the occurrence of selected hydrocarbons in food on sale at petrol station shops and comparison with food from other shops - a literature survey

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ABSTRACT

This study presents the results of a review of reports on the occurrence of some hydrocarbons in food in relation to the sales location, with a particular emphasis on petrol station shops. The principal selected hydrocarbons are volatile components of gasoline. The reported findings are discussed and compared, and put in the context of total daily exposure. The relevance of gasoline sales to the levels of the selected hydrocarbons in food items is assessed and compared with other sources of the hydrocarbons.

KEYWORDS

benzene, food, food sales, hydrocarbons, petrol station, service station, toluene, xylene.

CONTENTS

SUMMARY

This literature survey reviewing information on the occurrence of hydrocarbons in food products on sale at petrol station shops was commissioned by CONCAWE, the oil companies' European organization for environment, health and safety. The study was initiated to investigate concerns expressed about possible health effects related to the sale of food products at these locations. A limited number of gasoline hydrocarbons were selected for this survey: pentane, hexane, benzene, toluene, xylene and the ether MTBE. The results of the survey described in this report are based on 50 literature references, dating from 1980-1999.

The European Union has not established legal limits on the levels of these hydrocarbons in food products. The World Health Organisation has set values for the Tolerable Daily Intake of toluene and xylene via food.

Hydrocarbons are common contaminants in our environment. As a consequence, they have often been detected in a great variety of food products. For aromatic hydrocarbons, the UK Ministry of Agriculture, Fisheries and Food provided estimates for the average dietary intake of these compounds. There is, however, some variation in the background levels of hydrocarbons in food, as reported by various authors. All reported toluene and xylene levels in food are well below the TDIs set by WHO.

There are limited data available on the concentrations of (aromatic) hydrocarbons in food products sold at petrol station shops. These studies did not find significantly enhanced levels of hydrocarbons in foodstuffs from petrol station shops in comparison with food from other food shops.

However, the presence of newspapers and magazines near food products in shops was reported to increase the level of hydrocarbons in food, in the case of toluene by a factor of up to 10. The influence of traffic density at the location of the food shop on hydrocarbon levels in food is unclear; one study found higher levels of hydrocarbons in foods from shops located on busy roads, compared to food products from shops in residential areas, whereas another study did not detect any difference. Gasoline-driven engines placed in the same room in which olives are stored, were reported as a cause of the high levels of aromatic hydrocarbons in olive oil. Food contamination with hydrocarbons from other sources, such as packaging materials, cookware and food additives, is described in this report as well, but these sources only caused minor enhancements of hydrocarbon levels in food and contributions from some of these sources have since been reduced by reformulation of the product.

Partition coefficients of hydrocarbons between food and air were determined by several authors; the uptake of hydrocarbons was shown to depend on the fat content of the food product. In general, migration of hydrocarbons into food is slow. Only a small part of the total human exposure to benzene is due to consumption of contaminated food (<2.5%). The major pathway of benzene exposure is via inhalation of air.

Data about food contamination with pentane, hexane or MTBE from any source are scarce or non-existent.

This report identifies a number of factors which might contribute to the presence of selected hydrocarbons in food. The concentrations vary, but the limited data available indicate that the levels in food sold by retail petrol stations are comparable to those found in food purchased from other shops.

1. INTRODUCTION

1.1. BACKGROUND

Nowadays many different foodstuffs are sold at retail outlets in petrol service stations. The volume and range of food products sold by petrol station shops is expected to increase considerably over the next 5-10 years. In response to questions raised by various food hygiene authorities in eg UK, USA, Australia and Germany, a need was identified to provide reassurance that food sold in petrol stations does not present a risk to human health due to contamination with volatile hydrocarbons. Volatile hydrocarbons are inherent components of gasoline and increased concentrations of these compounds were detected in the air surrounding some petrol stations, as well as inside service station kiosks (Römmelt, 1989; CONCAWE, 1998). Once released into the atmosphere, volatile organic compounds may contaminate foods - especially those with a high fat content - in petrol station shops via direct absorption. The possibility of enhanced levels of hydrocarbons in foods sold at petrol station kiosks and the potential human health effects associated with consumption of these foods, were the subject of several newspaper articles in Germany. In 1997 a ZDF broadcast also dealt with the theme 'Food in Petrol Stations'. The German government has even answered questions from concerned members of parliament about this topic (Antwort der Bundesregierung, 1993).

In 1993 the European Union issued a Council Directive on the hygiene of food stuffs (European Community, 1993), which states that 'the...offering for sale or supply of foodstuffs shall be carried out in a hygienic way,' that 'food business operators shall identify any step in their activities which is critical to ensuring food safety and ensure that adequate safety procedures are identified, implemented, maintained and reviewed,' and that 'food business operators shall comply with the rules of hygiene as listed in the Annex'. The Annex describes general requirements for food premises, among which the protection of food 'against any contamination likely to render the food unfit for human consumption, injurious to health... In particular, food must be so placed and/or protected as to minimize any risk of contamination.' Obviously, shops at petrol stations selling food have to comply with the requirements of this Council Directive.

In order to assess any possible health risks related to the sale of food products at shops in petrol stations, CONCAWE - the oil companies' European organization for environment, health and safety - commissioned TNO to carry out a literature study on the occurrence of hydrocarbons in food sold at petrol stations, in relation to the contamination of foodstuffs with hydrocarbons from other sources and the 'natural' or background occurrence of hydrocarbons in food. Gasoline consists of a complex mixture of organic compounds. In agreement with CONCAWE, it was decided to concentrate on a selection of hydrocarbons: pentane, hexane, benzene, toluene, xylenes (ortho, meta and para), as well as MTBE (methyl tertiary-butyl ether).

1.2. SCOPE OF THIS SURVEY

The background to the current interest in the occurrence of hydrocarbons in food products on sale at petrol station shops is described in **Section 1.1**. In **Chapter 2** the legal limits and WHO guidelines for the levels of hydrocarbons in food are listed, as far as they have been laid down. **Chapter 3** describes the 'natural' or background occurrence of hydrocarbons in food, where 'natural' should be interpreted either as occurring naturally or as originating from unidentified sources of contamination (i.e.

the general presence of hydrocarbons as contaminants in our environment). Values determined for the average dietary intake of hydrocarbons via food are also included. **Chapter 4** deals specifically with the occurrence of hydrocarbons in food items on sale in petrol station shops. Because data about the levels of hydrocarbons in food sold in shops in which storage of food is close to printed matter or in shops on busy roads, are entangled with data about hydrocarbon levels in food from petrol station shops, the former data are also presented in this chapter. In most cases comparisons are made with the same food products purchased from shops at other locations. In **Chapter 5**, data about the contamination of food with hydrocarbons from other known sources, such as migration from packaging material or cooking ware, and food additives, are presented. The problems associated with the accurate determination of the levels of hydrocarbons in food and analytical methods are discussed in **Chapter 6**. **Chapter 7** contains a discussion of the factors determining the uptake of hydrocarbons in food from air. The levels of hydrocarbons measured in food purchased from petrol station shops are compared with the 'natural' occurrence of hydrocarbons in food, with the average dietary intake of hydrocarbons, with the contamination of food with hydrocarbons from other sources and with Tolerable Daily Intake values for hydrocarbons via food. Finally, a list of literature references used, is given in **Chapter 8**.

1.3. RESEARCH METHOD

The literature references on which this survey is based, were found by consulting several on-line databases. Literature searches were performed using the following keywords in various combinations (the truncation symbol (*) serves as a substitute for any string of zero or more characters):

- hydrocarbon*, pentane, hexane, benzene, toluene, xylene*, MTBE
- food*, drink*, snack*, sandwich*, candy bar*, chocolate*, vegetable*, fruit*, bread
- petrol, petrol station, gasoline
- migrat*, packag*
- print*, ink*

The TNO compilation, 'Volatile Compounds in Food' (TNO, 1996) was also consulted. A number of unpublished references were provided by CONCAWE and are included in this survey.

