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Soil quality — Assessment of impact from soil contaminated with petroleum hydrocarbons

Qualité du sol — Évaluation de l'impact du sol contaminé avec des hydrocarbures pétroliers

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Foreword

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International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 11504 was prepared by Technical Committee ISO/TC 190, *Soil quality*, Subcommittee SC 7, *Soil and site assessment*.

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Introduction

Petroleum hydrocarbons (PHCs) are common environmental contaminants. They are components of crude oil and products derived from it and are consequently found on a variety of sites including refineries, sites where they are used as feedstock (e.g. for manufacture of plastics), manufactured gas production sites, sites where hydrocarbons are used as fuel or lubricants and retail service stations. They may also be present as a result of spills and leaks during transportation.

Petroleum hydrocarbons can present unacceptable risks to the health and safety of humans, ecological systems, surface water, groundwater resources and to structures and building materials. Measuring the total concentration of petroleum hydrocarbons (TPH) in soil (and pore water and pore gas) does not give a useful basis for the evaluation of the potential risks to man and the environment. The variety of physical-chemical properties, and thus differences in the migration and fate of individual compounds, and the toxicity and carcinogenicity of different fractions and compounds in oil products, must be taken into account in human health and environmental risk assessments.

Only a limited number of individual compounds can be routinely identified and quantified. It is, consequently, necessary to adopt methods of analysis that provide information about the amount of different hydrocarbon fractions present, preferably distinguishing between aliphatic and aromatic fractions, and the concentrations of single compounds of particular concern in respect of the potential health and environmental risks that they pose.

Although most petroleum hydrocarbons found in soil are of an anthropogenic nature, there are some natural sources of these materials and other organic substances (e.g. peat and coal). The analytical methods historically used for the measurement of total petroleum hydrocarbons (TPH) tend to measure natural materials as TPH. This issue will not be dealt with in this International Standard, except to note that a method able to give a more precise determination of the petroleum hydrocarbons is less prone to giving results that can be misinterpreted and potentially lead to unnecessary or unsustainable remedial actions.

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The purpose of this International Standard is to give recommendations with respect to the choice of relevant fractions and individual compounds, and to give guidance on the appropriate use of the results. Decisions about which analytical methods to adopt must be based primarily on the need to provide the right type and quality of data for use in risk assessments. This requires consideration of how the results of the analysis are most appropriately used in a risk assessment, e.g. how can the fractions be used in exposure models and assessments, and is it sufficient to analyse soil or is it necessary to obtain related values in other media as well (pore water and pore gas).

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There are three published International Standards covering the analysis of the range of petroleum hydrocarbons of interest:

ISO 16703 can be used to measure mineral oil (C_{10} to C_{40}) and ISO 22155 or ISO 15009 to measure volatiles. However, revised methods are required to be able to properly measure the fractions and compounds recommended for determination in this International Standard. ISO/TC 190 is developing International Standards for methods of analysis designed to be compatible with the recommendations provided in this International Standard.

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Soil quality — Assessment of impact from soil contaminated with petroleum hydrocarbons

1 Scope

This International Standard gives recommendations with regard to the choice of fractions and individual compounds when carrying out analysis for petroleum hydrocarbons in soils, soil materials and related materials, including sediments, for the purpose of assessing risks to human health, the environment and other possible receptors. Since many products based on petroleum hydrocarbons often contain substances that are not hydrocarbons, the recommendations also encompass such compounds where relevant.

This International Standard also includes relevant background information on which the recommendations are based together with guidance on the use of the fractions recommended in the assessment of risk.

This International Standard does not set criteria or guidelines for use as assessment criteria, since this is typically a national or regional regulatory issue. This International Standard also does not include recommendations as to the specific model for the exposure assessment or the specific parameter values to be used; with respect to guidance on this matter, reference is made to ISO 15800.

