

# MEASUREMENT TOOLS: SOIL SYSTEMS

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## Summary

This article provides an overview of physical, chemical and biological methods to assess pollution of soils and strain imposed on them. The focus is on pollution with heavy metals and organic xenobiotica, and strain imposed by soil acidification. Some methods related to strain imposed by elevated nitrogen inputs, elevated atmospheric carbon dioxide concentrations, erosion, and salinity are also included. The article is subdivided into the investigation of the soil solid phase and the analysis of soil solution. The way, soil samples, that were collected in the field, are prepared and stored, can severely affect measured values. The inorganic pollution of a soil per se can be assessed by total elemental analysis of solid soil samples, if the lithogenic background is corrected for. However, with respect to ecotoxicological questions, extraction of mobile or bioavailable fractions provides more relevant results. Detailed element speciations in soils are obtained by sequential extractions, high resolution microscopy, and spectroscopic methods. Extraction methods for organic xenobiotica from soils are intended usually for complete recovery, while mobility of these compounds is either calculated from experimentally determined constants, or assessed by measuring soil solution concentrations. Soil microorganisms are good biomonitoring of soil pollution with heavy metals and organic xenobiotica. By analysing the soil solution composition, the medium is assessed which is seen by plant roots, and which is linked directly to the groundwater. Laboratory methods to collect soil solution are presented. With respect to analysis of the chemical composition, soil solution is very much like natural waters from lakes or rivers.

### 1. Introduction

In contrast to contaminants in water and atmospheric systems, in-situ measurement techniques for soil pollutants are only in the development stage yet. Only a few parameters, that are related almost exclusively to the physical and biological functionality of soils, can be measured directly in the field. Therefore, assessing soil pollution usually requires sampling of soil or soil solution in the field and measuring physical, chemical or biological parameters in the laboratory. This article provides an overview of such laboratory methods while the chapter "Field techniques: soil systems", describes the sampling methodology. In addition, a general introduction into the description of soils and into the problems associated with assessing the effects of a specific pollution can be found there.

Since soils, basically, are chemically altered rocks, which are the original source of most inorganic pollutants, often high background concentrations have to be taken into account, except for organic xenobiotica. This is most important when considering pollution of a soil per se when assessed by means of the total concentration of an analyte. However, this is often of minor interest. The major goal of soil analysis is much more directed to the effects of soil pollution on plants--as organisms themselves, or as starting point of the food chain--, on soil microflora and fauna, and on groundwater quality. For this purpose plant-available or mobile fractions of a contaminant have to be measured, which involves either extraction with an appropriate reagent and analysis of the extract, or analysis of the soil solution. It is equally important with respect to the effects on flora and fauna to assess the impact of pollution on the functionality of soils. The latter includes biological activity, nutrient balance and availability, as well as water

regime. In addition, biological activity is a good means for biomonitoring of soil pollution.

Soil science, in particular the basic description and classification of soils, historically, is greatly influenced by national practices. As a consequence, internationally accepted standards for assessing soil pollution are evolving only very slowly. Therefore, this article cannot be comprehensive. Rather it is tried to point out common principles and types of different approaches.

## **2. The Soil Solid Phase (Soil Matrix)**

### **2.1. Sample Preparation and Storage**

Due to the strong influence of soil structure on almost every physical, biological or chemical parameter, the immediate analysis/extraction of an undisturbed and "field-moist" soil core is by far the best way of characterizing a single soil or soil horizon. However, comparison of different soil samples is possible only after homogenizing their structure. A widely accepted standard is reducing the size of aggregates to less than 2mm, which is called the fine earth, and is accomplished as follows. For most physical and chemical parameters samples are dried at room to moderately high temperature. Then aggregates are crushed by means of jaw crushers or mortars, and finally passed through a sieve with 2 mm mesh size. At this point, rock fragments are retained, and not included in the analysis. For some sensitive parameters, the procedure has to be performed with "field-moist" soil, which can be difficult, particularly for clay-rich soils. For most parameters, analysing the fine earth is considered to provide more realistic results with regard to natural conditions than using fine ground material. Only for total elemental analysis a so-called analytical fineness of smaller than 100 $\mu\text{m}$  is required, which is accomplished by means of friction, ball or rod mills.