The number of references used for this survey totals 50, dating from 1980 to 1999.

2. LIMITS TO THE LEVELS OF HYDROCARBONS IN FOOD

2.1. LEGAL REQUIREMENTS

There are no existing European Union (EU) limits on the levels of the hydrocarbons benzene, toluene, xylene and pentane, and the ether MTBE in food.

The EU has however specified which organic compounds are allowed as solvents during the production or processing of food (European Community, 1993). Council Directive 88/344/EEC and several later additions to this directive list these solvents and the conditions under which they may be used. Of the gasoline-related hydrocarbons which are the subject of this literature survey, only hexane is mentioned in this directive. Hexane is allowed to be used for a restricted number of applications, such as production of oils and fats and extraction of flavours from natural products. For each specific application, a maximum residual level of hexane in foodstuffs is set (e.g. 1 mg/kg fat, oil or cocoa butter). Any other organic solvents which are not listed in the EC directive may not be used for food applications. Legal limits have not been defined for the chemical compounds which are not included in the directive.

2.2. WHO GUIDELINES

The World Health Organization (WHO) derived TDI values (Tolerable Daily Intake) for toluene and xylene on the basis of a LOAEL (lowest-observed-adverse-effect level) and a NOAEL (no-observed-adverse-effect level) respectively and an uncertainty factor (WHO, 1993 and WHO, 1996). The TDI is an estimate of the amount of a substance in food or drinking water expressed on a body weight basis (mg/kg or µg/kg of body weight) that can be ingested daily over a lifetime without appreciable health risk. TDIs are not so precise that they cannot be exceeded for short periods of time. Short-term exposure to levels above the TDI is not a cause for concern, provided that the individual's intake averaged over longer periods of time does not appreciably exceed the level set. On the basis of the TDI, guideline values (rounded figures) for toluene and xylene in drinking water were derived, allocating 10% of the TDI to drinking water and assuming a daily consumption of two litres of water and a body weight of 60 kg. Similarly, the EU's Scientific Committee on Food (SCF) took 10% of the TDI of toluene and xylene for exposure via food contact material to set specific migration limits for these compounds (European Union, 1999). The allocation of 10% of the TDI to drinking water and 10% to migration from food packaging materials is arbitrary as there are insufficient data to support these values. However, these default values are thought to ensure that in most cases, total daily intake from all sources does not exceed the TDI. In the case of benzene, a TDI has not been established because of the unequivocal evidence of the carcinogenicity of benzene in humans. WHO recommended a guideline value of 10 µg/l for benzene in drinking water, which corresponds with an excess lifetime cancer risk of 10^{-5}. In directive 98/83/EC on the quality of water for human consumption, the European Union set a much lower limit (1.0 µg/l) for benzene in drinking water (European Union, 1998). **Table 2.1** summarises the TDIs and guideline values for drinking water (set by WHO), the EU limits in drinking water and specific migration limits (set by SCF) for benzene, toluene and xylene. For pentane, hexane and MTBE, TDIs and guideline values for drinking water have not been set.

Table 2.1: TDIs, guideline values for drinking water, EU limits for drinking water and specific migration limits for benzene, toluene and xylene (WHO, 1993; WHO, 1996; European Union, 1998; European Union, 1999)

limit	**benzene**	**toluene**	**xylene**
TDI (µg/kg body weight) WHO	NV[1]	223	179
guideline value for drinking water (µg/l) WHO	10	700	500
Directive 98/83/EC on drinking water (µg/l)	1.0	NV	NV
specific migration limit (mg/kg food) SCF	NV	1.2	1.2

[1] NV: no value established

3. BACKGROUND LEVELS OF HYDROCARBONS IN FOOD

3.1. BACKGROUND OCCURRENCE OF HYDROCARBONS IN FOOD

Hydrocarbons have been identified in many different food products. They may occur naturally in certain food items, but hydrocarbons are generally present as contaminants in our environment, which may lead to increased levels of hydrocarbons in food. Most often, the source of the hydrocarbons measured in food items is not known and in these cases the occurrence of these compounds in food is described as 'natural', although this does not imply that they would be present naturally in food in an ideal, uncontaminated world. This chapter deals with the background occurrence of the selected hydrocarbons in food. In **Chapter 4** and **5** the contamination of food by hydrocarbons from known sources is described.

TNO edited a compilation called 'Volatile Compounds in Food', which contains literature data (both qualitative and quantitative) on volatile compounds identified in natural food products (TNO, 1996). Volatiles reported to be present in a product have only been included if the validity of identification could be judged. Compounds reported to originate from known sources have been omitted. **Table 3.1** summarises data from this compilation about the occurrence of selected gasoline hydrocarbons in food.

Table 3.1: Occurrence of selected hydrocarbons in food products (TNO, 1996)

hydrocarbon	number of food items in which hydrocarbons have been identified (number with quantitative data)	concentration range (µg/kg)
pentane	31 (4)	3-9100
hexane	49 (3)	4-40
benzene	89 (11)	0.1-7340
toluene	163 (35)	0.1-8100
o-xylene	82 (14)	0.1-50
m-xylene	75 (8)	0.9-130
p-xylene	73 (11)	1-500
xylenes	49 (11)	0.05-210
MTBE	1 (0)	-

The occurrence of monocyclic aromatic hydrocarbons in fruit and vegetables was investigated in 1996 (Górna-Binkul, 1996). Benzene was found at low concentrations (27-56 µg/kg dry mass) in only three species of fruit (apple, kiwi fruit and orange; fruit and vegetables contain 74-95% water). Toluene was detected in 8 species, with the concentrations in the Citrus species (orange, grapefruit, lemon and mandarin, 169-771 µg/kg dry mass) higher than in the other species (apple, kiwi fruit, pear and plum). Xylenes were only found in the peel extract of orange at low concentrations (3 and 111 µg/kg dry mass for o-xylene and m,p-xylene respectively). In the 14 species of vegetables examined, benzene was not detected. Toluene was detected in 4 species (cabbage, tomato, paprika, Brussels sprouts) at concentrations in the range 90-229 µg/kg dry mass, whereas xylenes were found in only two vegetables (parsley and paprika) at higher concentrations (up to 1890 µg/kg dry mass for m,p-xylene in parsley).

Interestingly, the distribution and amount of hydrocarbons present was found to be dependent on the morphological part of the plant species. Higher toluene concentrations were measured in peel than in pulp, which could be explained by the presence of lipophilic components in peel, exhibiting a higher uptake of hydrocarbons, or by the greater exposure of peel to polluted air than pulp. In the extracts of underground parts of vegetable species (roots, bulb), which are not exposed to air, hydrocarbons were not detected.

In 1995, 234 table-ready foods from the Total Diet Program of the US Food and Drug Administration (FDA) were surveyed for the presence of VOC (Volatile Organic Compounds) residues (Heikes, 1995), applying a purge and trap extraction method with GC-MS quantification with limits of quantitation of 9.3, 8.0, 5.5 and 3.7 µg/kg for benzene, toluene, m,p-xylene and o-xylene respectively. The Total Diet Program contains selected foods purchased from supermarkets in various regions of the US and prepared as they would be in a domestic kitchen. Raw fruits and vegetables and alcoholic beverages were excluded from this survey. Of the items studied, over 20 recipe (combined) food items (e.g. lasagna, tuna noodle casserole) or fast-food items such as pizza or quarter pound cheeseburgers were included. Thirty-six infant/toddler foods were represented. In **Table 3.2** the results of this survey for benzene, toluene and xylenes are listed. Unfortunately, Heikes et al. presented the analytical data of their survey in a highly condensed form, i.e. combined for all 234 food items, rather than separated into food types. The high level of benzene in sauerkraut (283 µg/kg) may be attributed to fermentation of cabbage.

