Flame retardants in the indoor environment. Part V: Measurement and exposure evaluation of organophosphate esters from automobile interiors

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ABSTRACT
Organophosphate esters are frequently applied as flame retardants in building products and other materials for indoor use. Using as example automobile interiors, the present study deals with the sampling, analysis procedures and assessment of this group of substances. Within the framework of standardized test stand investigations it was determined that for eight new vehicles clearly measurable concentrations of organophosphate esters can be present in the indoor air of the vehicle particularly at extreme climatic boundary conditions (air temperature 65°C; air exchange around 1 h^{-1}). However, under travelling conditions from the beginning no relevant concentration of organophosphate esters could be demonstrated due to the occurrence of high air exchange rates. The concentrations of organophosphate esters arising during travelling were all below the recommended guideline value for indoor rooms of 5 $\mu g/m^3$ by at least a factor of 10.

INDEX TERMS
Flame retardant; Exposure assessment; Automobile; Emission; Organophosphate ester

INTRODUCTION
Within the framework of preventative fire protection, flame retardants are often added to plastics to minimize the risk of a fire starting. The range of products used for flame retardants is wide ranging (WHO, 1997). The material property of the flame-retarding effect of plastic materials in the individual case depends on the flame retardant used and is based on preventing inflammation, hindering ignition or making combustion of the materials to be protected more difficult. An important class of flame retardants is the organophosphate esters. The original compounds (Carlsson *et al.*, 1997, 2000; Pardemann *et al.*, 2000; Pardemann and Wensing, 2003) and their decomposition products (Salthammer *et al.*, 2003) can be emitted to the environment from products under normal living conditions. Exposure of residents to flame retardants mainly results from accumulation in household dust and indoor air (Salthammer and Wensing, 2002). Some agents of these compound classes are suspected of causing adverse health effects. The German Federal Environmental Agency has published a literature survey on toxicological properties of flame retardants with the aim of substituting hazardous compounds (Umweltbundesamt, 2000). The present paper deals with organophosphate esters in automobile interiors. These flame retardants were determined within the framework of standardized test stand investigations together with measurements taken on the move. The toxicological assessment of the emissions is carried out using indoor air guideline values on the basis of utilization simulations.

METHODS
The passenger compartments of eight new vehicles (V-1–V-6 and V-8, V-9) were investigated for the emission of organophosphate esters on a special automobile test stand for

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indoor air investigations under standardized boundary conditions both at room temperature (RT; approx. 20°C) and in a heated-up state. The heating up of the vehicle interiors was carried out using a controlled heat radiator. Figure 1 shows the measured temperature profiles for various measuring points. During the test the vehicles were flushed with ultrapure nitrogen (volume flow 0.6 m^3/h, 23°C, 50% relative humidity). A detailed description of the test stand—Figure 2—can be found in Bauhof and Wensing (1999). An approximately 9-month-old used vehicle (V-7) was also tested. This vehicle was initially left outside in the sun for a number of hours. At an outside temperature of around 26°C the interior temperature, as measured between the front head restraints, increased to around 48°C. A first air sample was carried out under these boundary conditions in the stationary vehicle. Then, the vehicle was driven for 30 min. A second air sample was taken over the complete duration of the test drive. At medium ventilation settings the indoor temperature was kept at 20°C using the air conditioning control. Vehicle V-9 was also tested for organophosphate esters during a test journey immediately after the test stand investigation. For the investigations at the test stand the air sampling was carried out using a glass probe introduced into the vehicle's interior between the two front head restraints. For the air sampling during the test journeys the sampling point was located between the two front seats.

The collecting phase used was an XAD-2 (500 mg) specially cleaned using various solvents (acetone, methanol, dichloromethane) with upstream glass wool. The following sampling conditions were observed: 30–500 l total volume at a flow rate of 2 l/min. The quantitative assessment of the organophosphates was carried out using solvent desorption (dichloromethane) and GC/MS evaluation (DB 1701, HP 5890/HP 5989A) using original standard solutions (Aldrich), by applying the method of internal standard ($^{13}C_{12}$-DDE) in SIM mode (Pardemann and Wensing, 2003).

