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VOLATILE ORGANIC COMPOUNDS (VOCs) IN NEW CAR INTERIORS

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Summary

The types of VOCs and their concentrations have been determined in new cars from three different manufacturers, from their purchase on the Australian market to approximately two years later. Total VOC (TVOC) concentrations were initially very high (up to 64,000 μg/m^3) in two locally made cars which reached the market one to two months after manufacture. Such TVOC levels have been associated with sensory irritation and impairment of performance and memory in controlled exposure studies. These levels decreased approximately seven-fold in the first month, but still exceeded the NHMRC indoor air goal. The VOCs consisted mostly of substituted benzene compounds and alkanes, as well as some polar compounds. The third car was imported (reaching the market four months after manufacture) and the initial TVOC concentration was 2000 μg/m^3. Decays of car VOC concentrations occurred by an exponential process, with TVOC concentrations decreasing by approximately 20% per week after manufacture.

Keywords: Volatile organic compound (VOC), total VOC (TVOC), car, benzene, interior materials.

1. Background

1.1. VOCs in indoor air

There have been many studies of the types and levels of VOCs in established and new buildings in developed countries, summarised in recent reviews (Brown *et al*. 1994; Brown 1999). It has been commonly found that 100 or more VOCs can be detected in buildings, covering most compound types such as alkanes, aromatics, aldehydes, ketones and ethers. In established buildings, individual VOCs were generally at concentrations below 50 μg/m^3, with most below 5 μg/m^3. A measure of the total VOC (TVOC) quantity, total VOC (TVOC) defined as all VOCs in the boiling point range of 50–260°C (WHO 1989), had a mean of 200–1,100 μg/m^3, reflecting the large number of VOCs present. VOC concentrations were much higher in new buildings, with TVOC concentrations up to 20,000–40,000 μg/m^3 occurring in extreme cases. Recent measurements in some established and new Australian buildings (Brown 2000) have been consistent with these past findings.

1.2. VOC health effects and goals

The health significance of these levels of VOCs is an area of ongoing research. Much of this has focussed around the significance of TVOC exposures, since this appears related to occupant illnesses, such as effects seen in ‘sick building syndrome’, at levels much below those expected to cause illness in occupational exposures.

Controlled exposures of human subjects to a 22-compound mixture at TVOC concentrations of 7,000–33,000 μg/m^3 have observed effects within minutes, such as subjective reactions (odour, discomfort, drowsiness, fatigue/confusion), eye/nose/throat irritation, headache, and (in symptomatic subjects) neurobehavioural impairment. The consensus from the European Commission (1997) working group was that while effects were likely to increase with increasing TVOC, thresholds could not yet be established based on available data. However, it concluded that only sensory effects were likely at concentrations up to 25,000 μg/m^3, while other health effects became of greater concern above this level.

In Australia, the NHMRC (1992) recommended the following indoor air goals:

- TVOC not to exceed 500 μg/m3 (1-hour average); and
- any VOC not to exceed 250 μg/m^3 (1-hour average).

If these goals were exceeded, it recommended that the ventilation rate to the space be increased or the source of the pollutants be identified and reduced.

1.3. VOCs in car interiors

There have been several investigations into automobile exhaust-related VOCs in car interiors (reviewed in Brown 1999), particularly benzene. These have found car interior benzene concentrations ranging from 10–20 μg/m^3 during freeway travel, to 150 μg/m^3 in heavy urban traffic. An Australian study by Duffy and Nelson (1996) was consistent with these findings. An environmental goal for benzene has been recommended by the UK Health and Safety Executive as 5 ppb (16 μg/m^3) as a one-year average. The impact of car travel to this goal needs to consider the amount of time populations spend in heavy traffic.

Investigation into VOCs in new cars has been limited. Bauhof and Wensing (1999) described a standardised test procedure used in Germany in which car interior VOC concentrations were measured at 23–65°C. TVOC concentrations of 35,000–120,000 μg/m^3 were reported for six new cars (test temperature not specified), these concentrations decreasing exponentially over a 40-day period to about 10,000–30,000 μg/m^3. VOCs consisted of aromatics, glycol ethers and esters, aldehydes, ketones and amines. Grabbs *et al*. (1999) screened four new cars in the USA. Three exhibited initial TVOC concentrations of 300–600 μg/m^3 and the fourth 7500 μg/m^3. The latter decreased exponentially by about 90% within three weeks.

