# AT ANY SPEED

Chemicals in cars and the need for safe alternatives

THE ECOLOGY CENTER

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## Chemicals in cars and the need for safe alternatives

### A REPORT BY THE ECOLOGY CENTER

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### ECOLOGY CENTER

The Ecology Center is a nonprofit environmental advocacy organization that works for healthy communities, clean products and clean production. The Auto Project of the Ecology Center works to address toxic and health issues related to the production of automobiles and promotes cleaner vehicle technologies. The Ecology Center is based in Ann Arbor, Michigan.

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### EXECUTIVE SUMMARY

HEN MOST PEOPLE THINK about auto safety, seatbelts and air bags likely come to mind. But cars also pose hidden hazards that endanger drivers and passengers even before turning on the ignition. Chemicals used to make seat cushions, arm rests, floor coverings and plastic parts can break down into toxic dust that is inhaled, becoming a serious health risk.

According to the Environmental Protection Agency (EPA), indoor air pollution is one of the top five environmental risks to public health. Next to homes and offices, Americans spend the greatest amount of time in their cars—more than 100 minutes per day on average.

This study by the Ecology Center, *Toxic at Any Speed: Chemicals in Cars & the Need for Safe Alternatives*, found that concentrations of some toxic chemicals in automobile interiors were five to ten times higher than those found in homes and offices, thus making cars a significant contributor to overall indoor air pollution.

### **PBDEs and Phthalates**

This report examines two classes of toxic compounds: polybrominated diphenyl ethers (PBDEs) and phthalic acid esters (phthalates). PBDEs, used as flame retardants, and phthalates, used to soften plastics, were chosen due to their toxicity and ubiquity in the environment.

PBDEs are used in car interior fabric backing, wire insulation, electronic enclosures, arm rests, floor coverings and other plastic parts. These chemicals are known to cause neuro-developmental damage, thyroid hormone disruption and possibly liver toxicity in test animals. Given the high levels of PBDEs in cars compared to homes or offices, exposure during a 90-minute drive is similar to the exposure from eight hours at work.

Phthalates, the second group of toxic compounds examined in this study, are predominantly used as plasticizers and are found in a large variety of polyvinyl chloride (PVC) products in vehicles including seat fabrics, body sealers, instrument panels, and interior trim. These chemicals have been linked to birth



defects, impaired learning, liver toxicity, premature births, and early puberty in laboratory animals, among other serious health problems.

This study found that not only are drivers and passengers exposed to these toxic chemicals through inhalation of air and dust, but that these chemicals in cars pose a particular threat; frequent exposure to the sun's heat and UV light increases their levels and may exacerbate their toxicity. Since automobiles have 360degree windows, cars can heat up to 192°F; and UV exposure from parking in the sun creates a favorable environment for chemical breakdown.

### **Car Manufacturer Rankings**

The Ecology Center collected windshield film and dust samples from randomly selected 2000 to 2005 model cars made by 11 leading auto manufacturers. Rankings of these companies by the concentration of PBDEs and phthalates found on windshield films are presented in Table ES1.

### Table ES1: Ranking of Vehicles by Company(Windshield Film Concentrations)

Auto Company	Total PBDE, μg/m²	Auto Company	Total Phthalates, µg∕m²
Hyundai	0.054	Volvo	3
Volvo	0.152	BMW	3
BMW	0.178	VW	4
Honda USA	0.193	General Motors	5
Ford	0.280	Toyota USA	6
General Motors	0.301	Honda USA	6
Toyota	0.323	Mercedes	6
Honda	0.351	Honda	7
VW	0.594	Subaru	7
Subaru	0.744	Chrysler	7
Toyota USA	0.936	Toyota	8
Chrysler	1.021	Ford	10
Mercedes	1.772	Hyundai	24

### Alternatives

The presence of PBDEs and phthalates in automobile interiors, when coupled with the many other sources of exposure to these compounds in daily life, is both troubling and unnecessary, especially when alternatives exist and are already used by some automakers.

As seen in the above chart, Volvo was found to have the lowest level of phthalates and the second lowest level of PBDEs, making it the industry leader in terms of indoor air quality in cars. Volvo also proves the feasibility of replacing these harmful chemicals with safer alternatives. Volvo Group (the original parent company of Volvo), which produces trucks and buses, has prohibited the use of three types of phthalates and all types of PBDEs.<sup>1</sup>

Other manufacturers claim they have eliminated PBDEs and phthalates from particular applications. For example, Ford reports that it has eliminated PBDEs from "interior components that customers may come into contact with."<sup>2</sup> Honda also reports that it has eliminated most of its phthalate-containing PVC in its vehicles.<sup>3</sup>

Much of the motivation for these efforts is due to recent government initiatives in Europe and Japan. The European Union, for example, passed legislation in 2003 requiring the phase-out of PBDEs in electronic and electrical equipment. As a result, electronics manufacturers such as Apple, Dell, Hewlett-Packard, IBM, Panasonic and Sony have already eliminated PBDEs from their products. The European Union has also required phaseouts of phthalates in toys, childcare items, and cosmetics, resulting in similar elimination efforts in those industries. Other companies, like Volvo, have taken proactive action to get out ahead of future legislation.

