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Petroleum Products in Drinking-water

Background document for development of
WHO *Guidelines for Drinking-water Quality*

Preface

One of the primary goals of WHO and its member states is that "all people, whatever their stage of development and their social and economic conditions, have the right to have access to an adequate supply of safe drinking water." A major WHO function to achieve such goals is the responsibility "to propose ... regulations, and to make recommendations with respect to international health matters ...."

The first WHO document dealing specifically with public drinking-water quality was published in 1958 as *International Standards for Drinking-water*. It was subsequently revised in 1963 and in 1971 under the same title. In 1984–1985, the first edition of the WHO *Guidelines for Drinking-water Quality* (GDWQ) was published in three volumes: Volume 1, Recommendations; Volume 2, Health criteria and other supporting information; and Volume 3, Surveillance and control of community supplies. Second editions of these volumes were published in 1993, 1996 and 1997, respectively. Addenda to Volumes 1 and 2 of the second edition were published on selected chemicals in 1998 and on microbial aspects in 2002. The third edition of the GDWQ was published in 2004, and the first addendum to the third edition was published in 2005.

The GDWQ are subject to a rolling revision process. Through this process, microbial, chemical and radiological aspects of drinking-water are subject to periodic review, and documentation related to aspects of protection and control of public drinking-water quality is accordingly prepared and updated.

Since the first edition of the GDWQ, WHO has published information on health criteria and other supporting information to the GDWQ, describing the approaches used in deriving guideline values and presenting critical reviews and evaluations of the effects on human health of the substances or contaminants of potential health concern in drinking-water. In the first and second editions, these constituted Volume 2 of the GDWQ. Since publication of the third edition, they comprise a series of free-standing monographs, including this one.

For each chemical contaminant or substance considered, a lead institution prepared a background document evaluating the risks for human health from exposure to the particular chemical in drinking-water. Institutions from Canada, Denmark, Finland, France, Germany, Italy, Japan, Netherlands, Norway, Poland, Sweden, United Kingdom and United States of America prepared the documents for the third edition and addenda.

Under the oversight of a group of coordinators, each of whom was responsible for a group of chemicals considered in the GDWQ, the draft health criteria documents were submitted to a number of scientific institutions and selected experts for peer review. Comments were taken into consideration by the coordinators and authors. The draft documents were also released to the public domain for comment and submitted for final evaluation by expert meetings.

During the preparation of background documents and at expert meetings, careful consideration was given to information available in previous risk assessments carried out by the International Programme on Chemical Safety, in its Environmental Health

Criteria monographs and Concise International Chemical Assessment Documents, the International Agency for Research on Cancer, the Joint FAO/WHO Meetings on Pesticide Residues and the Joint FAO/WHO Expert Committee on Food Additives (which evaluates contaminants such as lead, cadmium, nitrate and nitrite, in addition to food additives).

Further up-to-date information on the GDWQ and the process of their development is available on the WHO Internet site and in the current edition of the GDWQ.

Acknowledgements

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The work of the following working group coordinators was crucial in the development of this document and others contributing to the first addendum to the third edition:

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The draft text was discussed at the Working Group Meeting for the first addendum to the third edition of the GDWQ, held on 17–21 May 2004. The final version of the document takes into consideration comments from both peer reviewers and the public. The input of those who provided comments and of participants in the meeting is gratefully acknowledged.

The WHO coordinator was Dr J. Bartram, Coordinator, Water, Sanitation and Health Programme, WHO Headquarters. Ms C. Vickers provided a liaison with the International Programme on Chemical Safety, WHO Headquarters. Mr Robert Bos, Water, Sanitation and Health Programme, WHO Headquarters, provided input on pesticides added to drinking-water for public health purposes.

Ms Penny Ward provided invaluable administrative support at the Working Group Meeting and throughout the review and publication process. Ms Marla Sheffer of Ottawa, Canada, was responsible for the scientific editing of the document.