2. Experimental Methods

2.1. Cars

Three new cars were evaluated from within three days of delivery to the purchaser. All were parked outdoors and were cleaned infrequently and never within a week of air sampling. The age of each car was measured from the middle of the month marked on compliance plates. One was fully imported and the others were locally made, and this was the major influence on the starting age of the cars for assessment.

2.2. Car test protocol

A consistent test protocol was utilised with the cars when sampling the interior air. This protocol was as follows:

(a) The car was moved to a shaded area for the test duration.

(b) It was aired by open windows for approximately 30 minutes before being closed up – doors, windows and vent closed.

(c) it was left closed for two to three hours, assuming it would reach a steady state pollutant concentration in this period.

(d) Air samples were collected at head height in the front of the car and concurrently outside the car at approximately 3–5 m away.

(e) Temperature and humidity outside the car were recorded.

A summary of the cars tested and protocol conditions is presented in Table 1.

2.3. Air sampling and analysis

Air sampling was by active sampling using controlled flow pumps at 100–200 mL/minute onto mixed sorbent tubes containing Tenax TA, Ambersorb and activated charcoal. Sample volumes were 0.2–5 L, with the lower volume being used for initial measurements of high concentrations in some cars.

Sorbent tubes were thermally desorbed at 280°C into a GC/FID/MS, with a DB5 column and programmed from 2–240°C. Compounds were identified by MS and quantified by FID, calibrated for each VOC relative to an internal standard of fluorobenzene (injected onto each sample tube). TVOC was estimated from the sum of all FID peaks eluting after 5 minutes (includes pentane and ethanol, but excludes methanol), expressed using the toluene calibration.

3. Results

Summaries of analytical results for the three cars are presented in Tables 2–4. Generally about 30–40 VOCs were identified in the air samples, but only the more dominant or toxic VOCs are presented here.

3.1. Types and quantities of VOCs

Air samples from Cars 2 and 3 contained mainly substituted benzenes and alkanes, initially at TVOC concentration of 20,000–64,000 μg/m^3. Car 1 also contained these types of VOCs plus several alcohols/ethers, indicating different source materials in this imported car. Car 1 exhibited much lower TVOC concentrations, although it is probable that the low TVOC concentration was the result of the long period (16 weeks) to reach the market, while the high TVOC concentration in Car 3 resulted from the short period (3 weeks) to market.

Overall, the more dominant VOCs found in the new cars (highest to lowest concentrations) were toluene, acetone/pentane, o-xylene/styrene, 1,2,4-trimethylbenzene, m,p-xylene, various $C_{7–12}$ alkanes, ethylbenzene, n-hexane and ethylene glycol butyl ether.

Table 1. Car descriptions and conditions of testing

Car number	Country of manufacture	Month/year of manufacture	Test conditions			
			Age (weeks)	Odometer (K)	T (C)	RH (%)
1	Korea	2/98	16–30	200–3500	13–14	50–80
2	Australia	4/98	10–98	20–27,000	12–20	40–80
3	Australia	7/98	3–91	40–27,000	14–20	40–80

Table 2. VOC measurements in Car 1

VOC	Concentrations (μg/m^3 at 0°C/101 kPa)			
	Car: 16 weeks	Car: 24 weeks	Car: 30 weeks	Outdoor: 16–30 weeks
Acetone + n-pentane	26	18	100	6.0
n-Hexane + MEK	10	6.1	37	<1
Benzene	10	6.5	21	3.0
MIBK	4.0	6.2	14	<1
Toluene	50	32	57	6.3
m+p-Xylene	31	23	37	2.3
Styrene + o-xylene	22	15	23	1.7
Ethylene glycol butyl ether	220	39	39	<1
1,2,4-Trimethylbenzene	34	18	20	0.6
n-Undecane	110	61	73	<1
n-Decane	57	42	60	<1
2-Propylheptanol	29	16	15	<1
n-Dodecane	85	42	44	<1
Other VOCs	<50	<30	<30	<1
TVOC	2100	1500	1800	180