The survey shows a close correlation between the levels of the volatile nonpolar analytes and the fat content of the food items analysed. The average fat level of the 47 foods found to be free of incurred VOC residues was only 1.8%. Another 144 items with total residues < 100 µg/kg had an average fat level of 7.8%, whereas 43 foods with total residues in excess of 100 µg/kg had an average fat content of 20%. The high levels of hydrocarbons in high-fat foods are related to the lipophilic character of the hydrocarbons, which is expressed by their high log P_{ow} values (P_{ow} is the partition coefficient of a compound between octanol and water, see **Appendix B**). In **Table 3.3**, results of analyses of the four food products with the highest levels of VOCs, sandwich cookies, butter, margarine and cake doughnuts, all with high fat contents, are presented.

Table 3.2: Selected results of a survey for hydrocarbons in 234 Table-Ready Food Items from the FDA's Total Diet Study (Heikes, 1995)

compound	**occurrence [a] (%)**	**average level (µg/kg)**	**range (µg/kg)**	**highest level food item**
benzene	12	50	9-283	sauerkraut
toluene	39	51	8-344	cake doughnuts
m/p-xylene	27	20	6-114	margarine
o-xylene	14	8	4-24	cake doughnuts
total average level of aromatic hydrocarbons [b]		129		

[a] Percentage of foods (of 234 food items) in which the analyte was detected >LOQ (limit of quantitation)

[b] Total average level of aromatic hydrocarbons refers to the sum of the average levels of the four aromatic hydrocarbons measured.

Table 3.3: Selected results of analyses of 4 food items with highest levels of VOC residues (µg/kg) (Heikes, 1995)

compound	**concentration in µg/kg for 4 food items**			
	sandwich cookies	**margarine**	**butter**	**cake doughnuts**
benzene	-[a]	-[a]	-[a]	11.0
toluene	26.3	171	248	344
m/p-xylene	12.9	114	54.8	35.0
o-xylene	6.31	21.7	12.5	23.5
total aromatic hydrocarbon [b]	46	307	315	414

[a] residue level <LOQ

[b] Total aromatic hydrocarbon refers to the sum of the four aromatic hydrocarbons measured.

In 1992 the American Petroleum Institute performed a study in which a variety of food products, selected to be representative of the foods consumed in the USA, were analysed solely for the presence of benzene (API, 1992). The foods were analysed by GC-PID (limits of detection between 0.01 and 2.31 µg/kg) and GC- MS. Of the 57 food products analysed, benzene was only detected in fried eggs and roasted peanuts with a concentration of 30 µg/kg for both items. On the basis of these results it was concluded that benzene seems unlikely to be a naturally occurring component of these foods. It was also suggested that at least some of the previous reports of the identification of benzene in food may be due to analytical mistakes.

In bottled drinking water, benzene was only detected in 1 of 182 samples at 2 µg/kg and toluene in 20 samples (range 0.5-63 µg/kg) (Page, 1993). In other beverages such as beer and carbonated soft drinks, any detected levels of benzene and toluene were also low (both <3 µg/kg) (McNeal, 1995), except in cases where the combination of the ingredients sodium benzoate and ascorbic acid caused higher levels of benzene (see **Section 5.4**).

3.2. AVERAGE DIETARY INTAKE OF HYDROCARBONS IN FOOD

The UK Ministry of Agriculture, Fisheries and Food (MAFF) carried out a survey of aromatic hydrocarbons in Total Diet Samples collected in 1993 (MAFF, 1995). Samples were collected from 10 UK locations for all twenty food groups of the Total Diet Study. Each food group consists of retail food products, which were prepared as for consumption. The results of the analyses are shown in **Table 3.4**.

Total dietary intakes of each hydrocarbon for the average UK consumer were estimated by multiplying the concentration of the compound analysed in a food group sample by the amount of that food group eaten in a day by one person, and summing the contributions of each food group. The average UK dietary intake of benzene was thus estimated to be 0.5-2.4 µg/person/day. Benzene was mostly detected in meat, fish, poultry and nuts, with hardly any benzene detected in other food products. Toluene was detected in most food groups analysed; the average UK dietary intake of toluene is 7.0-7.7 µg/person/day. The average dietary intakes of p/m-xylene and o-xylene are 1.2-4.9 and 0.9-4.6 µg/person/day respectively.

Table 3.4: Concentrations (µg/kg) of aromatic hydrocarbons in ten samples of each food group from the 1993 Total Diet Study (MAFF, 1995)

Food Group	**benzene[a]**		**toluene[a]**		**m,p-xylene[b]**		**o-xylene[b]**		**total aromatic hydro-carbon[c]**
	range	**mean**	**range**	**mean**	**range**	**mean**	**range**	**mean**	
carcase meat	1-7	3	2-6	4	<2-7	3	all<2	<2	10
offal	3-18	6	6-39	14	<2-12	4	<2-3	2	26
meat products	2-8	5	8-24	14	<2-30	7	<2-19	5	31
poultry	1-4	3	7-31	15	<2-34	11	2-7	4	33
fish	2-13	6	15-76	26	<2-19	5	<2-9	3	40
eggs	all<1	<1	4-12	7	<2-2	<2	all<2	<2	7
milk	all<1	<1	2-7	4	<2-2	<2	all<2	<2	4
milk products	<1-1	1	12-23	17	all<2	<2	<2-3	2	20
bread	all<1	<1	1-9	4	<2-14	3	<2-6	2	9
other cereals	all<1	<1	4-11	7	<2-7	3	<2-5	3	13
oils and fats	<1-1	<1	8-30	20	<2-3	2	all<2	<2	22
sugars	all<1	<1	4-19	8	all<2	<2	<2-3	2	10
green vegetables	all<1	<1	1-2	2	all<2	<2	all<2	<2	2
potatoes	all<1	<1	1-8	3	<2-4	2	<2-8	4	9
other vegetables	<1-1	<1	1-5	3	all<2	<2	all<2	<2	3
canned vegetables	all<1	<1	2-5	3	<2-2	<2	all<2	<2	3
fruit	all<1	<1	<1-1	<1	all<2	<2	all<2	<2	-
fruit products	<1-3	1	all<1	<1	all<2	<2	<2-4	2	3
beverages	all<1	<1	<1-1	<1	all<2	<2	all<2	<2	-
nuts	1-7	3	9-67	30	7-114	23	<2-39	7	63

[a] Limit of quantitation for benzene and toluene is 1 µg/kg

[b] Limit of quantitation for p/m-xylene and o-xylene is 2 µg/kg

[c] Total aromatic hydrocarbon refers to the sum of the four aromatic hydrocarbons measured.

A comparison between the MAFF Total Diet Study shown above (**Table 3.4**) and the FDA Total Diet Study described in **Section 3.1** (**Table 3.2**) reveals large differences in the aromatic hydrocarbon levels measured. In both studies retail food products were analysed, which were prepared as in a domestic kitchen. Both studies were also carried out by well-known research laboratories. The FDA study left out raw fruits and vegetables and alcoholic beverages, which may be expected to contain lower levels of hydrocarbons, but the total average level of aromatic hydrocarbons in the FDA Total Diet Study (129 µg/kg) is much higher than the total average level of aromatic hydrocarbons in any of the food groups in the MAFF study (highest total level of 63 µg/kg for nuts, average for all food groups is 15 µg/kg). It seems unlikely that the discrepancy in results between the two studies is caused by the different locations at which the food products were purchased (US vs. UK), which leaves the difference unexplained. The authors of the FDA study did not calculate average dietary intakes for the hydrocarbons measured.

