

HORIZONTAL STANDARDISATION FOR SOIL, SLUDGE,  
SEDIMENT AND BIOWASTE

Report of the Desk-Study “Pre-treatment for Organic  
Parameters” for the European Project HORIZONTAL

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# 1. INTRODUCTION

The objective of the project “HORIZONTAL” is to design an appropriate strategy towards the development of across-matrix, horizontal and harmonised European standards for the analysis of various inorganic and organic contaminants in soils, sludges and biowastes. Up to now considerable attention was given to the issues of sampling and the measurement processes themselves while the intermediate step of sample-pre-treatment was neglected. Therefore, the scope is the development of a desk study based on a critical evaluation of existing (vertical) International (ISO), European (CEN), and National Standards (EU, USA) as well as the of the CEN Committee Drafts dealing with pre-treatment and testing of soils (including sediments), sludges, biowaste and (soil-related) wastes concerning the current practices on the pre-treatment of samples prior to chemical and physico-chemical analysis. This part of the desk study is focused on organic constituents, of course, in accordance with the pre-treatment of the inorganic compounds. If points are not in conformity, this will be defined explicitly in the text. It must further be pointed out that hygienic and microbiological parameters are not included in this work.

The first part of the Project HORIZONTAL is, as already mentioned, the performance of the desk studies with additional elaboration of a proposal of a horizontal approach. After consultation with relevant CEN and ISO bodies and agreement in the Steering Committee, the next step will be the experimental examination of the proposed approach by a series of tests on soils, sludges and biowastes. To proof the validity (and applicability) of the draft, some comparative experiments need to be performed. The third part will then be the actual validation – proofing that a given standard is “fit for purpose”.

Unfortunately, the existing normative reference dealing explicitly with pre-treatment is scarce. Additionally, the borderline between the end of sampling procedure and the start of the pre-treatment as well as the end of the pre-treatment and the actual testing standard is fuzzy. In the context of this desk study, pre-treatment deals with the necessary steps applied to a fresh sample after sampling until the production of a test-portion, to be applied for a given testing procedure. In particular, this implies the issue of storage, homogenisation, and sub-sampling and includes operations such as stabilization (drying), particle size reduction (milling, grinding) and fractionation (sieving). It has to be pointed out that further analytical step such as the efficiency and characteristics of digestion and extraction are strongly influenced by the pre-treatment applied.

Since pre-treatment is critical and matrix-dependent it is necessary to define what sample materials will be relevant by the analysis of the organic micropollutants investigated. The following matrices are included:

- Soils with different structure (clay, sand etc.),
- Sewage sludge,
- Industrial sludge,
- Sediment,
- Compost (stabilized),
- Biowaste (not stabilized) with organic matter of mainly natural origin.

Other waste materials are not included at the moment, since no interest has been expressed so far.

Conditions of storage of samples of soils, sludges and wastes are often not described in detail. For instance freezing is recommended for most matrices for sample storage of NPs and LAS [Desk Study LAS and Nonylphenols, 2004].

## 1.1 Methodology

For documentation of the information provisioning first a literature search by internet was performed using different searching machines of diverse publishers. Searching phrases used in this context have been for instance soil, sludge, biowaste, water treatment, fate, environment in combination with LAS, PAHs, PCBs, NP, NPME, NPDE, DBP, DEHP etc.

Additionally, for receiving the Standards and Draft Standards several persons have been contacted by email and phone, namely:

- Andreas Paetz, Email: andreas.paetz@din.de
- Dr. Klaus Furtmann, Email: klaus.furtmann@lua.nrw.de
- Nina Zemann, Email: nina.zemann@lebensministerium.at
- Dr. Monika Kisser, UBA Niederösterreich
- Prof. Dr. Konstantin Terytze, Email: konstantin.terytze@uba.de
- Stefanie Kettner (Dr. Reimer Leschber), Email: stephanie.kettner@din.de
- Dr. Bernd Gawlik, Email: bernd.gawlik@jrc.it

Unfortunately, the receiving of the requested standards revealed much more difficult than expected. For instance the first contact was in the first week of October 2004 and all necessary information was obtained end of November 2004.

It is worth mentioning, that for some of the online publishers there was just limited access to the original literature.

## 1.2 Included Standards or Draft Standards in this Study

For pre-treatment explicitly very few official methods exist. Just for the matrix “Soil” two ISO methods, namely ISO/FDIS 14507 and ISO/DIS 11464 are available. It has therefore been very important to get information about ongoing work from the CEN and ISO bodies and about existing national methods. For sludge only an ongoing CEN/TC draft version from August 2003 was available [CEN/TC 308/WG 1/TG 4 N0058].

The following Standards and Draft Standards have been included in this study:

- |                        |  |
|------------------------|--|
| <b>ISO 14507:</b>      | Soil quality – Pre-treatment of samples for determination of organic contaminants (version 2002)         |
| <b>ISO/DIS 11464:</b>  | Soil quality – Pre-treatment of samples for physico-chemical analyses                                    |
| <b>Draft NEN 5709:</b> | Soil – Sample pre-treatment for determination of organic and inorganic parameters in soil (version 2004) |

- ISO 18381-1:** Soil quality – Sampling – Part 1: Guidance on the design of sampling programmes
- ISO 18381-2:** Soil quality – Sampling – Part 2: Guidance on Sampling techniques
- ISO/FDIS 10382:** Soil quality – Determination of organochlorine pesticides and polychlorinated biphenyls – Gas chromatographic method with electron capture detection
- ISO/DIS 22155:** Soil quality – Gas chromatographic determination of the content of volatile aromatic and halogenated hydrocarbons and selected ethers – Static headspace method
- ISO/FDIS 16720:** Soil quality – Pre-treatment of samples by freeze drying for subsequent analysis
- ISO/DIS 18287:** Soil quality – Determination of polycyclic aromatic hydrocarbons (PAH) – Gas chromatographic method with mass spectrometric detection (GC-MS)
- ISO 13877:** Soil quality – Determination of polynuclear aromatic hydrocarbons – Method using high-performance liquid chromatography
- ISO/FDIS 15175:** Soil quality – Characterization of soil related to groundwater protection
- ISO 11465:** Soil quality – Determination of dry matter and water content on a mass basis – Gravimetric method
- ISO 5667 – 13:** Water quality – Sampling – Part 13: Guidance on sampling of sewage sludges from sewage and water treatment works
- ISO 5667 – 15:** Water quality – Sampling – Part 15: Guidance on preservation and handling of sludge and sediment samples
- EPA 3540:** Extraction of Solid Samples of the Semivolatile or Nonvolatile Analytes
- TC 292 WI 028:** Determination of polychlorinated biphenyls (P.C.B.) congeners in soil, sludge and solid waste – Separation and quantitative determination of selected congeners by using capillary gas chromatography with electron capture or mass spectrometric detection.
- TC 308 WI 057:** Characterisation of sludges – Protocol for conducting inter-laboratory trials of methods for chemical, microbiological and physical analysis of sludges
- DIN 38402-30:** German standard methods for the examination of water, waste water and sludge, general information (Group A) – Part 30: Pre-treatment,

homogenisation and aliquotation of non-homogeneous water samples (A 30)

**DIN 38414-11:** German standard methods for the examination of water, waste water and sludge; sludge and sediments (Group S), sampling of sediments (S 11)

**DIN 38414-20:** German standard methods for the examination of water, waste water and sludge – Sludge and sediments (Group S) – Part 20: Determination of 6 polychlorinated biphenyls (PCB) (S20)

**DIN 38414-21:** German standard methods for the examination of water, waste water and sludge – Sludge and sediments (Group S) – Part 22: Determination of 6 polycyclic aromatic hydrocarbons (PAHs) by high performance liquid chromatography (HPLC) and fluorescence detection (S21)

**DIN 38414-22:** German standard methods for the examination of water, waste water and sludge – Sludge and sediments (Group S) – Part 22: Determination of dry residue by freezing and preparation of the freeze dried mass of sludge (S22)

**DIN 38414-23:** German standard methods for the examination of water, waste water and sludge – Sludge and sediments group (group S) – Part 23: Determination of 15 polycyclic aromatic hydrocarbons (PAH) by high performance liquid chromatography (HPLC) and fluorescence detection (S 23)

**DIN 38414-24:** German standard methods for the examination of water, waste water and sludge – Sludge and sediments group (group S) – Part 24: Determination of polychlorinated dibenzodioxines (PCDD) and polychlorinated dibenzofuranes (PCDF) (S 24)

**XP X 33 – 002:** Caractérisation des boues: Détermination de la matière sèche par lyophilisation

**DRAFT prEN 14899:** Characterisation of Waste – Sampling of waste materials: Framework for the preparation and application of a Sampling Plan

## 2. DESCRIPTION OF THE ANALYTES

The analytes to be included in the study are polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), phthalates (di-n-butyl phthalate and di-2-ethylhexyl phthalate), nonylphenol-polyethoxylates (NPnE) and linear alkylbenzenesulfonate (LAS). Since polychlorinated dibenzo-p-dioxins/furans (PCDD/Fs) and polybrominated-diphenyl-ethers (PBDE) show similar physico-chemical behaviour as PCBs, the sample pre-treatment could be extrapolated largely. Therefore, this group was not namely included into the desk study. It has to be remarked, that special laboratory equipment and security features are necessary for dioxine-analysis.

Although there is an intensive discussion about the environmental impact of pharmaceuticals [Díaz-Cruz et al., 2003], this large group is difficult to include into a proposed horizontal standard, due to their wide range of physical and chemical properties [Kümmerer, 2004].