2 Normative references

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The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

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ISO 11074, *Soil quality — Vocabulary*

ISO 15009, *Soil quality — Gas chromatographic determination of the content of volatile aromatic hydrocarbons, naphthalene and volatile halogenated hydrocarbons — Purge-and-trap method with thermal desorption*

ISO 15800, *Soil quality — Characterization of soil with respect to human exposure*

ISO 16703, *Soil quality — Determination of content of hydrocarbon in the range C_{10} to C_{40} by gas chromatography*

ISO 18512, *Soil quality — Guidance on long and short term storage of soil samples*

ISO 22155, *Soil quality — Gas chromatographic determination of volatile aromatic and halogenated hydrocarbons and selected ethers — Static headspace method*

ISO 25177, *Soil quality — Field soil description*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 11074, ISO 15800, ISO 25177 and the following apply.

3.1
aliphatic hydrocarbon
acyclic or cyclic, saturated or unsaturated carbon compound, excluding aromatic compounds

3.2
aromatic hydrocarbon
hydrocarbon, of which the molecular structure incorporates one or more planar sets of six carbon atoms that are connected by delocalized electrons, numbering the same as if they consisted of alternating single and double covalent bonds

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3.3
boiling point
BP
point at which the vapour pressure of a liquid equals the external pressure acting on the surface of a liquid

NOTE Units: degrees Celsius.

3.4
carcinogen
substance that causes the development of malignant cells in animals or humans

3.5
compliance point
location (in, for example, soil or groundwater) where the assessment criteria shall be measured and shall not be exceeded

3.6
equivalent carbon number
empirically determined parameter related to the boiling point of a chemical normalized to the boiling point of the *n*-alkanes or its retention time in a boiling-point gas chromatographic (GC) column

3.7
fraction
group of aromatic and/or aliphatic hydrocarbons with similar physico-chemical properties

NOTE In this International Standard: group of aromatic or aliphatic compounds with leaching and volatilization factors that differ by approximately one order of magnitude.

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3.8
gas chromatography
analytical method that is used to separate and determine the components of complex mixtures based on partitioning between a gas phase and stationary phase

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3.9
hydrocarbon
compound of hydrogen and carbon which are the principal constituents of crude oil, refined petroleum products and products derived from the carbonization of coal (at a high or low temperature)

3.10
indicator compound
compound chosen to describe properties, primarily toxicity, of a petroleum mixture or fraction

NOTE This method is often used to assess carcinogenic compounds.

3.11
NSO compounds
organic compounds that contain nitrogen, sulfur and oxygen

NOTE NSO compounds occur in organic matter and crude oil. Asphaltenes are examples of NSO compounds. NSO compounds can be separated from crude oil by polar solvents such as methanol.

3.12
partitioning
extent to which a compound of a hydrocarbon mixture separates into different media (or phases) based on its chemical and physical properties and the size and properties of the media in the specific situation

3.13
petroleum hydrocarbon
organic compound comprised of carbon and hydrogen atoms arranged in varying structural configurations which make up the principal constituents of crude oil and petroleum products

NOTE Mineral oil is a colloquial term for petroleum hydrocarbons or petroleum products.

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3.14
polycyclic aromatic hydrocarbon
PAH
compound whose molecules contain two or more simple aromatic rings fused together by sharing two neighbouring carbon atoms

NOTE Examples are naphthalene, anthracene and phenanthrene.

3.15
surrogate compound
representative compound with toxicological and/or physical properties indicative of a hydrocarbon fraction, which can therefore be used to represent the fraction in an exposure assessment

3.16
total petroleum hydrocarbons
method-defined parameter, depending on the analytical method used to measure it

4 Principle

A petroleum hydrocarbon product typically consists of a mixture of a very large number of individual compounds. When assessing exposure and risk related to a mixture of compounds, such as in a petroleum hydrocarbon product, evaluation has to be made with respect to the migration, fate and toxicity of the different compounds in the mixture and the toxicity of the mixture. During transport in the subsurface, the composition of a mixture may change due to different rates of dissolution, volatilization, retardation, biodegradation, etc. acting on different component compounds. As a result, the toxicity of the resulting mixture may vary with both time and distance from the source zone.

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Assessing the potential exposure to a mixture consisting of a large number of compounds is not feasible, neither in relation to the measurement of the concentration of all the compounds, in relation to the evaluation of the resulting mixture (after migration and degradation) in the relevant point of compliance (such as in the groundwater or in the indoor air), nor with respect to the resulting toxicity. A method, where only a number of compounds or surrogate compounds are measured and evaluated, is therefore preferable.

