



## Discussion Paper for TPH Workshop

### Introduction

In Australia, the normal approach for triggering further investigation during contaminated land investigations is to determine whether the concentration of contaminants of concern exceed published Health Investigation Levels (HILs) or Ecological Investigation Levels (EILs). In the case of petroleum hydrocarbons, a number of HIL's exist; however, these are limited and do not extend to the assessment of volatile hydrocarbons. There is guidance on how the assessment of risk associated with such contaminants should be carried out, and it is common practice to undertake a risk assessment to determine whether the concentrations might pose a human health or ecological risk. As such, there is a basis for developing a set of screening levels for petroleum hydrocarbons in soil and groundwater.

Health Screening Levels (HSLs) for petroleum hydrocarbons have been developed by the Cooperative Research Centre for Contamination Assessment & Remediation (CRC CARE) under the guidance of a Project Advisory Group (PAG) consisting of regulators, industry and researchers. These HSLs (which are proposed to assist in HIL derivation) are for a limited range of chemicals that may be regarded as indicators of the risk associated with a petroleum release. The indicators selected as chemicals of potential concern are:

Benzene, Toluene, Ethylbenzene, Xylenes, Naphthalene and carcinogenic PAHs.

The remaining constituents of petroleum mixtures are assessed as Total Petroleum Hydrocarbons (TPH). TPH have been assessed using a collapsed fractions approach similar to the approach adopted by the Canadian Council of Ministers for the Environment (CCME). These TPH fractions are defined as:

- C6-C10 (excluding BTEX)
- C>10-C16
- C>16-C34
- C>34

During the derivation of the HSLs, it became apparent that there were a variety of approaches adopted to the reporting of hydrocarbon fractions and the PAG recommended that CRC CARE sponsor a workshop to address this issue. This workshop is aimed at bringing together Australian analytical laboratories, environmental regulatory bodies and petroleum industry to a consensus to develop a consistent and harmonized approach to the analysis and reporting of TPH.

## **Fractions**

The fractions reflect those for which toxicity, fate and transport data are available through recognised sources. The adoption of these proposed new fractions requires discussion.

## **Naming**

The naming of this method has been discussed for many years. Most references and guidelines refer to Total Petroleum Hydrocarbons (TPH), however, is this correct terminology?

Alternatives include Total Recoverable Hydrocarbons (TRH), Total Recoverable Petroleum Hydrocarbons (TRPH), Solvent Extractable Hydrocarbons (SEH) or Total Extractable Hydrocarbons (TEH).

A recent survey showed that 7/10 member labs of the Environmental Laboratory Industry Group (ELIG) support the term TRH, unless a silica gel cleanup has been done, in which case the usual TPH term is acceptable.

## **How do the labs test for TPH?**

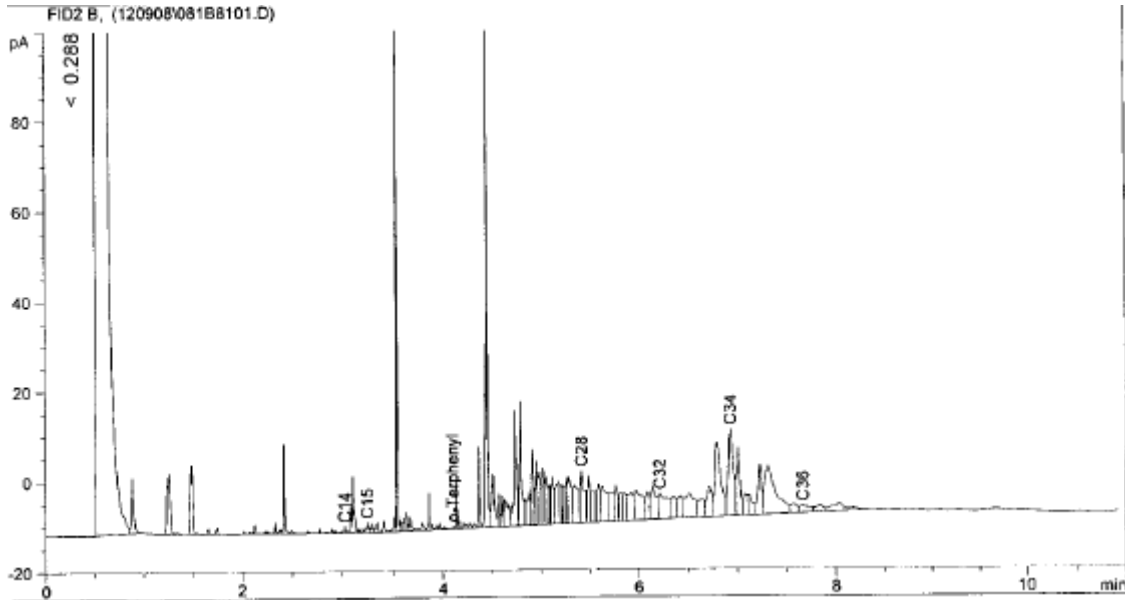
Very simply, the sample is extracted with an appropriate solvent, thereby transferring any material that can be extracted into this solvent. Remember that not only petroleum products will be dissolved into the solvent.

This solvent extract is then placed into a vial and analysed, in most cases by a Gas Chromatograph-Flame Ionisation Detector (GC-FID). Currently most labs will report the results as TPH.