Many individuals from various countries contributed to the development of the GDWQ. The efforts of all who contributed to the preparation of this document and in particular those who provided peer or public domain review comment are greatly appreciated.

Acronyms and abbreviations used in the text

EC	equivalent carbon
FAO	Food and Agriculture Organization of the United Nations
GDWQ	*Guidelines for Drinking-water Quality*
IRIS	Integrated Risk Information System (US EPA)
LOAEL	lowest-observed-adverse-effect level
MTBE	methyl *tertiary*-butyl ether
NOAEL	no-observed-adverse-effect level
PAH	polycyclic aromatic hydrocarbons
RfC	reference concentration
RfD	reference dose
TDI	tolerable daily intake
TPH	total petroleum hydrocarbons
TPHCWG	Total Petroleum Hydrocarbons Criteria Working Group
USA	United States of America
US EPA	United States Environmental Protection Agency
WHO	World Health Organization

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1. GENERAL DESCRIPTION

1.1 Identity

Petroleum products occur as complex mixtures of chemicals, primarily hydrocarbons. Hydrocarbons are organic compounds composed of carbon and hydrogen atoms arranged in varying structural configurations. At a simple level, they may be divided into two families: aliphatics and aromatics. The aliphatics may be further subdivided into four groups: alkanes (straight and branched chain), alkenes, alkynes and cyclic alkanes. Alkynes are not generally found in petroleum products and therefore will not be considered further. Within each hydrocarbon structural family and subfamily, there are homologous series. Each member of the series differs from adjacent members of the series by a repeating unit, such as a CH_2 group. Small amounts (mg/kg quantities) of constituents such as polycyclic aromatic hydrocarbons (PAHs) may also be found in some petroleum products.

Petroleum products are derived from crude oil, which undergoes fractionation in order to produce petroleum products for particular uses. Their composition varies according to the type of use and depends on their source and fraction. There are, therefore, significant compositional differences between petroleum products such as gasoline, diesel oil, aviation fuel and heating oil. Crude oil is distilled, and a variety of petroleum product fractions result, with distinct boiling point ranges. The chemical composition of all these products depends on the sources of crude oil or refinery streams from which they are produced (CONCAWE, 1985; IARC, 1989; ASTM, 2002). Petroleum products are not the only source of potential contamination of drinking-water with hydrocarbons. Other sources include petrochemical products such as solvents and coal-derived products.

The approach taken within the petroleum industry is to refer to aliphatic and aromatic fractions on the basis of their boiling point normalized to the boiling point of the *n*-alkanes or retention time on a boiling point gas chromatographic column. This is characterized by the equivalent carbon (EC) number. For example, the boiling point of hexane, which consists of six carbon atoms, is 69 °C, and its EC number is 6. Benzene also consists of six carbon atoms, but its boiling point is 80 °C, and its EC number is 6.5. The fractions for the aromatic compounds are presented on the basis of their EC numbers; since many of these relate to fractions of whole values, similar to the situation with benzene, they are usually represented as greater than the lower value. Fractions for aliphatic compounds are also presented on the basis of EC numbers; the EC numbers for aliphatic compounds are the same as the carbon (C) numbers for straight-chain alkanes, but differ for branched and cyclic alkanes. The EC number is used throughout this document.

Petroleum-derived products will often also contain additives, but these are normally present in very low concentrations. The exception is oxygenate fuel additives such as methyl *tertiary*-butyl ether (MTBE), for which a different analytical method will be required and which is considered in a separate guideline document.

1.2 Physicochemical properties

Within each homologous series of hydrocarbons, the physical properties of compounds change with the number of carbon atoms. For example, there is an increase in boiling point of approximately 20 °C for each carbon atom added to an *n*-alkane chain. The polarity of hydrocarbon structures governs the degree to which molecules interact with themselves and with water. Aromatic hydrocarbons are generally more polar than aliphatic hydrocarbons and therefore tend to be more soluble in water and less volatile than aliphatic hydrocarbons with a corresponding number of carbon atoms. Aromatic compounds above EC20 are neither volatile nor soluble in water, whereas aliphatic EC5–EC6 and EC7–EC8 fractions have relatively high volatility and low solubility in water.

