

## **Risk assessment for mineral oil: Development of standardized analytical methods in soil and soil-like materials**

**J. Harmsen (Alterra, The Netherlands)**  
**J.W. Hutter (ALcontrol, The Netherlands)**  
**T. Win (BAM, Germany)**  
**I. Barnabas (AES-labs, UK)**  
**P. Whittle (UK)**  
**N. Hansen (Eurofins, Danmark)**  
**H. Sakai (Japan Railway, Japan)**

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## ABSTRACT

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The present standard methods for the determination of mineral oil in environmental matrices give a total concentration. This concentration is not found to be a good estimate for ecotoxicological, human and agricultural risks. It is shown that the existing ISO standards for mineral oil and volatile compounds can be further developed to more risk based methods. This report is written to stimulate the discussion on the development of risk-based analytical procedures.

Keywords: [mineral oil](#), [TPH](#), [risk based assessment](#), [standardization](#)

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P.O. Box 47; 6700 AA Wageningen; The Netherlands

Phone: + 31 317 474700; fax: +31 317 419000; e-mail: [info.alterra@wur.nl](mailto:info.alterra@wur.nl)

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## Preface

Mineral oil in environmental matrices is one of the most often measured parameters. Different ISO-standard procedures are available. It is, however, very often not possible to explain toxicological effects observed in the field with the results of these analyses. Different approaches are on the moment in development to be able to explain toxicity. In several of these approaches, new measurement procedures are proposed to measure mineral oil. These methods often differ slightly from the existing ISO-procedures, but enough to make the results not comparable with result of the past. This is a non-desirable situation, because we think that the existing standards can be a good starting point for further development

This report is written to increase the participation of analytical experts also active in standardisation in the discussion. We hope that this will lead to a better results approach on the measurement of mineral oil in relation with toxicity. The report has been written to stimulate discussion. It reflects our opinion, but is not the official opinion of one of the organisation involved in writing this report.

Joop Harmsen  
Jaap Willem Hutter  
Tin Win  
Ian Barnabas  
Peter Whittle  
Nis Hansen  
Hiro Sakai



## Summary

The present standard methods for the determination of mineral oil in environmental matrices give a total concentration. This concentration is not found to be a good estimate for ecotoxicological, human and agricultural risks. There are world wide discussions on developments of methods that are a better estimate for risks. Another limitation is that not all relevant components are measured; specific, low boiling aliphatic hydrocarbons are missing. Target values for remediation can be higher than the reporting value.

There are several risk based approaches for measurement of mineral oil based on different mineral oil fractions. Difference in boiling point and polarity are both used. A method should not only be applicable for the small laboratory sample, but has to be representative for the site or lot. Pretreatment of the sample taken is therefore part of the procedure. Separate methods for volatile and non-volatiles are necessary. It is shown that the existing ISO standards for mineral oil and volatile compounds can be further developed to more risk based methods. Recommendations are given.

This report is written to increase the participation of analytical experts also active in standardisation in the discussion. We hope that this will lead to a better approach on the measurement of mineral oil in relation with toxicity.



## 1 Introduction

*The aim of the report is to describe the limitations of the current standardised methods for the determination of mineral oil in environmental matrices and possibilities to introduce standardised methods that give results usable for risk based assessment.*

This report is written on request of the Dutch Standardization Organization NEN. The two responsible Dutch authors are active in national and international standardisation bodies for the development of standardised methods. In these bodies they experienced that that problems on the determination of mineral oil are discussed world wide. Because standardisation is becoming an international process, the content of this report has been discussed with some experts also active in international standardisation committees (Tin Win active in ISO TC 190, I. Barnaby active in CEN 308, Peter Whittle active in ISO TC 190, Nis Hansen active in ISO TC 190 and CEN 308 and Hiro Sakai active in ISO TC 190). The content of this report is not the official opinion of any organisation, but is meant to be a help in the discussion on development of risk-based standard methods for the determination of mineral oil.

The main problems with the mineral oil determination concern:

- The present standard methods for the determination of mineral oil give a total concentration. This concentration is not found to be a good estimate for ecotoxicological, human and agricultural risks. Discussions have been world wide on developments of methods that are a better estimate for risks
- “Volatile oil”: there is no standard method available for determining the concentration of “volatile oil” which is in some cases a main part of the oil contamination (gasoline, white spirit). In practise laboratories have their own methods which are often not comparable and lead to different results. Furthermore there are no limit values set by the authorities for “volatile oil”. This is a problem because some serious hazardous compounds like hexane can be ignored.
- Limit values in the Netherlands are very low. The “streefwaarde” (lowest limit or soil) is 10 mg/kg d.m. for mineral oil C10-C40 in sandy soils (organic matter < 2 % on DM). This concentration is in practise, partially caused by co-extraction of natural organic matter and by blank levels of the petroleumether not reachable. In many Dutch samples a mineral oil concentration between 20 and 100 mg/kg d.m. is detected (in soil used as building material **60%** < 20, **9.8 %** 20-30, **6.6%** 30-40, **5%** 40-50, **9.5%** 50-100 en **9%** > 100 mg/kg d.m. (Alcontrol, 2005). The Danish health quality criteria in soil is 25 mg/kg for mineral oil measured as total hydrocarbons C10-C35.

