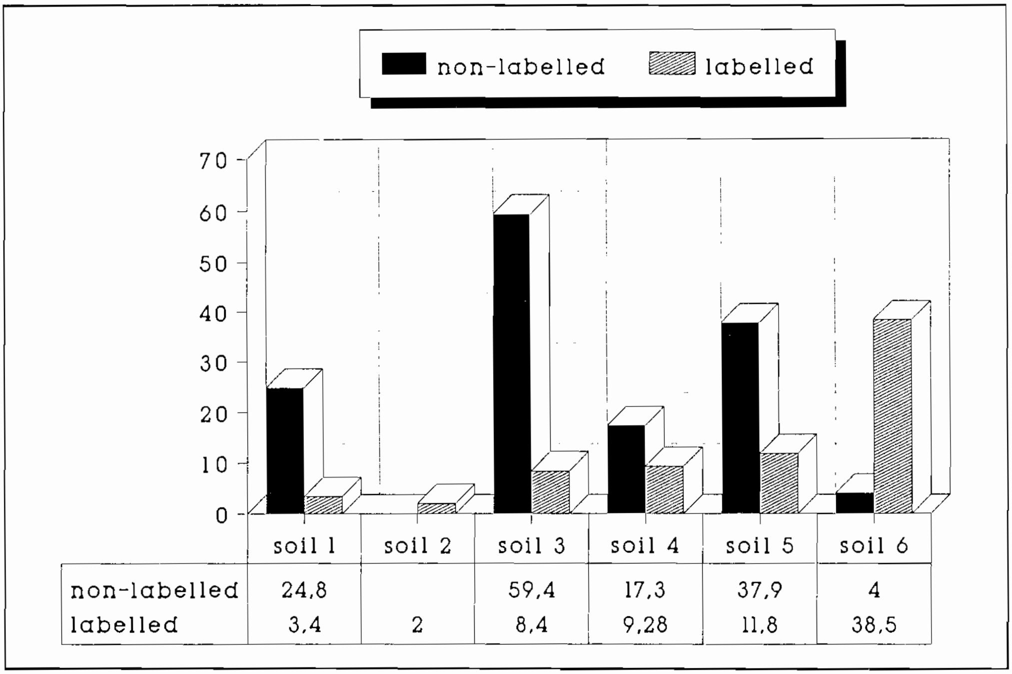


Fig. 6f: Sorption Kinetic of 2,4-D for Soil 6 (only representative data)

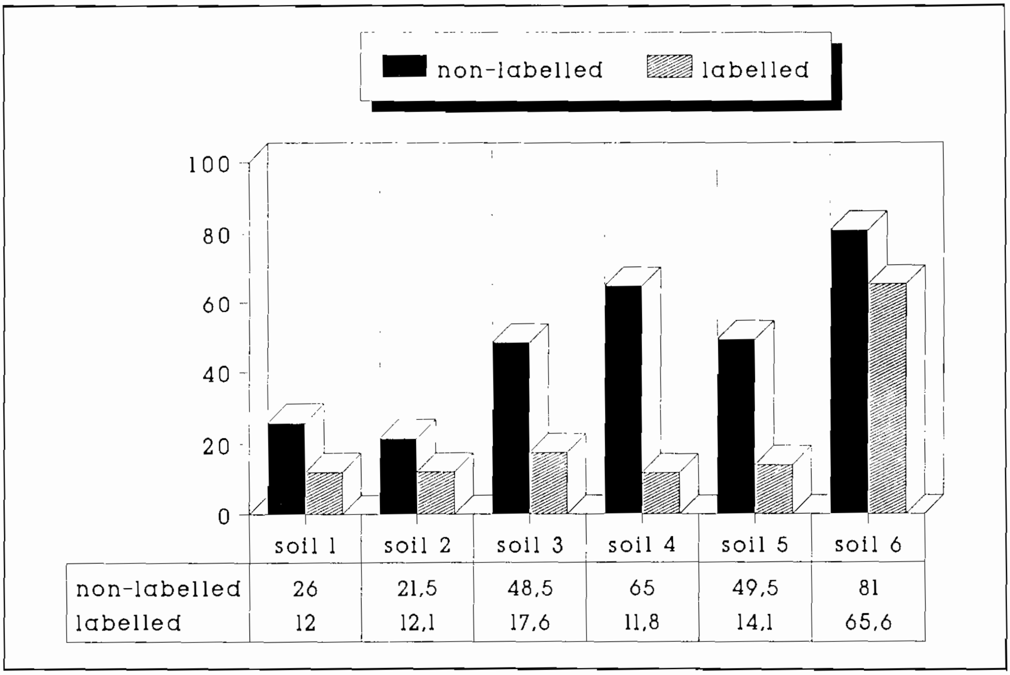
Soil equilibrium was reached within two hours to a large extent. The distribution coefficients (determined with ^{14}C-labelled substances) vary up to 28 % with the exception of soil 6 with a low sorption capacity. The results obtained with non-labelled substances scatter considerably (variation up to two orders of magnitude). These results cannot be compared with the results of the ^{14}C-2,4-D in contrast to Lindane and Atrazine. One reason may be that the sensitivity of the analytical determination method is much lower than that of the other substances under study.

The standard deviations of labelled and non-labelled values are depicted in Fig. 7a-c. The data show clearly that major part of the total variation must be attributed to analytical problems when using "cold" techniques.



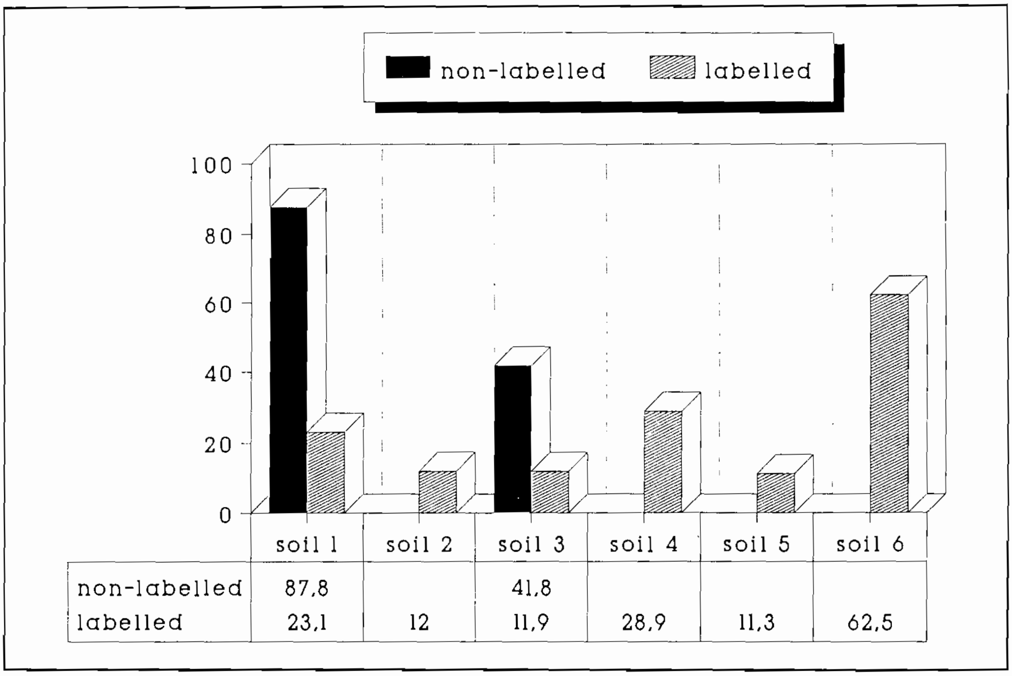
	soil 1	soil 2	soil 3	soil 4	soil 5	soil 6
non-labelled	24,8		59,4	17,3	37,9	4
labelled	3,4	2	8,4	9,28	11,8	38,5