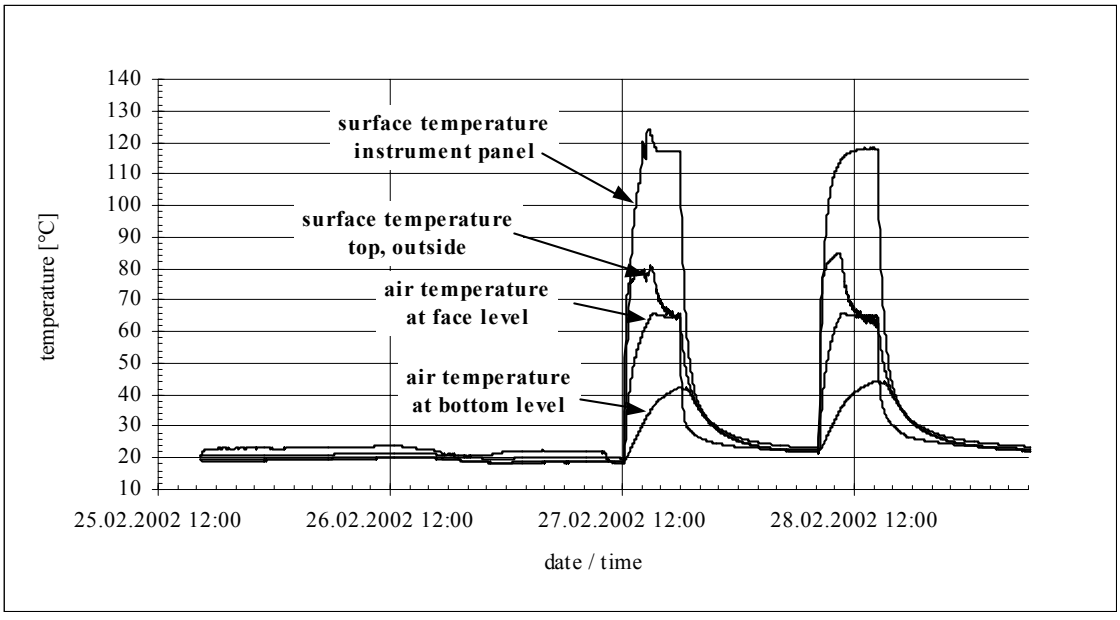
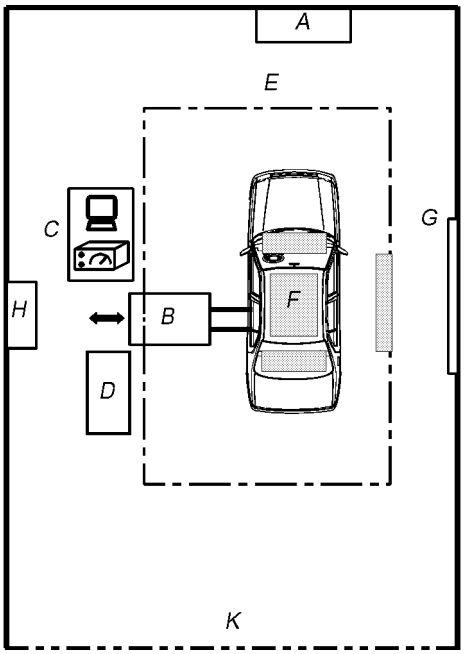


Figure 1 Temperature profiles of various measuring points during the test stand investigations with two heating phases at an air temperature of 65°C.



A: Gas supply

B: Movable carrier wagon with boom for probes and standard interface

C: Instruments and electronic data processing

D: Sampling devices

E: Mobile fastening rack for radiation heaters

F: Four fields of radiation heaters

G: Sockets of electrical supply for heaters

H: Semi-automatic controls for the electrical radiation heaters

K: Entrance gate for the test vehicle

Figure 2 Diagram of the test stand for automobile interior investigations.

