

# Guidance on petroleum hydrocarbon forensic chemistry for site investigation and remediation

## Volume 2

# GUIDANCE ON PETROLEUM HYDROCARBON FORENSIC CHEMISTRY FOR SITE INVESTIGATION AND REMEDIATION

Volume 2

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## FOREWORD

This guidance document has been prepared by Golder Associates (UK) Ltd. following commissioning by the Energy Institute (EI) under project identification number E1502, 2015.

The intention of the publication is to provide a practical introductory guide to petroleum hydrocarbon forensic chemistry, including a summary of changes in fuel specification and additives over time, the differences between petrogenic and non-petrogenic hydrocarbons, the effects of environmental processes such as weathering, and the application and limitation of various analytical techniques.

There is a wide range of literature relating to forensic chemistry available in the form of text books, peer-reviewed papers and internet data at various levels of complexity; it has not been our intention to duplicate these documents.

This guidance is aimed at site investigation and remediation practitioners, enabling them to confidently schedule appropriate sample analysis with an understanding of the purpose and limitation of each technology. By providing a solid background in the character and chemistry of hydrocarbons, and a thorough consideration of the interpretation of analytical results, the guidance document will allow consultants to demonstrate potential liability with greater confidence and reduced uncertainty.

The primary audience is anticipated to be environmental consultants involved in the investigation and remediation of hydrocarbon contamination, but this guidance document is also expected to be of use to regulators, site owners, and the insurance industry.

Although it is anticipated that this document will assist those involved in the investigation and remediation of sites contaminated with petroleum hydrocarbons, the information contained in this publication is provided as guidance only. While every reasonable care has been taken to ensure the accuracy of its contents, the EI, and the technical representatives listed in the acknowledgements, cannot accept any responsibility for any action taken, or not taken, on the basis of this information. The EI shall not be liable to any person for any loss or damage which may arise from the use of any of the information contained in any of its publications.

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Suggested revisions are invited and should be submitted to the Technical Department, Energy Institute, 61 New Cavendish Street, London, W1G 7AR.

Whilst written in the context of the UK legislative and regulatory framework, the principles set out in this publication can similarly be applied in other countries, providing national and local statutory requirements are complied with. Where the requirements differ, the more stringent should be adopted. A similar legislative and regulatory framework generally applies elsewhere in the European Union.

It is anticipated that this guidance will be updated as necessary to ensure it remains valid and of use to experienced practitioners involved in the investigation and remediation of sites contaminated with petroleum hydrocarbons. Where it is used as a reference and found to be deficient, users are encouraged to provide appropriate solutions and record them for incorporation into future editions of this EI document.

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## 1 INTRODUCTION

Significant resources are spent annually in the UK on the investigation and remediation of petroleum hydrocarbon contamination in soils and groundwater. The identification and characterisation of petroleum hydrocarbon contamination (including an estimate of its approximate age and source) is key to the attribution of liability in a regulatory and insurance context, and for making appropriately informed decisions on the need for, and extent of, any remedial actions. This is of particular relevance in the UK where the 'polluter pays' principle underpins contaminated land legislation.

Decisions on the apportionment of liability, and the need for intervention and remediation of petroleum hydrocarbon contamination in soils and groundwater in the UK, are typically based on chemical information from site investigations, and on the outcome of associated risk assessments. Standard analysis suites used in site investigations include an assessment of total petroleum hydrocarbons (TPH), often broken down into the carbon-based groupings identified by the TPH Criteria Working Group (TPHCWG). This information is focused on quantification, with only limited interpretation of the nature of the petroleum hydrocarbon. Whilst a significant step forward compared with the standard suite offered 10 to 20 years ago, such techniques do not allow for informed forensic interpretation of the original petroleum hydrocarbon source, point of release, or its composition and approximate age.

**Forensic Environmental Geochemistry:**  
*'Scientific methodology developed for identifying petroleum related and other potentially hazardous environmental contaminants and determining their sources and time of release. It combines experimental analytical procedures with scientific principles derived from the disciplines of organic geochemistry and hydrogeology'. (Kaplan et al.)*

An understanding and application of petroleum hydrocarbon forensic chemistry in site investigation, assessment, and remediation is therefore key to the correct attribution of liability in a regulatory and insurance context, and also to the correct identification of the original source of contamination, not only for soil and groundwater remediation, but also for identification of infrastructure repairs.