Several other authors have estimated the average dietary intake of benzene, but how these estimates were derived is not always as clearly presented as in the above mentioned MAFF study. Early estimates of the average dietary intake of benzene are very high (250 µg/person/day (NRC, 1980) and 31-108 µg/person/day (Gilbert, 1982)), suggesting that the consumption of food is an important pathway of human exposure to benzene. However, these high values are contradicted by the MAFF study and by other studies. A Canadian study gave an estimate of 1.2 µg/person/day for the average dietary intake of benzene (Holliday, 1989), which compares well with the MAFF results. The average dietary intake of benzene in Germany was reported to be <1 µg/person/day (Eikmann, 1992), whereas in an FDA Total Diet Study, the average dietary intake of benzene was calculated to be about 5 µg/person/day (Diachenko, 1997). Using various theoretical models, the average dietary intake of benzene was estimated to be 0.02 µg/person/day (Hattemeyer- Frey, 1990 and Travis, 1992) and 0.4 µg/person/day (Kokot-Helbling, 1995). The latter study also provided estimates for the average dietary intake of toluene (2.8 µg/person/day) and xylenes (12.0 µg/person/day).

Though there may be different opinions on the actual amount ingested via food, all authors (at least those of the more recent articles) seem to agree that consumption of food is not an important pathway for benzene exposure. Ingestion of food accounts for less than 1% of the average total daily intake of benzene from all sources, though Diachenko estimated the intake of benzene via food to be 2.5% (Diachenko, 1997). Inhalation of air is the cause of more than 99% of total human exposure to benzene (Wallace, 1996; Kokot-Helbling, 1995; Hattemeyer-Frey, 1990; Travis, 1992; Eikmann, 1992). This fact results in a major difference in the average daily intake of benzene between smokers and nonsmokers: smokers expose themselves to a 6-10 times higher intake of benzene compared with nonsmokers and they receive about 90% of their benzene exposure from smoking (Wallace, 1996). Smoking also causes significantly increased benzene concentrations in indoor air: in homes with smokers, the average benzene concentration is 50 to 67% higher than in homes without smokers (Wallace, 1996).

The Scientific Committee on Food also concluded that it is unlikely that intakes of benzene, toluene and xylenes via food would contribute significantly to the risk to human health from other sources, such as inhalation (European Union, 1999).

4. OCCURRENCE OF HYDROCARBONS IN FOOD SOLD AT PETROL STATIONS

The levels of aromatic hydrocarbons in food items sold at petrol station shops have been investigated by several authors. In these reports, comparisons are made with food sold in 'normal' supermarkets (i.e. shops believed to be remote from hydrocarbon sources), shops in busy roads, newspaper shops or supermarkets or petrol stations selling newspapers as well as food. The main results are summarised below.

Food products purchased from petrol station shops and food shops were tested for benzene and toluene (Rothenbücher, 1989 and Müller, 1990). Samples were extracted by steam distillation (Clevenger Principle) and analysed by GC-FID and GC-MS. The limit of quantitation for both compounds is 20 µg/kg. A preliminary study involved 43 food products from petrol station shops and 46 from food shops, all with relatively high fat content. Two out of 43 samples taken from petrol station shops contained benzene (2 ice cream samples with concentrations of 56 and 235 µg/kg); in food shops two out of 46 samples were found to contain benzene (2 sausage samples, 27 and 70 µg/kg). In petrol station shops, toluene was detected in almost all samples (41 out of 43 samples, median concentration 249 µg/kg), whereas the toluene concentrations in food shops were much lower (37 out of 46 samples, median concentration 22 µg/kg). In this preliminary study, however, no distinction was made between petrol station shops with or without sale of newspapers and magazines. The levels of toluene measured in high fat content foods bought at food shops are comparable to the levels found in the MAFF Total Diet Study for food groups with high fat content (see **Table 3.4**).

In the second part of this publication (Müller, 1990), hazelnut and whole-milk chocolate sweets were selected as suitable probes for a more detailed investigation into contamination with aromatic hydrocarbons. The retail outlets were specified further into food shops, food shops with printed matter (newspapers, magazines) stored close to the foodstuffs, petrol stations with and without sale of newspapers, and newsagents. Benzene was detected in only 15 of the total of 177 chocolate samples. Four samples contained benzene at concentrations of 20-53 µg/kg (one sample from a food shop, one from a petrol station shop with sale of newspapers and two from newsagents). Toluene was detected in the majority of samples; **Table 4.1** summarises the measured concentrations of toluene.

Table 4.1: Toluene levels of chocolate sweets purchased at various retail outlets (Müller, 1990)

retail outlet	number of samples	samples with toluene (%)	range (µg/kg)	mean (µg/kg)	median (µg/kg)
food shop	49	43 (88)	<20-695	70	47
food shop with newspapers	8	8 (100)	90-175	111	102
petrol station without newspapers	23	21 (91)	<20-214	57	47
petrol station with newspapers	33	33 (100)	27-1572	303	216
newsagent	64	64 (100)	<20-7897	1088	476

These results show that the toluene contamination of chocolate sweets is largely dependent on the presence of newspapers and magazines. In samples taken from petrol station shops that did not sell newspapers as well as in samples from food shops, the median concentration of toluene was reported to be the same (47 µg/kg).

The British Ministry of Agriculture, Fisheries and Food has carried out a survey of aromatic hydrocarbons in fatty foods purchased from petrol station shops (PS), shops situated on busy roads (RS) and shops assumed to be remote from any major sources of hydrocarbons (LC) (MAFF, 1996). No distinction was made between shops with or without sale of newspapers and magazines. Samples were analysed by static headspace gas chromatography with mass spectrometric detection. The detection limit was 1 µg/kg and the limit of quantitation was 10 µg/kg.

From each product sample, subsamples were taken from the surfaces and centre of the retail packs. Concentrations of contaminants are expected to be higher at the outer surfaces of the food than in the centre if contamination occurred by passive absorption from the atmosphere after packaging, whereas concentrations are expected to be constant throughout the bulk if contamination occurred before or during processing of the food. In the majority of food products analysed, the centre subsamples showed lower concentrations of aromatic hydrocarbons than the surface subsamples, independent of the site of the shops, indicating that hydrocarbon contamination of the packaged food product took place via absorption from the atmosphere.

In meat products, toluene was present above the reporting limit in 10 of the 33 retail packs (range 15-78 µg/kg), while benzene and m/p-xylene were each present in 1 of the 33 samples. The results for retail packs of butter, cheese, lard and margarine are shown in **Tables 4.2a-d**.

