

Constituents of potential concern for human health risk assessment of petroleum fuel releases

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Abstract: When petroleum-based vehicle fuels are released to the subsurface environment, only a small number of chemical constituents typically account for a large majority of human health risks associated with potential exposures to affected soil, soil gas or groundwater. In other words, the risk 'footprint' of most fuel constituents is most often contained within the footprint of key risk-driving constituents of potential concern (COPCs). Therefore, assessment and management of an appropriate set of COPCs can support robust management of all potential risks and eliminate unnecessary chemical analyses and evaluation of constituents that rarely (or never) give rise to unacceptable human health risks. This paper presents an approach for identifying COPCs for petroleum fuel releases, based on internationally adopted human health risk assessment practices and available information on fuel composition and chemical toxicity. COPCs are identified as all constituents that could potentially give rise to unacceptable human health risks, based on theoretical upper-bound exposure estimates for exposure pathways. COPC lists are presented to guide the investigation and evaluation of risks at sites where releases of petrol, diesel, and kerosene/jet fuel have occurred. Such lists are generically applicable and may underpin site-specific evaluation of environmental conditions and associated risks.

Supplementary materials: Risk equations, input definitions and values, the physical–chemical properties of the fuel components, human health criteria, complete results and rankings of the calculated risk values are available at <http://www.geolsoc.org.uk/SUP18789>.

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Petroleum-based vehicle fuels consist of mixtures of hundreds to thousands of hydrocarbon constituents, including numerous potentially hazardous substances. Releases of fuels to the environment can potentially cause adverse human health effects, safety hazards, ecological and aesthetic impacts, or other concerns, all of which should be considered in an assessment of site risks and the selection of appropriate response actions. Evaluating human health risks can prove especially challenging owing to (1) variability of fuel composition, (2) weathering of fuels following release to the environment, (3) degradation and generation of metabolites with a distinctive hazard profile, (4) site-specific heterogeneity of physical conditions, and (5) uncertainties in toxicity and chemical–physical property information for potential risk drivers. Consequently, it is virtually impossible to quantify health risks associated with every constituent of a petroleum fuel release.

Fortunately, in reality such efforts are not necessary to effectively manage risks. A focused evaluation of an appropriate subset of the highest priority fuel constituents (i.e. typical risk-driving fuel constituents for which toxicity criteria are established and which are relatively mobile in the environment) can support robust management of all potential risks. This approach can also help eliminate unnecessary expense and effort on chemical analyses and risk evaluation of constituents that rarely (or never) give rise to unacceptable human health risks, and may be easier to follow and communicate to stakeholders. In practical terms, at sites where risk management action is found to be necessary to address risk-driving constituents, such action will in most cases also address related, but lesser, risks associated with the presence of other (unquantified) substances. Other workers have advocated consideration of fully

fractionated total petroleum hydrocarbon (TPH) analysis for all fuel releases, including gasoline (e.g. Brewer 2012), but our analysis supports an assessment of constituents of potential concern (COPCs), supplemented with specific TPH fractions only for middle distillate fuels, as being sufficient to identify and manage significant human health risks.

Selection of an appropriate set of COPCs is an important early step of the site assessment and risk management process, and helps to ensure that the risk assessment identifies any unacceptable risks and allows an assessor to effectively manage those risks. COPCs comprise the specific target analytes that merit investigation in affected environmental media, such as soil, groundwater, surface water (if used for potable water supply), or soil gas (via vapour intrusion or exposure in confined spaces), to adequately manage risks to human health and the environment. Selection of COPCs should also consider the possible remedial treatment perspective to sufficiently mitigate any actual risks, and inform remedial system design. Detected COPCs should then be evaluated as part of a risk assessment, to identify any unacceptable risks to human health or the environment, and to support an appropriate risk management strategy. Meanwhile, fuel constituents other than COPCs for a given release are not expected to drive human health risk management decisions at most sites, and therefore investigative actions focused on non-risk-driving constituents may provide little or no value to the health risk management process.

This paper summarizes the results and technical basis of a process for selecting appropriate COPCs depending on the type of fuel that has been released and the potentially applicable human health exposure pathways. Generic lists of COPCs are presented

for evaluating releases specifically involving gasoline/petrol, diesel/gas oil, and kerosene/jet fuel, based on identification of the key risk drivers for each fuel, as associated with human exposure pathways commonly evaluated for petroleum release sites.

Background

Risk-based site management

Risk assessment is the process used to estimate the potential magnitude and likelihood of adverse health and environmental impacts, or of other concerns, associated with exposure to potentially hazardous substances. Established risk assessment frameworks and tools allow environmental professionals to make informed judgements on the type and degree of risks associated with chemical releases and appropriate corrective measures for managing such risks. The scientific concepts and procedures that form the basis of such tools have been developed and widely adopted in numerous countries over the past three decades, including the USA (National Research Council 1983; USEPA 1989, 1991, 1992, 2012); the Netherlands (Van den Berg 1995, 1997; Swartjes 1999, 2002), and the UK (Environment Agency 2002, 2005). Similarly, the World Health Organization has issued risk assessment guidelines (WHO 1999) and employed a risk-based approach for the development of international drinking water quality criteria (WHO 2011). Ferguson & Kasamas (1999) and Carlon (2007) have documented the extensive incorporation of human health risk assessment in regulatory programmes throughout Europe. In recent years, similar regulatory programmes have been established in Australia (EnHealth 2004), Latin America (SEMARNAT 2006; CETESB 2006) and Asia (HKEPD 2007).