In Japan, the Japanese Auto Manufacturers Association (JAMA) recently made headway toward improving air quality in cars when they announced a voluntary agreement of its members to reduce air concentrations of a number of volatile organic chemicals, including phthalates. These chemicals, also known as VOCs, are responsible for what is typically called "new car smell."<sup>4</sup> Several Japanese automakers have indicated efforts to reduce the use of these chemicals as a result of the initiative.<sup>5</sup>

In lieu of legislative action at the federal level, at least 9 U.S. states (California, Hawaii, Illinois, Maine, Maryland, Michigan, New York, Oregon and Washington) have passed laws banning two forms of PBDEs, penta and octa, which have been rapidly bioaccumulating in the environment. Additional legislation is being considered in at least six other states, as well as revisions of existing legislation that would extend PBDE phaseouts to all uses of deca, including automotive.





### Recommendations

### **FOR MANUFACTURERS**

Manufacturers should reduce the health risk to vehicle occupants by phasing out PBDEs and phthalates in auto interior parts, setting specific timelines for its material and component suppliers. As an interim step, North American automakers should voluntarily comply with recent Japanese and European initiatives that limit hazardous air pollutant levels in auto interiors.

### **FOR GOVERNMENT**

Congress and individual states should encourage rapid action to gradually eliminate the use of PBDEs and phthalates by requiring phase out timelines and providing research and technical assistance to vehicle manufacturers for assessment and development of alternatives. Government purchasers should further require disclosure on the use of these substances in their purchasing specifications. Voluntary efforts should also be given public recognition.

### **FOR VEHICLE OCCUPANTS**

Fortunately, car owners can take some direct actions to minimize health risks from PBDEs and phthalates in car interiors. Some of these actions will also reduce the risks associated with other interior car pollutants. Drivers can reduce the rate of release and breakdown of these chemicals by using solar reflectors, ventilating car interiors, and avoiding parking in sunlight.

### THE PROBLEM OF POLLUTANTS IN CAR INTERIORS

NDOOR AIR POLLUTION OF ALL kinds is considered a major potential health concern. The U.S. Environmental Protection Agency (EPA) notes:

In the last several years, a growing body of scientific evidence has indicated that the air within homes and other buildings can be more seriously polluted than the outdoor air in even the largest and most industrialized cities. Other research indicates that people spend approximately 90% of their time indoors. Thus, for many people, the risks to health may be greater due to exposure to air pollution indoors than outdoors.

In addition, people who may be exposed to indoor air pollutants for the longest periods of time are often those most susceptible to the effects of indoor air pollution. Such groups include the young, the elderly, and the chronically ill, especially those suffering from respiratory or cardiovascular disease.<sup>6</sup>

The American Lung Association, noting that Americans spend up to 90% of their daily lives indoors, also points out that the EPA has estimated indoor air pollution levels can be two to five times higher than outdoor air pollution levels.<sup>7</sup> The EPA has ranked indoor air pollution one of the top five environmental risks to public health.

Next to homes and offices, we spend our longest time in automobiles, 101 minutes per day on average.<sup>8</sup> Automobiles are unique environments. Air temperature extremes of 192°F (89°C) and dash temperatures up to 248°F (120°C) have been observed.<sup>9</sup> Homes and offices are typically maintained at much more moderate and stable temperatures, 68°–75°F (20°–24°C) in winter and 73°–79°F (23°–26°C) in summer.<sup>10</sup>

Automobiles also typically have windows 360 degrees surrounding the interior, resulting in five times the amount of glass per square foot of occupied space (90–100% of occupied space<sup>11</sup>) than homes (typically



12–17% of occupied space), resulting in much higher solar exposure.<sup>12</sup> Glass filters most light of smaller wave length (280-315 nm) in the ultraviolet (UV) region, but the transmission of longer wave UV (315-440 nm) through auto glass varies from 9.7% to 62.8% for laminated and nonlaminated glass respectively.<sup>13</sup> Around 90% of new cars have green tinted windows.<sup>14</sup> Chemicals, such as PBDEs, that are known to break down when exposed to the sun, may break down at much higher rates in solar-exposed cars then in other indoor environments.

While we do not typically occupy vehicles under extreme temperatures, the conditions in vehicles create an environment in which chemicals are constantly released from automobile components into the environment.

Awareness of the scope and extent of pollutants in automobile interiors has led to industry initiatives. For example, Yoshida and Masunaga identified more than 160 volatile organic chemicals (VOCs) in the interior air of a new Japanese car and reported that, during the summer, the concentration of total volatile organic chemicals (TVOCs) continued to exceed proposed indoor guidelines three years after purchase.<sup>15</sup>

Responding to government demands, the Japanese Automobile Manufacturers Association (JAMA) recently announced voluntary guidelines for the reduction of 13 volatile organic chemicals, noting that it "considers the cabins of motor vehicles to comprise one part of residential space." These chemicals are responsible for what is typically called the "new car smell."<sup>16</sup> One group of VOCs is phthalates, which have been associated with nose and throat irritation and other physical problems.<sup>17</sup> Other VOCs of concern include formaldehyde, toluene, xylene, ethyl benzene, and styrene. In place of solvents contained in paints, adhesives and other products, JAMA members will promote the use of waterbased solvents or eliminate solvents from the items altogether.