Table 4.2a: Concentrations of aromatic hydrocarbons in retail packs of butter purchased in petrol station shops (PS), road side shops (RS) and shops in locations remote from identifiable sources of hydrocarbon (LC) (MAFF, 1996).

compound		**petrol station shops (PS)**	**road side shops (RS)**	**shops far from hydrocarbon sources (LC)**
benzene	number of samples with benzene (%)	5 (56)	6 (54)	4 (33)
	range (µg/kg)	7-15	7-16	7-10
	average (µg/kg)	11	11	9
toluene	number of samples with toluene (%)	9 (100)	11 (100)	12 (100)
	range (µg/kg)	13-100	14-86	8-100
	average (µg/kg)	59	45	52
o-xylene	number of samples with o-xylene (%)	3 (33)	1 (9)	1 (8)
	range (µg/kg)	9-20	3	15
	average (µg/kg)	15	3	15
m,p-xylene	number of samples with m,p-xylene (%)	5 (56)	1 (9)	4 (33)
	range (µg/kg)	11-25	27	17-32
	average (µg/kg)	18	27	25

Table 4.2b Concentrations of aromatic hydrocarbons in retail packs of cheese purchased in petrol station shops (PS), road side shops (RS) and shops in locations remote from identifiable sources of hydrocarbon (LC) (MAFF, 1996).

compound		**petrol station shops (PS)**	**road side shops (RS)**	**shops far from hydrocarbon sources (LC)**
benzene	number of samples with benzene (%)	0 (0)	1 (17)	0 (0)
	range (µg/kg)	-	13	-
	average (µg/kg)	-	13	-
toluene	number of samples with toluene (%)	3 (50)	6 (100)	4 (80)
	range (µg/kg)	12-40	6-52	8-91
	average (µg/kg)	27	20	48
o-xylene	number of samples with o-xylene (%)	0 (0)	0 (0)	1 (20)
	range (µg/kg)	-	-	7
	average (µg/kg)	-	-	7
m,p-xylene	number of samples with m,p-xylene (%)	1 (17)	5 (83)	2 (40)
	range (µg/kg)	13	9-18	15-22
	average (µg/kg)	13	13	18

Table 4.2c: Concentrations of aromatic hydrocarbons in retail packs of lard purchased in petrol station shops (PS), road side shops (RS) and shops in locations remote from identifiable sources of hydrocarbon (LC) (MAFF, 1996).

compound		**petrol station shops (PS)**	**road side shops (RS)**	**shops far from hydrocarbon sources (LC)**
benzene	number of samples with benzene (%)	2 (33)	2 (33)	0 (0)
	range (µg/kg)	7-10	7-12	-
	average (µg/kg)	8	10	-
toluene	number of samples with toluene (%)	5 (83)	5 (83)	3 (50)
	range (µg/kg)	31-80	14-140	11-16
	average (µg/kg)	49	44	13
o-xylene	number of samples with o-xylene (%)	0 (0)	1 (16)	0 (0)
	range (µg/kg)	-	9	-
	average (µg/kg)	-	9	-
m,p-xylene	number of samples with m,p-xylene (%)	1 (17)	3 (50)	2 (33)
	range (µg/kg)	13	11-19	8-14
	average (µg/kg)	13	16	11

Table 4.2d: Concentrations of aromatic hydrocarbons in retail packs of margarine purchased in petrol station shops (PS), road side shops (RS) and shops in locations remote from identifiable sources of hydrocarbon (LC) (MAFF, 1996).

compound		**petrol station shops (PS)**	**road side shops (RS)**	**shops far from hydrocarbon sources (LC)**
benzene	number of samples with benzene (%)	4 (67)	-[1]	3 (38)
	range (µg/kg)	8-17	-	10-12
	average (µg/kg)	13	-	11
toluene	number of samples with toluene (%)	6 (100)	-[1]	8 (100)
	range (µg/kg)	21-230	-	19-320
	average (µg/kg)	139	-	90
o-xylene	number of samples with o-xylene (%)	1 (17)	-[1]	0 (0)
	range (µg/kg)	10	-	-
	average (µg/kg)	10	-	-
m,p-xylene	number of samples with m,p-xylene (%)	3 (50)	-[1]	2 (25)
	range (µg/kg)	13-24	-	19-26
	average (µg/kg)	17	-	22

[1] For unknown reasons, analysis data about retail packs of margarine from road side shops were not included in this survey

On the basis of a statistical analysis, the authors concluded that the location of the shops generally did not cause discernible differences in the concentrations of aromatic hydrocarbons in the fatty foods purchased from these shops. Only in the case of lard, overall concentrations of toluene were higher in PS retail packs than in RS and LC packs.

Compared with the MAFF Total Diet Study (MAFF, 1995, see **Section 3.2**), the milk products from all types of shops (PS, RS and LC) contained higher concentrations of aromatic hydrocarbons, which is probably explained by the higher fat content of the products analysed in this study than in the composite Total Diet Study samples, which also included low fat milk products.

The conclusion from the MAFF study that aromatic hydrocarbon levels in food do not depend on whether the food items are purchased in shops located on busy roads or in shops remote from any major source of hydrocarbon, is in contrast with a similar survey performed in Germany (Stüwe, 1991). The analyses were carried out according to the method described by Rothenbücher et al. (Rothenbücher, 1989). Stüwe et al. do not specify which food products were analysed and the data are presented in a very concise way, which makes it difficult to compare these results with the MAFF study. Nevertheless, Stüwe et al. reported that food items on sale at shops located on busy roads contain higher concentrations of aromatic hydrocarbons (average benzene level 26 µg/kg, average toluene level 77 µg/kg), than foods from shops in residential areas with much less traffic (average benzene level 12 µg/kg, average toluene level 26 µg/kg). Their results also showed a higher average concentration of benzene and toluene in food sold at petrol station shops located on busy roads than food sold at petrol station shops in rural areas. It is not clear whether the shops selected for this survey sell newspapers or not.

Furthermore, Stüwe et al. made a comparison between aromatic hydrocarbon levels in hazelnut chocolate sweets obtained directly from the manufacturer and the same sweets on sale at newsagents. The concentrations of aromatic hydrocarbons were found to be significantly higher in hazelnut chocolate sweets purchased from news agents (average toluene level 338 µg/kg), than in sweets direct from the manufacturer (average toluene level 43 µg/kg); these results are consistent with the increased levels of toluene reported by Muller et al. (Müller, 1990) for chocolate sweets sold at newsagents.

CONCAWE provided data from two unpublished surveys concerning aromatic hydro carbon levels in chocolate sweets from petrol station shops only, carried out by German research institutes. Again, there is no distinction made between petrol station shops with or without sale of newspapers and magazines. One survey analysed 17 chocolate sweets with a detection limit of 20 µg/kg (LEFO Institut, 1997). Only three samples contained benzene above the detection limit, whereas all samples were found to contain toluene (range 30-324 µg/kg, average 130 µg/kg, median 94 µg/kg). The second survey provides concentrations for 21 chocolate bars with a detection limit of 20 µg/kg (Lebensmittelchemisches Institut des Bundesverbandes der Deutschen Süsswarenindustrie, 1989). Benzene or p-xylene were not detected in any of these samples, o-xylene was detected in one sample and m-xylene in three out of 21 samples. Toluene was reported in 18 out of 21 samples (range 30-520 µg/kg, average 114 µg/kg, median 45 µg/kg). The toluene levels of these two surveys are comparable to those reported by Müller (Müller, 1990) for chocolate sweets from petrol station shops without sale of newspapers.

For clarity, **Table 4.3** contains the average toluene concentrations reported in the studies described in this Chapter, for food products sold at various retail outlets. Great care should be taken when interpreting the data presented in this Table. There are many variables such as food items investigated, retail outlet, analytical method and limit of quantitation, which may thwart a meaningful comparison between the reported studies.