Detailed physical and chemical properties are available for only about 250 petroleum hydrocarbons (TPHCWG, 1997a).

1.3 Organoleptic properties

A number of the more soluble aromatic components, particularly the alkyl benzenes, have extremely low taste and odour thresholds in water and can render drinking-water unacceptable to consumers at relatively low levels of contamination. Several such components have been considered separately in the Guidelines: benzene, toluene, ethylbenzene, and xylene. Other components of petroleum products will also be detectable by odour and/or taste in drinking-water at concentrations of a few micrograms per litre.

1.4 Major uses and sources in drinking-water

Petroleum products are used widely in a range of industrial applications. The largest quantities find use as fuels for a range of purposes, including gasoline, diesel oil, aviation fuel and heating oil.

1.5 Environmental fate

The differing chemical and physical properties of petroleum hydrocarbons mean that they will behave differently in the environment. Persistence of petroleum hydrocarbon compounds in the environment is reflected by physical properties such as volatility, so that generally the persistence increases as the boiling point increases. The main processes affecting environmental concentrations are volatilization, biodegradation and dissolution in water. Only a small proportion of the hydrocarbon constituents of petroleum products will be significantly soluble in water. The hydrocarbons present in contaminated drinking-water will not, therefore, reflect the hydrocarbon composition of the petroleum oil.

Petroleum products are stored and handled in a range of circumstances, and the primary concern for drinking-water is the potential for spills into source water or penetration of distribution systems or treatment works. In the event of water contamination by petroleum products, the actual nature of the contaminants present will largely be a function of their solubility in water. In general, the lower-molecular-weight aromatic compounds are the most water-soluble components.

2. ENVIRONMENTAL LEVELS AND HUMAN EXPOSURE

Spills and leaks of petroleum products are relatively common. This is not surprising in view of their extensive and widespread storage, transportation and use. Exposure to the constituents of petroleum products through drinking-water can be of short- or long-term duration. However, exposure is frequently the result of an accidental spill or short-term incident, in which the main issue for drinking-water is short-term exposure. Such incidents may lead to high concentrations of total petroleum hydrocarbons (TPH), in which case the probability of unacceptable taste and odour being detected by consumers will be significantly increased.

Although the term TPH is widely used, it is rarely well defined. In essence, TPH is defined by the analytical method — in other words, estimates of TPH concentration often vary depending on the analytical method used to measure it. No single method measures the entire range of petroleum-derived hydrocarbons, since petroleum products can include hundreds to thousands of individual compounds with a wide range of molecular weights, many of which may be present only in mg/kg amounts. The methods will usually result in some overlap in the measurement of the fractions.

It is not practical to analyse for all possible petroleum hydrocarbons in water, since it would be prohibitively costly to quantify each individual compound using current analytical technology. Because specific data are unavailable for many of the individual components of petroleum hydrocarbons, fractions were characterized from the available data in the literature by the Total Petroleum Hydrocarbons Criteria Working Group (TPHCWG, 1998a). This Working Group based its fractions on physicochemical properties and also on data from partitioning models. It was important that when delineating the fractions, the fractions were consistent with available analytical techniques. Hydrocarbon mixtures separate and partition based on these properties. There will be differences in both mobility and the level of adsorption, resulting in separation of the mixture. However, it was considered reasonable to assume that chemicals of a similar nature (e.g., aliphatic or aromatic) and boiling point would behave similarly. The TPHCWG specified the delineation of the different fractions on the basis on an order-of-magnitude differentiation in these simple partitioning properties (TPHCWG, 1997a).

