

INDOOR/OUTDOOR AIR QUALITY FACTORS WITH RESPECT TO VOC EMISSIONS FROM VEHICLES

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ABSTRACT

The last decade has seen significant change in vehicle emission legislation, particularly in countries that are highly industrialized. Such changes, from the hydrocarbon emission standpoint have been regulated by measurement of total and non methane hydrocarbon levels with little attention being given to specific hydrocarbons (VOCs), despite significant changes in fuel composition and refinery practice. The air quality situation however, often differs in developing countries where refinery practice is less complex and wider use is made of aromatics in compensating for lead reductions in fuel. In those countries where the very nature of urban dwelling indicates that indoor air quality is significantly affected by vehicle emissions, these indoor/outdoor air quality relationships are reviewed with reference to VOC air quality data monitored in London.

INTRODUCTION

Variation in resources have inevitably led to differences in refinery capability between countries and together with the moves to eliminate lead in gasoline have resulted in significant changes in fuel compositions. Such changes could lead to an increase in emissions of VOCs from vehicles, particularly from those not fitted with catalytic converters or other control equipment. This would result in a deterioration in outdoor air quality which in turn could lead to indoor air quality problems in poorly ventilated buildings in urban areas. The objectives of this survey therefore, were to set out the changes in fuel compositions and refinery practice and to study the relationship between indoor and outdoor air quality.

SOURCES OF VOC EMISSIONS

The pie chart in figure 1 shows the contributions to man-made hydrocarbon emissions in western Europe (1). Solvents are the largest single source, producing approximately 4Mt/yr (40%). Total vehicle and refinery related emissions are approximately 4.2 Mt/yr (2).

Thus, vehicle related emissions are a significant source of polluting hydrocarbons, representing approximately 40% of the 10 million tonnes of hydrocarbons released annually within western Europe (2). In other areas of the world these figures will not be identical, but it is likely that vehicle related emissions will contribute a large proportion of hydrocarbon emissions in countries which have a large car population, and few emission controls. Diesel fuelled vehicles contribute towards exhaust emissions of VOCs but are a negligible source of evaporative emissions. In total the gasoline sector is responsible for approximately 37% of total emissions, i.e the majority of vehicle emissions (2).

Within the EEC (European Economic Community) there is proposed legislation to attempt to control all vehicle related emissions, including distribution and refuelling

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operations, as well as exhaust and evaporative emissions (1). This, however, will take some years to implement and many more before the majority of vehicles have effective control equipment. Vehicle related hydrocarbon emissions are therefore likely to remain significant well into the next decade.

This situation is exacerbated in countries within the developing world which are not at a stage whereby such high technology controls could be introduced in vehicles and refining. To do so would require substantial investment in vehicle emission control technologies and changes in fuel composition.

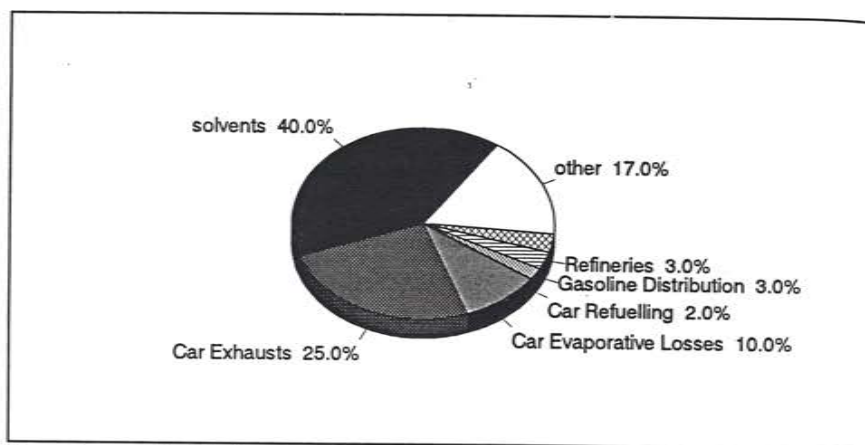


Figure 1 Contributions to man-made hydrocarbon emissions in Western Europe (1)

REFINERY PRACTICE AND GASOLINE COMPOSITION

Gasolines are made up of a wide range of components, each with different physical and chemical properties that affect the two crucial variables in gasoline blending; octane number and volatility. Refinery capability is therefore crucial to optimise the blend, the more flexibility the refineries can offer the easier it will be to change gasoline composition without impairing air quality.

In attempting to eliminate lead additives from gasoline, other blending components have been substituted in order to maintain octane ratings. Different countries have used varying approaches and this has affected vehicle emissions. One of the main alternatives to lead alkyls is the addition of reformate. This is a high octane product of catalytic reforming plants installed in many refineries that is high in aromatic compounds. In Western Europe countries that have used increased reformate, such as in Benelux and Scandinavia, they have produced gasolines with very high levels of aromatic compounds.