*In most cases the cause for the low exceeding of the limit value can not be found which leads to discussions between laboratory and client if this is really a contamination with mineral oil. In the Netherlands this is a problem in trading soil. Relevant here is the discussion about the risk of the*

*contamination found. In some cases there is a discussion if the result of the mineral oil analysis really is mineral oil. The concentration found could be related to additives in a soil decontamination process (e.g. polymers) which are detected as "mineral oil", which are not in the real sense of the word "mineral oil". In case of organic rich soils (peat) and in sediments high mineral oil concentrations (100-200 mg/kg d.m. can be measured in non-suspected and most probably clean soils (Jansen and Groenewegen, 1997)*

- "Target values in decontamination" In decontamination projects more and more the contractors are paid based on the oil concentration in the groundwater at the end of the project, for example the project is being paid for if the end concentration is  $< 300 \mu\text{g/l}$  and not if this is  $> 300 \mu\text{g/l}$ . Accounting for the large uncertainties in the determination (for the analysis as well as for the sampling) it is almost impossible to claim a statistical difference in result between 200 and 500  $\mu\text{g/l}$ . As a consequence in practise contractors sometimes take a few samples, send these to different laboratories and use the lowest value for proving the success of the project. In the UK no guideline values are available for remedial action for TPH<sup>1</sup>-contamination. Characterisation of the residuals present after remediation is necessary in order to do risk assessment of remediated soil (Pollard et al., 2005).
- In Japan, there is much more interest in smell and taste of chemicals including petroleum. The number of the carbon in it is 6 to 10. Hexane and benzene are controlled with a standard, which is designated by the Japanese Government (Ministry of Labour, 2001). Standards are necessary to evaluate these compounds

## 2 Mineral oil and risk-based analysis

In environmental samples, mineral oil or TPH (Total Petroleum Hydrocarbons) is one of the most often analysed parameters. In spite of the large amount of data available it is still difficult to relate the data to risks. In future a risk base assessment will be preferred all over the world. The difficulties for risk assessment are caused by the complexity of mineral oil. It is not a single compound, but it is a mixture of different hydrocarbons. The composition in the environment depends on:

- Type of mineral oil product (gasoline to lubricating oil)
- Origin of the crude the mineral oil product is made of
- Addition of additives to improve the quality of the product
- Fate of the mineral oil in the environment, Degradation volatilisation, solubility

In The UK, the term 'TPH' is considered as a misleading one and it is replaced by VPH (volatile petroleum hydrocarbons) and EPH (extractable).

Measurement of mineral oil was restricted to mineral oil as a total parameter, defined as all compounds with a boiling point between C<sub>10</sub> and C<sub>40</sub> or slightly different ranges

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<sup>1</sup> TPH (Total Petroleum Hydrocarbons) includes mineral oil and volatile hydrocarbons

and analysis of the most toxic and water soluble compounds of the group below C<sub>10</sub> (BTEX). Relating of the effects to measured mineral oil concentration, especially if volatiles are not present, showed that the total oil concentration is a too rough estimate of the risks (Concawe 1996; Brils et al, 2002). It is necessary to differentiate in groups of mineral oil components. This is worked out for toxicological effects as further described in this report, but also types of assessment ask for a more detailed mineral oil determination.

New questions ask for new methods and it is in human nature to develop a new method. In this report we connect the new questions with the possibilities of existing methods and more precisely the standardised ISO-methods. If it is possible to further develop these methods so that they can supply the answers, the assessment of mineral oil pollution will be a more constant activity in time. The first tier in assessment can still be the total concentration, which will be the same in the new and old approach, because the method is the same. The second tier will be the introduction of several different fractions.