Drying temperature, storage temperature and duration of storage before the analysis can have an influence on biological, chemical, and even physical parameters, the extent of which can depend strongly on the soil type. For most biological parameters, only immediate analysis of "field-moist" soil guarantees a relevant result. If samples cannot be analysed immediately, storage of the moist soil in the refrigerator or in the freezer (at -20°C) is recommended. However, some parameters like N mineralisation rate can change even in the frozen state. Chemical parameters, that are most affected by drying and storage are those that are strongly influenced by microbial activity, like all nitrogen forms and extractable phosphorus, or that are susceptible to oxidative transformations like oxidation states of chromium, iron or sulfur. If immediate analysis of the "field-moist" soil is not possible, storage of the moist soil at low temperature, or immediate air drying at room temperature and refrigerated or frozen storage of the dry soil are recommended, depending on the parameter. Addition of chemicals for inhibition of microbial processes is not applicable to soils, because this itself can alter chemical soil properties. Concentrations of volatile organic xenobiotica are also very susceptible. Recommendations for substances with boiling points below 300° include cool storage in sealed containers for a short period, or addition of the extractant to the moist soil in the field, and chemical drying with hygroscopic salts at low temperature for moderately volatile substances. For most other chemical and physical parameters immediate drying at 35 to 40°C in moving air is a widely recommended procedure. At higher drying

temperature, even particle size distribution can be affected. Long-time storage of dry soil for archiving is best at low temperature, and at low and constant humidity. In addition, adsorption of water vapour and gases like carbon dioxide, ammonia and sulfur oxides should be minimized by use of air-tight containers. Under such conditions, chemical parameters, except for the sensitive ones mentioned above, are expected to change only little over years. However, there are only few systematic investigations on this problem.

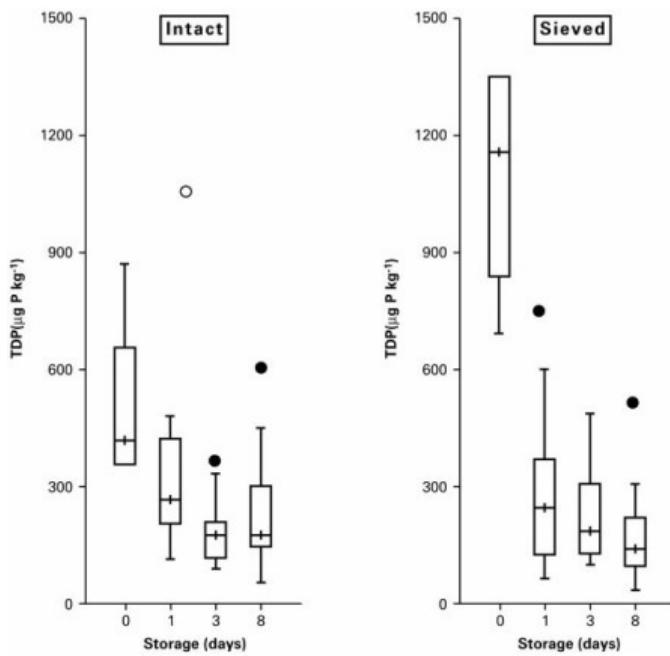


Figure 1. Total dissolved phosphorus in soil solutions obtained by centrifugation from a loamy sand (left: undisturbed soil core; right: sieved soil); the figure shows the effect of sieving and time of storage at 4°C (with permission from Chapman et al. 1997, *Soil Sci. Soc. Am. J.* 61:315-321).

With respect to analysing trace elements, contamination by abrasion from grinding and sieving instruments can be a problem. Agate is a good material for mortars and ball mills, tungsten coated stainless steel for friction mills.

For maximum comparability, results should be reported on a water-free basis, (i.e. dried at 105°C), irrespective of the specific pretreatment.

## 2.2. Basic Physical Description and Physical Parameters of Soil Functionality

Some of the physical parameters described in this chapter represent basic soil characteristics, which serve to put into perspective chemical parameters of pollution or strain. Others allow to estimate the extent of physical strain like erosion, compaction, limited aeration or limited water availability to plants.