Fig. 7a % SD of Mean of K' - of LINDANE



	soil 1	soil 2	soil 3	soil 4	soil 5	soil 6
non-labelled	26	21,5	48,5	65	49,5	81
labelled	12	12,1	17,6	11,8	14,1	65,6

Fig. 7b % SD of Mean of K' - of ATRAZINE



	soil 1	soil 2	soil 3	soil 4	soil 5	soil 6
non-labelled	87,8		41,8			
labelled	23,1	12	11,9	28,9	11,3	62,5

Fig. 7c % SD of Mean of K' - of 2,4 - D

If one analyses the relatively wide scattering of non-labelled values it becomes obvious that some participants had serious problems with their analytics. They provided continuously outlayer values (e.g. participant # 8, participant # 10) while others (e.g. participant 1) yielded values laying without any exception within the band width of the labelled "standard".

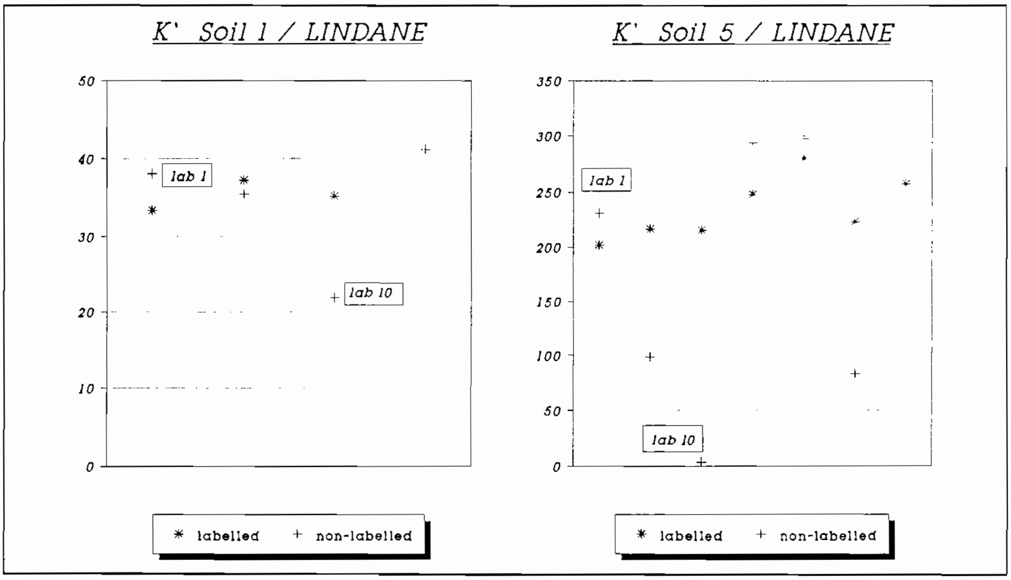


Fig 8a: K' - values for Lindane in soil 1 and soil 5

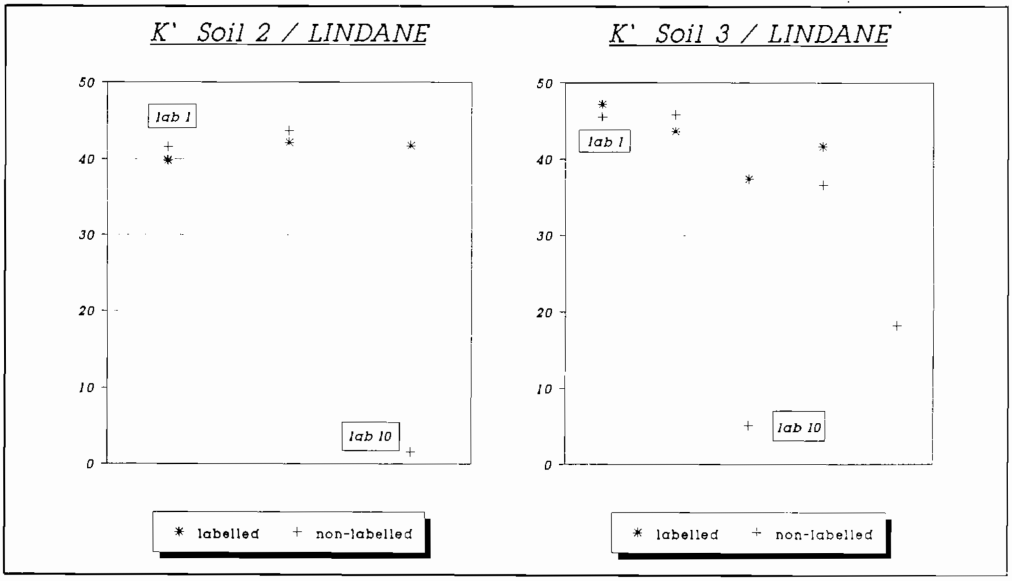


Fig 8b: K' - values for Lindane in soil 2 and soil 3

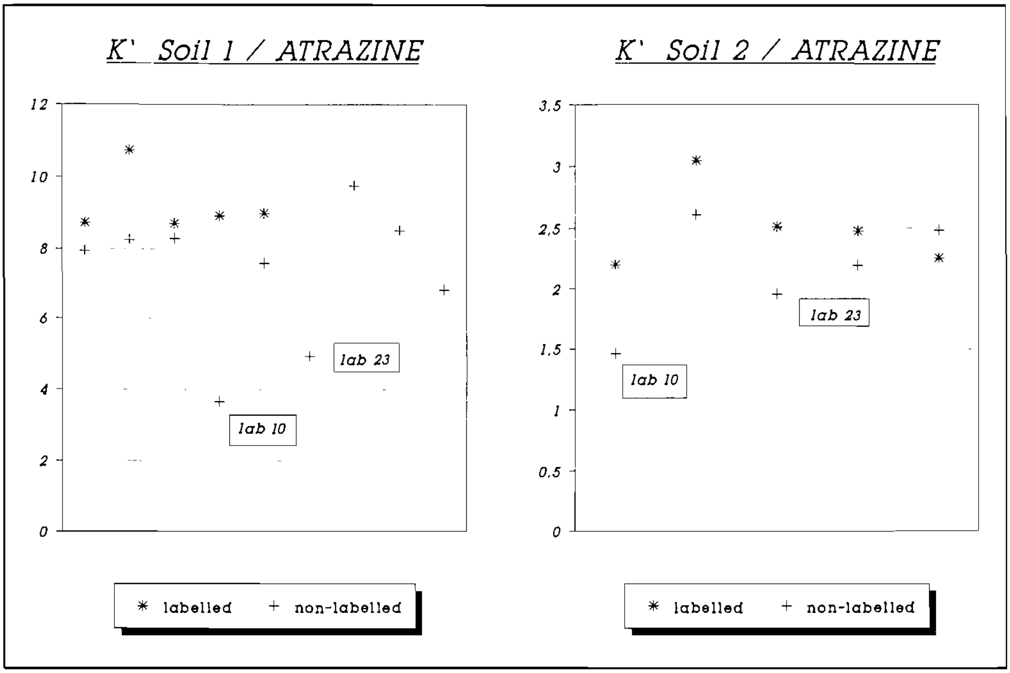


Fig 8 c: K' - values for Atrazine in soil 1 and soil 2

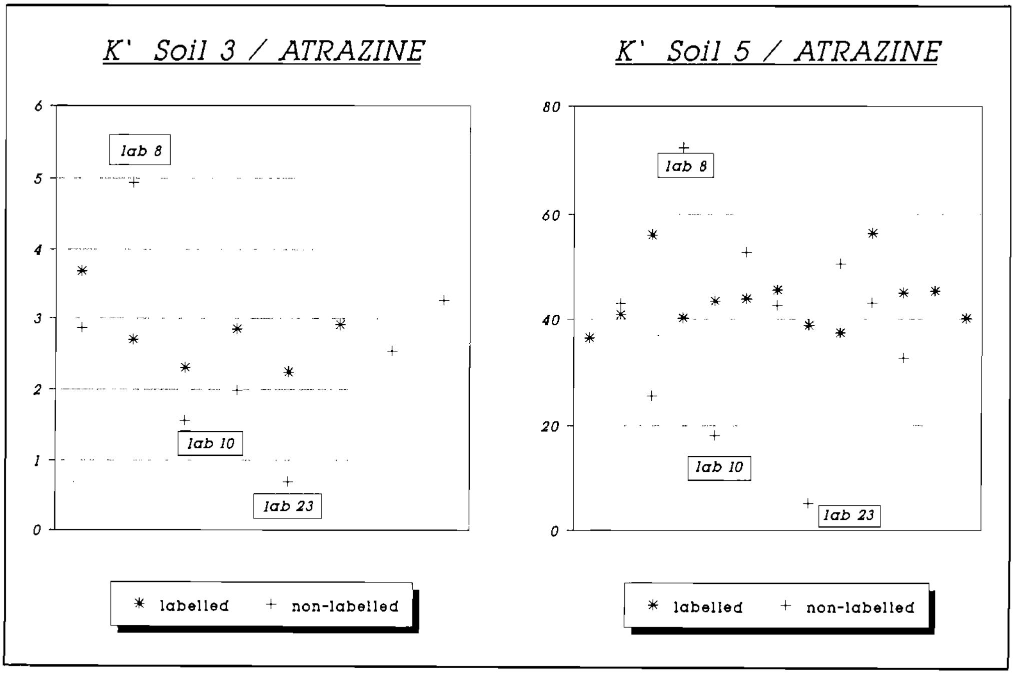


Fig 8 d: K' - values for Atrazine in soil 3 and soil 5

7.2 Desorption

The results (see raw data) show that the sorption is reversible to a large extent .