### 2.1 Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are a widely distributed group of organic pollutants containing two or more fused aromatic rings composed of only carbon and hydrogen atoms. Conditions for the formation of PAHs are most favourable during the pyrolysis of organic matter in air deficient environments at temperatures in the range 650 – 900 °C. The aromatic compounds formed are more stable than their precursors which include acetylene, butadiene and butyl benzene. PAHs occur naturally in the environment, due to their formation during forest and prairie fires and volcanic eruptions. However, the largest amount of PAHs is released into the environment by human activities including incomplete combustion of fossil fuels, which is the most important source of PAHs, as well as cigarettes, coke production, industrial processes and motor vehicles. Their great environmental concern is related to their mutagenicity, carcinogenicity and persistence [Chen et al., 2004; Woo et al., 2004; Criado et al., 2004]. The first cancers to be associated with PAH-containing substances were through skin contact which resulted in scrotal cancer of chimney sweeps and skin cancer among mule spinners in the cotton, wool and jute industries [Encyclopedia of Analytical Science, 1995]. Therefore their presence in the environment (air, water, soils) is regularly monitored and controlled. The US Environmental Protection Agency has included 16 PAHs in its priority pollutant list and they are also considered as priority contaminants by the European Union. Owing to their hydrophobicity PAHs are adsorbed strongly to the organic fraction of sediments and soils. Therefore it can be concluded that sediments and soils are usually considered as the main sinks for PAHs in the environment and PAHs with four or more aromatic rings are persistent in the environment [Harvey, 1996]. In the environment PAHs undergo reactions such as photo oxidation, sulfonation and nitration. These reactions are important not only because they represent a major pathway for the removal of PAHs but also because the reaction products are health hazards themselves and more toxic than PAHs. Two examples are the conversions of perylene and pyrene (nonmutagenic) to 3-nitroperylene (directly active mutagen) and 1-nitropyrene (highly mutagenic). These reactions are influenced by humidity, UV radiation, temperature and the nature of particulates onto which the PAHs are adsorbed. Mutagens may occur in ambient particulates because of reactions of PAHs with ozone, nitrous oxides, peroxyacetyl nitrate and free radicals present to varying degrees in polluted atmospheres.



Currently, there are no national or international standard limits for PAH levels in the environment. The scientific community is in general agreement that it is impossible to formulate a dose (or concentration) of a proven carcinogen or mutagen which is without a residual risk to health. Even the smallest doses of a carcinogen produce some genotoxic damage though no tumour formation is observed during finite experimental conditions.

## 2.2 Polychlorinated Biphenyls (PCBs)

Polychlorinated biphenyls (PCBs) are a class of synthetic aromatic compounds consisting of two benzene rings carrying from one to ten chlorine substituents. There are, thus 209 different molecular species (called congeners) that differ in the number and/or position of the chlorines [Luque García & de Castro, 2003; Abraham et al., 2002]. Typical industrial preparations obtained by random chlorination of biphenyl contain 20 – 60 congeners and they are widely used in the electronics industry mainly as a dielectric in capacitors and transformers, hydraulic fluids, in paper and cardboard manufacture, as additives in inks and as fillers. Due to their physical and chemical stability, and also to their lipophilic affinity, they are highly persistent and tend to accumulate in soils, sediments, adipose tissues and aquatic biota. About 1.5 million tons of PCBs were produced worldwide between the 1930s and the mid-1980s and a substantial fraction of this has entered or will ultimately enter the environment. PCBs are now widely distributed in most geographical areas and environmental compartments around the world and are found even in remote parts of the world, such as Antarctica and Northern Greenland [Lang, 1992].

PCBs are degraded aerobically and anaerobically. As a general rule, highly chlorinated congeners (which are highly stable and highly hydrophobic) are good substrates for anaerobic degradation, possibly via chlororespiration, but are poor substrates for aerobic degradation. Lower-chlorinated congeners are, in turn, poor substrates for anaerobic dechlorination, but are good substrates for aerobic degradation.

As already mentioned PCDD/Fs and PBDE can be extrapolated largely from PCB-behaviour.

## 2.3 Phthalates

The phthalates were introduced in the 1920's as softeners in plastic materials and are among the most important chemicals in various industrial products. The phthalates are diesters of phthalic acids and are produced from a reaction between phthalic acid and appropriate alcohols. Phthalates with short side chains have properties that are very different from those with longer side chains such as the widespread di-n-butyl phthalate (DBP) and di-2-ethylhexyl phthalate (DEHP). DEHP is one of the most used phthalates due to its stability, fluidity and low volatility. The smaller phthalates are rapidly degraded aerobically and anaerobically and have a lower tendency to adsorb, whereas long chain phthalates, such as DEHP, are predominately degraded aerobically. DBP and DEHP serve as important additives including flexible PVC materials and household products such as paint and glues. Since they are teratogenic, mutagenic and carcinogenic the US-EPA has classified them as priority pollutants [Jianlong et al., 2004; Yin et al., 2003; Jianlong, 2004]. Additionally, phthalic acid

esters (PAE) have been suspected to cause estrogenic effects in mammals including humans, and thus damage the reproductive system [Bauer & Herrmann, 1997].

Phthalic acid esters enter directly or indirectly into the environment. Due to their low water solubility and high octanol-water partition coefficients, they tend to accumulate in the soil or sediment and in the biota living in the phthalate containing waters. The level of accumulation depends on their solubility and partition coefficients and on their degradation rates through chemical or biological pathways. The environmental impact of DEHP is very strong: Its extremely high hydrophobicity makes it highly persistent and bio-accumulating. It has been discussed in the literature that the analysis of phthalate esters and alkylphenol ethoxylate lacks of suitable and well-validated methods. This fact can be attributed to different analytical problems. In case of phthalate esters, blank problems are very common since these compounds are ubiquitous and they can be found in tubing material, pipette tips, septa of vials, solvents and chromatographic sorbents [Cortazar et al., 2005].

## 2.4 Nonylphenol-Polyethoxylates

Nonylphenol-polyethoxylates (NPnE) are synthetic surface active substances that are used in the industry as tensides, emulgators and surfactants in paints, soaps, cosmetics, pesticides, detergents and insulating materials. They consist of a hydrophobic branched C<sub>9</sub>-alkyl-group and a hydrophilic alcohol polyethoxylate group in para-position.

Following use the NPnE's are primarily disposed to the sewer and led to waste Water treatment plants (WWTPs) where the parent oligomers are efficiently eliminated during biological treatment by shortening of the hydrophilic ethoxylate chain. The degradation products predominately comprise nonylphenol (NP), nonylphenol-monoethoxylate (NPME), nonylphenol-diethoxylat (NPDE) and nonylphenoxy carboxylic acids (NPCA). The abundance of the particular metabolite is dependent on the treatment conditions.

NP, NPME and NPDE are more lipophilic than their parent substances and are therefore more susceptible to bioaccumulation. NP is found to be toxic towards aquatic organism and furthermore to exhibit hormone disrupting effects. As a result of their toxicity, the large production volumes and their persistence in the environment, especially in sediments, the public concern about these compounds is leading to the withdrawal of these kind of compounds for many uses in the next future [Cortazar et al., 2005].

Nonylphenols are included in the EC priority list in the Water Framework Directive by the name of "nonylphenols".

## 2.5 Linear Alkylbenzenesulfonates (LAS) (not foreseen at present in contract!)

Linear alkylbenzenesulfonates (LAS) are used as an important anionic detergent in washing and cleaning agents in households and industry. They have caused significant concern due to their observed toxic effects on aquatic organisms [Carlsen et al., 2002]. Hence, LAS have entered the list of undesirable substances produced by the Danish EPA (DEPA, 1998), the main concern being the lack of degradation of LAS under anaerobic conditions, whereas the

compounds are readily degraded under aerobic conditions. LAS may enter the terrestrial environment by several pathways, such as irrigation with wastewater or by amendment of the soil by sewage sludge. Further LAS may enter the soil compartment through the use of pesticides, as detergents are found in pesticide formulations as emulsifiers, dispersing and spreading agents. LAS sorption on soils decrease with increasing pH and correlate positively with the organic matter content of the soils [Fytianos et al., 1997]. Due to their amphiphilic nature these surfactants in sewage sludge, soils and sediments can adsorb to the surface of resident particulate matter. Surfactants may also precipitate from solution in the presence of metal ions (particulately  $\text{Ca}^{2+}$ ). Such behaviour may result in a significant proportion of the surfactant load of raw sewage being associated with the particulated fraction [Scott & Jones, 2000]. After use LAS is degraded to SPC (sulphphenylcarboxylic acids). These are not included as an analyte in the method for LAS [Desk Study LAS and Nonylphenols, 2004].

### 3. GENERAL CONSIDERATIONS

Generally, it is advisable to minimize pre-treatment steps of the investigated sample, as every step may change the origin state. As it is mentioned in the normative references, the time elapsed between sample collection and analysis should be as short as possible. The addition of chemical preservatives or stabilizing agents is not a common practice for soil sampling. This is due to the fact that a soil sample is usually used for a large number of different determinations. Furthermore the sample has to undergo preparation procedures, e.g. drying or milling, during which unwanted and unquantifiable reactions of the preservatives may occur. A general point is to cool the sample right after sampling to avoid microbial activity. A further decreasing of the microbial activity would be the exclusion of oxygen.

The objective of the described pre-treatment methods is the preparation of a suitable test sample that contains a percentage of the compounds that is to be determined. That percentage shall resemble as closely as possible the percentage in the original sample.

The method used for the pre-treatment will depend on the substances or the groups of substances that are to be determined. A general distinction for the organic substances is made between two categories [ISO/FDIS 14507]:

- Volatile compounds (boiling point < 300 °C at 101 kPa) and
- Moderately volatile compounds (boiling point > 300 °C at 101 kPa).

The analytes (beside naphthalene) investigated in this study belong to the group of moderately volatile compounds. Naphthalene, which belongs to the polycyclic aromatic hydrocarbons, is volatile, since its boiling point is 218 °C at 101 kPa. For phthalates only boiling points at pressures lower 101 kPa were available from the literature, namely 160 – 164 °C for DBP at 2.7 kPa and 260 – 265 °C for DEHP at the same pressure of 2.7 kPa. The demarcation of the categories for volatile and moderately volatile compounds can, in principle, best be related to the vapour pressure. Since the vapour pressure for only a small number of substances is known, and in view of the relationship between vapour pressure and boiling point, the boiling point has been chosen as the criterion for distinction [ISO/FDIS 14507].