### 2.2.1. Bulk and Particle Densities, Porosity

Bulk density is defined as mass of dry soil material (105°C) per unit volume. This is an important basic parameter which serves to transform concentrations from the

analytically accessible mass basis to volume basis. It is very easily determined by drying and weighing the material taken with a core of defined volume. However, in particular for soils with a large content of rock fragments, the bulk density of the fine earth is a more relevant parameter. This can be determined by relating the mass of the fine earth contained in a soil core to the volume of the core minus the volume of the rock fragments. Particle density, which is defined as the mass of dry soil material per volume of soil solids or fine earth, is determined by means of a pycnometer. From the knowledge of both, bulk and particle density, soil porosity, another basic soil parameter, can be calculated. It is defined as the volume of water or air filled voids divided by the total volume.

### **2.2.2. Soil Structure and Texture**

Soil structure, i.e. the actual arrangement of aggregates forming cracks and channels together with soil texture, i.e. the size distribution of primary particles determine the soil's permeability for water and air.

The stability of aggregates, i.e. conglomerates of two or more primary particles, is a measure with which susceptibility can be estimated against erosion. The more large, stable aggregates the lesser the susceptibility to erosion. Size distribution of stable aggregates is estimated by sieving soil dry or, under water, through an array of sieves with decreasing mesh size, employing reproducibly working machines. While dry aggregate stability is a measure to estimate susceptibility to wind erosion, wet aggregate stability serves to assess susceptibility to the disruptive forces of falling rain drops and running water. Aggregate destruction by water can also lead to erosion, but, in addition, dispersed particles can be carried into soil pores, causing increased compaction and decreased porosity.

The primary particles within the fine earth smaller 2 mm are subdivided into clay, silt and sand fractions. Distribution among these three fractions defines the basic textural classes of soils. The upper limit for the diameter of clay particles generally is set at 2  $\mu\text{m}$ , and the most common values for the division between silt and sand are 50 or 63  $\mu\text{m}$ . Prior to the determination, organic material has to be destroyed, usually by treatment with hydrogen peroxide, in order to allow complete dispersion of aggregates. After aggregate dispersion, size distribution is determined by sieving (applicable for particles larger than 50  $\mu\text{m}$ ) or sedimentation. While the clay fraction with its large relative surface area basically determines the adsorption capacity of a soil for water and chemical substances, the silt and sand fractions represent a rather inert "filling material".

### **2.2.3. Water Regime**

Water desorption curves usually are recorded in the laboratory on undisturbed soil cores; they complement water content and water potential measurements that are carried out in the field. They are defined as the relation between matric potential (related to the capillary force by which water is retained in the soil pores), and water content during drying. Water desorption curves are related to pore size distribution, and can be interpreted with respect to aeration, water availability to plants, ability to store water, water flow, and infiltration. The water content at a specified potential is determined

either by means of tension tables, in which the soil core is brought into hydraulic contact with a hanging water column or vacuum, or in tanks in which the soil is set under pressure and is connected to atmospheric pressure via hydraulic contact with a ceramic plate.

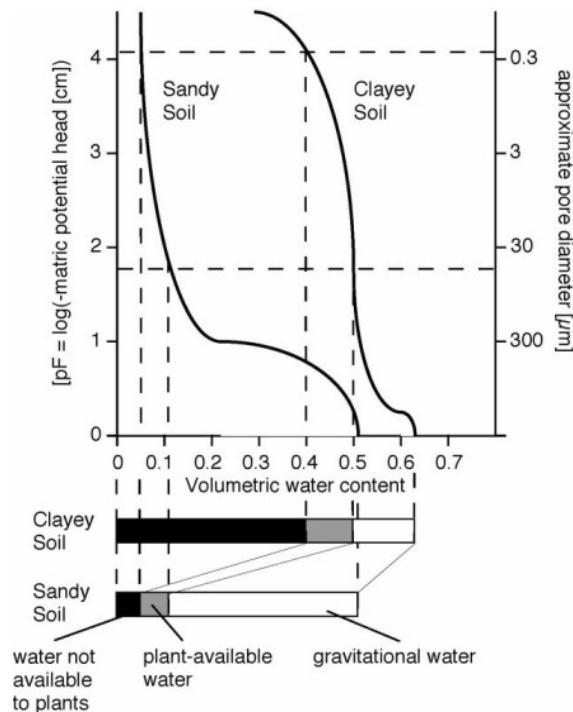


Figure 2 Characteristic water desorption curves for a sandy and a clayey soil; shown is a possible interpretation with respect to plant-available water (*modified from Gisi, U. et al. 1990. Bodenökologie, Georg Thieme Verlag, Stuttgart*)