Table 4.3: Average toluene concentrations measured in food products sold at various retail outlets, which are reported in the studies described in **Chapter 4**.

study	food type	retail outlet	number of samples analysed	percentage of samples with toluene (%)	mean concentration (µg/kg)
Müller, 1990	chocolate sweets	food shops	49	88	70
		food shops with printed matter	8	100	111
		petrol station shops without printed matter	23	91	57
		petrol station shops with printed matter	33	100	303
		newsagents	64	100	1088
MAFF, 1996	butter, cheese, lard and margarine	food shops remote from hydrocarbon sources	31	87	58
		petrol station shops	27	85	74
	butter, cheese and lard	road side shops	23	96	38
Stüwe, 1991	not specified	food shops in residential areas with little traffic	not reported	not reported	26
		food shops on busy roads	not reported	not reported	77
	hazelnut chocolate sweets	direct from manufacturer	not reported	not reported	43
		newsagents	not reported	not reported	338
LEFO Institut, 1997	chocolate sweets	petrol station shops	17	100	129
Lebensmittel-chemisches Institut BDSI, 1987	chocolate sweets	petrol station shops	21	86	114

In summary, the studies by Müller (chocolate sweets; Müller, 1990) and MAFF (fatty foods; MAFF, 1996) did not show any significant difference in aromatic hydrocarbon content, between food products on sale in petrol station shops and those in ordinary food shops. The MAFF study does not report any significant differences either, in hydrocarbon contamination of foodstuffs between shops situated on busy roads and shops at locations away from hydrocarbon sources. This latter result is contradicted by Stüwe et al., who reported higher levels of hydrocarbons in food sold at shops located on roads with high traffic density, than in food from shops in areas with little traffic (Stüwe, 1991). Müller et al. reported that the level of hydrocarbon contamination of food (especially toluene) is much higher if the foodstuffs are stored near newspapers and magazines than in the absence of printed matter, which is supported by the results of Stüwe.

5. OTHER POTENTIAL SOURCES OF HYDROCARBON CONTAMINATION OF FOOD

5.1. EXHAUST EMISSIONS AND EVAPORATIVE LOSSES FROM GASOLINE ENGINES

Car exhaust gases are a significant source of hydrocarbon contamination in air, therefore at least part of the background occurrence of hydrocarbons in food will probably be due to car exhaust. **Chapter 4** also contains data about hydrocarbon concentration in food products on sale in shops located on busy roads. The effect of exhaust from gasoline-driven engines on the level of hydrocarbons in food is clearly illustrated by two articles about the origin of high concentrations of aromatic hydrocarbons in virgin olive oil (Biedermann, 1995 and Biedermann, 1996). Olives on the tree were found to contain volatile aromatic hydrocarbons at concentrations exceeding those corresponding to the equilibrium with the environment. The process of enrichment is unknown, but it is assumed that virgin olive oil without direct contamination by the producers may contain up to 10 µg/kg of benzene and 250 µg/kg for the sum of benzene, toluene, ethyl benzene and xylenes. Further contamination occurs during processing of the olives. Apart from the oil mills, the rooms for intermediate storage of the olives are an important source of contamination by gasoline vapours, since they often contain vehicles and other gasoline-driven engines.

In a simulation experiment, a small grass mower was placed in a room similar in size to the storage rooms of olives (20 m^2) with the door and windows closed, after the mower had been used for about one hour (Biedermann, 1996). The engine was turned off outside the room, but it was still hot. After 3 hours, hydrocarbon levels in the air of the garage had risen to very high values (6.1, 20.6 and 7.1 mg/m^3 for benzene, toluene and xylenes respectively). Using the partition coefficients determined for aromatic hydrocarbons between air and oil (Biedermann, 1995), it was calculated that the oil phase of olives in equilibrium with the air analysed, would reach levels as high as 5 mg/kg for benzene and 50 and 70 mg/kg for toluene and xylenes respectively (Biedermann, 1996).

5.2. PACKAGING

The UK Ministry of Agriculture, Fisheries and Food reported a survey about the concentrations of benzene in plastic food packaging (MAFF, 1994). Raw material polymers contained the highest benzene concentrations. After further processing to form (unused) plastic food packaging, the benzene levels were reduced. Measured concentrations of benzene in plastics used to package retail food products are listed in **Table 5.1**. A worst case scenario, using the highest concentration of benzene (184 µg/kg for unused black polystyrene packaging) and assuming that all the benzene migrates into the food, provides an estimated maximum benzene concentration of less than 10 µg/kg. In practice, this value is expected to be much lower, because over 80% of the plastic samples contained less than 10 µg/kg benzene and not all of this would migrate into food.

Table 5.1: Benzene concentrations found in plastic packaging used for retail food samples (MAFF, 1994)

food category	number of samples	benzene concentration of packaging (µg/kg)
meat and poultry products	19	<1-161
fruit juice and soft drinks	15	<1-16
milk and cream	7	<1-13
yoghurts	21	<1-29
cheese	15	<1-15
other dairy products	14	<1-11
snack foods	10	<1-11
fats and oils	21	<1-25
bakery products	7	<1-22
microwave products	10	<1-7
miscellaneous	14	<1-45

Slightly higher levels of benzene were reported for commercial polypropylene packages such as yoghurt cups, salad tubs and cookie trays. Benzene concentrations ranged from none detected to 426 µg/kg with an average value of 133 µg/kg (Varner, 1991).

Two studies specifically deal with the migration of organic compounds from secondary recycled poly(ethylene terephtalate) (PET) into food. Using a theoretical approach for the determination of permeability constants, diffusion coefficients and solubility constants, it was concluded that organic compounds exhibit slow migration in PET and that the 'diffusion values are too low to provide toxic levels of uptake and exchange with food in second generation containers' (Sadler, 1996). The migration of benzene from PET sheets into food simulants (8% ethanol/water and n-heptane) has been determined experimentally (Komolprasert, 1997). The extraction data showed that migration of benzene from PET sheets containing 0.6 mg/kg of benzene, resulted in concentrations lower than 10 µg/kg in the food simulants. When migration experiments were performed with PET sheets spiked with benzene (218 mg/kg), higher concentrations of benzene were measured in the food simulants (24-40 µg/kg). These data also represent a worst case scenario, because the extruded PET sheets used were less crystalline (5-15%) than most commercial PET bottles (30% crystallinity) and diffusion/migration through polymers is inversely related to crystallinity.

Pentane was noted at a concentration of 18.7 µg/kg in one sample of spring water as a migrant from a foamed polystyrene cap liner (Page, 1993).

5.3. COOKING WITH PLASTIC COOKWARE

Plastic cookware is widely available for use in microwave and conventional ovens. Two samples of thermoset polyester compounded for the manufacture of plastic cookware were found to contain high concentrations of benzene (29 and 64 mg/kg), which was attributed to the use of t-butyl perbenzoate as an initiator in the manufacture of the polymer (Jickells, 1990). These contaminated samples showed migration levels of 1.9 and 5.6 mg/kg in olive oil after extraction for 1 hour at $175^{o}C$, whereas migration levels into olive oil from samples with a non-aromatic initiator were < 0.1 mg/kg. When thermoset polyester cookware purchased from retail outlets with benzene concentrations of 0.3 up to 84.7 mg/kg was used for cooking various foods, only low amounts of benzene (<0.01-0.09 mg/kg) were detected in the cooked food. Following these experiments, the plastic manufacturers have reformulated their products for food use, replacing t-butyl perbenzoate with an alternative initiator. Analysis of thermoset polyester cookware bought more recently, indeed showed much lower benzene concentrations (< 1 mg/kg) (Gramshaw, 1995).

Poly(tetrafluoroethylene) (PTFE) coatings of nonstick cookware were also reported to contain benzene at levels of <1-50 $\mu g/dm^2$ (Jickells, 1993). To determine the possible transfer of benzene from these coatings during normal use, several foods (puddings, cakes, roast potatoes) were prepared in previously unused cookware, but benzene was not detected in any of these foods at a limit of detection of 2 µg/kg, indicating that transfer of benzene is a very inefficient process (<0.5% transfer).

Microwave heat susceptors are typically packaged with foods intended for microwave use for the purpose of cooking these foods to golden crispness by conversion of electromagnetic energy into heat. Benzene and toluene were detected to be released by microwave susceptors at levels of <0.16-3.41 $\mu g/dm^2$ and 0.93-17.1 $\mu g/dm^2$ (McNeal, 1993). Jickells et al reported benzene release from microwave susceptors to be lower than 1 $\mu g/dm^2$ (Jickells, 1993). The latter microwave heat susceptors were used for cooking foods such as french fries and pizza according to the manufacturer's instructions. With a limit of detection of 2 µg/kg, benzene was not present in any of these cooked foods.