Table 3. VOC measurements in Car 2

VOC	Concentrations (μg/m^3 at 0°C/101 kPa)				
	Car: 10 weeks	Car: 14 weeks	Car: 22 weeks	Car: 115 weeks	Outdoor: 10–115 weeks
Acetone + n-pentane	100	240	180	36	7.5
n-Hexane + MEK	7.4	14	6.0	3.3	<1
Benzene	5.5	20	3.6	12	1.3
Toluene	78	58	21	37	4.0
n-Octane	120	3.1	1.5	0.7	<1
Ethylbenzene	140	7.9	3.6	0.9	<1
m+p-Xylene	220	48	20	20	<1
Styrene + o-xylene	280	51	12	12	2.4
Cyclohexanone	1300	22	12	<3	1.1
Alkene (C_{10})	480	35	11	7.5	<1
n-Decane	880	160	25	21	<1
1,2,4-Trimethylbenzene	1600	100	37	20	1.3
n-Undecane	520	140	45	2.8	<1
Other VOCs	<470	<50	<30	<15	<1
TVOC	20,000	3300	1500	390	50

Table 4. VOC measurements in Car 3

VOC	Concentrations (μg/m^3 at 0°C/101 kPa)			
	Car: 3 weeks	Car: 9 weeks	Car: 95 weeks	Outdoor: 9–95 weeks
Acetone + n-pentane	3700	1000	21	10
n-Hexane + MEK	500	34	5.7	<1
Benzene	84	26	20	2.4
n-Heptane	740	17	1.1	<1
Methylcyclohexane	630	22	0.7	<1
MIBK	590	43	4.1	<1
Toluene	9500	450	57	13
n-Octane	890	35	0.9	<1
Ethylbenzene	880	56	7.5	1.4
m+p-Xylene	2900	230	30	5.5
Styrene + o-xylene	2000	430	16	1.4
Alkene (C_{10})	1300	130	2.0	<1
n-Decane	3600	610	7.2	1.2
1,2,4-Trimethylbenzene	400	130	15	2.2
n-Undecane	870	310	4.6	<1
Other VOCs	<850	<190	<7	<1
TVOC	64,000	9500	410	100

Bauhof and Wensing (1999) reported fewer alkanes and greater numbers of polar VOCs in German cars.

Much greater concentrations were observed in the cars than outdoors, and so clearly the VOCs were emitted from the car interiors. Benzene concentrations in the cars varied from 4–84 μg/m^3, while outdoor levels were <1–7 μg/m^3. It is unknown if the benzene was emitted from the interior materials of the cars or from leaks from the petrol tanks into the car interior. It is feasible that both factors occurred in Car 3 since the benzene concentration in that car exhibited a large decrease from time of manufacture, similar to that observed for TVOC, and after 95 weeks was still much in excess of outdoor concentrations.

3.2. Toxicity of car VOCs

Benzene is a category 1 IARC carcinogen (known human carcinogen) for which an annual exposure goal of 16 μg/m^3 has been recommended (see Section 1.3). Since urban populations spend an average of one hour per day in car travel (Newton *et al*. 2000), these results indicate that car interiors can be contributors to total exposure to benzene.

Few environmental exposure goals are established for other VOCs. The NHMRC goal of 250 μg/m^3 for any compound was exceeded for many VOCs in Cars 2 and 3. Toxic effects of some of these VOCs and ambient air goals (μg/m^3) based on these effects (Calabrese & Kenyon 1991) are:

- acetone – mucosal irritation (8-hour goal, 39,000);
- cyclohexanone – possible human carcinogen (annual goal, 160);
- ethylbenzene – systemic toxin (24-hour goal, 140);
- MIBK – systemic toxin (8-hour goal, 530);
- n-hexane – neurotoxin (24-hour goal, 530);
- styrene – probable human carcinogen (annual goal, 29);
- toluene – central nervous system dysfunction (8-hour goal, 1500); and
- xylene isomers – foetal development toxins (24-hour goals: o-xylene 310, m-xylene 3100, p-xylene 61).