7.3 Sorption isotherm

The kf respectively the koc-values calculated by the participants are reported in appendix II. Based on the raw data of the participants the Freundlich-isotherms were calculated. Negligible deviations result from errors in rounding.

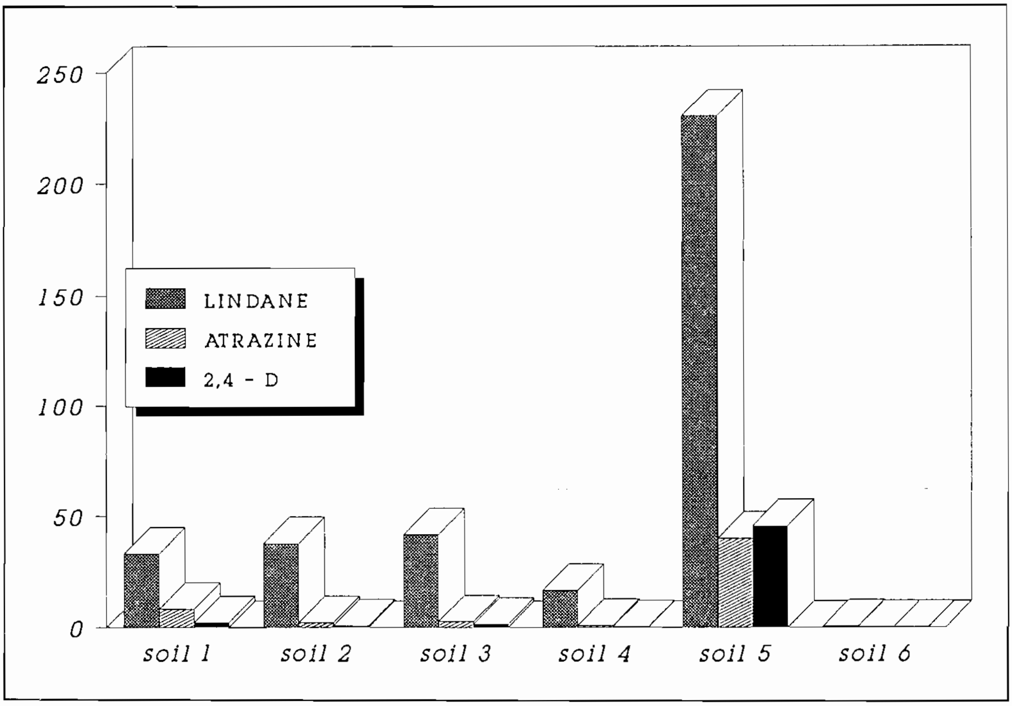


Fig. 9 Mean values of Freundlich coefficients determined in the ring-test

7.3.1 Lindane

Table 8: Test results

Soil 1	Lindane	labelled					
No.	kf	Koc	Mean	S.D.	%	Correl.	Slope
12	33.2	2550				0.999	0.89
Soil 1	Lindane	non-labelled					
No.	kf	Koc	Mean	S.D.	%	Correl.	Slope
1	48.15	3704				0.9989	1.36
8	36.32	2794				0.9999	0.91
Soil 2	Lindane	labelled					
No.	kf	Koc	Mean	S.D.	%	Correl.	Slope
6	37.02	1001				0.9999	0.96
12	38.61	1044				0.999	0.39
27	68.58	1854				0.976	1.54
			1300	480.5	37		
Soil 2	Lindane	non-labelled					
No.	kf	Koc	Mean	S.D.	%	Correl.	Slope
1	64.74	1750				0.9973	1.57
Soil 3	Lindane	labelled					
No.	kf	Koc	Mean	S.D.	%	Correl.	Slope
6	38.76	1123				0.9999	0.97
12	39.10	1134				0.999	0.96
13	47.30	1371				0.9991	1.05
			1209	140	12		
Soil 3	Lindane	non-labelled					
No.	kf	Koc	Mean	S.D.	%	Correl.	Slope
1	55.80	1617				0.9968	1.61
8	54.34	1575				0.9999	0.98