5.4. FOOD ADDITIVES

Several findings of benzene in food products are attributed to the presence of benzoates - mostly as an added preservative, rarely as a natural constituent - in combination with the presence of ascorbic acid (vitamin C) (Page, 1992; McNeal, 1993). **Table 5.2** lists benzene levels of several drinks with and without benzoate, which strongly suggests that the enhanced benzene levels are due to the benzoate additive.

Table 5.2: Average benzene levels in drinks with and without benzoates (Page, 1992)

sample	**average benzene concentration (µg/kg)**
fruit juices without benzoate	0.056
fruit juices with benzoate	0.672
noncarbonated fruit drinks without benzoate	0.116
noncarbonated fruit drinks with benzoate	0.395
carbonated soft drinks without benzoate	0.062
carbonated soft drinks with benzoate	0.793

In a second study, several food products containing added benzoates and ascorbic acid were analysed for the presence of benzene and compared with foods without benzoates (McNeal, 1993). Food products with benzoate and ascorbic acid were found to contain higher levels of benzene (range <1-38 µg/kg, with the highest concentrations measured for imitation strawberry preserves, taco sauce and duck sauce) than those without (≤2 µg/kg).

To investigate benzene formation from precursor compounds, aqueous solutions were prepared containing concentrations of both benzoate (0.04%) and ascorbic acid (0.025%), which are typical of those used in beverage formulations. After storage of these solutions for 20 hours in strong UV light or at 45°C, about 300 µg benzene/kg had formed, whereas only 4 µg benzene/kg was present in solutions stored in the dark at room temperature for 20 hours. Benzene was not found in identically treated control solutions containing benzoate or ascorbic acid alone. Although benzene levels in foods due to the combination of added benzoate preservatives and ascorbic acid are quite low, apparently some soft drink products have already been reformulated to avoid the formation of benzene from additives.

5.5. PRINTING INK

There are no articles in the open literature that exclusively deal with food contamination by hydrocarbons from printing ink of newspapers and magazines. Some useful data on this subject are provided intertwined in articles about contamination of food sold in petrol station shops (Müller, 1990 and Stüwe, 1991). These data are presented in **Chapter 4**.

Screen printing on packaging of food itself may also be a source of hydrocarbon contamination in food, since eg toluene is a common ingredient in printing inks. One may hypothesise that part of the background contamination of hydrocarbons in food sold in food shops is caused by printing ink on food packaging, especially in view of the enhanced hydrocarbon levels measured in food stored in the vicinity of newspapers and magazines. However, the open literature does not provide any information about this potential source of food contamination.

6. ANALYTICAL METHODS FOR THE DETERMINATION OF HYDROCARBONS IN FOOD

6.1. PROBLEMS ASSOCIATED WITH ANALYSIS OF HYDROCARBON LEVELS IN FOOD

Reliable analysis of hydrocarbon levels in food is dependent on the methodology chosen to eliminate (or at least minimise) two major problems relating to the analysis of hydrocarbons (Page, 1993; Barshick, 1995; Buschmann, 1990).

The first problem is analyte loss by volatility. The analysis of VOCs in (solid) food generally requires several transfer and preparation steps, during which the sample may be exposed to the atmosphere or may be heated, resulting in partial evaporation of the analyte. To reduce these losses, the number of manipulative steps should be minimised, or they should be performed in a closed atmosphere, and samples and equipment contacting samples should be cooled.

The second problem is contamination of the sample to be analysed with hydrocarbons during sample transport, sample preparation in the laboratory and/or the actual measurement. Air in laboratories may contain considerable levels of hydrocarbons, which could contaminate the food samples. The best solution would be performing sample preparations under a controlled atmosphere. Otherwise, sample contamination by laboratory air should be monitored by regular inclusion of blank samples.

Whatever the methods used for sample preparation and analysis, a thorough validation of the methods applied is essential.

6.2. ANALYTICAL METHODS FOR THE DETERMINATION OF HYDROCARBONS IN FOOD

For the determination of hydrocarbons in food, conventional sample preparation methods such as distillation and extraction have been used, followed by GC-FID and GC-MS (see for example Rothenbücher, 1989 and Müller, 1990). Currently, sample concentration is mostly carried out by headspace sampling or purge-and-trap methods; the latter technique is generally more sensitive (see for example Page, 1993; Heikes, 1995; McNeal, 1990; McNeal, 1993). The US EPA described several methods based on these techniques for the determination of VOCs in various matrices. Barshick et al. developed a new blender purge-and-trap method, which resulted in improved reproducibility and detection sensitivity, compared with conventional purge-and-trap methods (Barshick, 1995). The new blender unit described in this article, was designed in such a way that all sample handling can be performed in a closed system, which reduces loss of volatile analytes.

7. DISCUSSION

7.1. FACTORS DETERMINING THE UPTAKE OF HYDROCARBONS IN FOOD FROM AIR

The uptake of hydrocarbons in food from air depends on many factors such as the partition coefficient of the compound between food and air, the fat content of the food, the exposure duration, the hydrocarbon levels in air and the packaging of the food.

Partition coefficients of hexane, benzene and toluene between various food products and air have been determined (Halek, 1988; Grob, 1990; Kokot-Helbling, 1995). The partition coefficients between food and air were found to be linearly dependent on the fat content of the food, which is due to the high lipophilicity of these hydrocarbons. All hydrocarbons discussed in this survey are highly lipophilic (except MTBE), which is quantitatively illustrated by their high log P_{ow} values (see **Appendix B**).

Migration into foods is slow (Grob, 1990). After equilibration with a concentration of 1 mg/m^3 of benzene or toluene in air for 2 days, the top 5 mm layer of unpacked food products with high fat contents was just saturated to 25-50%. Experiments showed that transport from air to the surface layers of food samples is much faster than that from the surface further into the sample, which means that the sample surface is relatively rapidly saturated and that further uptake from the air is limited by the diffusion within the sample. The diffusion speed in the food sample itself was found to depend on the aggregate state of the food sample: the fastest migration was observed in rape seed oil, whereas diffusion is slowed down in solids or in samples containing fat particles enclosed by water (Grob, 1990).

Packaging of food products by sealed plastic films strongly reduces uptake of hydrocarbons form air (Grob, 1990). For example, after exposure for a period of two weeks, the relative saturation with toluene of a packed chocolate bar was only 7%. However, packed foods are often stored for much longer times than unpacked food products and some packaging materials are a source of hydrocarbon contamination themselves (see **Section 5.2** and **5.5**).

Using partition coefficients for fat and assuming that saturation is reached, Grob et al. calculated that a benzene concentration of 70 µg/m^3 in air would suffice to reach a benzene concentration of 50 µg/kg in fatty food. Similarly, a toluene concentration of only 21 µg/m^3 air would already result in a concentration of 50 µg/kg in fatty food. In practice such levels in air are easily reached. In two petrol service station shops, benzene concentrations were measured to be 11 and 87 µg/m^3 (CONCAWE, 1998) and in houses above small printing plants, toluene concentrations of up to 25 mg/m^3 were reported (Verhoeff, 1987). However, this approach is very theoretical and saturation concentrations in food are unlikely to be reached in practice, because migration and diffusion into food are relatively slow.