3. TOXICITY AND RISK ASSESSMENT

In general terms, alkanes have relatively low acute toxicity, but alkanes having carbon numbers in the range of EC5–EC12 have narcotic properties, particularly following inhalation exposure to high concentrations. Repeated exposure to high concentrations of *n*-hexane may lead to irreversible effects on the nervous system. Alkenes exhibit little toxicity other than weak anaesthetic properties. Most of the smaller aromatic compounds are of relatively low toxicity except for benzene, which is a known human carcinogen.

The fact that petroleum products are complex mixtures of hundreds of individual hydrocarbons is a complicating factor in determining their toxicity in the event of contamination of water. This means that the traditional approach of evaluating individual components is largely inappropriate. In order to overcome this difficulty, it

is more practical to consider a series of hydrocarbon fractions and to determine appropriate tolerable concentrations for those fractions. A number of groups have examined such an approach, but the most widely accepted is that developed by the TPHCWG in the USA. This is a multi-agency group, consisting of representatives from industry, government and academia, which has developed and published a series of five monographs detailing the data on petroleum hydrocarbons and, in addition, has developed tolerable intakes for a series of total hydrocarbon fractions.

Of the 250 individual compounds identified in petroleum by the TPHCWG, toxicity data were available only for 95. Of these 95, the TPHCWG concluded that there were sufficient data to develop toxicity criteria for only 25.

The approach used by the TPHCWG to make the problem more manageable was to divide TPH into a series of fractions based on the number of carbon atoms in conjunction with general structure. The toxicity data available on fraction-specific mixtures cover the aromatic fractions (>EC6–EC8, as described above) and the aliphatic fractions of TPH. Data on mixtures containing the higher-molecular-weight substances, >EC8–EC16 and >EC16–EC35 aromatic fractions, refer only to the EC8–EC11 range. There are no toxicity data on the highest-molecular-weight compounds, >EC35. However, compounds above EC20 are neither volatile nor soluble in water. In addition, compounds >EC35 are not likely to be absorbed by the oral or dermal routes of exposure (TPHCWG, 1997a, 1997b, 1998a, 1998b, 1999).

In view of the importance of the hydrocarbons arising from petroleum products and the relative frequency of exposure, an indicator/surrogate approach is probably the best available method for assessing the hazards and risks of TPH. However, some misallocations of specific substances to carbon fractions were made in the TPHCWG exercise. It is also important to consider changes in toxicity data with time. The TPHCWG approach provides a sound basis for evaluation of specific circumstances, but one that requires modification and updating as necessary for specific applications. The TPHCWG emphasizes that the approach presented is not intended to provide a "cookbook" but rather a framework.

3.1 Aromatic fractions

3.1.1 >EC5–EC6 and >EC6–EC8 aromatic fraction

These two fractions consist of one compound each, which are benzene and toluene, respectively. Benzene is a known human carcinogen following occupational exposure, although toluene is of lower toxicity. Drinking-water guidelines have been established for both substances (see section 5.1.1), and toluene has a very low reported odour threshold in water.

3.1.2 >EC8–EC10, >EC10–EC12 and >EC12–EC16 aromatic fraction

Within this carbon range, a number of individual compounds have been identified, but oral RfDs or drinking-water guidelines have been developed for only a limited number. These are ethylbenzene (EC8.5), xylenes (EC8.6–8.81), naphthalene (EC11.69), isopropylbenzene (EC9.13), acenaphthene (EC15.5) and biphenyl

(EC14.26). The TPHCWG concluded that there were no additional studies on individual compounds that could be used to develop additional RfDs.

However, oral data are available on a mixture within this EC number range consisting of naphthalene/methylnaphthalenes (EC11.69–13.87). An unpublished study, in which groups of male and female rats were dosed orally with 0, 300, 600 or 1000 mg/kg of body weight per day for 13 weeks, identified a lowest-observed-adverse-effect level (LOAEL) of 300 mg/kg of body weight per day. Centrilobular hepatocellular hypertrophy and hyperplasia and hypertrophy of the thyroid in both sexes were reported at all dose levels, while hyperplasia of the urinary bladder was reported in male rats at all dose levels and in female rats at 300 mg/kg of body weight per day. By applying a highly conservative uncertainty factor of 10 000, the TPHCWG calculated a reference dose (RfD, equivalent to a tolerable daily intake or TDI) of 0.03 mg/kg of body weight per day.