Soil 4	Lindane	labelled					
No.	kf	Koc	Mean	S.D.	%	Correl.	Slope
12	10.28	663				0.9998	0.92
13	10.24	661				0.9993	1.01
16	12.03	776				0.9999	0.94
27	12.42	801				0.9894	1.28
			725	74	109		

Soil 4	Lindane	non-labelled					
No.	kf	Koc	Mean	S.D.	%	Correl.	Slope
1	7.54	487				0.9929	1.54
8	10.47	676				0.9999	0.95
15	22.16	1430				0.9970	0.90
			864	499	58		

Soil 5	Lindane	labelled					
No.	kf	Koc	Mean	S.D.	%	Correl.	Slope
6	206.56	2238				0.9998	0.97
12	245	2654				0.999	1.04
16	247.4	2680				0.997	1.007
19	222.3	2408				0.9999	0.97
			2495	211	8		

Soil 5	Lindane	non-labelled					
No.	kf	Koc	Mean	S.D.	%	Correl.	Slope
1	1943.28	21054				0.9956	2.10
8	1120.54	12140				0.8583	1.10
(15	454.88	4928 (a)				0.9744	1.05)
15	214.31	2322 (b)				0.9999	0.85
			11839	9370	79		

Soil 6	Lindane	labelled					
No.	kf	Koc	Mean	S.D.	%	Correl.	Slope
12	0.566	226				0.997	1.01

(a) for the calculation of the Freundlich isotherm 4 concentrations were used

(b) for the calculation of the Freundlich isotherm only 3 concentrations were used according to the evaluation of the participant

A comparison of the koc-values show that the results are within one order of magnitude by neglecting the sub-soil 6, but vary up to factor 2-6 depending on the soil tested. The koc-value of soil 1 and 5 is quite similar but the sorption coefficients are twice as high as the koc values obtained for the other soils (2,3,4). The standard deviation of the ^{14}C-Lindane sorption coefficients for each soil is up to 12%. The use of non-labelled Lindane results in Koc-values higher then those determined for ^{14}C-Lindane.

7.3.2 Atrazine

Table 9: Test results

Soil 1 No.	Atrazine kf	labelled Koc	Mean	S.D.	%	Correl.	Slope
2	8.91	685				0.9999	0.88
11	7.80	600				0.9999	0.91
12	7.70	592				0.999	0.88
18	7.18	552				0.9984	0.90
20	9.74	749				0.9998	0.88
			636	80	13		
Soil 1 No.	**Atrazine kf**	**non-labelled Koc**	**Mean**	**S.D.**	**%**	**Correl.**	**Slope**
4	8.26	635 (a)				0.9977	0.66
4	5.32	409 (b)				0.9999	0.99
7	107.78	8290(*)				0.3557	0.90
12	7.02	540				0.995	0.89
24	11.05	850				0.9996	0.81
26	8.37	644				0.9991	0.87
			616	162	26		

(a) 1 g soil weight
(b) 2 g soil weight
(*) not considered for calculation of the mean value

Soil 2	Atrazine	labelled					
No.	kf	Koc	Mean	S.D.	%	Correl.	Slope
12	2.20	55				0.996	0.99
21	2.42	65				0.9998	0.96
27	2.36	64				0.999	0.96
			61.3	5.5	9		

Soil 2	Atrazine	non-labelled					
No.	kf	Koc	Mean	S.D.	%	Correl.	Slope
12	2.18	59				0.998	1.06
26	2.13	57				0.9987	0.89

Soil 3	Atrazine	labelled					
No.	kf	Koc	Mean	S.D.	%	Correl.	Slope
6	2.70	78				0.9997	0.95
12	2.47	72				0.991	0.94
13	2.97	86				0.9999	0.92
14	2.49	72				0.9997	0.93
21	3.01	87				0.9999	0.97
27	2.48	82					
			79.5	6.6	8		

Soil 3	Atrazine	non-labelled					
No.	kf	Koc	Mean	S.D.	%	Correl.	Slope
5	2.47	72				0.9999	0.94
8	1.80	52				0.6460	0.26
12	2.08	60				0.991	0.95
24	3.56	103				0.9950	0.90
26	2.68	78				0.9992	0.97
			73	19.5	27		

Soil 4	Atrazine	labelled					
No.	kf	Koc	Mean	S.D.	%	Correl.	Slope
3	0.92	59				0.9997	0.97
12	0.83	54				0.998	1.00

Soil 4	Atrazine	non-labelled					
No.	kf	Koc	Mean	S.D.	%	Correl.	Slope
8	1.74	112				0.9718	0.93
12	0.78	51				0.99	0.99
15	1.64	106				0.9982	1.03
			90	34	38		

Soil 5	Atrazine	labelled					
No.	kf	Koc	Mean	S.D.	%	Correl.	Slope
3	40.62	440				0.9999	0.92
6	36.10	391				0.9998	0.93
11	31.96	346				0.9999	0.89
12	39.6	429				0.998	0.97
16	43.58	472				0.9986	0.90
18	52.01	563				0.9993	0.90
19	35.33	383				0.9991	0.91
20	42.73	463				0.9998	0.93
21	38.75	420				0.9999	0.93
			434	63	15		

Soil 5	Atrazine	non-labelled					
No.	kf	Koc	Mean	S.D.	%	Correl.	Slope
4	36.17	392				0.9905	0.85
12	36.38	394				0.991	1.00
24	47.58	515				0.9950	0.83
26	41.94	454				0.997	0.88
			439	58.5	13		

Soil 6 No.	Atrazine kf	labelled Koc	Mean	S.D.	%	Correl.	Slope
12	0.19	75				0.999	0.75
20	0.26	102				0.9994	0.99
21	0.16	63				0.9859	1.08
			80	20	25		

With exception of soil 1 and 5 Atrazine is sorbed related to the organic carbon content of the soil. The variation of the sorption coefficients for each soil is 15 % (^{14}C-Atrazine) to 38 % (non-labelled). The determined sorption coefficient for soil 1 and 5 is similar but the sorption capacity is one order of magnitude higher than the Koc-values of the other soils. The results of ^{14}C-Atrazine and non-labelled Atrazine are in good agreement. Some participants obtained quite different results. Therefore the set up of a suitable analytical test method has to be performed carefully, especially with soil samples.