In a report on Environmental Risk Limits for mineral oil, Verbruggen (2004) summarised different steps and assumptions:

1. Oil is a mixture with compounds of different characteristics. In this exercise mineral oil is divided in blocks of equivalent carbon numbers (EC) within the group of aromatic and aliphatic compounds.
2. The environmental fate of these different blocks in water is well-defined ( $\log K_{ow}$ ,  $\log K_{oc}$ , solubility, and BCF).
3. It is assumed that the oil constituents affect the target organism mainly by narcosis: The effect of the different blocks is comparable when expressed in concentration (in moles) present in the target lipids (of the membrane).
4. The water concentration of the different blocks can be estimated by equilibrium partitioning between three phases: the organic matter of the sediment, oil and water.
5. The target lipid concentrations of the different blocks can be estimated from the water concentration by the equilibrium partition coefficient between water and cell membranes.
6. The internal molar concentrations of the individual blocks are added up to a total internal concentration.
7. For each type of oil a dose effect curve is made for the different species using the total internal concentrations, whether or not logtransformed.
8. Endpoints are estimated from these dose-response curves (EC10 or EC50) or from a statistical analysis of variance (NOEC).
9. The endpoints for the different species (EC10s) are brought together in making a species sensitivity distribution from which the HC5 and HC50 are estimated.
10. The HC5 and HC50 values, still based on internal concentrations, are recalculated to concentrations in water and sediment for each block individually using equilibrium partitioning equations.
11. For comparing measurements with the ERL it is necessary to measure the different blocks of aromatic and aliphatic compounds add the quotients of the

measured concentration and the ERL:  $\Sigma(\text{measurement}_i/\text{ERL}_i)$  conclude that the ERL is exceeded when the sum is greater than unity

His approach is in line with the work of the so-called Total Petroleum Hydrocarbon Working Group (TPHCWG, 2000). This group has made an intensive study on items related to the mineral oil contamination of soil and gives much information on toxicity data of oil compounds.

Verbruggen's concluding step 11 is important for this report, because it asks for differentiation of the mineral oil content in different fractions.

### **3 Development of the mineral oil analysis**

#### **3.1 Available chemical methods**

##### **3.1.1 Standard methods**

The analysis of mineral oil has developed from gravimetric analyses where the total amount was measured, to gas chromatographic analysis still focussed on the total amount, but with more possibilities. In between an infrared method has been applied (developed for the analysis in water, but also used in soils and sediment (ISO/TR 11046).

Before gaschromatographic analyses of oil in soil and sediments it is necessary to extract the mineral oil from the matrix and sometimes to concentrate the extract. Homogenisation of the matrix excludes the analysis of the volatile fraction of mineral oil. Therefore two lines have been followed. (1) the analysis of the non-volatile fraction of mineral oil ( $>C_{10}$ ) as described in ISO 16703 and (2) measurement of the volatile fraction of mineral oil. Because in this fraction the BTEX are often dominant present and are also the most risk-full compounds (toxic and risk for leaching), the methods for the volatile part of mineral oil are focussed on BTEX (purge and trap in ISO 15009 and headspace in ISO 22155).

In order to have the possibility to compare results of soil analysis with analysis in the other environmental matrix water, the developed methods followed as far as possible the definitions and procedures described in the methods for water analyses (EN-ISO-15680 for the volatile aromatic compounds and EN-ISO-9377-2 for the non-volatile fraction. On the moment this approach is called Horizontal standardisation (van der Sloot, 2003).

### 3.1.2 Volatile oil

Standards, as mentioned above, describe mineral oil as the fraction between C<sub>10</sub> and C<sub>40</sub> after an extraction of the sample with a solvent like petroleum ether or heptane and a clean-up with florisil or as volatile compounds. In practise however there are sites contaminated with chemicals like white spirit consisting of a mixture from alkanes with boiling points lower than C<sub>10</sub>. These contamination's are not completely triggered by other analyses like for example the BTEX analysis and therefore in practise in many cases ignored. In cases where this contamination is not ignored laboratories use their house methods in order to give an estimate of the concentrations. The method however largely differs from lab to lab. Some report the sum of BTEX+aliphatics as volatile oil, some everything seen by a MS detector between C<sub>6</sub>-C<sub>10</sub>, some between C<sub>5</sub>-C<sub>10</sub>, some subtract BTEX etc. As a consequence results from laboratories are not comparable. Table 1 gives an overview of methods used by some Dutch laboratories.

In Denmark soil is extracted with pentane and analysed with GC-FID to determine volatile oil and the sum from benzene to C<sub>10</sub> is reported as volatile oil. In Japan a guideline is developed to relief the irritation from the chemical species, which are released from materials for houses and buildings. The species are C<sub>6</sub> – C<sub>16</sub>.

Table 1. Methods used by some Dutch laboratories to determine the concentration of "volatile oil" in soil and water samples [2].