VOCs are just one of several classes of pollutants in car interiors. Two specific classes of compounds commonly used in auto interior parts, PBDEs and phthalates, have drawn significant attention for their potential impacts to human health in recent years. PBDEs, a class of chemical pollutants that includes compounds banned for use by some states and the European Union, raise important public health concerns. Phthalates, used primarily as an additive in PVC plastic, are also the subject of increased public health concern. In order to gain a better understanding of the air pollution exposure faced by drivers and passengers, the Ecology Center conducted its own tests of the presence of these chemicals in automobile interiors.

### What Are PBDEs?

PBDEs (polybrominated diphenylethers) are brominated fire retardants (BFRs) used primarily in plastics and textile coatings. In this class of compounds, two to ten bromines are attached to the diphenyl ether molecule. PBDEs are of significant environmental concern because they are toxic, bioaccumulative, and persistent, and levels in humans and wildlife are increasing exponentially.

Commercial production of PBDEs began in the late 1970s. PBDEs are used as fire retardants in plastics and textile coatings. Three commercial mixtures of PBDEs have been and continue to be produced: deca-BDE, octa-BDE, and penta-BDE. These commercial products contain a mixture of various congeners.

Since PBDEs have structures similar to other haloge-

### **Three PBDEs of Concern**

Public health authorities and regulators are particularly concerned about three forms of polybrominated diphenyl ethers (PBDEs).

The three commercial types of polybrominated diphenyl ethers are penta-, octa- and deca-BDE, which predominantly contain five, eight, and ten atoms of bromine per molecule, respectively. They also contain a smaller percentage of PBDEs with different numbers of bromine, such as tetra (four) and hexa (six), for example.

- Penta: used in polyurethane foam such as in mattresses, seat foam, other upholstered furniture and rigid insulation.
- Octa: used in high-impact plastics such as fax machines and computers, automobile trim, telephones and kitchen appliances.
- Deca: current automotive uses include cable insulation, electronics and textile coatings. Uses in other products include carpet foam pads, draperies, television sets, computers, stereos and other electronics, cable insulation, adhesives, and textile coating.

The only U.S. manufacturer of penta- and octa-BDEs, Chemtura (formerly Great Lakes Chemical Corporation), is phasing out their production after studies showed significant toxicity to laboratory animals. In addition, California and Maine banned the manufacture and use of penta- and octa- beginning in 2006. Seven other states, including Hawaii, Illinois, Maryland, Michigan, New York, Oregon, and Washington have also acted to phase out penta- and octa-BDE.

nated aromatic contaminants, such as polychlorinated biphenyls (PCBs), which are now banned, and dioxins, which are targeted for elimination as a byproduct of combustion processes, it has been proposed that PBDEs may have a similar mechanism of action.

Studies of the effects of PBDEs in laboratory animals suggest particular impacts on the developing brain, including "reduced adaptability, hyperactivity, and disturbances in memory and learning functions."<sup>18</sup> During the neo-natal period, which is characterized by rapid development and growth of the undeveloped brain, it had previously been shown that various toxic substances can induce permanent injuries to the brain function in mice exposed during this period of development. In mice and rats this phase lasts through the first 3–4 weeks after birth. In humans, on the other hand, it starts during the third trimester of pregnancy and continues throughout the first two years of life. In mice, exposure to PBDEs during this period led to permanently altered spontaneous behavior, reduced adaptability to new environments, as well as hyperactivity in the adult individual—deficiencies that grew worse with age.

Americans are exposed to PBDEs through house dust, food, and air.<sup>19,20,21</sup> However, recent studies increasingly point to indoor dust as the major route of exposure. One study estimated that foods contributed 16% of total PBDE intake of an average adult but that 90% of a toddler's dietary intake of PBDEs comes from dust ingestion.<sup>22</sup>

Two studies have found PBDE levels in the breast milk of U.S. women 10 to 100 times higher than those reported in Europe. Nearly one-third of 40 breast milk samples taken from women who live in the U.S. Pacific Northwest had greater concentrations of PBDEs than of PCBs.<sup>23</sup> Other food sources likely also play a part in total exposure. A study reporting the levels of PBDEs in a market basket survey of 30 food types from stores in Dallas, Texas, found significant PBDE residues, with the highest in fish and meat and the lowest in dairy products.<sup>24</sup>