In a separate reproductive toxicity study in rats with the same mixture, maternal body weight gain and food consumption were significantly decreased during the first 3 days of treatment, but no adverse development effects were observed at 450 mg/kg of body weight per day.

An RfD of 0.03 mg/kg of body weight per day was determined from the oral toxicity study on the naphthalene/methylnaphthalenes mixture, and this is broadly similar to, or lower than, RfDs and guidelines for other substances in this group. The only exception is 2-methylnaphthalene, which is found at concentrations of up to 1.5% by weight in some jet fuel and diesel. An RfD of 0.005 mg/kg of body weight (rounded value) was determined in 2003 (US EPA, 2005). This was based on a benchmark dose calculated from pulmonary proteinosis observed in mice given 2-methylnaphthalene in the diet for 81 weeks, with an uncertainty factor of 1000 applied to the benchmark dose of 4.7 mg/kg of body weight per day. There is some uncertainty over this value because there was no dose–response in this study, pulmonary proteinosis was observed in the controls and the authors stated that this had not been previously observed in controls (Murata et al., 1997). Deriving a group RfD using this value would be excessively conservative. However, methylnaphthalenes would not be the major contributor to this group of compounds in the case of a spill reaching water, and they also appear to have very low taste and odour thresholds in water.

3.1.3 >EC16–EC21 and >EC21–EC35 aromatic fraction

There are a small number of RfDs for chemicals in this EC range. These include fluorene (EC16.55), anthracene (EC19.43), fluoranthene (EC21.85) and pyrene (EC20.8). The RfD for pyrene was considered by the Working Group as a suitable conservative surrogate. The RfD of 0.03 mg/kg of body weight per day for pyrene (US EPA, 2005) is similar to the RfDs for fluorene, anthracene and fluoranthene and is, therefore, suitable to represent the fraction-specific RfD for the EC17+ carbon range. This is certainly conservative, since the higher-molecular-weight compounds are normally considered to be less toxic and more poorly absorbed. A number of these compounds are also considered to be PAHs, which are also considered as a separate group below.

3.2 Aliphatic fractions

3.2.1 EC5–EC6 and EC7–EC8 aliphatic fraction

The data for this group of compounds relate primarily to inhalation exposure because of their relatively high volatility and low solubility in water. The only aliphatic compound for which an inhalation reference concentration (RfC, equivalent to a tolerable concentration) has been developed is *n*-hexane. This is considered to be the most toxic compound in the fraction. The use of data on *n*-hexane to derive an RfD for the fraction would significantly overestimate the health risks and would be unnecessarily conservative in view of the relatively low concentration of *n*-hexane in petroleum fractions. The Working Group therefore considered that data for *n*-heptane should be used as the basis for deriving a fraction-specific RfD for this carbon range; however, *n*-hexane is considered as a separate substance.

There are only limited data on *n*-heptane from which an RfD can be derived. There is very little evidence for the peripheral neurotoxicity of *n*-heptane, but a possible metabolite, gamma diketone 2,5-heptanedione, has been shown to produce such effects in laboratory animals, with an approximately 38-fold lower production of the gamma diketone of *n*-heptane compared with *n*-hexane. On this basis, the Working Group determined that an oral RfD for *n*-heptane could be calculated from the oral RfD of 0.06 mg/kg of body weight per day for *n*-hexane by multiplying the *n*-hexane oral RfD by 38 to give a rounded oral RfD of 2 mg/kg of body weight per day.