Lab	Pre-treatment	Equipment	Remarks
A	Soil: acetone extraction Water: direct P&T	GC-MS	
B	Soil: methanol extraction Water: direct P&T	GCMS purge& trap	Detection in scan mode (mass to 450), calibration with alkane standard solution. Report: C6-C12.
C	Soil: methanol extraction Water: direct HS-GC	GC-FID after Headspace	<ul style="list-style-type: none"> <li>• Standard gasoline as cal. standard</li> <li>• Alkanes as marker for the fractions</li> <li>• report: C6- C12 (sum and fractions on even C's);</li> <li>• Aromatics inclusive &gt; No split in 'with and without' aromatics.</li> </ul>
D			Does not carry out a "volatile oil" test
E	Soil: methanol extraction Water: direct headspace	GC-MS after headspace	Calibration with alkanes (exclusive aromatics), report: C6-C10.
F			Does not carry out a "volatile oil" test
G	Soil: methanol extraction Water: direct Purge&trap	GC-FID after purge & trap	Calibration BTEX standard solution. Report: C6-C12, aromatics subtracted.
H			Does not carry out a "volatile oil" test
I	Soil: methanol extraction Water: direct Purge&trap	GC-MS after purge & trap	Report: - aliphatics n-C5 t/m n-C8 - aliphatics n-C8 t/m n-C10 Calibration with several n-alkanes Report: aromatics and alkylbenzenes: - aromatics C8 t/m C10 (without ethylbenzene / xylenes) - alkylbenzenes Calibration with several aromatics/alkylbenzenes.

There are no limit values set by the Dutch authorities for “volatile oil”. This is a problem because contaminations with solvents like white spirit (containing serious hazardous compounds like hexane) can be ignored.

### 3.2 Methods to predict toxicity

On different places methods are developed in order to measure the fraction of oil responsible for toxicological effects. All methods are using different boiling fractions, mostly combined with a separation of the extracted oil between aliphatics and aromatic (Table 2). In toxicological groups the TPHCWG-approach is becoming more popular because it seems simple because uses only one extraction for the whole range to be measured is used. In the UK most methods are based on the TPHCWG-approach, but it is, however, preferred to describe TPH as the fraction passing the florisil column, which may exclude several aromatic compounds.

**Table 2.** Methods developed to predict toxicity used in different institutions (given are the number of reported oil fractions)

		Total	Aliphatic fractions	Aromatic fractions	Target compounds included	Extraction methods <sup>1)</sup>	Carbon range
Massachusetts Department of Environmental Protection	MaDEP	3 (volatiles)	2	1	Y	2	5-36
Total Petroleum Hydrocarbon Criteria Working Group	TPHCWG		6	6	N	1	5-35
Canadian Council of Ministers of the Environment	CCME	4			N	2	6-34
Rijksinstituut voor Volksgezondheid en Milieu	RIVM		6	7	-	-	5-35
New Zealand, Ministry for the Environment		4			N	2	7-36
Texas Natural Resource Conservation Commission			7	6	N	1	6-35
American Petroleum Institute	API	1 (44+-fraction)	6	7	-	-	6-44+
Environmental Agency, UK	OK	1 (44+-fraction)	7	8			6-70 <sup>2)</sup>
Danish EPA	DEPA	3			N	1	Benzene-35
OSPAR <sup>2)</sup>		1	1	0	N	1	7-40
OVAM		1	7	8	Y	1	
RIKZ	RIKZ	4				1	10-40

1) 1= single extraction; 2 = extraction for volatiles + extraction for non-volatiles

2) OSPAR: Commission for Protection of Marine Environment of the North-East Atlantic

Some of the methods above have a broader scope. The OVAM method (based on the TTE oil characterisation) test is focussed on remediation and prevention of leaching. This implies additional measurements in water extract (OVAM, 2005).

<sup>2)</sup> Although the recently published documentation from the Environment Agency states up to C70, this is rarely being asked for at present in the UK.

## 4 Differences for water, soil and sediment

Measuring mineral oil in environmental matrices it has to be realized that due to the way of introduction in the environment, the properties of the oil and the properties of the matrix the composition of mineral oil may differ. In this chapter this is explained for the matrices (1) water, (2) soil and (3) sediment. This may have consequences for the analyses.