7.3.3 2,4-D

Table 10: Test results

Soil 1 No.	2,4-D kf	labelled Koc	Mean	S.D.	%	Correl.	Slope
6	1.70	130				0.9995	0.92
12	2.86	220				0.999	0.95
Soil 1 No.	**2,4-D kf**	**non-labelled Koc**	**Mean**	**S.D.**	**%**	**Correl.**	**Slope**
12	0.17	66				0.86	0.95
24	3.93	303				0.6204	0.23
Soil 2 No.	**2,4-D kf**	**labelled Koc**	**Mean**	**S.D.**	**%**	**Correl.**	**Slope**
12	0.70	19				0.997	0.95

Soil 3	2,4-D	labelled					
No.	kf	Koc	Mean	S.D.	%	Correl.	Slope
12	1.50	43				0.999	0.92
27	1.66	48				0.922	1.00

Soil 3	2,4-D	non-labelled					
No.	kf	Koc	Mean	S.D.	%	Correl.	Slope
24	3.43	99				0.6126	0.20

Soil 4	2,4-D	labelled					
No.	kf	Koc	Mean	S.D.	%	Correl.	Slope
3	0.34	22				0.9978	0.88
12	0.29	19				0.956	0.96

Soil 5	2,4-D	labelled					
No.	kf	Koc	Mean	S.D.	%	Correl.	Slope
3	39.10	424				0.9995	0.87
11	39.80	431				0.9999	0.98
12	67.38	730				0.996	0.902
13	41.47	449				0.9996	0.91
19	39.99	433				0.9984	0.92
27	43.12	467				0.9999	0.86
			489	119	24		

Soil 5	2,4-D	non-labelled					
No.	kf	Koc	Mean	S.D.	%	Correl.	Slope
24	no significant calculation of Koc-value possible						

Soil 6	2,4-D	labelled					
No.	kf	Koc	Mean	S.D.	%	Correl.	Slope
12	0.20	80				0.989	1.12

Only a few participants have performed the test with 2,4-D. The result scatter in a wide range (standard deviation up to 27 % for ^{14}C-2,4-D). Only 4 studies were performed with non-labelled substances. The results vary up to orders of magnitude. Based on the results of the tests with non-labelled substances an estimation of the sorption behaviour is not possible. One reason may be the lack of sensitivity in the analytical method.

The sorption capacity of soil 2-4 and soil 6 is very small (koc about 20-80). For soil 1 and 5 with an pH-value of 5.2 resp. 3.2 the koc-values are about 175 up to 500.

7.3.4 Comparison of sorption capacity

The results reveal that K_{oc} is not a substance-immanent value but a soil-related property. The sorption capacity of the selected soils can therfore not be contributed solely to their content in organic matter. It is a function of different components which vary within a wide range.

Table 11: Mean values of Koc for different soils.

Substance	Soil	labelled	non-labelled
Lindane	1	2550	3249
	2	1022.5	1750
	3	1209	1596
	4	700	864
	5	2495	11839
	6	226	---
Atrazine	1	636	616
	2	60	58
	3	79	73
	4	56.5	90
	5	434	439
	6	80	---
2,4-D	1	175	184.5
	2	19	---
	3	43	99
	4	20.5	---
	5	494	---
	6	80	---

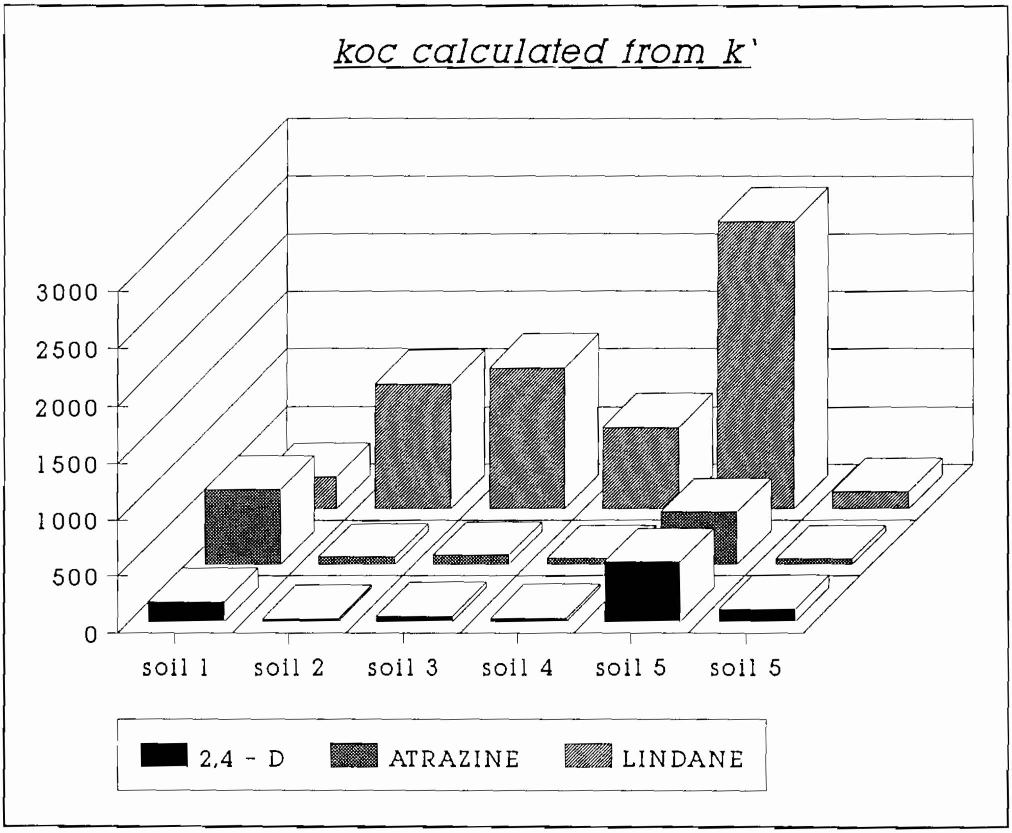


Fig. 10 K_{oc}-values for the tested soil/substance combinations

For Atrazine (K_{oc} about 80) soils 2,3,4 and 6 have nearly similar but low sorption capacities, whereas soil 1 and soil 5 adsorb to a high extent (K_{oc} 434 resp. 636). The investigation of 2,4-D leads for soil 2,3,4,5 to low K_{oc}-values (20 - 40), but for soil 1 and 5 to a higher K_{oc}-value, one order of magnitude higher (K_{oc} 175 - 500).Lindane is the substance with the highest sorption tendency (K_{oc} about 1000 for soil 2 - 4). The sorption capacity of soil 1 and 5 is two times higher. The sub-soil 6 shows only a slight sorption.

7.4 Comparison of K_{oc}-values

The results of the sorption coefficients calculated from distribution coefficients (initial concentration about 5 mg/l) and K_{oc}-values obtained from Freundlich isotherms are in a good agreement.