Extensive examination of commercial hexane, a mixture of hexane isomers containing approximately 53% *n*-hexane, was carried out, and these studies demonstrated no-observed-adverse-effect levels (NOAELs) ranging from 1840 to 5520 mg/m^3 in air. Using the NOAEL of 1840 mg/m^3 and making appropriate adjustments for exposure with an uncertainty factor of 100 to account for inter- and intraspecies variation, the group determined an RfC of 18.4 mg/m^3 for commercial *n*-hexane. From this RfC, an RfD of 5 mg/kg of body weight per day was calculated by the TPHCWG by assuming a 70-kg adult inhaling 20 m^3 per day.

The calculated RfDs for *n*-heptane and commercial hexane of 2 and 5 mg/kg of body weight per day, respectively, are both 2 orders of magnitude greater than the oral RfD for *n*-hexane of 0.06 mg/kg of body weight per day and demonstrate that *n*-hexane is not representative of this fraction. The TPHCWG therefore recommended an oral RfD of 5 mg/kg of body weight per day as being most appropriate given the levels of conservatism inherent in the development of the RfD and the relative concentrations of *n*-hexane and *n*-heptane in petroleum hydrocarbon fractions.

3.2.2 EC9–EC10, >EC10–EC12 and >EC12–EC16 aliphatic fraction

There are only very limited toxicity data available on individual compounds within the EC9–EC16 aliphatic range. The data that were used to develop oral and inhalation criteria for this fraction were studies on jet fuel JP-8 (EC9–EC16) and studies on dearomatized petroleum streams, which together cover the entire range of the fraction. Using data obtained from subchronic oral gavage studies on dearomatized aliphatics (EC9–EC12) and dearomatized aliphatics (EC10–EC13), an RfD of 0.1 mg/kg of body weight per day were determined by the Working Group. Based on similar

studies, an RfD of 0.75 mg/kg of body weight per day was determined for JP-8 jet fuel. The more conservative oral RfD of 0.1 mg/kg of body weight per day was protective of systemic toxicity and apparently adequately protective of reproductive/developmental toxicity.

3.3 PAHs

Most petroleum hydrocarbon mixtures contain very low concentrations of PAHs (TPHCWG, 1998b). A number of these are considered above under the appropriate carbon fractions. The major concern regarding PAHs is the potential carcinogenicity of some molecules (IPCS, 1998a). Benzo(*a*)pyrene and benz(*a*)anthracene are classified as probable human carcinogens, and a small number have been shown to induce skin tumours in skin painting studies in laboratory mice. Benzo(*a*)pyrene is normally considered to be the most potent carcinogenic PAH, but the carcinogenic potency of most PAHs is not well characterized. Only benzo(*a*)pyrene and fluoranthene have been considered in the guidelines. However, under circumstances of spills of petroleum products affecting water, PAHs are not usually a specific concern.

3.4 MTBE

MTBE may be used as an additive in the blending of some gasolines. The toxicity of MTBE is considered to be relatively low, so that the odour threshold in water of 15 µg/litre is well below the concentration that would be sufficient to protect health (IPCS, 1998b). MTBE is covered in a separate guideline document and will not be considered further here.

4. PRACTICAL ASPECTS

4.1 Analytical methods and analytical achievability

The methods for petroleum hydrocarbons are largely based on gas chromatography and liquid chromatography (TPHCWG, 1998a). These are relatively advanced analytical techniques and are not always readily available in many countries. The use of infrared spectrometry for total hydrocarbons may be of value in conjunction with analytical data on specific substances such as benzene and the low-molecular-weight aromatic hydrocarbons. The Japanese Standard Methods for Industrial Water and Wastewater specifies liquid–liquid extraction using 1,1,2-trichloro-1,2,2-trichloroethane. The extracts are measured by infrared absorbance at a wavelength of 3.4 nm. The average absorbance of three peaks observed in the range from 3.3 to 3.6 nm converted to the concentration of mixture. Taste and odour testing would also be a valuable adjunct to chemical analysis.