Effective risk management at petroleum-affected sites generally involves identification of applicable (1) pathways, (2) risk factors on a site-specific basis and (3) development and implementation of appropriate protective measures in the timeframe necessary to prevent unsafe conditions. Streamlined procedures for accomplishing these goals have been standardized by ASTM International via the Risk-Based Corrective Action (RBCA) process (ASTM 2010), and by CONCAWE (2003), both of which employ a tiered process for tailoring the response to petroleum or chemical releases to site-specific conditions and risks.

The primary factors influencing COPC selection are (1) the type of fuel or fuels released, whose composition dictates the type and relative abundance of toxic chemicals likely to have potential to enter the environment, (2) the likelihood of plausible source–pathway–receptor linkages between the affected environmental media and people living or working at or near the site of the release, and (3) the potential concentrations of fuel constituents at locations where human contact may be likely to occur.

Fuel composition and weathering

Following release to the environment, most petroleum-based products will weather with time, as the most volatile constituents evaporate, the most soluble constituents dissolve, and the product naturally biodegrades by both aerobic and anaerobic mechanisms. The degree of weathering depends highly on site-specific conditions (Stout *et al.* 2006); however, in general, a fresh release will present higher risks than a weathered release, as the most toxic fuel constituents also tend to be the most volatile and soluble. As weathering occurs, the principal risk-driving components typically shift from more to less volatile or soluble fuel components, and the overall risk reduces (e.g. Thornton *et al.* 2013).

Importance of the conceptual site model

A conceptual site model (CSM) underpins an environmental risk assessment and management by identifying plausible mechanisms by which chemicals could migrate through the environment and cause potential impacts to receptors. The CSM, including descriptions of light non-aqueous phase liquid (LNAPL) geometry, mobility, and partitioning behaviour into other phases (CL:AIRE 2014), should establish the likelihood of impact resulting from plausible source–pathway–receptor (S–P–R) linkages between a source (e.g. an LNAPL body) and a receptor. Illustrative conceptual models of LNAPL in the subsurface have been presented by CL:AIRE (2014), and partitioning relationships from an LNAPL source are illustrated in Figure 1. In some cases, the CSM alone may be adequate to determine that there is no plausible S–P–R linkage (i.e. no exposure means there is no potential risk) and, thus, no further work, such as chemical analysis of soil and groundwater samples, is required. Similarly, a CSM may be sufficient to identify that there is a clear and imminent threat and that emergency action is appropriate (prior to conducting a detailed risk assessment). More commonly, the CSM is used as the basis for planning site investigation activities (e.g. selection of COPCs, or sample collection and analysis), and later, if unacceptable risks are identified, it is used to guide development of an appropriate risk management strategy (e.g. comparison of mass reduction-based remediation alternatives versus containment, institutional or administrative controls to eliminate each complete S–P–R linkage).

Upper-bound risk estimation for fuel constituents

Risk evaluation methods

COPCs correspond to the specific chemical constituents most likely to pose unacceptable risks, and they must be identified based on very conservative (i.e. extreme), hypothetical exposure scenarios. Therefore, it is crucial to recognize that identification of a fuel constituent as a COPC by this study does not imply the existence of unacceptable risks at a site where these compounds are present. The key output of this study is a series of ranked lists of fuel constituents that are most likely to drive the risk management requirements for various combinations of fuel types and applicable exposure pathways. Consequently, COPCs are the constituents that merit inclusion in the site assessment and risk assessment processes.

The risk calculations used to identify and rank COPCs for a variety of scenarios are based on (1) the prevalence of each constituent in each fuel, (2) the fate and transport properties (e.g. solubility and volatility) of each constituent, (3) the capacity of each constituent to cause adverse chronic health effects (toxicity) and/or cancer (carcinogenicity), (4) conservative, upper-end estimates of potential constituent concentrations at assumed points of exposure, and (5) conservative assumptions regarding fate and transport (e.g. no biodegradation). Upper-bound human health risks values were calculated for each fuel constituent according to internationally adopted, standard risk assessment procedures for chronic (i.e. repeated, long-term) exposures (e.g. ASTM 2010) according to the assumptions described below. This exercise employed data published by internationally recognized sources on the composition of each fuel, the physical–chemical properties of the fuel components, and human health criteria. These procedures, in general, account for significant levels of uncertainties by the incorporation of conservative estimates of default exposure factors in addition to uncertainty