High levels of PBDEs in office and house dust (and thus available for inhalation) have also been detected. A study published earlier this year found flame retardants in the dust of all 16 homes tested in the Washington, D.C., metropolitan area, as well as one home in Charleston, S.C.<sup>25</sup> According to a source quoted in *Environmental* Science and Technology, "the study also shows that young children in the most contaminated homes may be ingesting enough polybrominated diphenyl ethers (PBDEs), which are suspected to be endocrine disrupters, from dust to raise public health concerns."26 A study by the Environmental Working Group of dust in 10 homes found "unexpectedly high levels of these neurotoxic chemicals in every home sampled." The average level of brominated fire retardants measured in dust from nine homes was more than 4,600 parts per billion (ppb). A tenth sample, collected in a home where products with fire retardants were recently removed, contained more than 41,000 ppb of brominated fire retardants, twice as high as the maximum level previously reported by any study.27

In the first nationwide study of PBDEs in dust samples from computers, toxic chemicals were found in all of the samples tested, including samples taken from a legislative office in Lansing and a computer lab at the University of Michigan.<sup>28</sup> Among the chemicals with the highest levels found were deca-BDE, one of the most widely used fire retardant chemicals in the electronics industry.

The presence of PBDEs in food products, homes and offices—and the fact that exposure of young children may be at levels close to public health concern—under-scores the importance of measuring PBDE levels and possible human exposures in automobile interiors.

### **Health Concerns Associated with PBDEs**

PBDEs can cross the placenta, exposing the fetus. Infants are exposed to PBDEs through breast milk. Children take in PBDEs from animal foods and house dust, and possibly from gases that vaporize from household products containing PBDEs. These will persist in their bodies though adulthood.

Studies with laboratory animals demonstrate the toxic effects of PBDEs. In these studies, PBDE exposure before and after birth caused problems with brain development, including problems with learning, memory and behavior. They also demonstrated that exposure to PBDEs during development can decrease thyroid hormone levels and affect reproduction.

These effects are observed mainly in studies with penta- forms of PBDEs. Some similar toxic effects are seen with octa- and deca- forms of PBDEs, but at higher exposure levels than for penta-. There is evidence from animal studies that deca-BDE may cause cancer at high exposure levels. Penta- and octa- have not been tested in cancer studies with animals.

PBDEs have a chemical structure similar to PCBs (polychlorinated biphenyls), which have been studied in humans. (The U.S. banned PCB manufacture in 1976. For more information on PCBs go to *http://www.atsdr.cdc.gov/tfacts17.html*). This suggests that PBDEs may be similar to PCBs in terms of toxic effects and their ability to build up in the environment and in people. PCBs are believed to cause skin conditions in adults and affect the nervous and immune systems of children. At high levels they may cause cancer.

### What Are Phthalates?

Phthalates (phthalic acid esters) are a group of chemicals predominantly used as plasticizers in soft plastics, such as in a large variety of polyvinyl chloride (PVC) products including seat fabric, cable insulation and interior and exterior trim in vehicles. They account for 30-45% by weight of most flexible PVC applications used in vehicles.<sup>29</sup> A wide variety of consumer products including cosmetics, building materials, clothing, food packaging, some children's toys, and even some medical devices also often contain phthalates. DEHP (di 2-ethyl-hexyl phthalate), which is used extensively in vehicles, in PVC medical tubing, and other devices, has been shown in animal studies to be hazardous at high levels of exposure.

Phthalates are among the most ubiquitous synthetic chemicals in the environment<sup>30</sup> and are nearly always found at some concentration in virtually all humans and wildlife.<sup>31</sup> Routes of exposure include food (from packaging), dust, and air, in declining order of exposure levels. They are found in the air and dust in homes and offices.<sup>32,33,34</sup> The United States Agency for Toxic Substance Disease Registry (ATSDR) estimates that 1.4 million kilograms of DEHP are vaporized to the air during plastics manufacturing every year and another 1.8 million kilograms are lost to the air from plastic product inventory every year.<sup>35</sup>

Phthalates and their metabolites are likely developmental and reproductive toxins, which have shown toxic effects in the liver, kidneys, and testes of laboratory animals and are linked to deteriorated semen quality, low sperm counts, and poor sperm morphology in men. A survey of chemical body burdens in Americans released in 2003 by the Centers for Disease Control and Prevention found levels of phthalates highest in children, creating the potential for developmental effects.<sup>36</sup> In Europe, DEHP is classified as "toxic to reproduction." Likewise, in California, DEHP is listed as a reproductive toxicant in the chemical list of Proposition 65.<sup>37</sup>

The daily intake of DEHP from all sources (food, dust and air) can exceed the EPA Reference Dose (RfD) (20 µg/kg body weight/day)—the level likely to be without an appreciable risk of adverse health effects over a lifetime—and is of great environmental and health concern.<sup>38</sup> Based on an analysis of urinary metabolites of DEHP, a German study estimated that 31% of the general population in that country may be regularly exposed to DEHP at levels that exceed the reference dose.<sup>39</sup> The U.S. Department of Health and Human Services recently



concluded that DEHP exposure levels are generally in the range of 2–30 µg/kg body weight/day but that some studies have shown levels as high as 65.0 µg/kg bw/day for men and 27.4 µg/kg bw/day for women.<sup>40</sup> Vulnerable populations, such as critically ill newborns, may be exposed to higher levels than the general population due to the extensive medical procedures they undergo using phthalate-containing materials. These levels of exposure are of great concern given the extent to which the RfD values are exceeded in the general population. They highlight the need to reduce exposure from all sources.