The United States Environmental Protection Agency (US EPA) has published methods for petroleum hydrocarbons in water. These include EPA 418.1, which also uses infrared absorbance; however, the detection limit is quite high, at 0.5 mg/litre, and the method does not discriminate between different hydrocarbons. The US EPA has also published different methods for TPH in water. These include modified EPA 3510C/8015B, which is based on gas chromatography with flame ionization detection. This method is for TPH as gasoline, jet fuel and diesel and allows the quantification

of the hydrocarbons EC6 through EC20. Other methods, such as EPA 5030B for aromatic volatile aromatics, using gas chromatography with a photoionization detector, are more specific for the more volatile aromatic components that are most likely to reach drinking-water; the detection limit for EPA 5030B is 0.5 µg/litre in water (US EPA, 1997a, 1997b).

4.2 Treatment and control methods and technical achievability

The first action to be taken if water is contaminated by a spill of petroleum products is containment. In the case of surface waters, floating booms can be used to contain the spill in as small an area as possible, away from drinking-water abstraction points. If a spill occurs and no containment equipment is available, containment booms can be improvised from whatever materials are at hand, such as wood or plastic pipes. Skimming, absorbents, or other methods can be used to remove the petroleum products contained on the surface of the water behind the containment boom.

Spills of petroleum products on land have the potential to pose long-term threats to groundwater quality. Temporary dykes and emergency pits can be used to confine the spill to the smallest possible area. Absorbent materials can be used to collect any free petroleum products, and contaminated soil should be removed.

Contaminated aquifers can be remediated by "pump and treat" or *in situ* methods (Shevah & Waldman, 1995). The first step is to pump out any floating petroleum products that can be recovered. "Pump and treat" involves flushing clean water through contaminated zones, recovering the contaminated water, treating it in above-ground reactors, then re-infiltrating the treated water. *In situ* remediation involves the utilization of microorganisms within the subsoil to degrade the contaminants.

There is relatively little information on the ability of treatment processes to remove petroleum products from water, although data for individual components may be available.

Relatively high concentrations of petroleum products are amenable to treatment by coagulation. In a laboratory study, a 1:1:1 mixture of unleaded gasoline, diesel oil, and jet fuel was spiked into brackish water at a total concentration of 3000 mg/litre. Coagulation tests were undertaken using a proprietary product consisting of a mixture of aluminium sulfate and poly(diallyldimethylammonium chloride) at a dose to give rapid floc formation. Percentage removal increased as the carbon number increased (Tansel & Eifert, 1999), as shown below:

Carbon number	% removal
7	10
8	20–25
9	75
10	70
>10	100

Laboratory flotation tests were conducted on *n*-octane in water emulsions with an initial concentration of 500 mg/litre. Ferric chloride (100 mg of iron per litre) gave >95% removal. Anionic or cationic polyacrylamides were ineffective (Zouboulis & Avranas, 2000).

Laboratory studies on the removal of oil from oil-in-water emulsions using hydrophobic polyvinylidene fluoride membranes have been reported. The emulsion was 1% kerosene in distilled water. Removals of up to 77% were obtained (Li, 1999). The paper reported that other studies using hydrophilic membranes achieved product water containing 10–100 mg of oil per litre from initial concentrations of 0.1–10%.

5. CONCLUSIONS

This document provides a pragmatic approach to assessing possible risks to health following a petroleum product contamination incident involving drinking-water. In most cases, this will relate to short-term exposure, although circumstances may arise in which longer-term exposure through drinking-water could occur. Where the latter is the case, it is appropriate to carry out a more detailed assessment, since there will be a relatively limited number of mobile and soluble substances present.

The approach used by the TPHCWG, as described above, has been followed by other national agencies responsible for environmental protection and is used here as the basis for providing guidance as to tolerable levels of hydrocarbon fractions in drinking-water, in the event of spills of petroleum products.