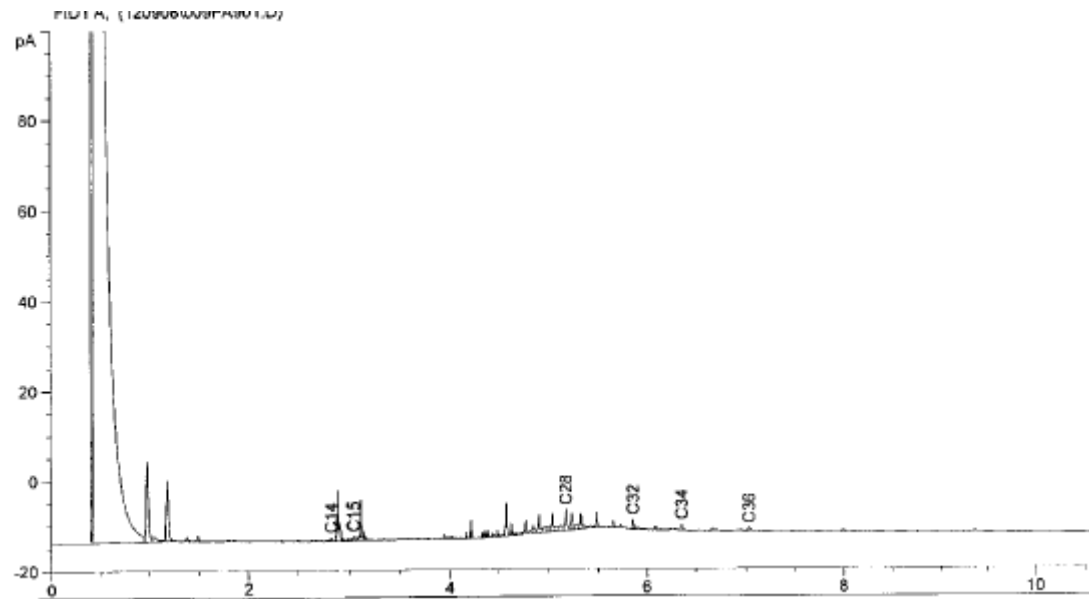
## **What is a silica gel cleanup?**

After a sample is extracted in solvent the extract is poured through a column containing silica gel. The solvent extract runs down through the column slowly, over the surface of the silica gel particles. The silica gel adsorbs any polar compounds that were extracted from the sample, allowing the non polar petroleum based compounds to flow through. General consensus from ELIG labs is that after a sample has been treated with silica gel the correct terminology is TPH.

## Some Examples



**Figure 1. Sample of Woodchips, extracted and run by GC-FID. In most cases all components would currently be calculated as Total Petroleum Hydrocarbons. As no silica gel cleanup was performed, perhaps the correct terminology should be Total Recoverable Hydrocarbons?**



**Figure 2. Sample of Woodchips, extracted and run by GC-FID, AFTER a silica gel cleanup. This appears to be truly Total Petroleum Hydrocarbons?**

## Instrumentation

There are different instruments that can be used for analysis. For the volatile fraction available instrumentation includes Purge & Trap followed by Gas Chromatograph-Mass Spectrometer (GC-MS), GC-FID or Headspace. For the semi volatile fractions it is GC-FID. Should instrumentation be specified in guidelines (prescriptive) or should any instrumentation, if deemed equivalent based on performance, be accepted.

## Calculating

There is no fixed way to calculate the current fractions. All labs calculate slightly differently. Examples of slight differences are:

Fractions	Lab A	Lab B	Lab C
C6-C9	Calculate from C5.5 to C9.5	calculate from start C6 to start C10	Calculate from >C5 to end C9
C10-C14	Calculate from C9.5 to C14.5	calculate from start C10 to start C14	Calculate from >C9 to end C14
C15-C28	Calculate from C14.5 to C28.5	calculate from start C14 to start C28	Calculate from >C14 to end C28
C29-C36	Calculate from C28.5 to C36.5	calculate from start C28 to end C36	Calculate from >C28 to end C36

A consensus needs to be reached to harmonise methodology. Such consensus should recognise the basis on which the fractions were derived.

A consensus should also be reached on how the fraction is calculated, for example, which standards are used in the calibration of each fraction. This could be aliphatics, aromatics, petroleum mix or BTEX compounds (for C6-C9).

## Method Performance Criteria

A poll conducted by ELIG suggests Australian laboratories use a number of different instrument configurations for TPH analysis. If the instrument is not prescribed in the method, then a performance measure will be required.

*A suggested protocol for a "performance based" method could be -*

A spiked homogenous soil can be prepared, which contains a mix of hydrocarbons. The homogenised spike sample can be distributed to laboratories and can be used as an in-house check on method performance.

An acceptance criterion can be derived for the material, which can be documented in the method. Using this approach, different detection technologies can be used for TPH determination as long as the sample concentration produced for the "reference" material lies within a specified acceptance criterion.

The success of this approach relies on a reference material, which is readily available, stable and well characterised. Some method harmonisation will be required e.g., definition of the bands and how they are calculated. The positive benefit should be improved consensus of TPH determinations for laboratories in Australia and increased confidence for the data user.