RESULTS

Table 1 shows the concentration ranges of organophosphate esters that were measured under test stand conditions at RT and 65°C in the indoor air of the eight different new vehicles from different manufacturers. The influence of the temperature on the release of the organophosphate esters can be clearly seen here. Whereas at RT the individual compounds could either not be detected or were clearly below 1 µg/m^3, at 65°C comparably higher concentrations were measured. The highest concentration at RT was measured at 0.48 µg/m^3 for the substance TCPP. In the heated-up state (65°C), the highest concentrations measured were for TCPP (11.1 µg/m^3) and TDCPP (8.64 µg/m^3).

Table 1 Organophosphate esters used as flame retardants, chemical name, synonym and concentration ranges (µg/m^3) for RT and 65°C

Chemical name	Synonym	Concentration, RT (µg/m^3)	Concentration, 65°C (µg/m^3)
Tributyl phosphate	TBP	<0.01–0.15	0.16–2.18
Tris(2-butoxyethyl) phosphate	TBEP	<0.01–<0.05	<0.05–0.69
Tris(2-ethylhexyl) phosphate	TEHP	<0.01–0.09	<0.01–0.19
Triphenyl phosphate	TPP	<0.01–0.09	<0.01–2.23
Tricresyl phosphate	TCP	<0.01–<0.05	<0.01–<0.05
Tris(2-chloroethyl) phosphate	TCEP	<0.01–<0.05	<0.01–0.10
Tris(chloropropyl) phosphate	TCPP	<0.01–0.48	0.07–11.1
Tris(2,3-dichloro-1-propyl)phosphate	TDCPP	< 0.01 – 0.20	0.07 – 8.64

Table 2 shows the concentration values of the organophosphate esters in the stationary vehicle and during the test journey for vehicle V-7, which was around 9-months old at the time of the sampling. In stationary state the comparably highest concentration of 1.7 $\mu g/m^3$ was measured for compound TCPP. Further positive results were found for TBP (0.4 $\mu g/m^3$), TPP (0.4 $\mu g/m^3$) and TCEP (0.1 $\mu g/m^3$). Compounds TBEP, TEHP, TCP and TDCPP could not be determined in the stationary vehicle. During the half-hour journey at medium ventilation setting the concentrations of all compounds were below the detection limit (0.2 $\mu g/m^3$). Table 2 also contains the results for vehicle V-9, which was initially measured under standard conditions at RT and 65°C on the test stand and then driven immediately afterwards. The highest concentration of organophosphate esters was for compound TDCPP with 8.64 $\mu g/m^3$ at 65°C on the test stand. With the measurements taken during the test journey low concentrations of TBP (0.49 $\mu g/m^3$) and TDCPP (0.47 $\mu g/m^3$) could only be measured in the first 12 min. During the further progression of the journey it could be confirmed within a matter of minutes, as with vehicle V-7, that no organophosphate esters were detectable in the indoor air.

Table 2 Organophosphate esters used as flame retardants, synonym and concentration ($\mu g/m^3$) for vehicles V-7 (stationary; travelling) and V-9 (test stand and travelling)

Synonym	V-7 #1[a] 48°C[h] ($\mu g/m^3$)	V-7 #2[b] 20°C[h] ($\mu g/m^3$)	V-9 #1[c] RT[h] ($\mu g/m^3$)	V-9 #2[d] 65°C[h] ($\mu g/m^3$)	V-9 #3[e] 65°C[h] ($\mu g/m^3$)	V-9 #4[f] 50°C[h] ($\mu g/m^3$)	V-9 #5[g] 40°C[h] ($\mu g/m^3$)
TBP	0.4	<0.2	0.02	1.83	0.49	<0.53	<0.34
TBEP	<0.1	<0.2	<0.01	0.26	<0.39	<0.53	<0.34
TEHP	<0.1	<0.2	0.09	0.43	<0.39	<0.53	<0.34
TPP	0.4	<0.2	<0.01	0.22	<0.39	<0.53	<0.34
TCP	<0.1	<0.2	<0.01	<0.05	<0.39	<0.53	<0.34
TCEP	0.1	<0.2	<0.01	0.10	<0.39	<0.53	<0.34
TCPP	1.7	<0.2	<0.01	0.60	<0.39	<0.53	<0.34
TDCPP	<0.1	<0.2	0.03	8.64	0.47	<0.53	<0.34

[a]Stationary vehicle. [b]Measurement when travelling. [c,d]Measurement on the test stand.
[e]Measurement when travelling, immediately after test stand measurement, duration 12 min.
[f]Measurement when travelling, immediately following #3, duration 12 min.
[g]Measurement when travelling, immediately following #4, duration 25 min.
[h]Air temperature at the start of sampling.