The European Parliament in July 2005 voted to prohibit the use of three phthalate plasticizers in toys and child-care items and to restrict three other plasticizers throughout the European Union.<sup>41</sup> In 2003, the European Parliament banned two phthalates commonly used in cosmetics—dibutyl phthalate (DBP) and DEHP —because they are suspected reproductive toxins.

### The Potential Risks from Phthalates in Auto Interiors

Studies have documented that phthalates used in indoor plasticizers are found in indoor air and dust, regardless of the ventilation rate. One study noted, "[A] small area of plasticizer-containing products emits almost as much as a large area. Therefore, if the surface materials contain plasticizers, it is impossible to avoid the phthalates in indoor air."<sup>47</sup>

The technical literature also documents the offgassing of DEHP from soft PVC. Elevated interior air temperature in cars, as high as 192°F, and dash board temperatures as high as 248°F can cause accelerated release of phthalates from materials and dramatic increases in DEHP levels in the air (see Tables 11 and 12). At car interior temperatures of 140°F, DEHP levels can reach extremely high levels. The combination of high interior temperatures from parking in sunlight and the off-gassing of DEHP, in particular, make autos a significant source of phthalates being released to the outdoor environment. A German study estimated that 31% of the general population in that country may be regularly exposed to DEHP at levels that exceed the EPA reference dose. While no one has quantified in detail the contribution of phthalates from dust and air in cars to the total exposure, it is important to con-sider that humans spend 101 minutes each day in their vehicles and that continued releases of phthalates contribute to overall environmental levels.

Global production of phthalates is an estimated 3.5 million metric tons per year,<sup>42</sup> of which 80–90% is used as additives in flexible PVC.<sup>43</sup> Roughly 50% of the market share for phthalates is accounted for by diethylhexyl phthalate (DEHP),<sup>44</sup> at least 95% of which is added to PVC to give it flexibility.<sup>45</sup> As noted by Koch et al., "This is of greatest importance for public health since DEHP is not only the most important phthalate with respect to its production, use and occurrence and omnipresence but also the phthalate with the greatest endocrine disrupting potency."<sup>46</sup>

### SAMPLING FOR PBDES AND PHTHALATES IN AUTOMOBILE INTERIORS

RIVATELY OWNED VEHICLES were solicited to participate in the study as they arrived at a local household recycling center. The Ecology Center collected 15 composite samples (13 windshield films, 2 dust samples) and analyzed these for 11 PBDE congeners and 8 phthalates (see Appendix 2 for complete list). The samples were collected from 133 vehicles. Fewer dust samples were collected due to the greater amount of time required to collect the samples.

Separate windshield film composites were collected for each manufacturer, depending on whether the vehicle was made in the U.S. or abroad. The Vehicle Identification Number (VIN) was used to determine the country of manufacture for each vehicle sample. Between six and ten vehicles from each manufacturer were grouped for



Sample	Number Vehicles	Surface Area Sampled, m <sup>2</sup>	Ambient Air Sampling, Temperature (Average °F)	Average Vehicle Model Year	Average Interior Volume, ft <sup>3</sup>
BMW	7	1.4	45.0	2001	97
Chrysler	10	2.0	57.5	2002	142
Ford	10	2.0	55.2	2002	117
GM	10	2.0	58.5	2003	116
Honda Import	8	1.6	56.6	2002	119
Honda USA <sup>1</sup>	10	2.0	56.7	2002	135
Hyundai	6	1.2	57.7	2003	135
Mercedes	8	1.6	37.4	2001	91
Subaru	6	1.2	53.2	2002	126
Toyota Import	8	1.6	56.6	2003	114
Toyota USA <sup>1</sup>	10	2.0	52.9	2003	153
Volvo	10	2.0	57.0	2003	109
VW	8	1.6	53.0	2001	100

### **Table 1: Window Wipe Sample Vehicles**

1 manufactured in the United States

each composite. Vehicles produced primarily between 2000 and 2005 were sampled for this study (see Appendix 4). Vehicles that had windows cleaned within the last two weeks were not sampled. The characteristics of the sampled vehicles are shown in Tables 1 and 2.

The experimental details for the collection and analysis of dust and film samples are described in Appendix 1.

### **Results: PBDEs**

Dust and window film samples were analyzed for 11 PBDEs (see Appendix 2 for full list). The highest concentration of PBDE congeners in the dust samples was of deca-BDE, followed by the penta-, tetra-, and hexacongeners at an order of magnitude lower than the levels found for deca-BDE (see Table 3). This finding is consistent with the major usage of deca-BDE in vehicular textile backings, wire insulation, electronic enclosures, carpet backings, and plastics. Technical grades of penta-BDE were historically used primarily in automobiles in polyurethane foams. But significantly, and in contrast to findings reported for vertical windows in buildings, the deca-congener concentration was significantly lower or completely absent

in films from the interior car windshields we sampled.