Table 12: Comparison of K_{OC} and K'

labelled Substance	Soil	results of distribution coefficients		results of Freundlich isotherms	
		K'	K_{oc}	K_f	Koc
Lindane	1	36.81	2832	33.2	2550
	2	40.36	1091	37.815	1300
	3	42.51	1232	41.72	1209
	4	11.17	721	10.85	725
	5	231.38	2507	230.32	2495
	6	0.39	156	0.566	226
Atrazine	1	8.76	674	8.27	636
	2	2.47	67	2.31	61.3
	3	2.84	82	2.73	79.5
	4	0.85	55	0.88	56.5
	5	43.59	472	40.08	434
	6	0.122	49	0.20	80
2,4-D	1	2.21	170	2.28	175
	2	0.75	20	0.70	19
	3	1.59	46	1.50	45.5
	4	0.45	29	0.32	20.5
	5	48.38	524	45.55	489
	6	0.16	64	0.20	80

7.5 Mass balance

The mass balance was performed according to table 13, 14, 15; the participants used different extracting agents revealing good results.

7.5.1 Lindane

Table 13: % of recovered substance

No.	soil	labelled	non-labelled	solvent
1	1	----	98.8	Dichloromethane or Benzene/Hexane
	2	----	100.9	
	3	----	98	
	4	----	96.8	
	5	----	99.9	
	6	----	103	
6	2	84.86/84.27	----	Quickszint100
	3	93.65/90.16	----	
	4	68.22	----	
	5	99.09/88.91	----	
8	1	----	65.8	Dichloromethane
	3	----	64.7	
	4	----	64.7	
	5	----	96	
9	3	96.7	----	Acetonitrile Water (7:3)
	4	95.9	----	
	5	95.3	----	
13	3	82.3	----	Acetone
	4	86.8	----	
	5	56.2	----	
15	4	----	91/84	Acetone
	5	----	91/90	
	6	----	96/94	
16	4	97.9/99.4/96.1/95.4	----	Methanol
	5	96.7/96.4/94.6/95	----	
17	1	----	81	Hexane/Water (2:1)
	2	----	92.6	
	3	----	81.5	
	4	----	116	
	5	----	66	

No.	Soil	labelled	non-labelled	solvent
22	3	----	55/78.5	HCl/ Toluene/Acetone (1:2.5:2.5)
	4	----	100/92.6	
	5	----	82.6/80.1	
	6	----	100/89.1	
27	1	75.2/69.6	----	Methanol
	2	85.7/85.8	----	
	3	72.1/86.1	----	
	4	86.2/79.6	----	
	5	79.5/86.9	----	
	6	68.9/67.8	----	

7.5.2 Atrazine

Table 14: % of recovered substance

No.	Soil	labelled	non-labelled	solvent
2	1	88/91	----	Acetone
3	4	97.41/97.43	----	Methanol
	5	95.8/95.66	----	
4	1	----	95.5	Methanol
	5	----	70.5	
5	3	----	94.5/92.3 (0.2 g/l)	Dichloromethane
	3	----	90.6/90.4 (0.04 g/l)	
6	1	77.92/66.71	----	Quickszint100
	3	97.86/95.74	----	
	5	90.05/91.56	----	
7	1	----	96.99/95.16	Dichloromethane
	5	----	90.797/92.04	
8	1	----	90.6	Dichloromethane
	3	----	81.7	
	4	----	84.2	
	5	----	42.7	

No.	Soil	labelled	non-labelled	solvent
9	3	96.9	----	Acetonitrile/ Water (7:3)
	5	99	----	
11	1	92/91.4	----	Ethanol
	5	98.6/86.6	----	
13	3	94.2	----	Acetone
	5	63.4	----	
14	3	99.9/99.7	----	Methanol
15	4	98/97	89/89	Acetonitrile/ Water (65:35)
	5	62/62	14/14	
	6	98/97	96/102	
16	5	96.7/94.1	----	Methanol
18	1	39.9/41.06		Dichloromethane
	5	57.93/57.7		
19	5	104/103	----	not specified
20	1	96.9	----	Dichloromethane/ Methanol (1:1)
	5	99.2	----	
21	2	97.6/96.9	----	Methanol
	3	97.3/95.4	----	
	5	92.8/91	----	
24	1	----	88.3/86	Methanol
	3	----	90.3/93.6	
	5	----	62.5/63.3	
26	1	---	93.8/94.8	CH_3CN
	2	---	94.9/93.5	CH_3CN
	3	---	96.2/94.8	CH_3CN
	5	---	59.5/58.2 and CH_2Cl_2/H_2O	CH_3CN
27	1	67.8/64.4	---	Methanol
	2	84.2/82.8	---	
	3	81.9/82.4	---	
	5	53.3/50.6	---	

At least for the set of test substances the use of a sub-soil leads to no additional information concerning sorption behaviour. Even though some participants felt it was important to test a subsoil the greater majority agreed that a weak absorbing topsoil should be substituted to the subsoil sample.

The sorption equilibrium (adsorption plateau) was attained rapidly after two hours. The plateau was reached to a large extent for all substances. Therefore an equilibration time of 16 hours seems to be sufficient for most organic chemicals. Nevertheless some chemicals could reach equilibrium after a period longer than 16 hours. Therefore a statement should be introduced in the test protocol that, according to the case, this period may be prolonged.

Some participants applied very strict criteria for reaching the equilibrium. So these participants didn't perform further investigation. Therefore the criteria for reaching of the plateau should be fixed more concretely. It was decided that equilibrium is reached if three consecutive measurements do not vary by 10 % of their mean.

Due to the reasons mentioned above only some participants have determined the sorption isotherms. Furthermore for some substances and soils the test performance was not demanded according to the results of the adsorption experiments.

Some participants felt that it would be preferable to work below the concentration of 5 [mg/l]. It was decided to maintain this recommendation in the protocol and to specify that, in the case of poorly soluble substances, the concentration to be used is half of the saturation value.

Although analytical well documented methods were available for all substances studied, the sorption coefficients, k' as well as K_f values, determined with non-labelled substances show a much higher variation than the results obtained with ^{14}C radio-labelled substances (e.g. Lindane, soil 5). Therefore the set up of a suitable analytical test scheme has to be performed more carefully especially with different soil samples. The concentration of the test substance in the supernatant of the soil should be determined immediately before test material is lost by other mechanism.

All participants have performed the investigation under different conditions concerning temperature leading to a further variation of the sorption coefficients. In general the variation of sorption coefficients was too high to identify a specific effect of temperature.

Concerning the calculation of sorption isotherm it has to be strengthened that the considered kf-values may vary within a factor of about 2. This depends on the number of concentrations included in the calculation of Freundlich isotherm (e.g. non-labelled Lindane soil 5, (3 and 4 values included, see page 42)).

The slopes obtained from the calculation of Freundlich-isotherms vary between 0.8 - 2.5 for one substance and soil by using non-labelled substances. However these variations decrease significantly by using labelled substances. In these cases all slopes vary between 0.8 and 1.2. Analytical determinations of low concentrations may cause problems and doubtful results. Therefore in these cases the determination of concentration has to be checked with regard to analytical errors.

A comparison of sorption coefficients calculated from distribution coefficients (initial concentration about 5 mg/l) and koc values obtained from Freundlich-isotherms show that the results are well comparable.

The desorption data show that sorption is reversible to a large extent. It was recommended by the meeting that the calculation of the desorption distribution coefficient should be included to elucidate whether sorption is completely reversible or not.