Figure 2 shows the relatively high level of aromatics present in West German gasolines, where reformate is the main octane blending component, in comparison to other European gasolines. Great Britain, for example, has adopted the use of light hydrocarbon components to maintain octane ratings and consequently produces fuels with a significantly lower aromatic content (4), but with a higher olefin content.

High levels of aromatic compounds in fuels have been shown to produce emissions containing VOCs, for example high benzene contents in gasolines produce elevated benzene

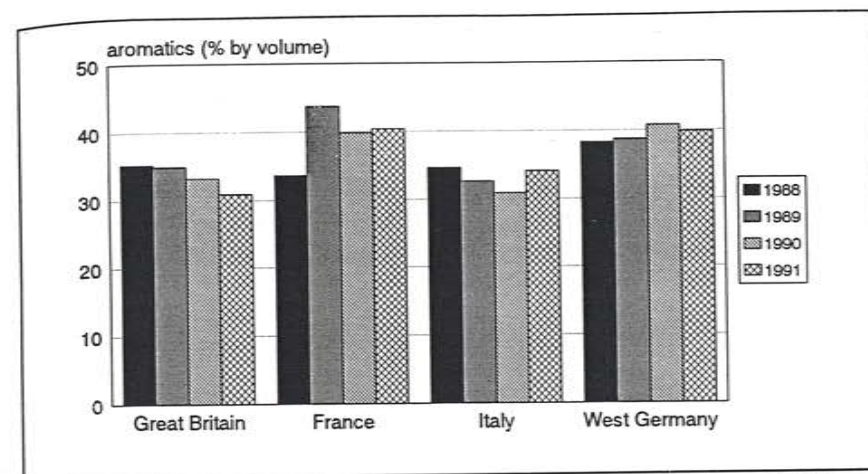


Figure 2 Aromatic hydrocarbon content of Western European gasolines - total leaded and unleaded gasolines (3)

emissions (5-7). Table 1 summarises the trends in fuel composition and the probable effects on vehicle emissions.

The use of fuels containing high levels of aromatic hydrocarbons is only a significant concern in countries which do not utilise catalytic converters on cars. In the US all cars are fitted with catalytic converters which will remove the majority of VOCs from exhaust emissions. In West Germany a large proportion of cars are fitted with similar devices and they are being introduced in most other European countries. It is in the rest of the world and in the developing world in particular, where catalytic converters are not being used and are unlikely to be introduced in the foreseeable future, that use of such fuels is a major problem.

Many VOCs found in vehicle emissions such as benzene and PAH (Poly aromatic hydrocarbons) have long been established as carcinogenic or mutagenic (8). Long term exposure to benzene is implicated in leukaemia and the PAH benzo-a-pyrene in lung cancer(3). Toluene and xylene are currently not thought to be as carcinogenic as benzene, but are sources for irritant decomposition products after photochemical reactions and may have other health effects (7,8). The use of aromatic hydrocarbon rich fuels will have a significant health effect in countries not utilising catalytic converters or other exhaust emission controls.

Table 1 Summary of probable results of changes in fuel composition for non - catalyst equipped vehicles (5-7,9,10)

Increased	HC	CO	NOx	Aldehydes	Aromatics	Benzene	Evaporative
reformate	▲	▲	▲	▼	▲	▲	-
MTBE	▼	▼	▼	▲	-	-	▲
isomate	▼	▼	▼	-	-	-	-
RVP	-	-	-	-	-	-	▲
reduced lead	▲	-	-	-	▲	▲	-

High octane fuels which are low in aromatics can be generated by alkylation and isomerism processes or by the use of oxygenates. Alkylation and isomerism plants require high level of investment at the refinery and result in increases in energy consumption and a reduction in product yield. Oxygenates, although reducing hydrocarbon and CO emissions (9,10) are expensive and there is evidence that their use produces more oxides of nitrogen and traces of aldehydes in exhaust emissions. They are being increasingly used in many countries but there is a limit to their availability.

The other main variable in gasoline quality, i.e. its volatility, is also affected by changes in gasoline composition. In Great Britain the use of light hydrocarbons, predominantly butanes, has resulted in very high vapour pressures (4), increasing fuel volatility and resulting in increased evaporative losses.

INDOOR/OUTDOOR AIR QUALITY RELATIONSHIPS

Methods

In order to examine the relationships between indoor and outdoor air two sites adjacent to a moderately busy road in London, UK, were examined during June 1991. At the first site, located 5m from the roadside, outdoor air quality was monitored for transport related VOCs. The second site, in an office overlooking the road, was located 25m further back from the roadside site, at which the same VOCs were monitored (11).