Table 4 shows the total PBDE concentration by company. These results were based on an average of 6–10 randomly selected vehicles sampled for each company. The overall congener profiles for each company were similar. The highest total PBDE concentrations found were recorded under unique conditions. The

#### Table 2: Dust Sample Vehicles

### Samples

#### DaimlerChrysler

2002 Dodge Ram 1500 Pickup 2001 Chrysler Town & Country LXI

### **General Motors**

2000 GM Sierra Pickup 2000 Oldsmobile Integra 2000 Pontiac Grand Am 2001 Buick Century 2002 Chevy Silverado 2002 Chevy Venture 2003 Chevy Venture

#### Ford

1999 Ford Escort 2002 Ford Focus SE 2002 Ford Escape 2002 Ford F-250 Pickup 2003 Ford Taurus 2005 Ford Taurus

### Honda

2002 Honda CRV

#### Mazda

2000 Mazda Protégé (2)

#### Nissan

2001 Nissan Pathnder 2005 Nissan Murano

Toyota

2004 Toyota Camry 2001 Toyota Highlander Mercedes composite sample was obtained at a used car dealership where these vehicles were parked for an unknown length of time. Due to the large surface area of materials in car interiors, gas phase concentration of the chemicals in parked vehicles may approach equilibrium relatively fast. This may lead to an increase in condensation on windows when exterior temperatures are low compared to the inside. When driving and ventilation is resumed, gas phase concentrations of chemicals will decrease and subsequent evaporation of film deposits can also be expected.

Several factors may explain the virtual absence of deca-BDE on interior windshields (see Table 3) in contrast to the results obtained with interior building windows. One possibility is that deca-BDE did not deposit on the windshields. However, studies have shown deca-BDE presence on a variety of building windows (see Table 6).

The fact that significant quantities (more than 50% of all PBDEs analyzed) of the deca congener were found on interior building windows suggests two possible routes of its deposition in vehicles. Due to elevated temperatures (up to 192°F) in sun ex-

posed vehicles, vapor phase deposition on cooler windshields is expected in addition to deposition of small dust particles on the "sticky" window films composed of semivolatile chemicals, such as hydrocarbons and phthalates. This was likely followed by rapid photolytic debromination within the film matrix with subsequent formation of lower brominated congeners. This assumption is

### Table 3: Mean Concentration of PBDEs in Vehicle Dust Samples, mg/kg; and Windshield Films, µg/m<sup>2</sup>

Sample Type, Size	BDE-28	BDE-47	BDE-66	BDE-77	BDE-85	BDE-99	BDE-100	BDE-138	BDE-153	BDE-154	BDE-209	Total
Dust N=2	<dl< td=""><td>0.600</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>0.600</td><td>0.085</td><td><dl< td=""><td>0.100</td><td>0.065</td><td>9.500</td><td>10.950</td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	0.600	<dl< td=""><td><dl< td=""><td><dl< td=""><td>0.600</td><td>0.085</td><td><dl< td=""><td>0.100</td><td>0.065</td><td>9.500</td><td>10.950</td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>0.600</td><td>0.085</td><td><dl< td=""><td>0.100</td><td>0.065</td><td>9.500</td><td>10.950</td></dl<></td></dl<></td></dl<>	<dl< td=""><td>0.600</td><td>0.085</td><td><dl< td=""><td>0.100</td><td>0.065</td><td>9.500</td><td>10.950</td></dl<></td></dl<>	0.600	0.085	<dl< td=""><td>0.100</td><td>0.065</td><td>9.500</td><td>10.950</td></dl<>	0.100	0.065	9.500	10.950
Film N=13	0.003	0.065	0.000	0.000	0.024	0.158	0.053	0.008	0.041	0.032	0.006	0.365

### Table 4: Concentration of PBDEs (μg/m<sup>2</sup>) in Windshield Films

Auto Company	Total PBDE, μg/m²
Mercedes <sup>1</sup>	1.772
Chrysler	1.021
Toyota USA	0.936
Subaru	0.744
VW	0.594
Honda	0.351
Toyota	0.323
General Motors	0.301
Ford	0.280
Honda USA	0.193
BMW	0.178
Volvo	0.152
Hyundai	0.054
Median	0.323
Mean	0.365

### Figure 1: BDE-99/BDE-100 Mass Ratio in Films, Automotive Dust and Commercial Products



supported by analysis of the congener profiles, and particularly the mass ratios of the congeners in automotive dust and films, and films collected from interior building windows.

The congener profiles and the mass ratios of PBDEs in automotive dust, house dust, and interior building window films closely resemble that of commercial penta-BDEs, whereas this ratio deviates significantly in samples taken from interior windshields of vehicles. Figure 1 shows the BDE-99/BDE-100 mass ratio in films, automotive dust and commercial products. The mean BDE-99/BDE-100 mass ratio found on windshields is 3.3 compared to the commercial penta mass ratio of 5.5–6.1.