The selection of an appropriate solvent is a key question of the quality of mass balance data. Different extracting agents, choosen by the participants showed satisfying results. The meeting decided to leave the option of solvent open according to the experience of each laboratory.

9. References

- OECD-Guidlines for testing of chemicals, Paris OECD, revised version (1983)
- W. J. Dixon 'Processing data for outliers' Biometrics 9 (1953) 74 - 89.

Appendix I

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CONCLUDING REMARKS

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Following the recommendations of the ad-hoc meeting of individual experts on soil (Brussels, 22.06.1988) an EU-wide laboratory-intercomparison-test was organised by the German Umweltbundesamt in order to test the feasibility and applicability of the revised guideline on adsorption / desorption of chemicals in soil.

Beside the modified operating procedure given in the test protocol special interest was focused on the sorption characteristics of the test set of selected soils. 27 individual laboratories from nine different member countries participated in the common exercise. Three test substances were chosen from several proposals at a preparatory meeting of the participants, (Brussels, 04.09.1988). LINDANE, ATRAZINE and 2,4-D were selected for the following reasons:

- The water solubility ranges from 8 mg/l to 600 mg/l, the log Pow ranging from 3.7 to 0.1. The set of test chemicals cover therefore a broad range of chemical properties.
- Extensive information on sorption behaviour was already available from numerous data in the literature
- It was supposed that the test substances would not cause too much analytical problems.
- The substances do not hydrolyse during the testing period
- The substances can be purchased easily also in ^{14}C-labelled form.

All test substances, including $CaCl_2$, as well as the soil samples were shipped to the participants from one common source, respectively, in order to prevent charge-specific variations.

The air dried fine soils were gamma-irradiated prior to shipping to the participating laboratories in order to guarantee that no biodegradation would occur during the test procedure. This method of sterilization leaves the physical structure undisturbed and in contrast to autoclaving or chemical treatment minimizes the alteration in sorption properties.

The results of the ring-test were presented and discussed at a participant's meeting in Ispra/Italy, 03.-04.12.1990. The main results under the aspect of appropriate and representative soil selection are reported.

The amount of test substances adsorbed from the test solutions at equilibrium (16 h) is summarized in Table 1 for all combinations of six test soils and three test chemicals.

Tab. 1 Adsorbed amount of test substance at equilibrium (mean values of the laboratories using labelled material) in [%]

	LINDANE	ATRAZINE	2,4-D
soil E1	88	60	30
soil E2	90	32	16
soil E3	90	38	23
soil E4	70	18	10
soil E5	99	90	93
soil E6	9	2	0

These data give a first rough information on the sorption tendency for each individual test substances/soil sample combination. For a more detailed interpretation and deeper understanding of the differences the values must be compared in context with the sorption relevant parameters. Table 2 summarizes the sorption controlling properties:

Tab. 2 Sorption relevant parameters of the EURO soil set (in parenthesis the code number of the soil is given with the highest/lowest value for this parameter)

PARAMETER	Minimum	Maximum
% clay	(E5) 6.00	(E1) 75.00
% silt	(E5) 12.70	(E6) 82.40
% sand	(E6) 1.70	(E5) 81.60
% organic carbon	(E6) 0.25	(E5) 9.23
C/N ratio	(E1) 7.65	(E5) 30.77
pH value (KCl)	(E5) 3.40	(E2) 7.50
amorphous FE (‰)	(E2) 0.18	(E3) 4.75
amorphous Al (‰)	(E2) 0.17	(E3) 1.58
C.E.C (mval/100 g)	(E6) 11.40	(E5) 32.70

As can be seen from the listed minimum and maximum values in Table 2 a wide range for each pedological parameter is realized within the set of test soils. For many but not all of these parameters the soil samples E5 and E6 (sub-soil) represent the highest or lowest level. All but one (soil E4) samples mark at least one extreme position of the list of parameter governing type and strength of adsorption. On the other hand soil sample E4 stands for medium values of all parameters.

The Vertic Camibisol soil from Sicily (soil E1) has the highest clay content, mainly consisting of kaoline and illite minerals, its organic material showing the most valuable composition under ecological conditions (C/N = 7.65). The second soil from the Mediterranean region, the Greek Rendzina is characterized by a high pH-value, resulting from a high content of carbonates. On the other side the content of amorphous iron and amorphous aluminium is the lowest of all samples. This parameter reaches a maximum position in the pattern of the Dystric Cambisol (E3) from the more temperate Atlantic zone with intensive weathering. The Orthic Podzol (E5), also a very common form of soil in Northern Europe combines several extreme values at the same time. It shows by far the lowest pH (3,4) value among all samples. As a consequence of this highly acidic milieu an accumulation of organic material (> 9 % o.c.) at a low degree of humification (partly litter material) is observed. Apart from the maximum of particle size distribution allocated in the sand fraction with very low sorption capacity the high content of organic matter is responsible for the highest cation exchange capacity among all 'other' soil samples.

In contrast the sub-soil sample (E6) shows by far the lowest value in cation exchange capacity although it shows the highest silt content (around 80 %) of all test materials. In the composition of this soil, organic material is utmost completely absent (o.c = 0.25 %; N_{total} = 0.02 %).

One approach in interpretation of the differences in adsorption is to constellate pairs of samples from the soils with nearly identic values for one parameter but with significant differences in other ones. E.g. soil samples E1 and E3 show pH-values at the same level, while sample E3 closely resembles soil E6 in clay content. For content of organic carbon E2 and E3 on one side and E1 and E4 on the other side form pairs of very similar pH-values. Relationships in C.E.C. can be found for the combinations E1/E2 and E3/E4. With these pairs of similar contents of one component one can study the influence of other parameters on the over-all adsorption rates.

In general (but not for all participants) the results of the ring test obtained with non-labelled test substances showed a higher degree of standard deviation. In order to minimise the variation contributed by eventual analysis error the data in Table 1 were therefore restricted to the averaged values obtained from those laboratories which employed exclusively labelled material. The observed differences in adsorption should therefore nearly exclusively be caused by the differences in composition of sorption related parameters.

What can be easily noted at a first glance is that the sorption behaviour of the test chemicals as well as the sorption capacities of the soil samples vary considerably. They reflect the different sorption mechanisms, realized and interrelated in the various test soils to different extents and their relevance for chemicals of different properties.

As one result of the ring test it becomes clear that the extention of the set of originally 5 topsoils to 6 soil samples by including a sub-soil sample with extremly low sorption capacity (demanded by some of the experts at the meeting of the subgroup, 01.-02.06.1986) led to no additional information. This soil adsorbed none of the test chemicals to an extent exceeding significantly the analytical variation limit. Therefore no differences could be noticed which could be properly attributed to the variation in physico-chemical properties of the test substances or the pedological characteristics of the soil. Soil samples however which do not reflect these differences are of at least limited purpose in determining adsorption capacities and do not fulfill the prerequisites to serve as a reference material. Furthermore the retardation effect of this kind of sub-soil for chemicals which have already past the top horizon of a soil profile can be neglected under the aspect of exposure analysis for groundwater contamination.