Outdoor VOCs were sampled for 25 minutes every hour using an auto-TCT injector (Chrompack UK Ltd) and were analysed using a Chrompack CP9000 chromatograph fitted with a 25m Poraplot U column and a flame ionisation detector (programme: 50°C for 2 minutes, 15°C/min to 200°C, 200°C for 28 minutes).

Indoor VOCs were analysed by a thermal desorption procedure. Sample air was drawn through stainless steel sampling tubes (89mm x 5mm i.d.) packed with 200mg of Tennax-TA, 60-80 mesh (Chrompack UK Ltd) for 55 minutes. The tubes were thermally desorbed at 250°C for 15 minutes using a Perkin elmer ADT-50, which was coupled to a Perkin Elmer 8320 gas chromatograph fitted with a CPSIL-8 column and an ion trap detector (programme: 42°C for 7 minutes, 5°C/min to 90°C, 20°C/min to 150°C, 30°C/min to 275°C, 275°C for 6 minutes).

The two methods showed agreement to within 10% in a previous study.

Results

It can be seen from table 2 that a significant amount of VOCs have infiltrated from the outdoor environment into indoor air during the summer. Concentrations of these compounds were high, highlighting the significant contribution outdoor pollutants, particularly from vehicles, make to indoor air quality.

All the VOCs measured showed higher concentrations outdoors as would be expected with the main source being attributable to vehicles and using an office without strong indoor VOC sources which might be associated with recent refurbishment.

Infiltration exhibited a strong dependence on meteorological conditions, but there were some indications that VOC volatility was also a controlling factor.

This data supports the concerns discussed in the earlier sections that changes in fuel compositions, particularly in countries which do not adopt measures to reduce VOC emissions from vehicles, will result in a significant deterioration in both outdoor and indoor air quality.

Table 2. Summary of the air quality survey conducted in London during June 1991 (11)

Pollutant ($\mu\text{g}/\text{m}^3$)	Site	Mean	S.D.	% of outdoor value
Benzene	outdoor	48.0	29.0	68
	indoor	38.0	15.3	
Toluene	outdoor	35.4	17.1	68
	indoor	24.0	8.8	
Ethylbenzene	outdoor	7.2	4.1	65
	indoor	4.7	1.3	
m+p-Xylene	outdoor	23.2	11.4	61
	indoor	14.1	5.3	
o-Xylene	outdoor	8.8	3.6	61
	indoor	5.4	1.7	
1,3,5-Trimethylbenzene	outdoor	3.6	1.8	53
	indoor	1.9	0.5	
1,2,4-Trimethylbenzene	outdoor	10.7	4.7	58
	indoor	6.2	1.7	

DISCUSSION

VOCs in the urban environment can be attributed to two main sources, solvents and vehicle related emissions, with vehicles contributing approximately 40% of man made hydrocarbon emissions. There is growing concern that unregulated VOCs produced by vehicles are contributing to a deterioration in urban air quality, particularly following the recent changes in gasoline compositions. In countries that do not fit catalytic converters to vehicles, such changes in fuel compositions can result in increased levels of aromatic hydrocarbons, olefins, aldehydes etc in outdoor air, depending upon refinery practice.

The survey data have shown that there is considerable outdoor pollution by VOCs in London during the summer and that a large percentage of these infiltrate into indoor air in naturally ventilated homes and offices. Given these high infiltration rates and the carcinogenic properties of these compounds, there is considerable cause for concern.

In developing countries or those that are unlikely to be able to introduce stringent vehicle emission controls, or place considerable investment in new refining processes, alternative strategies will have to be sought to prevent future impairment of indoor and outdoor air quality. Such steps could, for example, include a delay in reducing lead levels of gasolines until adequate emission controls can be introduced.

Clearly indoor/outdoor interactions are a significant factor in indoor air quality and control of outdoor emissions is a vital component in any strategy to improve the quality of indoor air.

CONCLUSIONS

- Despite significant changes in vehicle emission legislation little attention has been paid so far to individual VOCs.
- Differences in refinery practice produce a wide range of fuel compositions with distinct emission characteristics.
- Following the steps to eliminate lead from gasolines in developed countries, fuel compositions have changed significantly. In many countries where catalytic converters are not used, the use of gasoline components with high aromatic hydrocarbon contents has resulted in an increase in VOC emissions.
- In developing countries, where refineries do not have the capability to produce alternative fuel blending components, premature steps to reduce lead from gasoline could lead to increased VOC pollution of outdoor air.
- The survey of indoor and outdoor air in London has shown that a large percentage of VOCs in the outdoor environment infiltrate into indoor air. Any increases in VOC emissions by vehicle related sources in the urban environment will therefore lead to a deterioration in indoor air quality.

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