Hydraulic conductivity is a measure of a soil's ability to transmit water at a certain water potential (see above), which depends on particle size distribution and structure of the soil. It is easiest to determine hydraulic conductivity at zero water potential, i.e. at saturation. Methods for saturated hydraulic conductivity measure the flow of deaerated water or dilute salt solution, which, ideally, mimics the actual soil solution, through an undisturbed saturated soil core under the influence of a constant or falling head.

#### 2.2.4. Specific Surface

The specific surface area, expressed in  $\text{m}^2/\text{g}$ , determines or is closely related to many physical and chemical soil properties: soils' capacities to retain water, to exchange and adsorb ions and molecules, and to control biological processes. The specific surface area usually is determined for organic-matter free soil material. It can be calculated either from the volume of adsorbed gases like nitrogen, ethane, water vapor, or ammonia, or from the retained amount of a polar liquid like ethylene glycol (mono)ethyl ether.

#### 2.3. Total Elemental Analysis

Total elemental analysis of soil material provides an overview of its overall chemical composition. In addition, this analysis can yield an estimate of a soil's pollution per se, without information on biological availability or mobilizability of individual components, however. With respect to anthropogenic origin, nothing can be said about such a source without an estimate of the lithogenic background.

### **2.3.1. Suitable Methods of Analysis for a Large Part of the Periodic Table**

A large array of elements can be determined by neutron activation analysis directly, and non-destructively on small amounts of soil material of analytical fineness. Because this method is based on properties of the atomic nucleus, it is virtually uninfluenced by chemical matrix effects. Combined with digestion and chemical separation techniques the method's sensitivity is sufficient to quantitatively detect also low concentrations of trace elements. However, the need for accessibility to a neutron source limits the method's suitability for routine analyses.

X-ray fluorescence analysis is a second method that allows direct and non-destructive analysis of soil samples. Another advantage is that instruments can be built with microfocussing capabilities, which allows for the analysis of single soil particles. However, matrix effects due to chemical composition and particle size inhomogeneities can be severe, and vary greatly for different soil materials. Therefore, for accurate quantitative analyses, a common procedure of matrix effect reduction is to fuse finely ground soil with lithium or sodium borates, cast the melt in a mold to form transparent discs, and analyse the discs. In principle, the method is suited for all elements heavier than oxygen. However, detection limits are relatively high when compared to other methods, in particular for the lighter elements.

All other instrumental methods generally require digestion of the soil material, for which two different approaches are used. One of them involves heating of ground soil with a mixture of acids in open or closed vessels, usually made from platinum or Teflon, until the entire material is dissolved. There are a lot of different procedures described in literature, differing in the composition of the acid mixture, the construction of the vessel, and the heat source used. In most procedures, however, hydrofluoric acid is an important component of the acid mixture which is needed to dissolve silicates. A second method is the fusion of ground soil material with salts like sodium carbonate or lithium (meta)borate, followed by dissolution of the melt in dilute nitric or hydrochloric acid. Evaporation loss of elements that are volatile, or form volatile products during digestion is a common problem with both, heating with acids in open vessels, and fusion.

Within the family of methods that are used for the analysis of digests, every method has its own advantages and disadvantages. Atomic absorption spectrometry (AAS), using acetylene flames for atomization, is relatively cheap and offers good sensitivity for group one elements and some volatile elements like Pb, Zn and Cd. However, since only one element can be analysed at the same time, it is practical, if only few elements need to be analysed as a routine. A relatively cheap method that offers high sensitivity for single elements is AAS, using atomization in graphite furnaces. Direct, but destructive analysis of soil powder is possible with this method, but good analytical