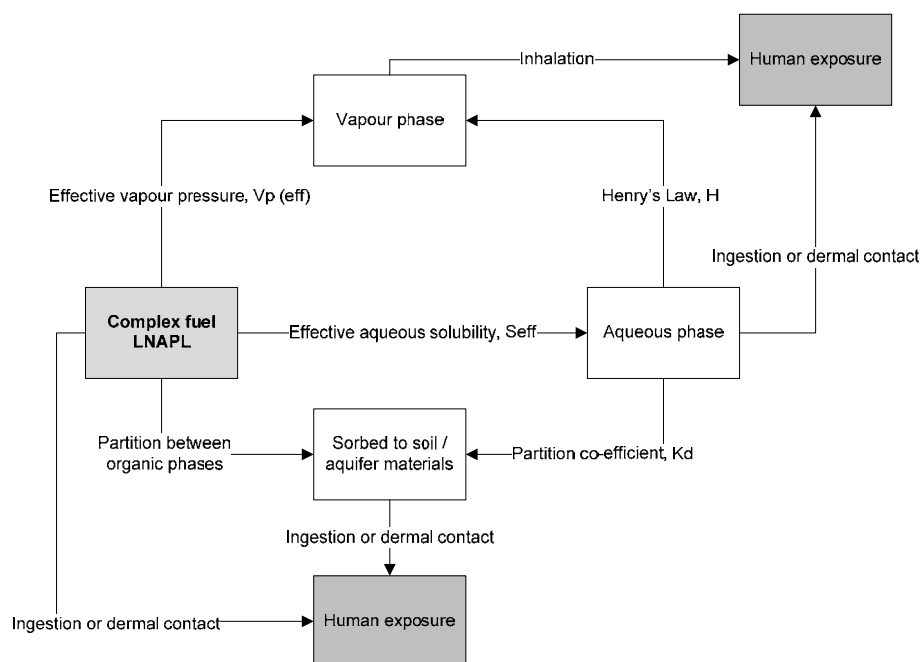


Fig. 1. Illustrative process-based CSM of hydrocarbon partitioning from an LNAPL source.

factors and modifying factors for toxicological parameters. Even further conservative assumptions have been employed in the risk calculations and for identifying COPCs, as described below.

Key assumptions

Acceptable risk thresholds

For the purposes of this study, COPCs have been identified as the fuel constituents for which the maximum predicted hazard quotient might exceed a value of 1.0, or the maximum predicted excess lifetime cancer risk might exceed a target limit of 10^{-6} (i.e. one in 1000000).

A hazard quotient is the estimated exposure concentration divided by a corresponding reference concentration (or tolerable intake); therefore no adverse health affect is expected to occur below this threshold. A hazard quotient greater than or equal to 1.0 for any constituent indicates a possibility of adverse health effects owing to exposure by the corresponding exposure route.

Potential excess lifetime cancer risk is calculated, using the ASTM (2010) approach, as the estimated exposure concentration multiplied by a corresponding unit risk factor (or slope factor). This value represents a predicted increase in the probability of an individual developing cancer during their lifetime as a result of the assumed exposure. In other words, an estimated excess lifetime cancer risk of 10^{-6} indicates that an individual exposed to the constituents in accordance with the CSM would have an increased one in 1000000 (0.0001%) chance of developing cancer during their lifetime (not the loss of life due to cancer). For comparison, in the USA, men have slightly less than a one in two lifetime risk of developing cancer, and for women the risk is slightly more than one in three (American Cancer Society 2011). The USEPA and other regulatory bodies have frequently referred to an acceptable target range of 10^{-4} to 10^{-6} for increased lifetime cancer risk. Target risk limits have been set by policy in some jurisdictions, and many regulatory frameworks establish a target excess lifetime cancer risk of 10^{-5} , being the centre of this range (e.g. World Health Organization 2011). However, for small populations of exposed individuals, theoretical excess lifetime cancer risks of up to 10^{-4} (one in 10000 or less) are considered acceptable (Van den Berg 1997). For purposes

of identifying COPCs, the use of 10^{-6} as a screening criterion represents a very conservative approach; however, this does not suggest that using higher target risk levels would not be appropriate for other generic or site-specific risk evaluations.

COPC content in fuels

The composition of a single fuel type can vary as a function of initial crude oil composition, refining processes, addition of performance-enhancing additives, and local legislative or market requirements. To ensure that the assessment captures the chemical constituents most likely to present the highest risk levels, fresh (unweathered) product compositions were assumed. The concentration of each reported constituent in each fuel was assumed to equal the average or, when available, upper-end average (e.g. 95% upper confidence limit) of the range reported by the Total Petroleum Hydrocarbons (TPH) Criteria Working Group (TPHCWG 1998). For diesel, more recent data presented by Chevron (2007) were also used. It is possible, however, at the market or site-specific scale that particular fuel compositions, such as ethanol-based gasolines, may occur that differ from those assumed in the screening evaluation for COPCs. One exception to the assumption that fuel releases would consist of entirely fresh, unweathered products was allowed for hydrocarbons lighter than carbon range C6 and other very highly volatile constituents, such as alcohol additives (e.g. ethanol). Given their low boiling points, such compounds will evaporate rapidly following release in relation to assumed exposure durations and therefore are not considered to pose significant chronic risks via inhalation, nor considered to be COPCs.

Maximum theoretical COPC concentrations in soil, soil gas and groundwater

Upon a hypothetical release to the environment, the concentration of each fuel constituent in each environmental medium (soil, soil gas or water) was assumed to equal its maximum theoretical value, corresponding to effective saturation of that medium, based on partitioning into each environmental compartment (Fig. 1). For vadose zone soils, this very conservatively assumes that the air-filled soil porosity could be completely displaced by

the fuel in question, corresponding to equivalent TPH concentrations in soil greater than $100000 \text{ mg kg}^{-1}$ in every case. Maximum soil concentrations were then estimated based on the assumed mass fraction of each chemical constituent. Concentrations in groundwater were assumed to equal effective solubility (i.e. for each constituent, its estimated mole fraction in the fuel times the pure-component aqueous solubility; Thornton *et al.* 2013), and soil gas concentrations were assumed to equal effective saturated vapour concentrations (i.e. for each constituent, effective solubility times its Henry's Law coefficient). In actuality, observed maximum concentrations in soil gas (Golder Associates 2008) or groundwater (Bruce *et al.* 1991) are typically less, by an order or magnitude or more, than the predicted theoretical concentrations used to identify COPCs.