Further decisions are depending on the situation and the leaching test to be performed and following the pre-treatment. It may be necessary to subject the soil to pre-treatment including liquid/solid separation, drying, sub-sampling, particle size reduction, compaction and/or conservation. It may also be necessary to dry humid soil samples prior to particle size reduction. There will always be a risk of losing volatile components (e.g. mercury and various organics, as well as water of crystallization), and any drying operation should therefore be carried out as gently as possible at the lowest convenient temperature. The sub-sampling techniques used (coning and quartering or application of riffles or other dividing apparatus) should ensure that the sub-samples obtained are truly representative of the bulk sample. Some contaminated soils, particularly when humid, may undergo ageing, carbonation and oxidation reactions with the atmosphere as well as microbial degradation reactions if stored prior to testing [ISO/FDIS 15175]. And finally it has to be taken into account, for which use the pre-treated test-portion is produced. It is obviously, that a provisionary sample, which should be stored for a long time and should not undergo any changes in that time, demand different sample pre-treatment efforts than a sample for providing environmental monitoring data.

A method proposed by the Umweltbundesamt (UBA) Berlin for instance is quick-freezing after sieving to a particle size of < 2 mm usable directly for field samples. This is possible with a special device, where the material is collected after sieving on a tray, which is cooled with liquid nitrogen from below. For isolation this device is surrounded by styrofoam to reduce the amount of liquid nitrogen required. The frozen soil-material can be transferred with a ceramic or stainless steel spatula into food carriers (probably tight plastic boxes) for transportation. The thickness of the layer on the tray should not exceed 2 cm, as otherwise the material needs more time for freezing and additionally clump formation could increase. Homogenisation of this material is carried out by the use of a jaw crusher cooled with liquid nitrogen to guarantee a sample processing under frozen condition. The advantage of this method is to obtain a sample which is very well flowable and which allows the discharge of test portions without thawing the complete sample. Additionally, this method is well suited for long-time storage under frozen conditions with the original water content [Weinfurtner et al., 2002]. Unfortunately, this method is not applicable to analytical methods which demand dried samples and possibly not applicable to the analysis of DBP and DEHP.

Further physico-chemical parameters to be paid attention to are:

- Volatility (vapour pressure, Henry's Law constant, boiling point),
- Stability (isomerisation, photodegradation, microbial degradation),
- Sorption behaviour ( $\log K_{OW}$ ,  $K_{OC}$ ),
- Water solubility.

### 3.1 Volatility

Vapour pressure is a chemical-specific property, defined as the partial pressure of a chemical, in the gas phase, in equilibrium with the pure solid or liquid chemical. Vapour pressures are very temperature-dependent and are expressed in Pa and, generally, reported at temperatures in the range 20 – 25 °C. Experimental measurements are not easily made. Additionally, reported vapour pressure values often exhibit wide discrepancies, up to tenfold between different authors. An other parameter for an appropriate indication of compounds volatility is the Henry's Law constant, denoted H or  $K_H$ . The Henry's Law constant represents a partitioning coefficient defined as the ration of a chemical's concentration in air to its concentration in water at equilibrium. In general, a high value favouring volatilisation and samples containing such compounds must be handled carefully in order to avoid loss. For instance, evaporation steps should not be included in the sampling process. The H value can be estimated from experimentally-determined solubilities and vapour pressures. Therefore in this case, since the vapour pressure (and also the H value) for only a small number of substances is known, and in view of the relationship between vapour pressure and boiling point, the boiling point has been chosen as the criterion for distinction.

### 3.2 Stability

Photodegradation is the photochemical transformation of a molecule into lower molecule weight fragments, usually in an oxidation process. This term is widely used in the destruction (oxidation) of pollutants by UV-based processes. PAHs, for instance, are known to be

sensitive to photodegradation [Villar et al., 2004; Sabaté et al., 2001] and exposure to direct sunlight or other strong light should be avoided or at least minimized to a minimum during all steps of sample storage and pre-treatment. The simplest pre-requisite to minimize UV-based degradation is storage and transportation in amber glass bottles or sample containers covered with foil. An other process, which leads commonly to transformation products with the same or a very similar molecular weight, is isomerisation. In general, transformation processes – UV-based, microbiological, etc. – are also depended on the matrix type (cation exchange capacity, pH value, organic matter, etc.), humidity, oxygen saturation and temperature. It is well known that the matrix type has a profound influence on the persistence of compounds and their degradation products. For example, a compound and its degradation products persist longer in sandy soils than in organic-rich soils. Organic matter and temperature are two other parameters that essentially affect the formation of the transformation products of pollutants in sample. In general, by increasing the organic-matter content and the temperature, the degradation is enhanced. When the organic-matter content increases, the biomass of the active microbial population also increases and so does the degradation. Additionally, it is clear, that high temperatures lead to higher microbiological activities and, therefore, to faster degradation. A general possibility to avoid microbial degradation is to cool the sample right after sampling and store it at low temperatures. A further decreasing of the aerobic microbial activity would be the exclusion of oxygen.

### 3.3 Sorption Behaviour

The mobility of environmental relevant chemicals in soils/sediments/sludges is largely dominated by sorption processes following a variety of mechanisms. These processes depend on the lipophilicity of the compounds, the matrix mineralogy and organic matter content, and especially the matrix humidity. In general, it has been stated that a decreasing water content increases adsorption and reduces the mobility, increasing temperature reduces the adsorption and increase mobility, increasing clay-mineral content and organic-matter content increase adsorption and reduce the mobility, and that plant cover increase metabolism and reduces leaching. The adsorption and mobility are interrelated, and the mobility depends essentially on the degree of interaction between the pollutant molecule and the soil/sediment/sludge components. The role of the organic matter in solid matrices is very important. It could be shown that the most persistent complexes result from the direct covalent binding of pollutants to soil humic matter or clay. In the case of soils, the clay content should also be taken into consideration. Adsorption is there often correlated with the clay content of soils and the mineral fractions of clay play an important role in adsorption of pollutants. Nevertheless, organic matter has a stronger effect, but the adsorption of environmentally relevant pollutants onto clay is important, because many soils contain much more clay than organic matter.

*Water-octanol partition coefficient:* This parameter is usually reported as a logarithm usually as  $\log K_{OW}$  or  $\log P_{OW}$ . It is defined as the ratio of the equilibrium concentrations of the two-phase system consisting of water and n-octanol. This parameter is characteristic of the lipophilicity of the molecule and gives an indication of the compound's tendency to accumulate in biological membranes and living organisms. It is generally considered that substances with a  $\log K_{OW}$  value higher than 3 can show accumulation. The polarity of a molecule is strongly correlated with  $K_{OW}$ . As a rough rule, non-polar analytes are characterized by  $\log K_{OW}$  values above 4 – 5, whereas polar analytes have  $\log K_{OW}$  values below 1 or 1.5. Between these two values, compounds are classified as moderately polar.  $\log K_{OW}$  values have been proved

valuable for prediction of mobility and persistence in solid environmental matrices and of soil/sediment/sludge sorption, particularly in solid matrices with large amounts of organic matter. PCBs show a log  $K_{OW}$  above 4. In detail, about 4.6 for monochloro biphenyl and log  $K_{OW}$  greater than 8 for decachloro biphenyl [Baker et al., 2000; Römpp, 2004]. Similar values are reported for PAHs, for instance naphthalene shows a log  $K_{OW}$  value of 3.3 and for Benzo[g,h,i]perylene a value of 7.2 is found in literature [International Chemical Safety Cards, 1997]. DBP shows a log  $K_{OW}$  of 4.6 and DEHP of 4.9 [Römpp, 2004]. For NP a log  $K_{OW}$  between 4 and 6 is indicated [Serôdio & Nogueira, 2004], for NPME and NPDE 4.2, respectively [Ahel & Giger, 1993a]. However, some special attention should be given to the partitioning of non-polar compounds having low solubilities. This is because they have a high potential to adsorb everywhere, on matrix particles in the environment or on sampling as well as laboratory equipment.

$K_{OW}$  cannot be used as a predictor of bioaccumulation for compounds that transform because the enzymatic reaction of a compound is not related only to hydrophobicity [<http://conference.ifas.ufl.edu/landapp/organics.htm>].

### 3.4 Water Solubility

Water solubility is a fundamental, chemical-specific property defined as the concentration of a chemical dissolved in water when the water is both in contact and at equilibrium with the pure chemical. Water solubilities are measured in mg/L and at temperatures in the range 20 – 25 °C (ambient temperature). Water solubility indicates the tendency of a chemical to be removed from soil/sediment/sludge/waste by runoff and to reach the surface or ground water. It also indicates the tendency to precipitate at solid particles. The water solubility or the solubility ranges in mg/L for the analytes under investigation are given in Table 1 [values from: Römpp, 2004; International Chemical Safety Cards, 1997; Brix et al., 2001; Ahel & Giger, 1993b].

Table 1: Water solubility ranges in mg/L of the analytes of interest.

Analyte	mg/L
DBP	10
DEHP	0,05 - 05
PCBs	up to 6
PAHs	up to 4
(besides Naphthalene)	31,7
Nonylphenol	~ 5

An other parameter, which is related to the water solubility and the leaching behaviour of a pollutant, is the acid-base ionisation constant, which is inter alia to the equilibrium concentration of the non-ionic and ionised forms. The ionisation constant is usually expressed as negative logarithm of  $K_a$  ( $= -\log K_a = pK_a$ ), the ratio of the equilibrium concentration of the ionised forms and the equilibrium concentration of the non-ionic form. The higher the  $pK_a$  value, the weaker is the acid and its tendency to be ionised.