### 4.1 Water

The solubility of the individual mineral oil components in water differs a lot. The solubility of the C<sub>7</sub>-aromatic compound toluene is 522 mg/l, while the solubility of the C<sub>7</sub>-aliphatic hydrocarbon heptane is only 2.7 mg/l (Bosman, 1986). Larger compounds are less soluble. The final amount of a compound present in water depends on the fraction of that compound in the oil and follows Henry's law. This results of a change in composition. For instance a light fuel oil consisting of 66.7% aliphatics, 27.3% aromatics and 6% more polar compounds in equilibrium with water, gives a dissolved oil with percentages of 2.9; 11.4 and 85.7 respectively (Harmsen, 1986). The ratio between aliphatics and aromatics is completely changed. If a floating layer of oil on water is sampled another more aliphatic oil will be analysed.

### 4.2 Soil

Mineral oil in soil is the result of activities where oil is used or transported. Leakage of pipelines can introduce large amount of mineral oil in the environment. Soil is able to absorb an amount of oil in pores and organic matter until a residual concentration. Larger amounts are transported in the soil. Due to biodegradation and evaporation the composition may change. On larger depths where these processes are negligible the original mineral oil product can be found.

### 4.3 Sediment

Mineral oil is one of the most commonly occurring organic contaminants in sediments. It is persistent in sediments due to the existence of anaerobic conditions. Under aerobic conditions mineral oil in sediments and soil is biodegradable (Harmsen, 2004).

The typical mineral oil pattern that is found in polluted soils is not seen in sediments. The reason for this is logical. The density of spilled oil is usually lower than the density of water; oil, therefore, will float on water and tends not to go into the sediment. Exceptions are some greases or special oil products, but these products are not released into the environment in large amounts. Due to evaporation the most volatile compounds will disappear quickly. Movement of the water is responsible for

presence of suspended particles in the water and break up of the oil film in the water. Oil particles will adsorb to the solid particles and settle out together with these particles. The water layer above the sediment, including the top layer of the sediment, is aerobic and can be considered a bioreactor. The easily degradable compounds are partly removed in this layer. The easily degradable low boiling compounds and the n-alkanes are visible at the beginning of the upper chromatogram in Figure 1. The remaining in the sediment is weathered oil (second and third chromatograms in Figure 1); weathered oils are also present in a polluted terrestrial soil after a period of active bioremediation. The amount of oil components visible in the beginning of the chromatogram is low.