It is seen that several of these goals were exceeded in the cars for several weeks after manufacture.

TVOC concentrations also occurred at levels that may affect occupants (see Section 1.2) for weeks to months after car purchase, although not for years. The effects that could be caused by this TVOC exposure include eye irritation, and performance and memory factors, all of which may be important car safety issues, as well as occupant health and comfort issues.

3.3. VOC persistance in new cars

Overall, the VOC concentrations in the cars are seen to decrease with time from manufacture, especially for Cars 2 and 3. The rate of this decrease was estimated for TVOC concentrations by combining the data for all cars. The combined data exhibited good fit to an exponential decay curve, as presented in Figure 1, with a decay rate constant of 0.23 weeks^{-1}. Thus, the TVOC concentrations in new cars is estimated to decrease by a proportion of $e^{-0.23}$ each week, i.e. a decrease of approximately 20% each week. An overview of the data in Figure 1 shows that the NHMRC TVOC goal will be

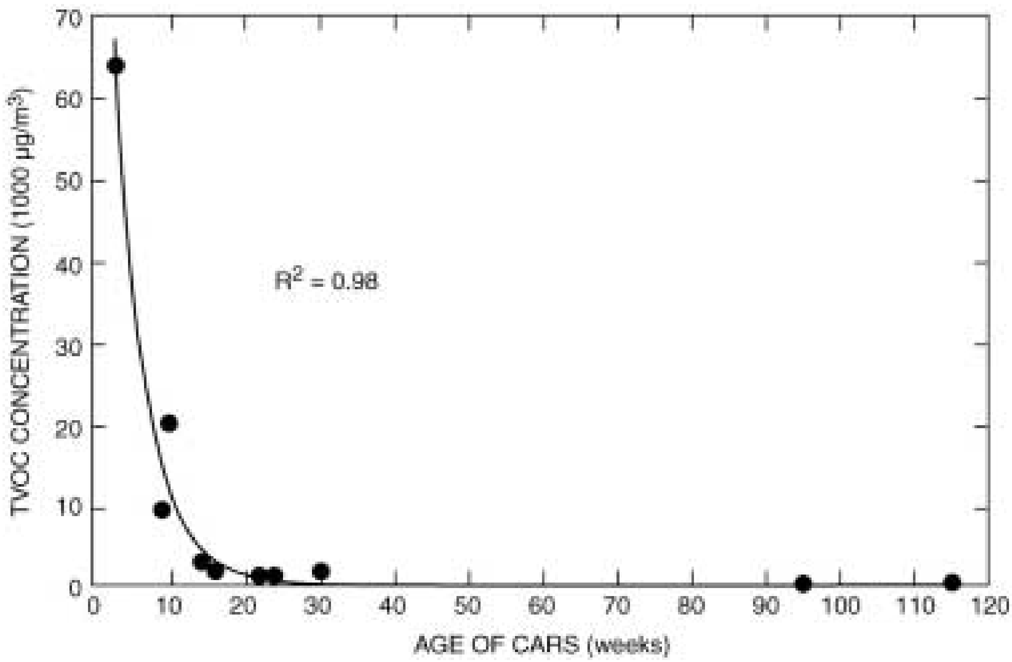

Figure 1.

reached in approximately 24 weeks or 6 months, showing that the pollution of the new car interiors is a transient event to some extent. However, it is clear from long-term measurements in Cars 2 and 3 that after the VOCs from the car interior have depleted, VOCs associated with small fuel tank leaks may be present.

4. Conclusions

High concentrations of VOCs were found in new cars, especially those reaching the market soon after manufacture, i.e with minimum path-to-market. The total VOC (TVOC) levels found have been observed previously to cause sensory irritation and performance and memory impairments to human subjects, showing that the pollution of new car interiors may be a safety issue. Several of the VOCs observed have potential toxic effects, an aspect that should be explored in further study. The decay of TVOC concentrations was found to be exponential, at approximately 20% per week, with the NHMRC indoor air goal being reached after approximately 6 months.

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