## 4. STATE OF THE ART

### 4.1 Appropriate Containers for Shipping

The main purpose of the container is to protect the sample from contamination by foreign substances from the environment or from losses due to adsorption and volatilization, respectively. The choice and the preparation of containers used for sampling, transportation, storage and preparation are therefore very important to ensure that the materials do not alter the organic micropollutants. The choice of the wrong device may cause several problems. Adsorption onto the walls of the container may occur, e.g. for PAHs the use of plastic materials for sampling and sample storage shall be avoided since adsorption on the walls may result in losses [DIN 38414-23]. For the group of phthalates it must be considered that plastic containers cannot be used either, since phthalates are commonly used as plasticizers and are easily extracted from plastic materials.

To summarize, the most frequently encountered problems regarding containers are [ISO 10381-1]:

- Adsorption onto the walls of the containers,
- Improper cleaning resulting in contamination of the container prior to sampling,
- Contamination of the sample by the material of which the container is made,
- Reaction between constituents of the sample and the container,
- Reaction with atmospheric components by permeation of gases (air).

General problems to be considered are the improper cleaning resulting in contamination of the container, contamination of the sample by the material of which the container is made and reaction between constituents of the sample and the container. A general cleaning procedure for glass containers for sampling PCBs in soils and sludges is recommended in DIN 38414-20. Therein it is advised that the cleaned containers shall be flushed with acetone before usage. After complete evaporation of the acetone the containers shall be baked out bottom-up for at least 1 hour at 150 °C.

As known, borosilicate glass is well adapted for several types of sediments and soils, dry or wet and, in general, brown glass is preferred to prevent light effects. For sludges it is recommended to use glass containers too, in combination with a PTFE-lined cap. A further mentioned possibility is the use of glass containers with aluminium foil protection [ISO 5667-15]. Metal as shipping material is not advisable, since it may cause catalytic activities.

For a bigger amount of the sample the usage of glass containers is questionable due to the bigger required sizes of the containers. Maybe therefore it would be better to use plastic containers with tightly sealed caps.

Another point to take into consideration is the ease of re-opening the container. The use of ground-in stoppers may cause seizing but greasing of the stoppers is not advisable since contaminations have to be avoided. Therefore, as already mentioned, PTFE-lined caps are advisable [Popek, 2003].



Other factors to be considered in selection of the sample container used to collect and store the sample include:

- Resistance to temperature extremes,
- Resistance to breakage,
- Water and gas tightness,
- Ease of re-opening,
- Size, shape and mass,
- Availability and costs,
- Potential for cleaning and re-use [ISO 10381-1].

In most standards it is recommended that the sample mass shall be about 500 g to 1000 g [ISO 10381-1; ISO/DIS 18287]. Due to the high water content of sludge samples it is necessary to know before sampling how much dry sample is needed for the analysis. Otherwise several litres of a 3 % sludge sample may not be enough [CEN/TC 308/WG 1/TG 4 N0058, 2003].

Furthermore it is advisable to fill the containers completely to avoid loss of volatile species. Since naphthalene is volatile and belongs to the group of PAHs this has to be taken into consideration as well.

Temperature is the most important factor affecting the samples, from the time of sample collection through handling to the final analyses. Samples should be transported and stored wherever possible at  $+ (4 \pm 2) ^\circ\text{C}$  so as to avoid the possible loss volatiles and to minimize microbiologically induced change or deterioration [ISO 10381-1]. Refrigeration is easily carried out with cool boxes and ice. It is normally preferable to maintain the samples in a cooled condition all the time of transportation from the sampling site to the lab. Any deviation should be recorded in a sampling protocol.

Transportation and storage should be carried out in dark containers to prevent light effects (photooxidation processes) as well as to avoid the stimulation of biological activity.

Preparation steps and analysis should be examined as soon as possible. The maximum storage time for a sample kept in the dark at low temperatures depends on the parameters to be determined. For moderately volatile compounds the maximum storage period is recommended not to exceed 7 days after sampling [Draft NEN 5709, 2004]. Storage for several months in the dark is only admissible for dried samples. For sludges maximum storage duration of 6 months is recommended for frozen samples ( $\leq - 20 ^\circ\text{C}$ ) as well as for dried samples [ISO 5667-15].

## 4.2 Sample Packaging and Shipment

After sampling, the sample has to be shipped to the laboratory in the most expedient manner. If samples cannot be transported on the day of collection, they should be kept on ice or under refrigeration overnight. Factors which have to be taken into account are type of samples, volume of samples, their transportation time, and distance to the laboratory, the available transportation options, and others. While in transport, the packaged samples must be kept on ice at  $+ (4 \pm 2) ^\circ\text{C}$ ; hence the need for insulated coolers. In general, coolers with sample usually do not keep the required inside temperature of  $+ 4 ^\circ\text{C}$  for more than 24 – 48 hours. To

prevent water damage from melting ice or condensation, the ice or the cooling unit should be double-bagged in resealing bags. A temperature blank placed with the samples inside the cooler is a good tool for determining the true temperature of the samples upon arrival to the laboratory [Popek, 2003].

To package samples for shipping, the following supplies are advisable:

- Sturdy plastic or metal coolers without spouts or spouts taped shut,
- Resealing plastic bags of various sizes,
- Ice or cooling units,
- Temperature blank,
- Cushioning packing material, such as bubble wrap,
- Clear strapping tape,
- Warning labels (e.g. 'This side up', 'Fragile'),
- Shipping labels,
- Waterproof ink pen.

### 4.3 Determination of Dry Matter and Water Content

It is important to state if the results of the analysis are related to soil mass or soil volume. For the determination of dry matter and water content on a mass basis a standard exists. In ISO 11465 the gravimetric method is described. The principle is to dry the soil samples to constant mass at  $+ (105 \pm 5) \text{ }^\circ\text{C}$ . The difference in mass of an amount of soil before and after the drying procedure is used to calculate the dry matter and water contents on a mass basis. A thermostatically controlled drying oven with forced air ventilation is used that is capable of maintaining a temperature of  $+ (105 \pm 5) \text{ }^\circ\text{C}$ . Constant mass is reached when, during the drying process, the difference between two successive weightings of the cooled sample, with an interval of 4 h between them, does not exceed 0.1 % (m/m) of the last determined mass. It has to be remarked that if volatile organic substances are present, this method will not give a reliable determination of the water content. Therefore, Karl-Fischer-titration method [Schulz, 1983] will give steady results and is already ASTM standard test method for the determination of free water and water of hydration in most solid and liquid organic and inorganic compounds [ASTM E203-01].

### 4.4 Drying Methods

Drying is performed primarily to stabilise the material and allow it to keep in a cool dark store with the minimum deterioration of the matrix and the determinedness. In general, the drying process should be carried out mildly in order to prevent to occurrence of rearrangement processes [Rump & Kristi, 1988].

Different drying methods are listed in Table 2. As already mentioned, naphthalene belongs to the group of volatile organic compounds. For this group (boiling point  $< 300 \text{ }^\circ\text{C}$  at 101 kPa) no sample pre-treatment is recommended to be carried out. The test samples should be taken from the sample as soon as possible after sampling, to avoid losses.

Furthermore some extraction procedures require a field-moist sample. For these drying and grinding are not possible.

For sludges, one recommendation for trace organics is to perform the determinations on as-received samples, which implies that drying is not applicable [ISO 5667 – 13; ISO 5667 – 15].

Homogenisation of field-moist samples is carried out by shaking vigorously (e.g. sewage sludge samples) and the usage of an Ultraturax or dough-mixer, respectively.

Table 2 gives an overview about the drying methods recommended in diverse Standards and Drafts as well as other references. Most literature is available for PAHs and PCBs whereas for the other organic micropollutants very few literature is procurable.

Drying of the samples is advisable since water may disturb quantitative extraction of the organic micropollutants. Another objective is to obtain a sample that can be ground using the chosen grinding method.

Table 2: Overview of recommended drying methods.

Matrix	Compounds	Drying Methods	Reference
Soil	Volatile compounds	- No drying	ISO/FDIS 14507
	Moderately volatile compounds	- Grinding necessary: Chemical drying with anhydrous sodium sulphate/magnesium silicate - Grinding not necessary/possible: Just mixing by hand	ISO/FDIS 14507
Soil		- Air drying - In a drying oven - Freeze-drying	ISO/DIS 11464
Soil	Moderately volatile compounds	- Chemical drying with sodium sulphate	Draft NEN 5709
Soil	Organochlorine pesticides and polychlorinated biphenyls	- Chemical drying with anhydrous sodium sulphate in accordance with ISO 14507	ISO/FDIS 10382
Soil	PAHs	- If using method B: Sir drying in accordance with ISO 11464	ISO 13877
Soil	Polycyclic aromatic hydrocarbons	- Extraction of the field moist sample - Chemical dried soils samples according to 14507 can also be used	ISO/DIS 18287
Solid waste	Polychlorinated biphenyls	- Chemical drying with sodium sulphate - Alternatively lyophilisation or other drying techniques	TC 292 WI 028
Soil	PAHs, PCBs	- Air drying - Freeze drying	DIN, 2004
Sludge, Sediment	PCBs	- Freeze drying	DIN 38414-20
Soil, Sludge, Biowaste	PCBs	- Drying oven (max. temperature: + 35 °C) - Freeze drying	DIN, 2004
Soil, Sludge, Biowaste	PAHs	- Drying oven (max. temperature: + 35 °C) - Freeze drying	DIN, 2004
Sludge		- Freeze drying	AbfKlärV 1992, Anhang 1
Soil	PAHs	- Air drying - Drying oven at + 40 °C - Chemical drying with anhydrous sodium	Belkessam et al. (2005)