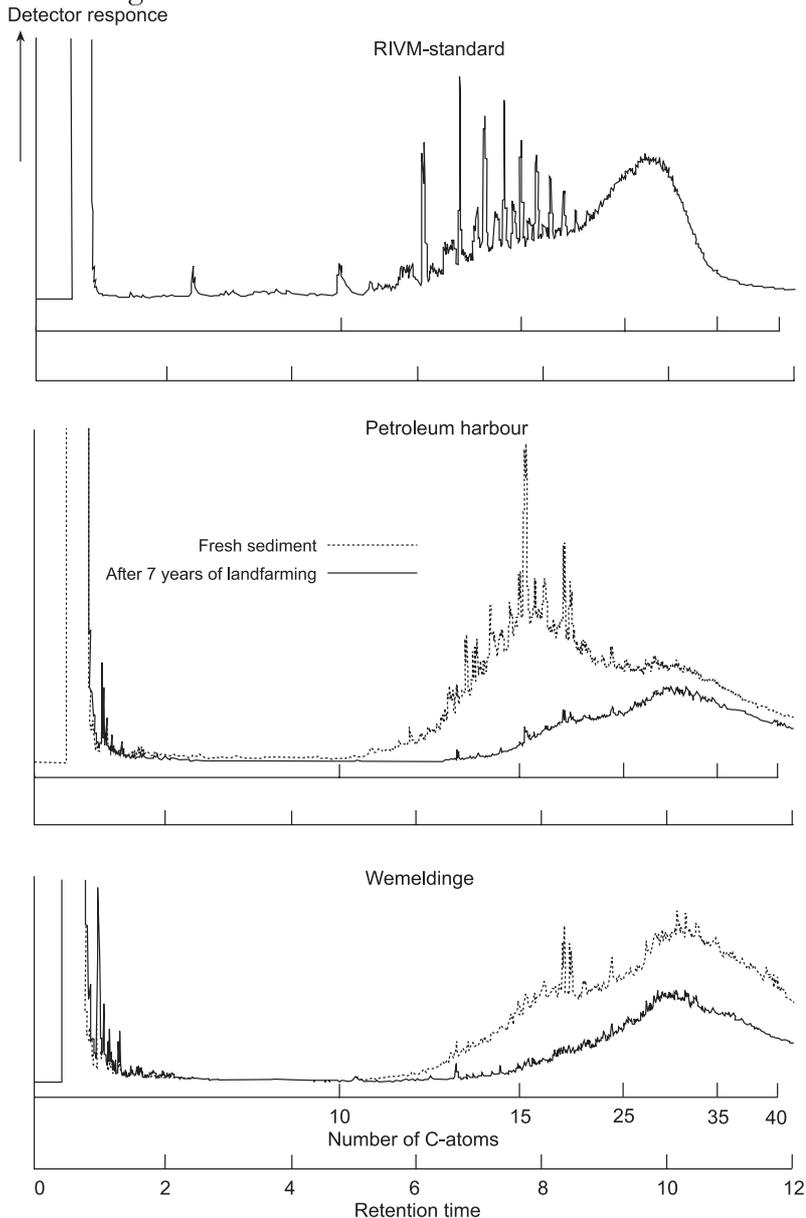


Figure 1 Chromatograms of mineral oil.  
 - Mixture of mineral oil as present in the RIVM standard (commercial calibration mixture used by Dutch laboratories).

- *Mineral oil in the original dredged sediments from Petroleum Harbour and after 7 years landfarming.*
- *Mineral oil in the original dredged sediments from Wemeldinge and after 7 years landfarming.*

Mineral oil in sediments is present in different physical forms (Harmsen and Zweers, 2000; Brils et al., 2002):

- Free occurring un-bound droplets.
- Droplets bound to sediment particles.
- Mineral oil adsorbed on the surface of organic matter.
- Mineral oil absorbed in the organic matter.
- Mineral oil present between mineral particles.

## 5 Transformation of ISO-standards to risk based standards

It is easier to relate risk to the concentration of individual compounds or groups of related compounds than to a group parameter like mineral oil. However, this is also a limited approach. Risks can be better predicted using the approach of bioavailability (ISO/CD17402, NRC Committee, 2003, Harmsen et al., 2005). In contradiction to heavy metals and PAHs, no methods are available to predict the bioavailability for target organisms for mineral oil. This is also related to the way mineral oil is present, adsorbed as individual molecules, but also as a separate phase. The concept of bioavailability has to be kept in mind in developing chemical methods for predicting risks. As long as a free oil phase is present, this phase will be in equilibrium or close to equilibrium with the water phase and risks can be related to total concentration of compounds present in the mineral oil. Having low concentration or low residual concentration as present after bioremediation of soil or sediment, the equilibrium approach is not valid and a method based on total concentration will overestimate the risks.

The ISO-method for mineral oil measures the part having retention times between  $C_{10}$  and  $C_{40}$ . The two available methods for volatile compounds have a limited scope, but these methods can measure all mineral oil compounds from  $C_5$  up to at least  $C_{10}$ . There is no standard method available that measures the whole range. In the ISO-approach this is also not possible. Standard methods are starting with a sample as homogenous as possible. This pretreatment is described in ISO-14507 and ISO 16720. For volatile compounds it is not allowed to mix the sample in order to prevent losses. The extraction liquid is added as soon as possible. In air-dried soils (< 30 °C) losses up to  $C_{16}$  can be observed. Volatile compounds are more homogenous distributed compared to the less volatile and without homogenisation acceptable standard deviations can be obtained. If samples are not pretreated, the result will have a low reliability because of the large standard deviation (see the results from for example the Dutch ANVM236 Project).

As long as there is no reliable pre-treatment method for volatile compounds it is advisable to follow the ISO-approach i.e. no homogenisation for volatiles as

described in ISO-14507 and homogenisation for the non-volatiles as described in ISO-14507 or ISO 16720 freeze drying). If all compounds have to be measured using one method, this implies that homogenisation cannot be allowed and a low accuracy for the low-volatile compounds will be obtained.

The detailed information wished for risk assessment is not yet in the scope of the ISO-methods. ISO 15009 and ISO 15680 are limited to the volatile aromatics and ISO 16703 (soil) and ISO 9377-2 (water) give the sum of the hydrocarbons with retention times between C<sub>10</sub> and C<sub>40</sub>. It is however possible to extend the scope of the methods.

Using ISO 15009/22155 and ISO 15680 it is possible to measure all volatile compounds in environmental matrices and to extend the scope with volatile hydrocarbons between C<sub>5</sub> and C<sub>10</sub>. If a GC/MS system is used it is even possible to identify and quantify all individual compounds. These individual results can be linked with toxicological data. It is also possible to summate specific compounds (e.g. aromatics and aliphatics) but this will mean a loss of information if toxicological data of all individual compounds are present.

ISO-16703 measures all hydrocarbons between C<sub>10</sub> and C<sub>40</sub>. The chromatogram is mostly not suitable for measurement of all individual compounds. Some specific compounds like n-alkanes can be recognised, but most compounds are resolved in a hump. Using an MS-system may increase the number of individual measurable compounds.