performance is difficult to achieve. Inductively coupled plasmas (ICP) are versatile heat sources of very high temperature that are coupled either with a detector for atomic and ionic emission lines (ICP/AES), or with a mass spectrometer (ICP/MS). Both methods allow multielement analysis over a large dynamic range. Sensitivities for most elements are better with more expensive ICP/MS. In addition, this method allows to determine ratios of different isotopes of an element. On the other hand, the tolerance for high amounts of dissolved solids is much better for ICP/AES, which generally makes this method more suitable for the analysis of soil digests. Both ICP methods can be coupled with a laser ablation unit, in which material from a small spot of soil is vaporized by a laser. This allows direct localized analysis with high spatial resolution. Very sensitive analysis of elements like arsenic and selenium is achieved by transformation into volatile hydrides, which then are introduced into an AAS flame or an ICP. Similarly, mercury compounds can be transformed into elemental Hg vapour, which is directly analysed by AAS, or is introduced into an ICP. Although instrumental methods are most commonly used today, it should not be forgotten, that there are wet-chemical methods, e.g. gravimetry, titrimetry or colorimetry, for almost all elements. An often used approach for routine analysis of a large number of samples, is the concept of "total extractable" concentrations as opposed to "real total" contents. Instead of preparing digests, soil samples are extracted with either aqua regia, or, more often, 2 M boiling nitric acid. The extracts are analysed by AAS, ICP/AES or ICP/MS. The major problem with this approach is, that the proportion extracted with these strong acids depends very much and unpredictably on the soil type.

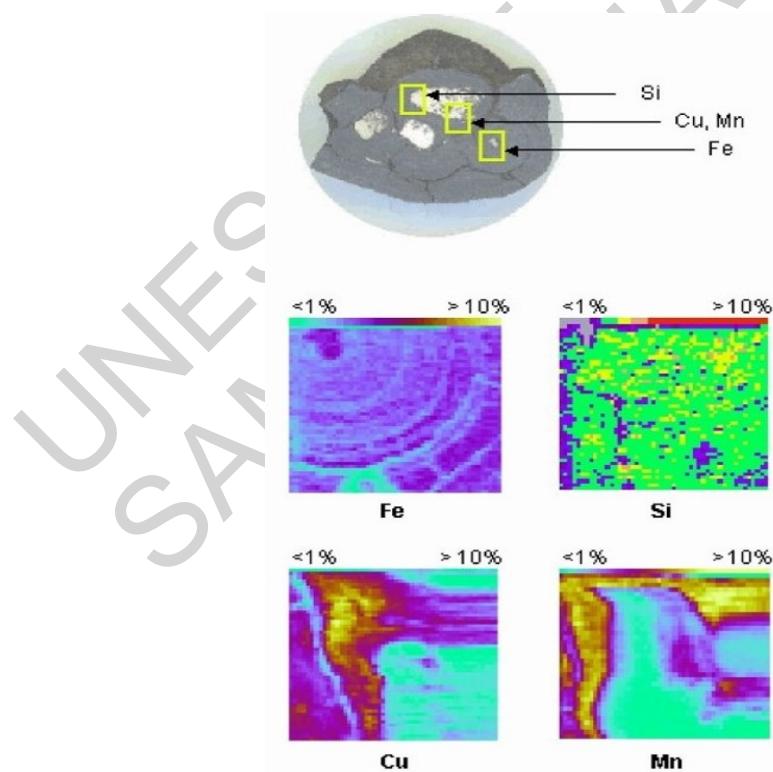


Figure 3. Element distribution patterns in a polished Mn nodule section as obtained by mapping with laser induced plasma spectrometry, a technique similar to laser ablation/ICP spectrometry (with permission from Yoon, Y.Y. et al. 1997. Analyst 122:1223-1227)

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## Biographical Sketch

**J. Luster** received a M.S. and Ph.D. in chemistry from the Swiss Federal Institute of Technology at Zrich in 1985 and 1990, respectively. For two years he was then postdoctoral research fellow at the University of California at Berkeley in the group of Prof. G. Sposito, where he performed analytical-chemical and complex-chemical investigations on the interactions between metal ions and dissolved soil organic matter, as well as spectroscopic studies of trace metals in mineral phases. From 1992 to present, Dr. Luster has been research scientist in the department of Soil Ecology at the Swiss Federal Research Institute WSL. He has been involved in various projects on acidification and heavy metal contamination of forest soils. In addition he has been responsible for running the departments analytical-chemical laboratory.