		<ul style="list-style-type: none"> <li>sulphate/talcum powder</li> <li>- Freeze drying</li> </ul>	
Soil		<ul style="list-style-type: none"> <li>- Air drying</li> <li>- Drying oven at + 40 °C</li> </ul>	<a href="http://www.icp-forests.org/Manual.htm">www.icp-forests.org/Manual.htm</a>
Soil	PAHs	<ul style="list-style-type: none"> <li>- Thermal drying (+ 25 °C – + 40 °C)</li> <li>- Chemical drying with anhydrous sodium sulphate/talcum powder</li> <li>- Freeze drying</li> </ul>	Berset et al. (1999)
Sludge, Sediments	PAHs	<ul style="list-style-type: none"> <li>Using sample preparation by method B:</li> <li>- Freeze drying according to DIN 38414-21</li> <li>- For sediment samples: Alternatively air drying</li> </ul>	DIN 38414- 23
Sludge		<ul style="list-style-type: none"> <li>- Drying oven: Max. temperature + 105 °C</li> <li>- Freeze drying</li> <li>- Chemical drying with sodium sulphate</li> </ul>	CEN/TC 308/WG1/TG4 N0058
Soil	PAH	<ul style="list-style-type: none"> <li>- Chemical drying with sodium sulphate according to ISO/FDIS 14507</li> </ul>	ISO/TC 190/SC 3/ WG 9 N0110
Soil, relatively dry sludge, solid waste	Non-volatile and semivolatile organic compounds	<ul style="list-style-type: none"> <li>- Chemical drying with anhydrous sodium sulphate</li> </ul>	EPA 3540
Sludge	PAHs	<ul style="list-style-type: none"> <li>- Freeze drying</li> </ul>	Pérez et al. (2001)
Sludge	PAHs	<ul style="list-style-type: none"> <li>- Freeze drying and sodium sulphate</li> </ul>	Manoli et al. (1996)
Sediment	PCBs, PAHs	<ul style="list-style-type: none"> <li>- Freeze drying</li> </ul>	Fernández et al. (1996)
Sediment	PAHs	<ul style="list-style-type: none"> <li>- Freeze drying</li> </ul>	Lee & Part, (1993)
Soil, Sediment	PAHs	<ul style="list-style-type: none"> <li>- Freeze drying</li> </ul>	Budzinski et al. (1999)
Soil	PAHs	<ul style="list-style-type: none"> <li>- Freeze drying</li> </ul>	Deuster et al. 1997
Sediment	PAHs	<ul style="list-style-type: none"> <li>- Freeze drying</li> </ul>	Letellier et al. (1999)
Sludge	PAHs	<ul style="list-style-type: none"> <li>- Oven drying at + 40 °C</li> </ul>	Villar et al. (2004)
Soil	PAHs	<ul style="list-style-type: none"> <li>- Air drying in a fume hood</li> </ul>	Gong et al. (2005)
Sludge	PAHs	<ul style="list-style-type: none"> <li>- Oven drying at + 40 °C</li> </ul>	Flotron et al. (2003)
Solid Sample	Polar and hydrophobic pollutants	<ul style="list-style-type: none"> <li>- Air drying at + 30 °C overnight</li> </ul>	Pörschmann & Plugge (1999)
Soil	PAHs	<ul style="list-style-type: none"> <li>- Air-drying for 10 days at room temperature</li> </ul>	Sun et al. (1998)
Soil	PAHs	<ul style="list-style-type: none"> <li>- Air-drying in a fume hood</li> </ul>	Ma et al. (2005)
Soil	PAHs	<ul style="list-style-type: none"> <li>- Air-drying</li> </ul>	Wenclawiak (1992)
Soil	PAHs	<ul style="list-style-type: none"> <li>- Air-drying</li> </ul>	Barnabas et al. (1995)
Soil	PAHs	<ul style="list-style-type: none"> <li>- Air-drying</li> </ul>	Saim et al. (1997)
Soil	PAHs	<ul style="list-style-type: none"> <li>- Air-drying</li> </ul>	Lundstedt et al. (2000)
Soil, Sediment	PAHs	<ul style="list-style-type: none"> <li>- Air-drying</li> </ul>	Noordkamp et al. (1997)
Soil	PAHs	<ul style="list-style-type: none"> <li>- Air-drying</li> </ul>	Dean et al. (1995)
Soil	PCBs	<ul style="list-style-type: none"> <li>- Air-drying</li> </ul>	Folch et al. (1996)
Sediment	PCBs	<ul style="list-style-type: none"> <li>- Air-drying</li> </ul>	Tong & Imagawa (1995)
Soil	PCBs	<ul style="list-style-type: none"> <li>- Air-drying</li> </ul>	Van der Velde et al. (1992)
Sediment	Nonylphenols, phthalate esters	<ul style="list-style-type: none"> <li>- freeze drying</li> </ul>	Cortazar et al. (2005)
Soil	PAHs	<ul style="list-style-type: none"> <li>- Thermal drying</li> <li>- Freeze drying</li> <li>- Chemical drying</li> </ul>	Berset et al. (1999)
Soil, heap	PAHs, PCDDs,	<ul style="list-style-type: none"> <li>- Air-drying</li> </ul>	Popp et al.

material, sludge	PCDFs		(1997)
Soil, Sediment	PCBs	- Freeze drying	Lopez-Avila V. (1995)
Sludge, compost	DEPH	- Chemical drying with anhydrous sodium sulphate	Bagó et al. (2005)
Soil	DBP	- Air drying	Jianlong et al. (2004)
Sludge, Sediment	DBP, DEHP	- Freeze drying	Fromme et al. (2002)
Sediment	Nonylphenol, DBP, DEHP	- Freeze drying	Cortazar et al. (2005)
Sediment	LAS	- Freeze drying	Ding & Fann (2000)
Soil	LAS	- Air drying	Carlsen et al. (2002)
Soil	LAS	- Air drying	Fytianos et al. (1998)
Sediment	NP, NPEOs	- Freeze drying	Valsecchi et al. (2001)
Sediment	Phthalates	- Freeze drying	Klamer et al. (2005)
Sludge	NPEOs	- freeze drying	Petrović & Barceló (2000)
Sludge, compost	PAHs, PCBs	- Freeze drying	Lazzari et al. (1999)
Sludge	NPEOs	- Air drying	Lee et al. (1997)
Sediment	Phthalates	- Freeze drying	Fromme et al. (2002)
Sludge	Phthalates	- Freeze drying	Marttinen et al. (2003)
Sludge, Sediment	NPEO	- Freeze drying	Gomes et al. (2003)

#### 4.4.1 Freeze-Drying

Samples can be dried by different procedures, e.g. air drying, drying at elevated temperatures in a drying oven, chemical drying with anhydrous sodium sulphate and freeze drying, which is also known as lyophilisation or vacuum drying. Freeze drying has become a popular drying technique and is recommended for the analysis of nonpolar micropollutants. For this method an International Standard, (ISO/FDIS 16720, Soil quality – Pre-treatment of samples by freeze drying for subsequent analysis), exists. During freeze drying, water is removed from the sample under vacuum conditions by direct conversion from ice to vapour (sublimation) which is collected in a condenser where it releases its heat energy and turns again into ice. A sample in a thin layer form is required for suitable lyophilisation. The thickness of the sample should not exceed 2 cm. If the representative amount exceeds 2 cm thickness multiple drying may be applied. Others recommend the depth of the layer not to be exceeding 10 mm. Furthermore it must be pointed out that throughout the drying process the pressure inside the apparatus and the temperature of the samples shall be such as to avoid sample thawing and loss of any compound of interest. It has the advantage that the sample rarely dries out into clods and usually crumbles into fractions. To avoid losses of volatile components, the sample should be cooled during lyophilisation. Without cooling, the temperature of the sample will increase to room temperature after sublimation of the moisture and this may again lead to losses. Modern freeze-drying instruments have an additional device to cool the sampler holder.

For sludges and sediments it is shown that compared to drying at 105 °C, freeze drying shows significantly lower losses of volatile compounds [DIN 38414-22].

In the case of very humid or clayey soils, the technique of freeze drying compared with air or oven drying at temperature < 40 °C in accordance with ISO 11465 has the advantage of a quicker drying process and to provide a dried sample that can be reduced in size more easily. One problem of freeze drying can be that substances may volatilize during freeze drying and may partly be released to the ice condensate or be found in the release gas to the vacuum pump. In addition to using a lower temperature it is advisable to cover each sample in its container with a lid that has a ca. 2-3 mm hole. The water vapour, which is removed primarily through heat transfer to the sample causing evaporation, is not impeded, whereas any contamination can only reach the sample through the small hole by diffusion. This strategy also allows very contaminated materials to be prepared since each sample is self contained and does not contaminate the inside of the freeze dryer or other samples in the chamber [Barceló, 2000].

Belkessam et al. [2005] showed that for PAHs in soils freeze drying seems to induce the volatilization of the light PAHs since some of the most volatile compound concentrations were lower than those measured after drying at room temperature or 40 °C. Berset et al. [1999] made similar observations. In his studies he showed when analyzing the concentrations of the single PAHs it turned out that all soils had above all lower naphthalene recoveries compared to the thermal dried ones. Therefore, it must be concluded that although freeze-drying is much faster than thermal drying and contamination through the ambient air can be minimized the volatile compound naphthalene is partly lost and no quantitative results can be obtained.

For sludges with high water content a previous centrifugation to get rid of part of the water is recommended [AbfKlärV, 1992]. The released centrifugate should not contain any particles. Lyophilised samples are hygroscopic among others due to the relatively large surface. They absorb moisture when stored in the open, even after a short time [Otto, 2000]. One possibility to avoid moisture absorption after lyophilisation is to store the samples in a desiccator over phosphorus pentoxide or other drying agent.

In CEN/TC 308/WG 1/TG 4 N0058 it is advised to dry the freeze-dried material before analyses with sodium sulphate, if the storage time of the material is longer than 2 hours.