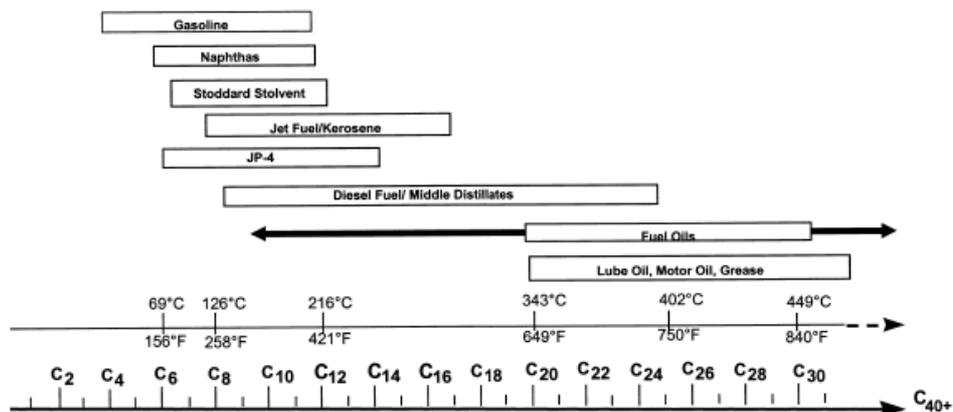


Figure 2. Approximate Carbon and Boiling Ranges of Petroleum Products [15]

### Mineral oil fractions

Based on the measured chromatogram, it is very easy to divide the total range in boiling ranges, separated by the retention times of the n-alkanes. All ranges are possible. There are several possibilities for a distinction in fractions:

1. Based on the most common used mineral oils like gasoline (C<sub>6</sub>-C<sub>12</sub>), diesel (C<sub>10</sub>-C<sub>30</sub>), fuel oil (C<sub>8</sub>-C<sub>20</sub>), kerosene/petroleum, lubricating oil (C<sub>30</sub>-C<sub>40</sub>), (Figure 2) .

2. Based on toxicity: it is well known that the higher the boiling point of an alkane the lower the toxicity of the compound.

It would be recommendable to combine both arguments mentioned above. The TPHCWG uses the fractions summarised in Table 3 (TPHCWG, 2000)

Table 3. Fractions defined in the TPHCWG-approach. Range of Equivalent Carbon Number

Aliphahtic	Aromatic
5-6	Benzene (6.5)
>6-8	Toluene (7.6)
>8-10	>8-10
>10-12	>10-12
>12-16	>12-16
>16-35	>16-21

Having the extract obtained with ISO-16703, it is possible to make a separation into aliphatic and aromatic compounds. This can be done using column chromatography with a silica gel column. The aliphatic fraction and aromatic fraction can both be analysed again using gas chromatography and the chromatogram can be divided into different boiling fractions (for an example see Table 3).

In ISO-16703 uses florisil to remove polar compounds originated from natural organic matter that are co-extracted. This is a separation on polarity and also less polar compounds can be partly removed. The florisil-column also removes part of the PAHs. This is not a problem, because PAHs can be easily and more accurate being determined using ISO 13827 or ISO 18287 or the Horizontal standard in development.

It should be realised that reporting limit of the ISO-standard do not change by extending the scope. For the non-volatile compounds the presence of co-eluted natural organic matter and quality of the solvents is responsible for a background signal in the chromatogram. This background signal will, however, be higher if methods are applied without a clean-up (i.e. Florisil) to remove the polar organic compounds. For the volatile compounds a much lower reporting limit is possible, because individual compounds can be measured. If a summation, by integrating the total surface is used the reporting limit will be higher.

## 6 Conclusion

From toxicological point of view, the result of the determination of mineral oil as measured using ISO16703 (fraction C<sub>10</sub>-C<sub>40</sub>) gives no prediction of the toxicity because it gives no detailed information concerning individual compounds found and

boiling point of the oil fraction. A more specific analysis is necessary. This observation has led to the development of methods analysing the range between  $C_6$  and  $C_{40}$  and the possibilities to distinguish in boiling point and fractions with different polarities. From chemical analytical point of view, especially the analysis of volatiles has a high inaccuracy, because it is not possible to homogenise the sample to prevent losses of the volatile compounds. Furthermore at present there is no standardised method if more than aromatic compounds have to be measured as a consequence of which laboratories use different methods especially for volatile compounds and report different results.

It is possible to use the existing ISO-methods to produce the data wanted by toxicologists. Such a method is based on two existing methods (ISO15009/22155 for the analysis of volatile compounds and ISO 16703 for the analysis of less volatile compounds).