Conservative fate and transport models

Simple analytical models were employed to predict estimated maximum exposure point concentrations, based on CSM assumptions illustrated in Figure 1, maximum steady-state source concentrations (i.e. no source attenuation) and pathway distances based on ASTM (2010). These models are generally conservative in that they tend to overestimate predicted exposure point concentrations. Specifically, the models employed are those presented in ASTM International guidelines (ASTM 2010), including the following: (1) surface soil volatilization and particulates to outdoor air (including mass-balance limitations); (2) surface soils and groundwater volatilization to indoor air (including mass-balance limitations for soil, but neglecting biodegradation for both soil and groundwater on the vapour intrusion pathway); (3) soil leaching to groundwater. It should be noted that fate and transport modelling do not apply for direct exposure pathways, such as soil ingestion and dermal contact, because predicted exposure concentrations for these pathways are equivalent to assumed source medium concentrations.

Most sensitive residential receptor

Conservative default exposures factors were assumed for all risk calculations, corresponding to a child resident for non-cancer (threshold) effects and an adult resident (30 year exposure) for cancer (non-threshold) effects. Although some risk assessment frameworks employ age-weighted exposure factors for calculating cancer risks, which assume a child receptor who grows into an adult during the 30 year exposure period, for simplicity, cancer risks for our evaluation have been evaluated assuming an adult receptor only. However, the results of the evaluation show that considering a child versus adult receptor was not significant for this exercise, as all carcinogenic compounds have been identified as COPCs for every evaluated scenario.

Results

The generic lists of COPCs determined for gasoline/petrol, diesel/gas oil, and kerosene/jet fuel are summarized in Table 1, which shows the key risk drivers associated with human exposure pathways commonly evaluated for petroleum release sites. The charts in Figures 2–4 depict the relative magnitudes of the maximum theoretical cancer risks (CR) and hazard quotient (HQ) values calculated for each evaluated combination of fuel and exposure pathway.

For each fuel type, the specific list of risk-driving constituents varies from pathway to pathway, depending on the relative importance of key chemical and physical properties. For inhalation exposures, the greatest potential risks are associated with compounds that (1) are the most volatile constituents and (2) have the greatest

toxicity via inhalation uptake. In addition, other volatile compounds, such as methane, could pose a safety risk in certain circumstances and may warrant evaluation based on site-specific conditions. Water exposure risks are generally driven by compounds that have a combination of the highest aqueous solubility (and mobility) and the highest toxicity via oral uptake (ingestion). Risks associated with direct exposures to soil (incidental ingestion and dermal contact) are essentially proportional to the amount of each key risk-driving constituent present in the released product multiplied by its toxicity.

Discussion

For gasoline/petrol releases, the applicability of certain COPCs will depend on knowledge of site history and the nature of the particular released product. For example, considering the widespread use of ether oxygenates and their metabolites, such as TBA (API 2012), in some locations, these compounds may warrant consideration as COPCs unless specific information precludes their possible presence at the site (e.g. if they were banned or limited to less than 0.5% v/v in fuel by law over the lifetime of the site being investigated). Similarly, lead scavengers may warrant consideration as COPCs only for releases known or suspected to involve leaded gasoline/petrol. For sites where the release history is unknown or uncertain, professional judgement may be required for selection of appropriate COPCs, based on a range of potential sources, accounting for all different types of fuel that have been handled at the site, and whether oxygenates or lead scavengers are likely to be present. Additional considerations regarding the applicability of some potentially risk-driving COPCs are discussed in the notes of Table 1 and should be evaluated on a site-specific basis.

The approach, results, and recommendations of this study are based on numerous, highly conservative assumptions, and are therefore considered suitable for global application at sites where the evaluated fuel types and exposure pathways are known to be present. For cases where mixtures of fuels may have been released, or where the source of a release is unknown (e.g. during an initial investigation), additional analyses may be advisable, such as gas chromatograph (GC) scans or use of full-range TPH fraction analysis to identify the fuel type(s) present and to allow selection of appropriate COPCs for further more detailed risk estimation. In addition, risk assessors should exercise care to evaluate the need for additional COPCs for cases where exposure pathways not considered in this study are also determined to be complete.

For most petroleum-based vehicle fuel releases, site investigations and risk assessments focused on the COPCs identified in Table 1, as applicable, should be sufficient, in terms of sample point location, monitoring frequency and measurement quality, to allow for effective evaluation and management of potential risks to human health. Fuel constituents other than COPCs for a given release are not expected to drive risk management decisions at most sites; therefore investigative actions focused on non-risk-driving constituents may provide little or no value to the risk management process. This does not mean, however, that evaluation of additional analytical parameters may not be necessary or beneficial to support risk-based site management decisions, including the design of treatment systems.

Examples of additional information or criteria that may warrant site-specific evaluation include the following.