#### 4.4.2 Chemical Drying

ISO/FDIS 14507 recommends chemical drying for organic micropollutants in soils. Before chemical drying, it is advised to remove all parts not representative for the soil, e.g. all visible metallic contents if subsequent grinding is necessary. 200 g of sodium sulphate and approximately 50 g of magnesium silicate are added to a glass container. After sealing the container the two substances are mixed by shaking and cooled to a temperature below 10 °C. In the Draft NEN 5709 a temperature of 2 °C to 5 °C is recommended. For each sample, approximately 250 g of soil are added to the glass container. Draft NEN 5709 recommends reducing the amount of sample to 140 g as well as the admixtures (110 g sodium-sulphate and 30 g magnesium silicate). Mixing by shaking, placing to the fridge to stand cold for 12 to 16 h

is advised. Furthermore shaking vigorously every 4 h is advised to avoid clod formation. If large clods are formed in the initial phase, this can be crushed manually by cutting with a spatula in the container. This may particularly be necessary with heavy clay soils. If the moisture content is greater than 60 % it is recommended to add extra sodium sulphate instead of reducing the amount of sample.

Furthermore it is noted, that drying with sodium sulphate is less suitable for the determination of moderately volatile organic compounds in sludges or sediments with high water content. Chemical drying of such a sample before crushing can cause problems due to insufficient drying and clod formation. In CEN/TC 308/WG 1/TG 4 N0058 it is therefore recommended for sludges that drying with sodium sulphate can only be used, if the dry content is bigger than 85 %.

Belkessam et al. [2005] found that moisture seems to inhibit extraction, as results obtained with bulk soils or chemically dried soils are lower than those obtained after drying (ambient temperature or 40 °C).

For PAHs compared to thermal drying at 40 °C, chemical drying with sodium sulphate revealed similar results. The main striking difference was the partly much higher recovery of naphthalene in the case of chemical drying [Berset et al., 1999].

However, it has to be noticed, that the addition of a desiccant increases the bulk of the sample, dilutes the contaminants and reduces the effective sample mass that maybe taken for methods where there is an upper limit on the amount of material that may be extracted in any on batch, e.g. containerised following extraction methods like SFE, ASE, or MAE or even the Soxhlet if the sample is very large.

#### 4.4.3 Air-Drying

In ISO/DIS 11464 a further possibility is given, namely air-drying. Air-drying is a very sparing method but often can last a couple of days and hence, is very time-consuming. To accelerate the drying process, the samples could be crushed lightly by hand using a wooden hammer or a mortar and pestle. In ISO/DIS 11464 it is advised to spread all the material in a layer not thicker than 5 cm on a tray, which does not adsorb any moisture from the soil and which does not cause contamination. Additionally, performing the drying procedure under an extractor is advisable [DIN 38414-23]. Furthermore it is essential to avoid direct sunlight, since this could create large temperature differences in the sample, especially between the partly or completely dried top layer and the lower layers which are still wet. Furthermore, the temperature must not exceed 40 °C. If the soils tend to agglomerate during air-drying they have to be crushed again in a mortar.

Belkessam et al. [2005] investigated PAHs in two different soils. They found that for the more clayey soil, which is mainly polluted by light PAHs like naphthalene, acenaphthene, fluorene etc., the concentrations measured after drying at room temperature of 40 °C were the highest ones compared to other drying techniques. In contrast, Campangpangan and Suffet [1996] reported that air and oven drying resulted in losses of the more volatile PAHs.

#### 4.4.4 Oven-Drying

Among the different drying techniques thermal drying is certainly a very common one. An important question related to that technique is at which temperature and how long the soil should be dried. In ISO/DIS 11464 it is recommended to break down the size of larger aggregates to accelerate the drying process. The material should be spread in a layer, not thicker than 5 cm, on a tray, which does not cause contamination. The tray should be put in the ventilated drying oven and the temperature should not exceed 40 °C. Other literature recommends the layer not be thicker than 15 mm [[www.icp-forests.org/Manual.htm](http://www.icp-forests.org/Manual.htm)]. The advantage of oven-drying compared to air-drying is the increased speed that limits changes of the sample condition due to microbial activity [Markert, 1994].

Berset et al. [1999] performed experiments on sewage sludge samples for PCBs and PAHs. They dried the sewage sludge at 25 °C, 40 °C, 80 °C and 105 °C and the results show that a significant loss of analytes occurred when drying temperature exceeded 40 °C. Therefore drying soil samples between 25 °C and 40 °C might be a good choice. Samples containing a high percentage of moisture could take several days to dry sufficiently. Drying at lower temperatures will reduce volatilisation losses but also exposes the sample to the ambient environment for longer periods of time, which serves to increase the risk of contamination through laboratory air. This might become a problem, especially in low contaminated samples as they are common in the field of environmental monitoring [Gawlik et al., 2004].

A new approach of drying samples in an oven is Microwave-drying, a very fast drying procedure. Microwave-drying exhibits the same problems as oven drying. An exact control of the microwave energy is necessary to prevent overheating of the sample and losses of volatile compounds [Knapp & Schramel, 2003].

Every drying technique has its advantages and disadvantages. Which method to use will finally not only depend on the questions addressed but also on economical factors.

#### 4.5 Crushing and Removal of Coarse Materials - Homogenisation

If soil samples have dried into large aggregates, crushing is necessary. Parts, that are not representative and obviously not representative for the investigated sample shall be removed by sieving and hand picking. This can for example be all visible metallic contents, gravel, and fragments of glass and rubbish. It is advised to determine and record the total mass of the dried sample and the mass of any material removed in this step. Devices for prior crushing might be scale grinder, jaw crusher or simple a wooden hammer

Generally, in ISO/DIS 11464, after removal of extraneous material, it is recommended to crush the dried large particles into particles no larger than 2 mm using suitable apparatus.

In ISO/FDIS 14507 cryogenic crushing is recommended after drying with sodium sulphate. It is noted, that samples have to be completely dry before cryogenic crushing to avoid contamination. It is advised to fill the Dewar vessels to be used with sufficient liquid nitrogen for the PE containers to be fully covered by the liquid nitrogen when placed in the Dewar



vessels. The content of each glass container with soil and additives is quickly transferred into a PE container. The PE container should be sealed and completely immersed in the liquid nitrogen. The container shall be allowed to stand still until the liquid nitrogen no longer boils vigorously, for approximately 10 min. After the container is completely cooled, the container shall be retrieved from the liquid nitrogen and the contents transferred to the cross-beater mill. In Draft NEN 5709 it is advised to use PE pots instead of glass pots when chemically drying is applied to ensure the material does not have to be transferred for cryogenic crushing. Since phthalates are used as softeners for plastics and are easily extracted, it is not advisable to use plastic pots in case of examination of phthalates.

ISO 13877 for example recommends the soil samples to be crushed in a mortar after air-drying. Another recommended possibility is the usage of a ball mill [DIN, 2004; DIN 38414-23; Cortazar et al., 2005]. To avoid contamination it is recommended to use materials like agate and corundum, respectively [Camann, 2001]. For biowaste or compost it could be necessary to use a shredding machine, as advised in ISO 13877, prior to drying and homogenisation.

Belkessam et al. [2005] found that the use of jaw-crushers instead of mortar leads to reproducible measures by improving matrix homogeneity for 2 soils among the 3 ones investigated by them.

Grinding equipment can be subdivided into various groups. In Draft NEN 5709 it is distinguished between homogenising and non-homogenising devices, because they influence the way in which the test sample is taken out from the treated sample.

As homogenising pre-treatment device for moderately volatile compounds a grinder/mixer or a comparable device like a disintegrator (together with a sieve) is recommended. It is remarked, that during the validation of Draft NEN 5709 only one type of device (Sample Mate) was tested with which field wet samples could be ground under cryogenic conditions. As non-homogenising pre-treatment devices a disintegrator with a sieve with a mesh width of 1 mm and a wheel grinder, respectively, are cited.

## 4.6 Sieving

ISO/DIS 11464 advises to sieve the dried and crushed sample by hand or using a mechanical shaker. In DIN ISO 13877 it is advised for soils to sieve already the field moist sample prior drying through 2 mm.

Most analytical tests are performed on the fine fraction of the solid sample – in particular soils and sediments –, which is obtained by sieving through a 2 mm-mesh [Rump & Krist, 1988], ISO/DIS 11464 recommends a sieve width of 2 mm. For sediments and soils the sieving removes grit, small stones, macro-benthos and detritus. This aids preservation by removing the large part of biological material in the sample. Numerous trace organic contaminants are associated with the fine fraction of the soil or sediment which contains the soot and the organic carbon [Barceló, 2000]. The stones and fresh plant fragments, glass, etc. remaining on the sieve shall be removed and weighed. Any aggregates left on the sieve shall be crushed separately and returned to the sample. If required, a separated treatment of all or part of the material left on the sieve is carried out.

In Draft NEN 5709 a wire sieve with a mesh width of 1 mm for organic micropollutants is recommended. A sieve with a mesh size of 1 mm after usage of a cross beater mill is advised in ISO/FDIS 14507 as well. The application of a nylon mesh is published, too [Sastre et al., 2001].

Some literature recommends the samples to pass through a “20 or 30 mesh screen” [Ding et al., 2000; Ding & Fann, 2000; Fytianos et al., 1997]. Mesh is a notation for the number of apertures of a sieve related to the edge length in Inch. This specification serves as a description of the particle sizes for instance for sieving analysis. Increasing mesh values comply with decreasing mesh sizes. It must be indicated that at least 4 different sieving-types do exist wherewith mesh values vary as well. For instance the values of the US Bureau of Standards indicate a mesh width of 0.84 mm for a 20 mesh sieve and 0.59 mm for a 30 mesh sieve [Römpp, 2004].