ISO 15009/22155 gives the concentration of all individual compounds between  $C_6$  and  $C_{10}$ . These data can be linked with toxicological data in order to predict the toxicity. More accurate results will be obtained compared to the TPHCWG-approach in which approach this fraction of the mineral oil is distinguished in 4 fractions, knowing the great difference in toxicity of the individual compounds in this range. Regarding cost, the amount of work in the laboratory will be the same for measuring individual compounds and 4 groups. Interpretation of the chromatogram to establish the individual compounds may take more time, but automating is possible.

ISO 16703 gives the total mineral oil fraction between  $C_{10}$  and  $C_{40}$ . This method can be easily expanded to a method where boiling points are differentiated. The extract is suitable for column chromatography in order to obtain an aliphatic and an aromatic fraction. As a result the measures for this fraction are comparable with the results obtained from the methods described in table 2.

In environmental matrices like sediments, surface soils and biologically cleaned soils volatile compounds are not present. For these samples only ISO 16703 has to be used. In cases a high amount of volatiles is present this will be observed during sampling, pretreatment or as residual peaks present in the chromatogram before  $C_{10}$ .

## 7 Recommendations

Based on the discussions in this report the next recommendations are given:

1. Develop a method in order to determine “volatile” mineral oil which gives an indication of contamination with non-aromatic compounds with a boiling point  $< C_{10}$ . It is recommended to focus on compounds with a boiling point  $> C_5$ .
2. Link the proposed method as much as possible to existing international standards like ISO 15009 or ISO 22155 (soil, volatile compounds), ISO 15680

(water, volatile compounds), ISO 16703 (soil, mineral oil) and EN-ISO 9377-2 (water, mineral oil).

3. The reported mineral oil concentration should give insight in the different oil fractions. It is possible to use fractions related to common used mineral oil products like gasoline, diesel, lubricants etc., but also a risk-based approach could be used.
4. Develop a scheme which shows in which cases which test is relevant (e.g. for sediments and biologically cleaned soils volatiles are not relevant. Use of screening and other observations
5. Develop a definition for “volatile oil” (C<sub>5</sub>-C<sub>10</sub>, only aliphatics, inclusive volatile aromatics etc.).
6. Develop new limit values for contaminations with “volatile oil” (C<sub>5</sub>-C<sub>10</sub>) and semi-volatile mineral oil (C<sub>10</sub>-C<sub>40</sub>). Link these to different oil fractions and or individual components.

Appendix 1 contains a proposal for the procedure to be followed and for the tests to be carried out and the oil fractions to be reported.



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## Appendix 1 Proposed procedure and test methods

For analysing soil and water samples on mineral oil a procedure with the next steps is proposed:

### STEP 1

Decision on methods that have to be applied. The following possibilities have to be discussed:

- 1 Decision scheme based on experience  
Sediments only C10- C40  
Soil depended on origin of sample
- 2 Starting with method for > C10 (ISO16703). If compounds < C10 are visible in the chromatogram, measure also <C10 (based on ISO 15009 or ISO 22155)
- 3 Starting with method for <C10. If compounds > C10 are visible in the chromatogram, measure also >C10 (based on
- 4 Start with a screening method<sup>3</sup>

### STEP 2

Application of selected method. If concentration measured is above a certain limit go to step 3

### STEP 3

Aliphatic – aromatic split method for non-volatiles  
Measurement of individual volatile compounds

Discussion points:

- “Total volatile oil”: sum of only aliphatic or also aromatic compounds?
- Is it allowed to report "higher then" values of the screening test and compare with reference values?

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<sup>3</sup> 1. Pre-screening oil test

The pre-screening oil test can be a very fast and simple (and therefore cost effective) test in order to assess if there is a mineral oil contamination present.

Proposed test procedure: make an acetone/n-hexane (soil) or n-hexane (water) extract and analyse the extract (after removal of the acetone (soil)) with a GC-FID system. As it concerns here a pre-screening no clean-up is required. Calibrate with a standard mixture of aliphatics (e.g. the Dutch RIVM mixture) and report the total content of C8-C40 and in case of a positive result send a copy of the chromatogram to the client.

Remarks:

- Sometimes Pentane as extraction solvent is proposed. This solvent however is very volatile and therefore not practical to deal with in summer conditions. Therefore, like in the OVAM compendium, n-hexane is proposed.
- With a n-hexane extract information can be given for boiling points > C8. Some oil types contain compounds with lower boiling points, but together with the GC-FID chromatogram it can easily be assessed there are also volatile compounds present.