Vapour intrusion potential

Analysis for oxygen (O_2) in soil gas samples can be used to determine potential for subsurface aerobic biodegradation of

Table 1. Summary of generic COPCs for fuel release sites

Exposure pathway	Environmental medium				Fuel type ¹		
	NAPL	Soil	Soil gas	GW ²	Gasoline/petrol	Diesel/gas oil	Kerosene/jet fuel
Indoor inhalation	■	■	■	■	Benzene Toluene Ethyl benzene Xylenes Naphthalene ⁽³⁾ n-Hexane ⁽⁴⁾ Ether oxygenates ⁽⁵⁾ EDC/EDB ⁽⁶⁾ %LEL (soil gas) ⁽⁷⁾	Benzene Xylenes Naphthalene TPH ⁽⁸⁾ : Arom >C10–C12 TPH: Aliph >C8–C10 TPH: Aliph >C10–C12 %LEL (soil gas)	Benzene Toluene Ethyl benzene Xylenes Naphthalene TPH: Arom >C10–C12 TPH: Aliph >C5–C6 TPH: Aliph >C6–C8 TPH: Aliph >C8–C10 TPH: Aliph >C10–C12 %LEL (soil gas)
Soil ingestion, dermal contact and outdoor inhalation of vapours and particulates	□	■	□	□	Benzene Toluene Ether oxygenates ⁽⁵⁾ EDC/EDB ⁽⁶⁾	Benzene 2-Methyl naphthalene Benzo[a]pyrene ⁽⁹⁾ TPH: Arom >C10–C12 TPH: Arom >C12–C16 TPH: Aliph >C12–C16	Benzene 2-Methyl naphthalene TPH: Arom >C10–C12 TPH: Arom >C12–C16 TPH: Aliph >C8–C10 TPH: Aliph >C10–C12 TPH: Aliph >C12–C16
Groundwater ingestion; soil leaching to groundwater	□	■	□	■	Benzene Toluene Ethyl benzene Xylenes Ether oxygenates ⁽⁵⁾ EDC/EDB ⁽⁶⁾	Benzene Toluene 2-Methyl naphthalene TPH: Arom >C10–C12	Benzene Toluene Ethyl benzene Xylenes TPH: Arom >C10–C12 TPH: Arom >C12–C16

■, Applicable medium for sample analysis; □, medium not recommended for sample analysis.

¹The table presents COPCs for use where the fuel type is known. At sites where the fuel type(s) is unknown (e.g. at the time of an initial site investigation), or where there is known to be a mixture of fuel types, then it will normally be necessary to undertake a screening analysis (e.g. gas chromatography, GC) to identify the fuel type(s) present, or to combine all of the above COPCs presented in this table (e.g. full-range TPH fraction analysis). In subsequent investigations or monitoring events, the COPC list may then be selected from the relevant COPC suite(s) presented above.

²GW, groundwater. However, this may include surface water or drinking water where there is potential for receptor exposure to that water.

³Our evaluation suggests that naphthalene has potential to present unacceptable risk from gasoline via the indoor inhalation pathway, but field evidence (e.g. USEPA 2013) suggests this is rarely observed. Evidence from field sites may be reviewed in the future to determine if naphthalene should remain a COPC for this exposure pathway. A similar review of evidence from field data may be considered for TPH fractions and naphthalene for both diesel and kerosene via the indoor inhalation pathway.

⁴Where NAPL is in contact with building or enclosed space, n-hexane should be replaced by TPH fraction analysis, to include TPH aliphatic fractions >C5–C6, >C6–C8, and >C8–C10.

⁵Ether oxygenates (e.g. MTBE, ETBE, DIPE, TAME, and associated TBA) are applicable as COPCs for releases of gasoline/petrol unless they were banned or limited to less than 0.5% v/v in fuel by law over the lifetime of the asset.

⁶EDC, 1,2-dichloroethane (ethylene dichloride); EDB, 1,2-dibromoethane (ethylene dibromide). Evaluation of these lead scavengers is applicable only for releases of leaded gasoline/petrol.

⁷%LEL, per cent of lower explosive limit.

⁸TPH, total petroleum hydrocarbons, aromatic or aliphatic fractions, as indicated.

⁹Benzo[a]pyrene may be omitted as a COPC if the threshold for acceptable excess lifetime cancer risk is increased from 10^{-6} to 10^{-5} , or above (see Fig. 3). Caution should be exercised when evaluating risks associated with the presence of benzo[a]pyrene, with specific regard to the potential for other (non-fuel) sources of benzo[a]pyrene in the environment.

vapours, which can be a significant factor in preventing the occurrence of indoor vapour intrusion at many petroleum release sites (Rivett *et al.* 2011). Where sampling of indoor air is necessary, analysis for petroleum marker compounds that are not typically expected to occur in indoor environments, such as cyclic alkanes, may prove useful for evaluating the potential occurrence of vapour intrusion.

Worker safety criteria

In addition to %LEL (per cent of lower explosive limit), analyses of soil gas samples for carbon dioxide (CO₂), methane

(CH₄) and carbon monoxide (CO) or field screening for organic vapours (e.g. using a photo-ionization detector) may be suggested to monitor the need for emergency response at sites where workers or others may be working nearby in confined spaces.

Other receptor types

Consideration should be given to collection of data relevant to other receptor types, where they are present, including risks to terrestrial and aquatic ecology. This decision should be based on