The forensic environmental geochemistry (forensic chemistry) approach combines the use of appropriate laboratory analytical methods and scientific principles, with interpretation around the movement, fate and transport of contaminants in soil and groundwater, to identify the source and potential timing of contamination. However, environmental consultants, supporting petroleum hydrocarbon site operators, and owners, often have limited or no direct knowledge and experience of forensic chemistry techniques. Apportionment of liability and decisions on risk and remediation are largely based on the results of relatively simple environmental techniques, and their interpretation can lead to incorrect allocation of resources and unnecessary costs.

This guidance is therefore aimed at experienced site investigation and remediation practitioners. It will provide information to support them in confidently scheduling appropriate sample analysis for petroleum hydrocarbon forensic chemistry studies, and will give an understanding of the purpose and limitation of each technique. It is intended that this guidance document will allow consultants, with the support of forensic chemistry experts, to plan site investigations, assess risks, design mitigation measures, and demonstrate potential liability for petroleum hydrocarbon impacts with greater confidence, reduced uncertainty, and without unnecessary costs.

## 1.1 SCOPE AND APPLICATION

This guidance relates to environmental contamination in the subsurface (soil and groundwater media only); it does not extend to inland waters or to the marine environment. The scope of the document covers petroleum hydrocarbons comprising crude oil and its refined products, and does not include chlorinated hydrocarbons or any other contaminant groups. Biofuels are not considered, other than when blended with petroleum products.

The primary audience is anticipated to be experienced consultants involved in the investigation and remediation of petroleum hydrocarbon contamination. However, the guidance document is also expected to be of use to regulators, site owners, site leaseholders, site operators, and the insurance industry.

This document is not intended as a step-by-step reference manual, or specific framework for petroleum hydrocarbon forensic chemistry interpretation. It provides an overview of petroleum hydrocarbon chemistry, forensic chemistry analysis, and interpretation methods, as a supporting document for experts in contaminated site investigation and remediation.

It is intended that this document will assist environmental consultants in seeking advice and support from specialist analytical laboratories and environmental forensic chemistry experts, to enable appropriate decisions in sample collection for laboratory testing as part of site investigation design, and in the correct identification of petroleum hydrocarbon type, contaminant source, approximate age, distribution and apportionment of liability. Some prior knowledge and experience of basic organic chemistry, the character, fate and transport of petroleum hydrocarbons in the environment, standard contaminated land investigation methods, and laboratory analysis is assumed.

In terms of geographical relevance, it is anticipated that the primary readership for this document will be based in the UK, and the document has therefore been written mainly with reference to UK and European information, where available. However, the vast majority of relevant literature sources, references, and relevant product composition relate to the US, and these have been referenced to illustrate key points, examples and case studies, where appropriate.

It is important to note that crude oil composition, refining and blending methods, product composition and additive use vary globally from region to region (and in some cases within individual countries or refineries), with time, and in the context of local regulatory requirements. The composition of a single product may vary daily due to the choice of crude oil, the availability of different refinery streams for blending, or due to seasonal variations on product specifications (for example, winter gasoline is blended to have a higher vapour pressure than summer gasoline, in the same refinery). Local and site-specific research is therefore critical to any successful petroleum hydrocarbon forensic study.

## 1.2 HOW TO USE THIS DOCUMENT

This document has been structured in two volumes:

- Volume 1 presents an overview of the procedures and processes carried out in a forensic investigation of petroleum hydrocarbon contamination and their application. It is intended to form an introductory guide for an environmental consultant embarking on such an investigation. A number of case studies are provided as an Annex.
- Volume 2 provides extensive background information on petroleum hydrocarbon chemistry, laboratory analytical methods and forensic interpretation. It is not intended that Volume 2 is read from start to finish. Rather, it is recognised that all readers are likely to have detailed understanding of some aspects presented, but only a working knowledge of others. Volume 2 has therefore been designed as a reference document to support Volume 1, to be consulted when required.

Throughout both volumes, text boxes have been included to highlight particular points:

For each topic, further reading is suggested in reference boxes. These are not intended to be a full or comprehensive list of reading matter, but are suggestions to assist guidance users in learning about a specific topic in greater depth, if desired.

Important points and definitions have been highlighted in dark green boxes

Short case studies are provided within the main body of the report in light green text boxes, to illustrate specific points. Further short case studies and four more detailed case studies are presented in Volume 1 (Annex C).