7.2. COMPARISON BETWEEN HYDROCARBON LEVELS IN FOOD FROM PETROL STATION SHOPS WITH HYDROCARBON CONTAMINATION OF FOODS FROM OTHER SHOPS

Any comparison between the studies described in this survey regarding hydrocarbon levels in food is hampered by the different methodologies applied. The analytical methods, detection limits, food products analysed (low/high fat content) and packaging of the food products are usually different. Time periods for which the food items analysed have been stored in the shop are unknown. As common contaminants in our environment, hydrocarbons may originate from many sources, which complicates the measurements. It is clear however, that the presence of newspapers and magazines in close proximity to food products may have a major influence on aromatic hydrocarbon levels in food, but more often than not, this important variable is neglected.

Reports about levels of hydrocarbons in foods on sale in 'normal' food shops differ, which makes it difficult to determine a background level against which 'contaminated' food products can be compared. In a MAFF Total Diet Study, average daily intakes of benzene, toluene, o-xylene and m,p-xylene were estimated at 0.5-2.4, 7.0-7.7, 0.9-4.6 and 1.2-4.9 µg/person/day respectively. Some authors mentioned lower estimates, whereas food products analysed in an FDA Total Diet Study generally contained higher levels of aromatic hydrocarbons (see **Chapter 3**). Quantitative data on concentrations of pentane and hexane in food products are scarce and MTBE has only been determined qualitatively in one food item.

The European Union has not set legal limits for the selected hydrocarbons in food. The World Health Organization has derived TDIs only for toluene and xylene (see **Chapter 2**). For a person weighing 60 kg, the Tolerable Daily Intake (via food or drinking water) amounts to 13.4 mg toluene and 10.7 mg xylene. Clearly, these values are much higher than the average daily intakes via food products described in **Chapter 3**.

When the results from the few studies dealing with the analysis of hydrocarbons in foodstuffs on sale in petrol station shops are compared with the hydrocarbon levels reported for food products in 'normal' food shops, there are no significant differences between the levels in food products from these two locations. Only concentrations of aromatic hydrocarbons (primarily benzene and toluene) in food items purchased from shops at petrol stations have been measured. There are no data about levels of pentane, hexane or MTBE in food from petrol station shops.

The MAFF study does not report any significant differences either, in hydrocarbon contamination of foodstuffs between shops situated on busy roads and shops at locations away from hydrocarbon sources. This latter result is contradicted by Stüwe et al., who reported higher levels of hydrocarbons in food sold at shops located on roads with much traffic, than in food from shops in areas with little traffic (Stüwe, 1991).

Müller et al. reported that the level of toluene contamination of food is much higher (up to 10x) if the foodstuffs are stored near newspapers and magazines than in the absence of printed matter, which is supported by the results of Stüwe for aromatic hydrocarbon levels. In fact, storage of food products in close proximity to newspapers and magazines, seems to be the most important source of hydrocarbon contamination of food, bearing in mind that this conclusion is based on only two investigations.

7.3. CONCLUDING REMARKS

On the basis of the literature references described in this survey, the following concluding remarks are made:

- The European Union has not (yet) imposed legal limits to the concentrations of pentane, hexane, benzene, toluene, xylene and MTBE in food. The World Health Organization derived Tolerable Daily Intake values only for toluene and xylene of 223 and 179 µg/kg body weight respectively. Because of its carcinogenicity, WHO did not set a TDI for benzene. For drinking water, the WHO guideline for benzene is 10 µg/l, whereas Directive 98/83/EC sets a tenfold lower limit for benzene in drinking water (1.0 µg/l).

- The British Ministry of Agriculture, Fisheries and Food estimated the average dietary intake for benzene, toluene, o-xylene and m,p-xylene to be 0.5-2.4, 7.0-7.7, 0.9-4.6 and 1.2-4.9 µg/person/day respectively. Other studies found both higher (FDA) and lower values for the average levels of aromatic hydrocarbons in food products, which thwarts an accurate determination of background levels in food. There are very few quantitative data about the levels of pentane and hexane in food and there are no data about the level of MTBE in food products.

- The concentration of (aromatic) hydrocarbons in food increases with the fat content of the food item. This may be different for the ether MTBE, because MTBE is much less lipophilic than the selected hydrocarbons (lower log P_{ow} value).

- There are few studies about the levels of aromatic hydrocarbons in food on sale at petrol station shops and there are no investigations about the concentrations of pentane, hexane and MTBE. For aromatic hydrocarbons, the levels in food products sold at petrol stations shops were not found to be significantly different from the levels in food from other food shops.

- Two studies in which the levels of aromatic hydrocarbons in food sold at newsagents or in shops in which the food products were stored in close proximity to printed matter, were investigated, found enhanced levels of aromatic hydrocarbons in these food products (up to 10x higher toluene levels than in food from shops without newspapers and magazines).

- Two studies concerning analysis of aromatic hydrocarbon levels in food products sold at shops located on busy roads reported contradicting results. An investigation by MAFF did not show any discernible differences with levels in food from shops situated on roads with little traffic, whereas a German survey reports higher concentrations in foods from shops on busy roads.

- A significant source of hydrocarbon contamination of olives is storage in a relatively small room together with gasoline-driven engines. These storage conditions may lead to high levels of hydrocarbons in olives.

- Other investigated sources of hydrocarbon contamination of food (e.g. packaging materials, cookware, food additives) do not cause greatly enhanced levels of hydrocarbons in food. In some cases (thermoset polyester cookware and food additives), the manufacturers have reformulated their products to minimise formation of benzene.

- Consumption of food is not an important pathway for exposure to benzene, accounting for at most 2.5% of the total average daily intake of benzene. The vast majority of human exposure to benzene is caused by inhalation of contaminated air. Smoking increases a person's benzene exposure by a factor 6-10.

7.4. CONCLUSION

This report identifies a number of factors which might contribute to the presence of selected hydrocarbons in food. The concentrations vary, but the limited data available indicate that the levels of hydrocarbons in food sold by petrol stations shops are comparable to those found in food purchased from other shops.

8. REFERENCES

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APPENDIX A

LIST OF ABBREVIATIONS

API	American Petroleum Institute (US)
EPA	Environmental Protection Agency (US)
FDA	Food and Drug Administration (US)
FID	Flame Ionisation Detection
GC	Gas Chromatography
LOAEL	Lowest-Observed-Adverse-Effect-Level
LOQ	Limit of Quantitation
MAFF	Ministry of Agriculture, Fisheries and Food (UK)
MS	Mass Spectrometry
MTBE	Methyl-t-butyl ether (2-methoxy-2-methylpropane)
NOAEL	No-Observed-Adverse-Effect-Level
NRC	National Research Council (US)
PET	Poly(ethylene terephtalate)
PID	Photo Ionisation Detection
PTFE	Poly(tetrafluoro ethylene)
SCF	Scientific Committee on Food (EU)
TDI	Tolerable Daily Intake
UV	Ultraviolet
VOC	Volatile Organic Compounds
WHO	World Health Organisation
ZDF	Zweites Deutsches Fernsehen

APPENDIX B

PHYSICAL CONSTANTS OF SELECTED ORGANIC COMPOUNDS

compound	**pentane**	**hexane**	**benzene**	**toluene**	**o-xylene**	**m-xylene**	**p-xylene**	**MTBE**
formula	C_5H_{12}	C_6H_{14}	C_6H_6	C_7H_8	C_8H_{10}	C_8H_{10}	C_8H_{10}	$C_{15}H_{12}O$
molecular weight	72.15	86.18	78.11	92.14	106.17	106.17	106.17	88.15
boiling point (°C)	36.1	69	80.1	110.6	144.4	139.1	138.3	55.2
density (g/cm^3)	0.6262	0.6603	0.8765	0.8669	0.8802	0.8642	0.8611	0.7405
log P_{ow}	3.4	3.9	2.1	2.7	3.1	3.2	3.2	0.9