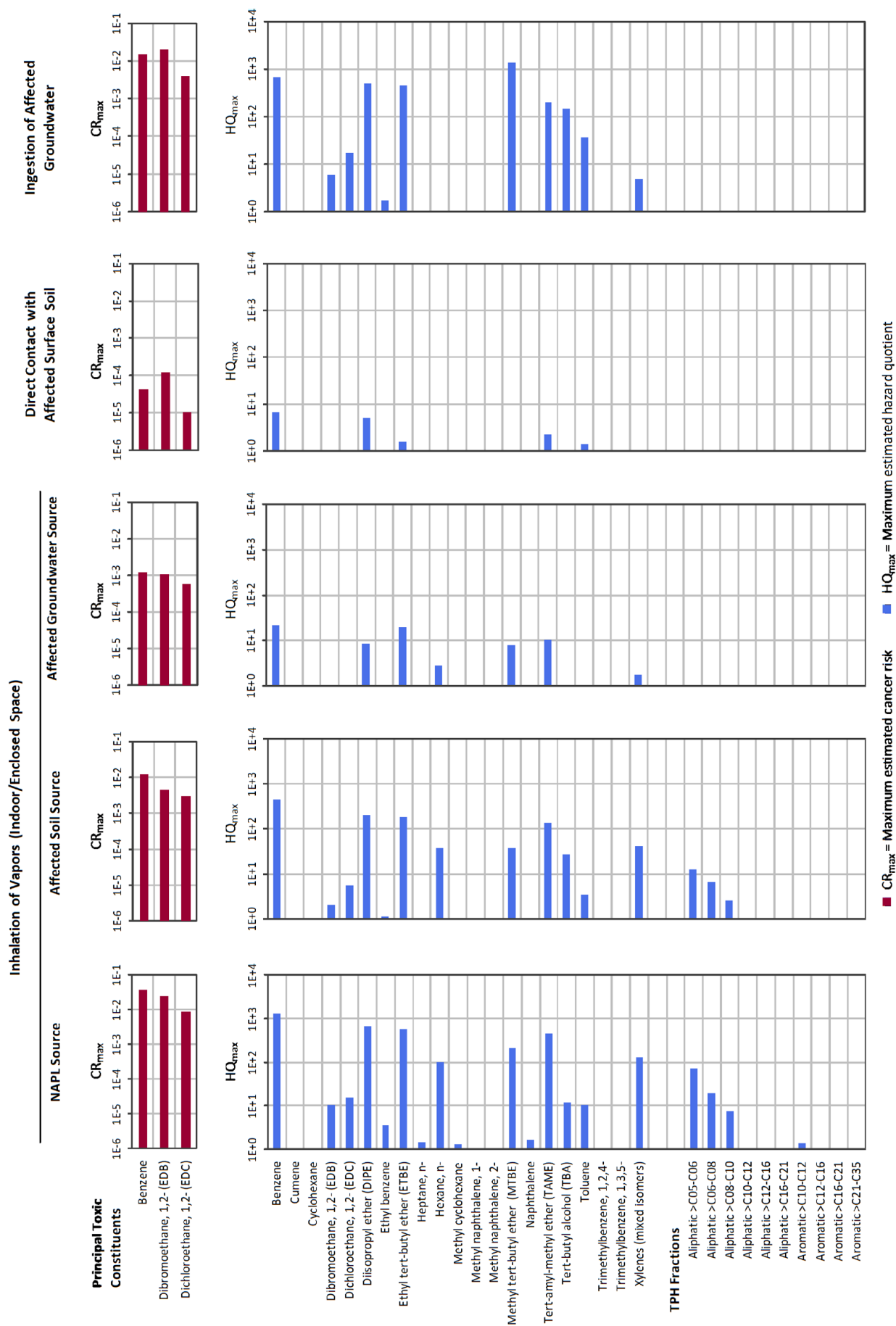
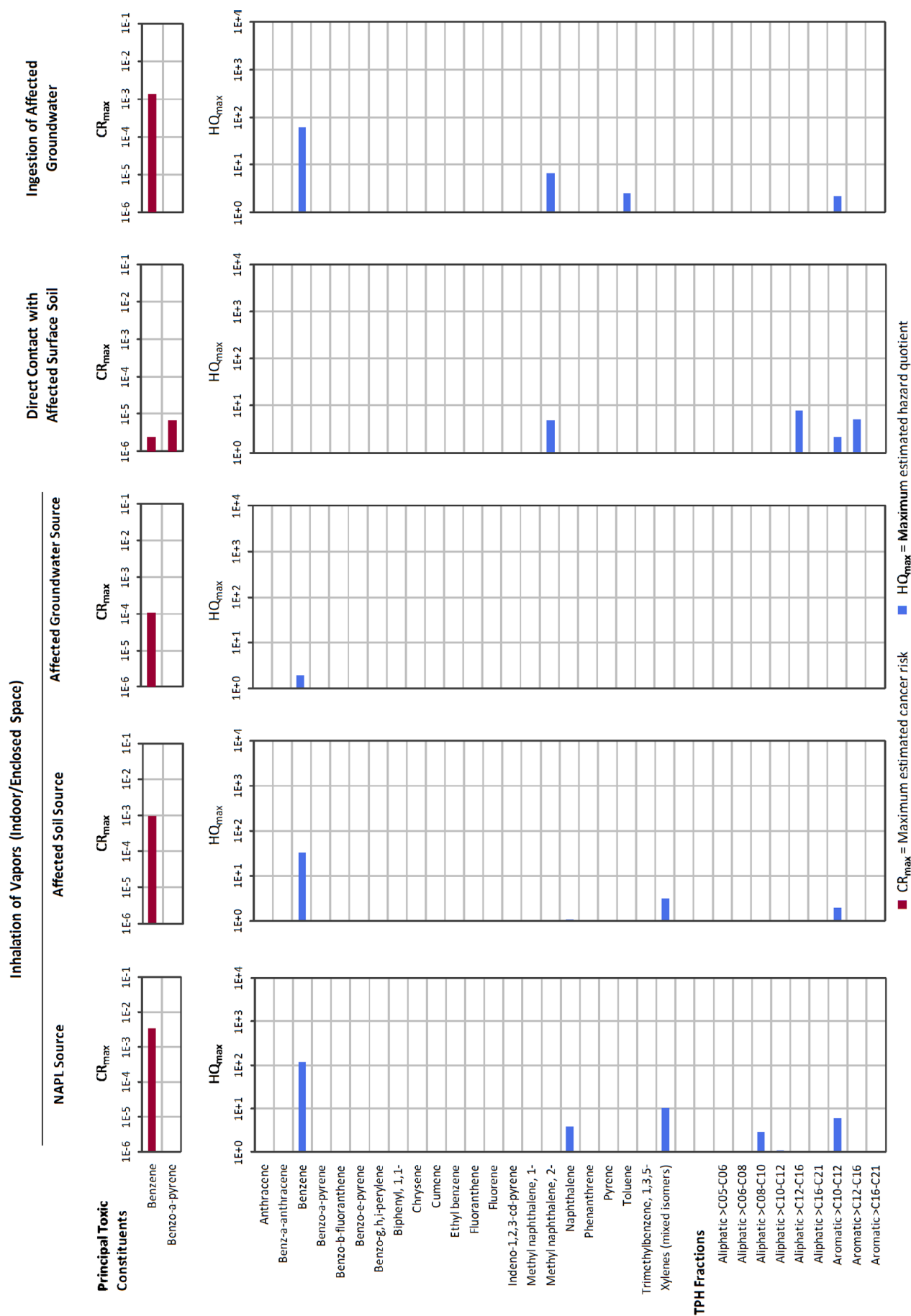