All soil samples, except E6, adsorbed LINDANE to a comparatively high degree (>70 %). This must probably be attributed to the very hydrophobic nature of this chemical. Even smaller amounts of organic material are sufficient for high adsorption rates. For this reason differences in sorption relevant parameters (e.g. high clay content of E1 or high content of organic matter of E5) do not dominate the adsorption behaviour. During the adsorption experiments equilibrium was attained rapidly. Not unexpectedly, the range of pH (E2/E5) is also of minor influence. The results confirm the already known potential for a high affinity to almost all kinds of soil substrates and the tendency of the chemical to accumulate in this environmental compartment.

In contrast to LINDANE the test chemical ATRAZINE revealed a much more differentiated spectrum of adsorption behaviour in soils of different composition. The amount of test substance adsorbed from the test solution ranges from 18 - 90 %, with sample E2 and sample E4 showing the lowest adsorption amounts. These two samples are at the same time those of the highest pH values. And this parameter is the only one on a similar scale for both samples. Even more, the triple of soils which show the highest adsorption is identic with the triple of lowest pH values. Therefore the pH value of the soil substrate is one of the important factors influencing the sorption behaviour of ATRAZINE.

Neither the similarity in clay content between soil sample E2 and soil sample E4, nor the comparable organic matter content of sample E2 and E3 results in comparable sorption amounts of ATRAZINE. At the same time however it are obviously these two parameters which must be made responsable for both of the highest sorption rates (soil E1 with the highest clay content and soil E5 with the highest content of organic matter).

It becomes clear from the ATRAZINE data that for this kind of substances one single soil parameter cannot explain the sorption behaviour in different kinds of soils in a satisfying way. Obviously the influence of the composition of the clay fraction and the provenience and genesis of the organic material cannot be described sufficiently with mere %-values. Additionally the pH has a marked influence on the pH-dependent sorption sites, thus leading to varying sorption capacities of the "same" material. Those processes play an increasing role especially for polar or even dissociating chemicals.

The influence of pH which already became important for ATRAZINE unambiguously dominates the sorption behaviour of 2,4-D in soils (pK_a w 3.6). Clay content and organic matter content are only of limited importance. A pH-ranking list of the soil samples is reciprocal to the adsorption-ranking of 2,4-D. Soil sample E5 (pH = 3.4) shows an adsorption amount for 2,4-D which is even higher as for ATRAZINE (with 2,4-D showing a tenfold solubility in water in comparison to ATRAZINE). Because of the small clay content in sample E1 it is unequivocally the organic matter which despite of its low degree of humification is the most effective adsorption component. The mechanism of sorption under the given conditions is anionic binding to protonated sites.

Combining high concentrations of clay (> 80 %) and low pH (5.1) as in the case of soil E1 is obviously more effective in adsorbing 2,4-D to soil than higher rates of organic matter (6.45 %) at the same pH conditions (5.2) as in the case of soil E3

The results of the EU laboratory-intercomparison test substantiate the concept for selection of representative soils for adsorption of chemicals. The five test soils are appropriate to represent the majority of top soils occuring within the Union. Their different composition and properties cover the spectrum of sorption relevant parameters.

For adsorption experiments these soils cannot be replaced by any synthetic adsorber material, e.g. silica gel. The kind of information got from the full set of five soils can also not be combined in one single soil because the sorption properties of different soils result from different sorption mechanism on qualitative as well as quantitative scale. This could be well demonstrated in the ring test exercise mainly for ATRAZINE and 2,4-D. The sorption behaviour of this kind of substances can only be fully understood when comparing the sorption in different kinds of soil.

Adsorption tests with the full test set of representative soils are an indispensable prerequisite for estimating the mobility in soils for a broad spectrum of chemicals with different physicochemical properties on one side and specified for different kinds of soil in the member states on the other side.

Since 1982 when the German Federal Environmental Agency in co-operation with the European Union, the Department of Soil Science and the Department of Geography of the University of Kiel started the project which meanwhile is called 'EURO-Soil Project', lots of institutions and research centers as well as numerous industrial laboratories where involved in the improvement of the OECD Test Guideline 106 and the selection, sampling, treatment and analysis of the EURO-Soil samples. All the efforts undertaken so far and yet not completely finished not only prove that the Guideline in its present, revised form is a suitable tool for the assessment of the behaviour of new chemicals in soil and that the topsoils selected fully cover the requirements for representative test soils. In the course of the comprehensive analyses and tests carried out with the reference material lots of information on the six soil samples where collected and it certainly can be stated that the EURO-Soils belong to the best known soil samples of the European Union.

Through complex mathematical procedures the soil types and sampling sites have been selected in order to obtain material which is representative with respect either to frequency distribution or regional situation. The suitability of treatment and homogenization procedures applied were checked by comprehensive tests on homogeneity which revealed that each bottle of the reference material can be called homogenous within defined limits. The pedological analyses led to the observation that the samples cover wide ranges not only of sorption controlling but of other important pedological parameters. The analyses of trace elements and bound residues of organo-chlorine compounds showed that they are not present at interfering levels. Therefore the material is of optimum suitability to form reference material for adsorption/desorption testing according to the OECD Test Guideline 106.

However, although the EURO-Soil Project was exclusively designed to prepare a common concept for soil sorption testing within the European Union, it seems that it can also help to solve some other soil related problems. One of the major problems of the European Union is the poor comparability of soil classification and pedological analysis in the various EU Member States. Each country has its own way of mapping, classifying and analysing soils and the present state of soil documentation is far from being equal. On the other hand there is an urgent need of harmonization in order to effectively promote the protection of the limited and non-renewable resource soil. This is the more imporant since soils are highly complex three-phase entities which vary in space and time and which form the essential basis of life. Without any doubt a co-ordinated EU-wide soil protection requires a common data base and a complex network to bring the countless results of soil related studies together. One of the first steps to fulfill this task is the definition of reference material being comprehensively analyzed and available in sufficient quantities. For example, to link the soil data bases of different EU Member Countries the data have to be standardized first because the different analytical methods used sometimes lead to remarkable differences in the results. This data conversion could easily be performed if reference material is analysed first by the laboratories of the respective Member States using their standard methods and subsequently defining a common basis to level the data by applying certain correction factors.

Of course, since the soil selection was influenced by certain sorption related criteria, the soils might not totally meet the requirements for 'global' reference material in any case. Regarding the determination procedures and the properties of the material sampled, however, a quite satisfactory situation appears to be given to use the EURO-Soils not only as adsorption/ desorption reference. Consequently, there is a rapidly rising interst in the EURO-Soils from different directions which is understandable on the background of a nearly complete lack of reference material.

Since all the efforts undertaken in connection with the EURO-Soil project and documented in this report improved the knowledge on sampling, preparing and distributing reference soil material, the authors take the liberty to suggest, that together with potential notifiers a modified and extended concept should be implemented in order to establish a scientifically well founded and technically feasible European reference soil system for a more efficient protection of the soil environment.