The presence of deca-BDE coupled with a near commercial ratio on interior building windows, in contrast to our findings on automotive windshields, reflects data obtained under significantly different environmental conditions. Building windows are vertical and solar exposure is limited due to the angular configuration of windows in relation to the sun's position. Also, window glass often contains reflective coatings. Slanted automotive windshields are more directly exposed to solar radiation. Moreover, in contrast to the ambient interior temperatures of buildings (~68°F), temperatures in solar exposed vehicles may easily reach 192°F, a difference that may accelerate reaction rates by several orders of magnitude.

A recent study highlighted the impact of temperature on volatilization of flame retardants.<sup>48</sup> An electronic

1 7 of 8 vehicles sampled were cars for sale on a used car dealership lot.

### Table 5: Emission Rates to the Air FromTelevision Case (ng/m³ per hour) at 23°C

PBDE	Television set housing (ng/m³ per hour)
TriBDE (BDE-17)	-
TriBDE (BDE-28)	0.2
TetraBDE (BDE-47)	6.6
TetraBDE (BDE-66)	0.5
PentaBDE (BDE-100)	0.5
PentaBDE (BDE-99)	1.7
PentaBDE (BDE-85)	-
HexaBDE (BDE-154)	0.2
HexaBDE (BDE-153)	1.0
HeptaBDE	4.5
OctaBDE	1.5
NonaBDE	0.8
DecaBDE	0.3

### Table 6: Total PBDE Concentrations in Window Films in Different Environments

Sample Location	Location	∑ PBDE-ng/m²
Toronto; urban¹	exterior	2.5-14.5
Ontario; suburban <sup>1</sup>	exterior	1.1
Ontario; rural <sup>1</sup>	exterior	0.56
Electronics Recycling Facility <sup>3</sup>	exterior	38.7
Toronto; urban <sup>2</sup>	interior	19.4–75.9
Ontario; rural <sup>2</sup>	interior	10.3
Electronics Recycling Facility <sup>3</sup>	interior	755
Ann Arbor; urban cars in continuous use⁴	interior	54–1,021, average: 440
Ann Arbor: urban cars parked in dealers lots⁴	interior	1,772

#### Notes on percent deca (BDE-209) in the samples

1 On average the percentage of BDE-209 for exterior samples is 67% of total PBDE.

2 On average the percentage of BDE-209 for interior samples is 53% of total PBDE.

3 At the electronics recycling facility, the BDE-209 percentage found was 50% and 80% for exterior and interior window levels, respectively.

4 In contrast, the interior window films in vehicles contained an average of only 1.6% BDE-209 of total PBDE.

### Table 8: PBDE Concentrations in AutomotiveFilms by Location of Manufacture

Continent of Manufacture	PBDE Average µg∕m²
U.S.	0.55
Asia	0.37
Europe	0.31

circuit board and enclosure was studied and BDE-28 and BDE-47 were the only PBDEs detected being released at  $73^{\circ}$ F ( $23^{\circ}$ C). However when the temperature was raised to 60°C, eight additional PBDEs were detected (BDE-17, BDE-99, BDE-17, BDE-66, BDE-100, BDE-85, BDE-154, and BDE-153) and the concentrations of BDE-28 and BDE-47 increased by up to 500 times. BDE-47 increased from 1 ng/m<sup>3</sup> to a maximum of 500 ng/m<sup>3</sup> at 140°F (60°C). The study noted that both PBDEs and organophosphoric flame retardants exhibit the same temperature dependent behavior. Higher-brominated, i.e. lower-volatility compounds like deca-BDE, were not detected in air due to sorption onto test chamber glass. Experimental results showing that about 25% to 100% of the emitted flame retardants are adsorbed by the chamber walls confirm this expectation.

A deca emission rate of 0.28 ng/m<sup>3</sup>/hour was determined for TV casings at a temperature of 23°C.<sup>49</sup> Emission rates from television set housings for specific PBDE congeners are shown in Table 5.

Table 6 presents a comparison of total PBDE film concentrations of our data with those obtained from indoor and outdoor windows of residences and offices in Ontario, Canada.<sup>50</sup> Total PBDE concentrations of interior film for in-use vehicles are about 10 times higher than those reported for interior residential and office windows and are comparable to data obtained at the electronics recycling facility cited in Table 6. For parked vehicles, interior total PBDE concentrations even exceed the recycling facility values by factors of 2–4. As discussed above, in contrast to the Canadian