Fig. 2. Relative upper-bound risk owing to exposure to fuel constituents: gasoline/petrol.



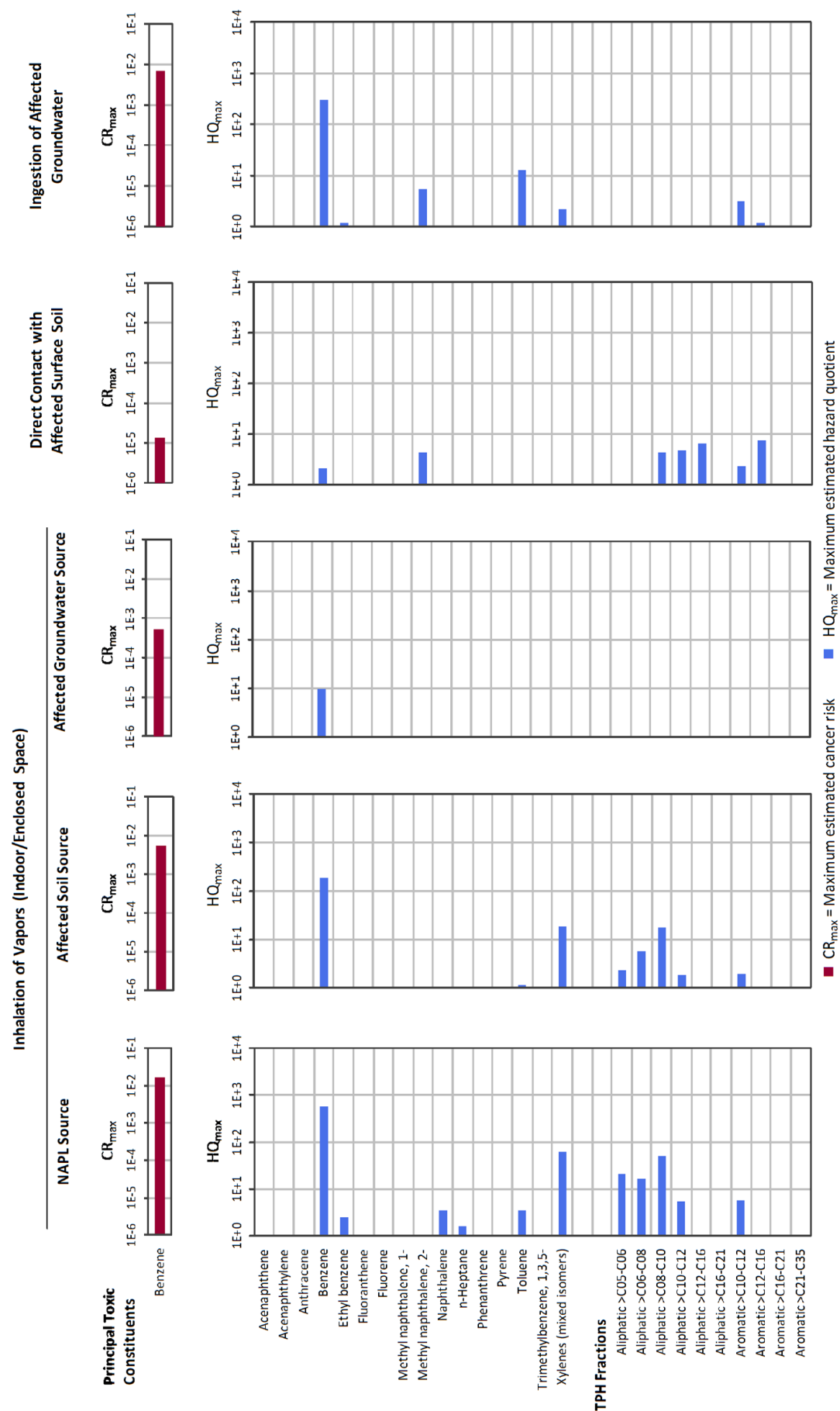


Fig. 4. Relative upper-bound risk owing to exposure to fuel constituents: kerosene/jet fuel.

the presence of plausible source–pathway–receptor linkage(s) to ecological features in the conceptual site model.