On the other hand, it is necessary when choosing the relevant compounds and surrogate compounds (such as relevant fractions of the total oil product) to ensure that the resulting evaluation of either overall exposure or toxicity is a reasonable estimate of the exposure and toxicity related to the oil product as a whole. Furthermore, selection of surrogate compounds should ensure that, if risk-management action is necessary, the risk-management applied for the surrogate is also likely to mitigate the risks associated with other (unquantified) substances present in the mixture.

Studies on migration, fate and toxicity of petroleum hydrocarbons show substantial differences between the properties of individual compounds and fractions of aliphatic and aromatic hydrocarbons. Similar differences exist between hydrocarbon compounds with different carbon content. The choice of surrogate compounds for assessing exposure and toxicity of petroleum hydrocarbons should be based on fractions of the total hydrocarbon mix in a mineral oil product and on individual compounds and fractions with similar properties.

This International Standard gives recommendations about the choice of relevant individual compounds and fractions as a basis for the assessment of risks to humans and the environment at relevant compliance points using established risk assessment models. It should be noted that, for the suggested combination of fractions and singular compounds, it is necessary that comparable analytical methods exist for the suggested fractions, etc. not only for soil, but also for water, air and petroleum hydrocarbons present as non-aqueous-phase liquids (NAPL) in order to verify exposure assessment calculations and the assumptions employed in the risk assessment model.

As mentioned in the introduction, the choice of fractions and indicator compounds should, apart from the above, be based on the performance characteristics of the possible analytical methods, and on the overall cost of the analysis in relation to the goal of the assessment to be carried out.

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5 Recommendation of relevant fractions and individual compounds

5.1 General

This clause summarizes the recommendations given with respect to relevant petroleum hydrocarbon fractions and individual compounds to measure and use in risk assessment, unless local or national regulations set other requirements. The recommendations are based on the arguments given in the following subclauses.

5.2 Fractions

It is recommended that the fractions given in Table 1 should be used when measuring and assessing risk related to petroleum hydrocarbons. These fractions will ensure that the calculation of exposure can be carried out using surrogate physico-chemical properties for the fractions that represent all compounds within the fraction reasonably well and that toxicity of the compounds within the fractions will be reasonably similar, except for the specific compounds of significant toxicological potency that will also have to be assessed as individual compounds, see 5.3.

Surrogate physico-chemical properties can be set for each of the fractions suggested, either by using a single property for each fraction or by using a set of relevant indicator compounds representing the fraction by set percentages and then using their properties. The first method is the one utilized by TPHCWG[30]. The other method is used, for instance, in the Danish exposure assessment tool for contaminated soils, JAGG[12]. Some jurisdictions may have specific requirements regarding the properties to be used in risk assessments. If not, it is recommended to use the properties listed in Annex A.

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Table 1 — Recommended petroleum hydrocarbon fractions for use in risk assessment related to human health and the environment, based on Equivalent Carbon (EC) number

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Aliphatic fractions	Aromatic fractions
> 5 to 6	> 5 to 7
> 6 to 8	> 7 to 8
> 8 to 10	> 8 to 10
> 10 to 12	> 10 to 12
> 12 to 16	> 12 to 16
> 16 to 35	> 16 to 21
> 35 to 44	> 21 to 35
	> 35 to 44
> 44 to 70	

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NOTE Depending on the available knowledge concerning the contaminant situation on the site in question, not all fractions may be relevant on a specific site.

5.3 Individual compounds

Since petroleum hydrocarbon mixtures may contain specific compounds with a toxicity that is substantially higher than the other compounds in the fraction it is part of, it is recommended to carry out separate exposure and toxicity assessments of these compounds, unless the initial desk study and conceptual model of the site in question shows that it is not relevant. Table 2 gives the recommended list of specific compounds to include.