5.1 Health-based group values

5.1.1 >EC5–EC6 and >EC6–EC8 aromatic fraction

Drinking-water guidelines have been developed for the two compounds in this range that are found in petroleum products: benzene (10 µg/litre) and toluene (700 µg/litre). Toluene has a very low reported odour threshold in water and may be detected by odour at concentrations below the guideline value.

5.1.2 >EC8–EC10, >EC10–EC12 and >EC12–EC16 aromatic fraction

Drinking-water guidelines have been developed for a number of substances in the >EC8–EC10 fraction. These include ethylbenzene (300 µg/litre), *m*-xylene, *o*-xylene and *p*-xylene (500 µg/litre) (WHO, 2004). Another is methylethylbenzene, for which there is no specific guideline value; however, all of these have low reported taste and odour thresholds and, particularly as a mixture, will cause the water to be unacceptable to consumers at concentrations below those of concern for health and usually well below the guideline values.

To determine a value for use in assessing drinking-water contamination for the fractions >EC10–EC12 and >EC12–EC16, for which the proposed group RfD was 0.03 mg/kg of body weight, it would be appropriate to assume a 60-kg adult drinking 2 litres of water per day. A conservative allocation of 10% of the RfD of 0.03 mg/kg of body weight per day to drinking-water would give a value of 0.09 mg/litre. However, as exposure from other sources would be expected to be very small, it would be possible to allocate a greater portion of the RfD to drinking-water if required. [note: right-hand justify paragraph on web, use en dashes in line 2, add space in 0.03 mg/kg in line 3, and hyphenate as marked above]

5.1.3 >EC16–EC21 and >EC21–EC35 aromatic fraction

To determine a value for use in assessing drinking-water contamination, it would be appropriate to assume a 60-kg adult drinking 2 litres of water per day. A conservative allocation of 10% of the RfD of 0.03 mg/kg of body weight per day to drinking-water would give a value of 0.09 mg/litre.

5.1.4 EC5–EC6 and EC7–EC8 aliphatic fraction

In the context of drinking-water, assuming a 60-kg adult drinking 2 litres of water per day and allocating 10% of the RfD of 5 mg/kg of body weight per day to drinking-water would give a value of 15 mg/litre for this fraction of aliphatics. However, this concentration would be significantly above the solubility in water.

5.1.5 EC9–EC10, >EC10–EC12 and >EC12–EC16 aliphatic fraction

In terms of drinking-water, the RfD of 0.1 mg/kg of body weight per day would give a guideline value of 0.3 mg/litre, assuming a 60-kg adult drinking 2 litres of water per day with an allocation of 10% of the RfD to drinking-water.

5.1.6 PAHs

WHO (2004) has proposed a drinking-water guideline value for benzo(*a*)pyrene of 0.7 µg/litre, but it was not considered necessary to propose a formal guideline value for fluoranthene. Other PAHs have not been considered for the development of specific guideline values. However, some PAHs were used to develop fraction-specific RfDs, as indicated above.

5.2 Guidance on petroleum products in drinking-water

The above approach provides a sound basis for assessing the potential health risks associated with large-scale contamination of drinking-water by petroleum products. The allocation of 10% of each of the RfDs or TDIs for the five fractions to drinking-water provides allowance for potential additive toxicity and also simultaneous exposure from other sources. This approach would require the analytical capability to determine the concentration of each of the fractions, but since most are of low solubility, the most soluble fractions will be present in the greatest concentration. In some cases, the only method available is the measurement of total hydrocarbons. This is less satisfactory, but, by using the lowest drinking-water value, it would provide a conservative assessment.

However, it is of particular importance that these values should only be used in conjunction with sensory assessment for taste and odour, which will, in most cases, be detectable at concentrations below those concentrations of concern for health, particularly with short-term exposure. In particular, substances such as ethylbenzene, trimethylbenzene and MTBE have recorded taste and odour thresholds of a few micrograms per litre. In view of the above, it is not considered appropriate to set formal health-based guideline values for petroleum products in drinking-water.

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