DISCUSSION

The plastics used in today's automobile manufacture for a wide range of purposes are furnished with flame retardants for safety reasons (preventative fire protection). The use of flame retardants can generally lead to a formal conflict of interests, namely with regard to the product specifications on safety on the one hand and the aspect of health protection on the other. The results of the present study show that particularly under the extreme climatic boundary conditions of the test stand investigations (heated to 65°C air temperature; air exchange around 1 h^{-1}) measurable concentrations of organophosphate esters can be demonstrated in the automobile interior. Test stand investigations are very useful for automobile manufacturers to obtain information on possible emission sources in the vehicle interior and their emission potential under standardized boundary conditions within the framework of comparative investigations. However, the results are not suitable for

comparison within the framework of exposure evaluations, e.g. with recommended guidelines for indoor air, because in addition to the air temperature the air exchange rates in the vehicle interior are fundamentally different in test stand investigations and during measurements when travelling. Depending on the ventilation system setting the air exchange rate in the travelling vehicle is up to approx. 240 h^{-1} (Schmidt and Lüßmann-Geiger, 1996) and is therefore higher than the air exchange of a stationary vehicle by a multiple (≈0.5–1 h^{-1}), or that of other indoor rooms.

For exposure evaluations only those measured values should be used that have been obtained under conditions similar to the actual use. For this reason the present study also carried out measurements under travelling conditions with regard to an exposure evaluation of organophosphate esters in addition to the test stand investigations. The consideration of possible exposure of vehicle occupants is of importance, as automobile drivers can spend a considerable part of the day in the vehicle, as results of relevant studies in the USA have shown. For example, a period of 1–4 h per day in the automobile in the general population is cited (Weisel *et al.*, 1992). According to another source (Park *et al.*, 1996), adults spend on average around 7% of their day (approx. 1.7 h) in a motor vehicle.

In view of exposure an evaluation of the concentration values during travelling can be done on the basis of an assessment concept that was introduced some time ago: A German commission has developed a scheme for calculating indoor air guideline values on the basis of toxicological data (Ad-hoc Working Group, 1996). Here Guideline II (RW II) defines a value that requires immediate action. Guideline I (RW I = RW II/10) is the concentration not to be exceeded for lifelong exposure. For TCEP, Sagunski and Roßkamp (2002) have derived values of RW II = 50 µg/m^3 and RW I = 5 µg/m^3. In view of the insufficient toxicological data for other organophosphorous compounds the authors suggest RW I/II as sum values for concentrations for TCEP, TCPP, TBP, TBEP, TEHP and TPP.

Concentration values in the magnitude of RW II (50 µg/m^3) were not achieved in any case in the present study even under the extreme climatic boundary conditions of the test stand investigation. The results at the test stand at RT (see Table 1) revealed only very low concentration values across the board with individual maximum values in the magnitude of 1/10 RW I and are therefore regarded as being irrelevant. In the test stand measurements at 65°C individual cases of concentration values in the magnitude of RW I (5 µg/m^3) and above were obtained. As expected, however, the present measurements under travelling conditions (Table 2) clearly revealed that even in the 'hot' state (F-9) in comparison to RW I no relevant concentrations of organophosphate esters could be demonstrated in the interior vehicle air due to the occurrence of high air exchange rates. The detection level lay in the magnitude of 1/10 RW I; even a life-long exposure to this value is not regarded as critical.

CONCLUSION AND IMPLICATIONS

The results of the present study clearly show that the materials used in automobile interiors do not cause relevant air concentrations of organophosphate esters during travelling. With regard to the mentioned guideline value (RW I) materials equipped with these compounds can be used in the automobile field.

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