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Table 2 — Recommendations for individual compounds to be included in assessments (the list is not comprehensive)

Non-threshold compounds	Threshold compounds
Benzene	*n*-Hexane
Benzo[a]pyrene	Toluene
Benz[a]anthracene	Ethylbenzene
Benzo[b]fluoranthene	Xylenes
Benzo[k]fluoranthene	Styrene
Benzo[ghi]perylene	Naphthalene
Chrysene	Methylnaphthalenes
Coronene	Anthracene
Dibenz[a,h]anthracene	Fluoranthene
Indeno[1,2,3-c,d]pyrene	Phenathrene
	Pyrene

NOTE Other PAHs are potentially of concern and can be included if found relevant at the specific site.

Other compounds of this type include compounds containing nitrogen, sulfur and oxygen (NSO-compounds) that can also be found in petroleum hydrocarbon mixtures (e.g. benzo[b]thiophen, carbazole). Many products based on petroleum hydrocarbons also contain additives of different types with purposes specific to the products [e.g. methyl *tert*-butyl ether (MTBE), ethyl-*tert*-butylether (ETBE), *tert*-amyl methyl ether (TAME), ethanol, fatty acid methyl ester (FAME)]. These may have different environmental fate and characteristics, such as a higher solubility, a lower biodegradability or lowest olfactory and taste detection thresholds. When choosing the individual compounds to include in an investigation of a specific site, these issues should be taken into account.

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It is recommended that the NSO-compounds and additives given in Table 3 are considered, when deciding which compounds should be considered in the risk assessment. Not all compounds may be relevant at all sites.

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Table 3 — List of NSO-compounds and additives to be assessed if relevant

NSO-compounds
Benzo[b]thiophene
Dibenzofuran
Dibenzothiophene
Acridine
Carbazole
Aniline
Dimethyl disulfide
4-methyl aniline
4-methyl quinoline
Thiophene
Quinoline
Additives
Ethyl *tert*-butyl ether (ETBE)
Methyl *tert*-butyl ether (MTBE)
Di-isopropyl ether (DIPE)
Methanol
Ethanol
Butanol
Tert-butyl alcohol (TBA)
Fatty-acid methyl esters (FAME)
Tert-amyl methyl ether (TAME)
Amino ethyl ethanolamine
Diethylene triamine (DETA)
Ethylene diamine
Tetraethylenepentamine (TEPA)
1,2-dibromoethane
1,2-dichloroethane

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It should be noted that other compounds can be relevant at a specific site (e.g. lead additives and fuel dyes). There are potentially approximately 14 000 different NSO compounds in crude oil belonging to different heteroatomic classes, e.g. asphaltenes, carboxylic acids and oxygenates. The compounds suggested are typical of NSOs found at fuel and gasoline spill sites and similar.

In the risk assessments based on the fractions and individual compounds measured, the properties listed in Annex A should be used, unless local jurisdictions require otherwise. Since acceptance criteria and guideline values usually are regulated nationally or regionally, this International Standard does not give recommendations with respect to such criteria/guidelines.

6 Petroleum hydrocarbons in soil

When talking about petroleum hydrocarbons, the difference between the term petroleum hydrocarbons as such and the term total petroleum hydrocarbons should be noted. Petroleum hydrocarbons (PHC) typically refer to the hydrogen- and carbon-containing compounds that originate from crude oil, while total petroleum hydrocarbons (TPH) refers to the measurable amount of petroleum-based hydrocarbons in an environmental matrix and thus to the actual results obtained by sampling and chemical analysis.

TPH is thus a method-defined term. In other words, estimates of TPH concentrations will vary depending on the analytical method used to measure them.

Historically, this has been a significant source of inconsistency, as laboratories have different interpretations of the term TPH. By defining PHC fractions for risk assessment, this International Standard improves consistency in reporting and PHC risk assessments.

Petroleum hydrocarbons are constituents of crude oil, which on the other hand is the basis for the production of a large number of processed hydrocarbons/products. Crude oil contains aliphatic and aromatic hydrocarbons plus NSO compounds, etc. Hydrocarbon products can be either aliphatic or aromatic hydrocarbons or a mixture of both plus the addition of other organic and inorganic compounds (e.g. naturally occurring NSO

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