## 4.7 Subsampling

Subsampling is necessary when the sample cannot be stored (laboratory sample and archive sample) or used (test sample) completely, because of its size. For the preparation of a laboratory sample, the dried, crushed and sieved sample (now < 2mm) should be divided into representative portions of 200 to 300 g. Several methods of subsampling exist, e.g. coning and quartering (subsampling by hand), the use of a sample divider, or by mechanical subsampling. A variety of appropriate equipment for subsampling is available. For further detailed information see ISO/DIS 11464 and Draft NEN 5709.

Generally, it is essential that the material is completely homogenised prior to sampling the specific mass for analysis. This may be achieved by extensive ball milling with agate balls for 8-10 h. The sample, if stored for any time prior to analysis, should be re-homogenised by shaking the container with an agate or Teflon ball inside to re-mix the contents which will have settled [Barceló, 2000].

If a test sample of less than 2 g is to be taken for the analysis, it is essential to further comminute the fraction less than 2 mm [ISO/DIS 11464]. Therefore it is necessary to mill a representative subsample of the dried, pulverized and sieved soil until the complete subsample just passes through a sieve of 250 µm or a size otherwise specified in the test method. As a general rule the correlation of the sample size with sample amount is valid. That implies that the test sample has to contain at least 10times the largest grain size particle. It is noted that if more than one analysis has to be carried out, sufficient material should be ground to the smallest particle size specified, to enable all the analyses to be made on this one subsample.

Draft NEN 5709 [2004] advises that for determination of organic compounds a D<sub>95</sub> that is smaller than 1 mm has been assumed for the used size in relation to the test sample.

Samples may be milled or ground immediately before analysis for those analyses for which finely ground material is required [[www.icp-forests.org/Manual.htm](http://www.icp-forests.org/Manual.htm)].

## 4.8 Storage Conditions

In all cases samples for trace level analysis must be stored in a separate physical location from analytical standards, and any other material which may contain a high concentration of the pollutants under investigation. Storage is usually in a completely segregated and dedicated room and the sample should be protected from light, elevated temperature and/or humidity [Prichard et al., 1996]. In general, most analytes and sample matrices are more stable at low temperatures. For checking temperature fluctuations during storage, it could be necessary to use a maximum/minimum thermometer. At deep freeze temperatures ( $-18^{\circ}\text{C}$  or lower), most enzymatic and oxidative reactions are reduced to a minimum. Nearly all Standards and Draft Standards recommend storage of the sample at least in a refrigerator at low temperatures, generally  $+ (4 \pm 2)^{\circ}\text{C}$ . This implies already dark and dry conditions. Before opening the sample container the samples should be allowed to reach ambient temperature. Special care should be taken to avoid hygroscopic samples (freeze dried samples) taking up water, both when stored and when warming back to room temperature. Additionally, in many Standards and Drafts a maximum storage time prior to analysis is recommended. For instance, Draft NEN 5709 [2004] proposes a maximum storage period for a sample under refrigerated conditions ( $2 - 5^{\circ}\text{C}$ ) in relation to the volatility of the analytes:

- |                                      |                            |
|--------------------------------------|----------------------------|
| ▪ For volatile compounds:            | Four days after sampling;  |
| ▪ For moderately volatile compounds: | Seven days after sampling; |
| ▪ For non-volatile compounds:        | Unlimited                  |

Or in relation to the specific provisions:

- |  |                            |
|--|----------------------------|
| ▪ For dry substance:                                   | Seven days after sampling; |
| ▪ For lutite materials (fraction $< 2\ \mu\text{m}$ ): | Unlimited                  |

## 4.9 Integrated Method

Draft NEN 5709 exposes an integrated method for soils. With this pre-treatment method, a subsample is obtained, that is suitable for organic and inorganic parameters that are moderately volatile and non-volatile. The soil sample is treated while wet in relation to this method. It is advised to take at least 140 g of sample material from the original sample with a core sampler. At least ten random cores shall be taken over the complete height of the sample. Parts, that cannot be ground shall be removed and weighed. The sample shall be put in the grinding beaker and a coolant, e.g. liquid nitrogen or fixed carbon dioxide shall be added, if moderately volatile compounds are also being determined, so that the temperature of the sample is below  $5^{\circ}\text{C}$  in any case after grinding treatment. Additionally, the coolant shall be stirred through the sample before starting the grinding treatment.

For security reasons it is recommended to wear suitable gloves whenever using liquid nitrogen, fixed carbon dioxide and the refrigerated soil.

If the grinding method is homogenising, it is therefore sufficient to use one handful taken directly from the grinding beaker to obtain a test sample. When using a non-homogenising grinding method it is recommended to take the test sample from cores or by first

homogenising. Since the sample is field wet, it is not usually possible to divide it with a sample divider.

## 5. EVALUATION OF DRAFTING A HORIZONTAL STANDARD

A straightforward and low cost sample pre-treatment with common instrumentation should meet a number of criteria. The proposed suggestion should be in accordance to the inorganic sample pre-treatment. Therefore, special emphasis has to be given for the selection of the materials for crushing and milling machines, in order to avoid contamination with inorganic elements, as well as for the drying methods, in avoidance of losses of volatile trace elements or organic components. Draft NEN 5709 [2004] proposed an integrated sample pre-treatment method applicable to organic as well as to inorganic parameters. The main sample pre-treatment steps in this Draft for the integrated method are the following:

- (1) Wet field soil sample with a mesh < mm;
- (2) If the sample contains free water, this should be siphoned off, after this step subsamples for volatile substances like BTEX, halogenated hydrocarbons, cyanides, mercury and others should be taken;
- (3) Remove 'artefacts' (which means parts that cannot be ground), nature and mass of these artefacts should be recorded;
- (4) Divide into subsample by: (a) Quartering; (b) Using a static slotted divider; (c) Taking at least 10 cores, subsamples for this step should be used for measuring the dry substance, the organic substance, pH, lutite and for allocating subsamples for any required reanalysis;
- (5) Grind/mill the sample to a particle size < 500 µm, if also moderate volatile substances are being determined, grinding/milling must take place below 0 °C.
- (6) Divide the sample by: (a) Rotational division; (b) using a static slotted divider; (c) at least 3 cores after homogenization.
- (7) Take subsamples for treatment for: EOXs and PAHs, Mineral oil, OCPs and PCBs, other moderately volatile substances, metals, anions, organic substances.

It has to be noticed, that in Draft NEN 5709 [2004] a detailed description of the applicable tool-material is missing as well as for the sample pre-treatment step 'homogenization', which is mentioned but not explained.

Following CEN/TC 308/WG 1/TG 4 N0058 (Sludge quality – Pre-treatment of sludge for subsequent analysis) it has to be discussed whether the sludge sample is treated like sludge or soil. It is mentioned to treat the samples like sludge as long as they are not proof (stichfest), otherwise like a soil sample. Additionally the partly high water contents of raw sludges have to be considered. As already mentioned, in Draft NEN 5709 [2004] free water from the sample should be siphoned off. This step may be applicable to PAHs and PCBs, which are nearly insoluble in water. Whereas, LAS, phthalates, NP and NPDE are frequently found in surface waters and receiving water of sewage treatment plants [Gomes et al., 2003; Fauser et al., 2003; Fromme et al., 2002; Marttinen et al., 2003b]. In order to draft a horizontal standard for all of the named compound groups siphoning off free water seems not advisable.

A similar discussion might be necessary for the application of drying step, since some compounds are more volatile than others (e.g. naphthalene) and notable losses during drying could occur for these compounds. The best solution, however, for more volatile compounds would be the analysis of the field moist sample. As a matter of fact, in many cases field moist samples are difficult to handle (homogenizing, grinding, milling) and during storage the water amount could change dramatically. At this point it should be discussed whether drying should be applied, taking into account losses of these volatiles – especially naphthalene. This might

be less a problem than drawn, since as soon as the drying method has become a standard; the losses of naphthalene will be comparable, which could be enough for providing monitoring data. A second possibility would be to exclude naphthalene from the PAH-group.

The following flow sheet (Figure 1a and 1b) contains the proposed sample pre-treatment.