Groundwater natural attenuation parameters

At many sites, simple visual inspection or statistical analysis of COPC concentration trends over time may yield meaningful interpretations of plume stability and direct evidence of the effects of natural attenuation processes in groundwater and/or the vadose zone (Rivett & Thornton 2008). Collection and evaluation of electron acceptor (O_2 , NO_3^- , SO_4^{2-}) and degradation product (e.g. COPC metabolites, Fe^{2+} , Mn^{2+} , CO_2 , HCO_3^- , CH_4) data may help to explain the mechanisms of the observed attenuation processes for use in a lines-of-evidence assessment of natural attenuation.

Bulk TPH measures

Bulk TPH, TPH-gasoline range organics (GRO) and diesel range organics (DRO) screening analyses have very limited value for assessing or managing human health risks (Zemo & Foote 2003). In general, TPH-GRO and DRO are not recommended for investigating human health risks, as these analyses are not compound-specific and can frequently include organic compounds other than petroleum constituents, including naturally occurring organic matter. In cases where TPH-GRO and DRO may have already been evaluated at a site, these data may potentially be of use for comparison with aesthetic or other non-health risk criteria, or for characterizing the nature or extent of petroleum impacts of unknown origin. In addition, this may be helpful for treatment system design. In general, however, petroleum hydrocarbon fractionation or chemical fingerprinting results, if available, will provide better, more relevant information with respect to release characterization than TPH-GRO and DRO. Bulk TPH analysis may be helpful in determining (1) if there is a significant level of organic compounds not accounted for by use of individual COPCs during risk assessment, and (2) if there is a significant level of organic compounds not accounted for by use of COPCs that influence design of water treatment systems.

Fractionated TPH

Evaluation of TPH carbon range fractions (e.g. Texas TCEQ Methods 1005/1006, TPHCWG 1999; Environment Agency 2005) can be useful for evaluating risks in cases for which there are a large number of potential risk-driving constituents (e.g. TPH fractions greater than about C10, when the number of compounds present in a single TPH fraction becomes large, and assessment of a TPH fraction is more practicable than assessment for each of the constituent compounds). As shown in Table 1, specific TPH fractions are identified as COPCs for certain exposure pathways for diesel/gas oil and kerosene/jet fuel. Evaluation of TPH fractions can also be useful for identifying the nature of impacts from an unknown source or mixtures of impacts from different sources, based on knowledge of the general composition of potentially released fuels.

Other parameters necessary for risk estimation

In common with normal site characterization to inform a site-specific risk assessment, collection of other non-chemical data may help to understand the potential for migration of COPCs along potential pathways (Smith & Lerner 2007). This may include information on soil and aquifer geochemical and physical properties, such as fraction of organic carbon (f_{OC}), cation exchange capacity (CEC), porosity and soil moisture content.

Other parameters relevant to reuse or disposal of water or soils

The potential for reuse of abstracted water (e.g. treated water for irrigation), or for disposal of materials to a sewer or to a waste management facility, may require additional analysis to ensure compliance with waste classification criteria and discharge consent requirements, or to ensure the reuse of materials or water does not give rise to any new unacceptable risks that were not evaluated in the conceptual site model and risk assessment.

Other parameters necessary for specialist forensic analysis of site conditions

Additional data may be useful to age a spill (e.g. GC scan, sulphur content, presence of lead or various ether oxygenate compounds), to identify the presence of fuel resulting from more than one release, or to understand the mechanisms of biodegradation processes (e.g. stable isotope analysis).

Conclusions

The generic COPC lists presented in Table 1 for releases of gasoline/petrol, diesel/gas oil and kerosene/jet fuel can be used as a guideline, allowing for focused, robust investigations and risk assessments at sites where releases of these fuels have occurred, and eliminating unnecessary expense and effort on chemical analyses and evaluation of chemical constituents that do not give rise to unacceptable human health risks. These lists are based on currently available knowledge, especially as pertains to the availability and numerical values of applicable chemical-specific toxicity criteria. Furthermore, environmental processes are complex, and some of the constituents identified as COPCs by this study may be found to degrade relatively quickly after release, resulting in no potential health risks. For example, additional research or experience may show that certain prevalent fuel constituents are rarely encountered in affected soil samples or that certain exposure pathways (e.g. indoor vapour intrusion) are rarely complete for petroleum constituents. Conversely, new fuel formulations could be brought to market that require different COPCs to be considered. Therefore, the presented lists of COPCs may require updating when justified by the development of additional information.

Finally, the approach and recommendations resulting from this study are not a substitute for local regulatory requirements, which may mandate an alternative approach for COPC selection or indeed for site evaluation and risk management. Users themselves must be aware of and fully comply with all applicable laws and regulations when applying the results of this study to address a fuel release at a particular site. Nevertheless, the identification, assessment and management of an appropriate set of COPCs can support robust, cost-efficient risk management at most fuel release sites, whether utilized in conjunction with existing regulatory requirements and guidance or for cases where such requirements or guidance do not exist.

Acknowledgements. Funding for this research was provided by Shell Global Solutions (US) Inc. The authors gratefully acknowledge the contributions of M. Lahvis, F. Sierra, G. DeVaul, I. Rhodes and C. Stanley of Shell Global Solutions (US) Inc., I. Fielding of Shell Global Solutions (UK) Ltd., and L. Beckley and R. Kamath of GSI Environmental Inc. The authors also wish to thank the anonymous reviewers for their careful review and constructive feedback.

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Received 15 January 2014; accepted 13 August 2014.