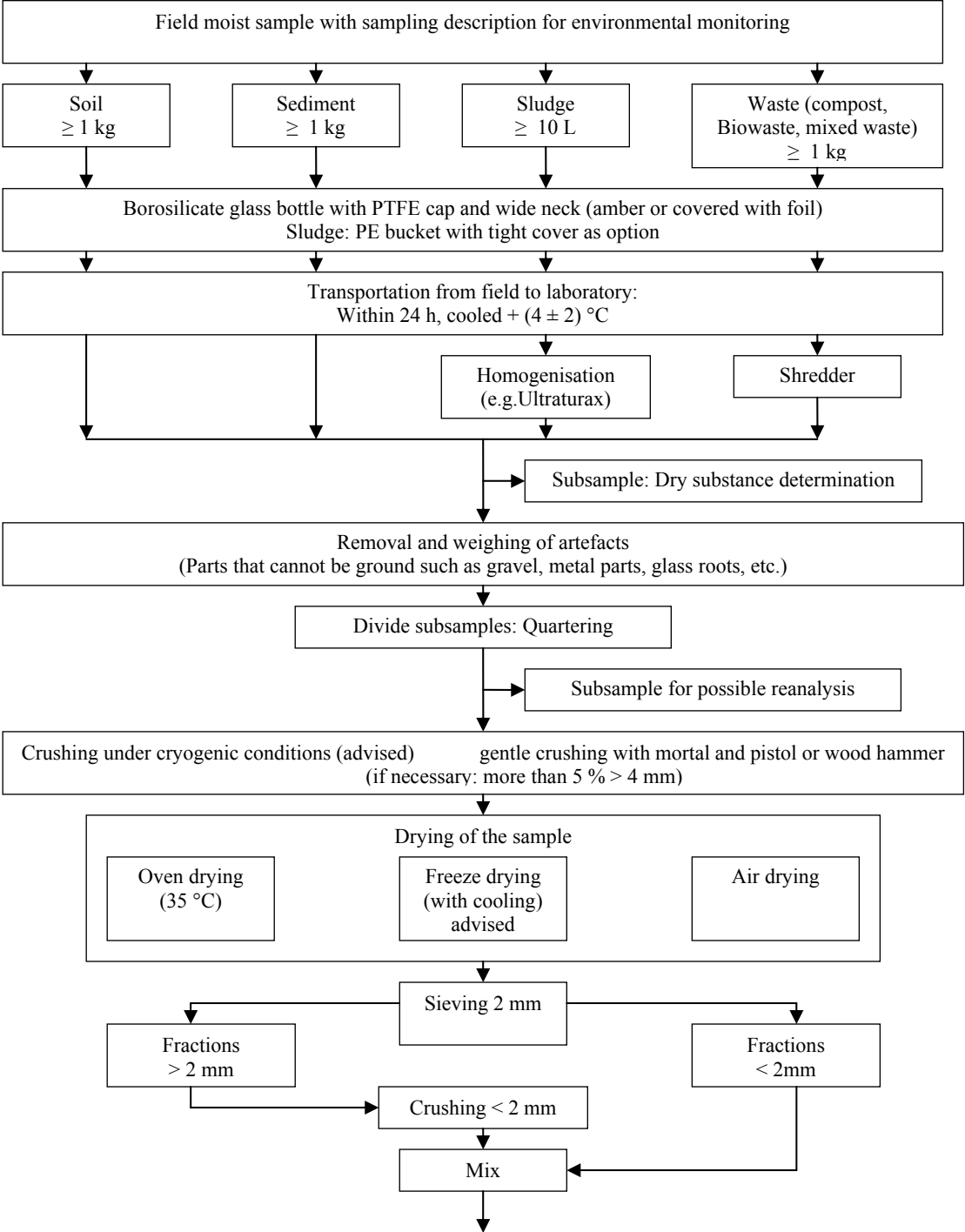


Figure 1a – Diagram for sample pre-treatment.

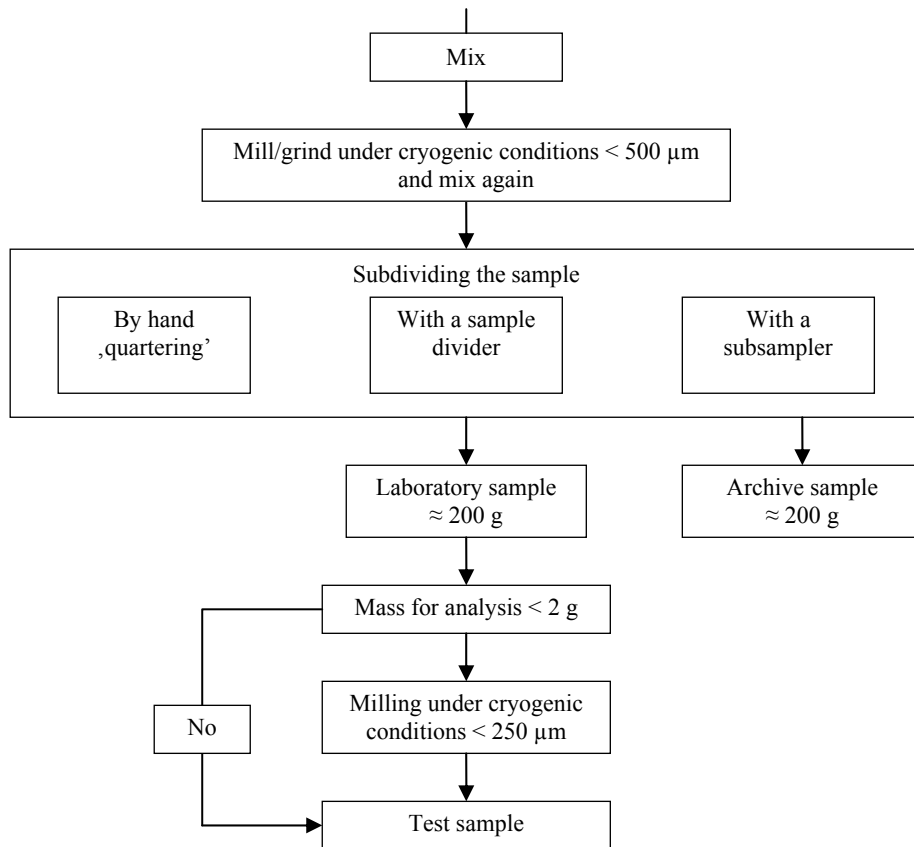


Figure 1b – Diagram for sample pre-treatment, continued.

## 6. ADDITIONAL CONSIDERATIONS

Once the sample has been obtained it is essential to maintain the quality of the material in such a way that the final chemical information is representative of the concentrations of determinant in the original sample. This requires a strict protocol for the sample treatment and storage both in the field, on the way and in the laboratory [Barceló, 2000]. The sample pre-treatment report should be as detailed as necessary for the special aim of investigation (monitoring or provisioncy sample). Beside the sampling sheet, which should include a very detailed description of the site as well as the sampling plan/protocol [Paetz & Crößmann, 1994] additional information should be provided with the sample. This information – a so-called ‘Sample Sheet’ – should at least include:

- Title data (sample name, sample number),
- Sampling sheet (site data, sampling procedure),
- Transportation data (container, temperature, time, etc.),
- Storage (location, temperature, time),
- Homogenisation, grinding, milling, sieving (materials, equipment and tools used),
- Drying (type, equipment and tools used),
- Sub-sampling (equipment and tools).

Such information may relate to the movement of the sample from one location to another or to sub-sampling from the sample for analysis. It is also important to decide how the documentation is to be stored [DOC ISO/TC 190/SC 3 N0431].

At this stage it has to be pointed out that, for all the sample pre-treatment steps mentioned in this study, the use of certified reference materials (CRMs) for quality control is not enabled. The reason is that existing matrix-CRMs for pollutant control, in particular in the area of soil, sewage sludge or sediments, CRM have already passed all these steps during the production cycle.

In order to obtain a Horizontal Standard for sample pre-treatment for organic as well as inorganic micropollutants some critical remarks should be discussed:

- *Sample containers:* The purpose of a sample container is to protect the sample from interaction with its surroundings during transport and storage. Changes that may occur include loss of components to or contamination from the surroundings, as well as reaction with atmospheric components, especially oxygen, water, or carbon dioxide. Therefore, containers should have closures that seal completely, and do not introduce contamination into the sample. For trace element analysis, containers of Teflon or linear polyethylene are advised, which introduce the least contamination, but should be carefully cleaned with HCl and HNO<sub>3</sub> (both in appropriate purity) before use. This procedure seems not advisable for organic components. Borosilicate glass is also widely used for sample containers for inorganic analysis. This material is relatively inexpensive, non-reactive to most organic compounds, and impermeable to gases. Though it sorbs a variety of molecules and ions, this is normally a problem only when the analytes are present in very low concentrations. Closures for borosilicate containers are usually screw caps with liners of Teflon or other inert plastic (which could lead to contamination problems for the analysis of phthalates).



- *Drying*: Drying procedures for volatile and semi-volatile organic as well as inorganic trace components are critical. Only freeze-drying seems to be advisable for such components, even though, it is recommended that the sample be cooled during lyophilisation to  $< 10\text{ }^{\circ}\text{C}$  [Knapp & Schramel, 2003]. For non-volatile trace components oven-drying at lower temperatures could be applied. In case of inorganic sample-pretreatment chemical drying can not be used due to contaminations by added drying agents.
- *Homogenisation (grinding, milling and sieving)*: Containers and tools for homogenisation can lead to contaminations and losses as in the other analytical steps. In inorganic trace analysis grinding and milling in vibrating ball mills applying PTFE or PFA containers and PTFE coated balls (made from stainless steel or tungsten, etc.), eventually under cooling with water or liquid nitrogen, are preferred. Mixers made from stainless steel should be avoided in trace element analysis. For these instruments materials such as Ti, W or special ceramic materials should be used. A Horizontal standard for organic and inorganic trace analysis for this step seems possible as far as stainless steel materials are avoided.

## 7. ACRONYMS

The short cuts used in this text are:

ACRC	Institute for Analytical Chemistry and Radiochemistry
ASE	Accelerated solvent extraction
ASTM	American Society of Testing and Materials
BTEX	volatile aromatic hydrocarbons (benzene, toluene, ethylbenzene and xylenes)
CEN	European Committee for Standardisation
CRM	Certified Reference Material
DBP	Di-n-butyl phthalate
DEHP	Di-(2-ethylhexyl) phthalate
DEPA	Danish Environmental Protection Agency
DIS	Draft International Standard
EC	European Communion
EOX	Extractable organohalogen compounds
EPA	Environmental Protection Agency
FDIS	Final Draft International Standard
H/K <sub>H</sub>	Henry's Law constant
ISO	International Standardisation Organisation
LAS	Linear Alkylsulfonates
MAE	Microwave assisted extraction
NEN	Nederland's Normalisatie-instituut
NP	Nonylphenols
NPDE	Nonylphenol-diethoxylates
NPCA	Nonylphenoxy carboxylic acids
NPME	Nonylphenol-monoethoxylates
NPnE	Nonylphenol-polyethoxylates
OCP	Organochlorine pesticides
PAE	Phthalic Acid Esters
PAHs	Polycyclic Aromatic Hydrocarbons
PBDE	Polybrominated-diphenyl-ethers
PCBs	Polychlorinated Biphenyls
PCDD/Fs	Polychlorinated Dibenzo-p-dioxins/furans
PE	Polyethylene
PFA	Perfluoroalkoxy
PTFE	Polytetrafluoroethylene
PVC	Polyvinylchloride
SFE	Supercritical fluid extraction
SPC	Sulfphenylcarboxylic acids
TC	Technical Communittee
TG	Technical Group
TUG	Graz University of Technology
UBA	Umweltbundesamt
UV	Ultraviolet
WG	Working Group
WWTP	Waste Water Treatment Plant

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