#### Table 7: Deca Concentrations and Deca Percentage of Total PBDEs in Dust

	Location	Mean Deca (ppm)	Deca % Total PBDE	Range Deca
Homes	Atlanta	2.0 ppm	53%	0.12-21 ppm (Sjodin, 2004)
	Cape Cod	1.2 ppm	30%	0.9-1.5 ppm (Rudell, 2003)
	Belgium	4.4 ppm	98%	Unknown (Al Bitar, 2004)
	DC	1.4 ppm	10-90%	0.78-30.1 ppm (Stapleton, 2004)
	Germany	1.4 ppm	80%	0.2-19 ppm (Knoth, 2003)
	UK	10 ppm	98%	4-20 ppm (Greenpeace, 2003)
	US	4.6 ppm	55%	0.9-10 ppm (CSP, 2005)
	US	2.4 ppm	10-85%	0.4-7.5 ppm (EWG, 2004)
Office	EU Parliament Office	2.1 ppm	85%	0.3-7 ppm (Greenpeace, 2002)
Autos	Michigan	9.5 ppm	83-91%	9.5 ppm (this study)

Sample, size	DMP	DEP	DPP	DBP	DIBP	BBP	DEHP	DOP	Total
Dust, N=2	0	0	0	3	1	6	49	4	63
Film, N=13	0	0	0	3	0	2	5	1	8

**Key:** Di (2-ethylhexyl) phthalate (DEHP); Butyl benzyl phthalate (BBP); Di-isobutyl phthalate (DIBP); Di-octyl phthalate (DOP); Di-n-butyl phthalate (DBP); Di-n-octyl phthalate (DNOP); Diethyl phthalate (DEP); and Dimethyl phthalate (DMP).

window film study, BDE-209 (deca-BDE) was found to be absent or at considerably lower concentrations in interior vehicle films.

The average dust concentration for deca in homes and offices is 1-2 ppm. Levels found in auto dust are 9.5 ppm, which is up to five times higher than dust in other indoor environments (see Table 7).

No significant correlations between concentration levels and any of the vehicle characteristics (volume, vehicle age, area sampled or ambient temperature) were observed. However, as shown in Table 8, there is a potential difference in the total PBDE concentrations of these films relative to the continent of their production. Although Table 8 indicates the possibility of significant differences in total PBDE windshield film concentrations based on the country a vehicle was produced, the sample size was inadequate to be conclusive.

### **Results: Phthalates**

Five phthalates were found in automobile dust, Di-nbutyl phthalate (DBP); Di-isobutyl phthalate (DIBP); Butyl benzyl phthalate (BBP); Di (2-ethylhexyl) phthalate (DEHP) and Di-octyl phthalate (DOP) (see Table 9). However, the predominant phthalate found in the dust samples (78%) was DEHP. Windshield films contained 4 out of the 5 phthalates that were found in dust. DEHP was also the dominant phthalate on windshields, accounting for 63% of the total.

As shown in Table 9, by far the major phthalate found in the dust samples (78%) was DEHP, at a concentration of 49 ppm. This appears low in comparison to dust found in apartments<sup>51</sup> (562 ppm median) and dust collected from U.S. homes in several states<sup>52</sup> (329 ppm mean). This difference may be related to the larger variety and quantity of vinyl products used in homes and due to greater dust formation via abrasion. Vehicles, in contrast, use less PVC in places where abrasive dust formation may occur, such as seats and carpets.

Table 10 shows the concentrations of DEHP and total phthalates by company. In general, levels found on

windshield films were very similar between companies with the exception of one sample, Hyundai. Very little research has been done on the presence and behavior of phthalates on window films. It is possible that the heat to which auto windshields are exposed limits accumulation of DEHP on windshields. Photo degradation may also be a factor.

While air concentrations of phthalates were not measured as part of this study, outgassing of DEHP from soft PVC has been well recognized throughout the technical literature. Plasticizers, including DEHP, are not chemically bound to the polymer. They reside between the PVC molecules and this gives PVC the flexibility

### Table 10: Concentration of DEHP in Windshield Films, µg/m<sup>2</sup>

Auto Company	DEHP µg/m²	Total Phthalates $\mu$ g/m <sup>2</sup>
Hyundai	24	24
Ford	7	10
Honda	7	7
Subaru	7	7
Toyota	6	8
Toyota USA	6	6
Honda USA	5	6
General Motors	5	5
Chrysler	4	7
Mercedes <sup>1</sup>	4	6
VW	4	4
BMW	3	3
Volvo	3	3
Median	5	6
Mean	6	7

1 7 of 8 vehicles sampled were cars for sale on a used car dealership lot.

	VP (hPa; 1 hPa = 0.75 mm Hg)							
Temperature (°C)	DEHA	BBP	DEHP	DIDP				
20	6.3 X 10 <sup>-7</sup>	6.5 X 10 <sup>-6</sup>	2.2 X 10 <sup>-7</sup>	3.3 X 10⁻ <sup>8</sup>				
50	2.7 X 10 <sup>-5</sup>	1.5 X 10 <sup>-4</sup>	1.0 X 10 <sup>-5</sup>	1.8 X 10 <sup>-6</sup>				
100	3.7 X 10 <sup>-3</sup>	9.1 X 10 <sup>-3</sup>	1.6 X 10⁻³	3.4 X 10 <sup>-4</sup>				
150	0.16	0.21	0.076	0.019				
200	3.10	2.50	1.600	0.460				
Volatility grouping	high	high	medium	low				

Table 11: Vapor pressure (VP) of plasticizers and volatility groupings

From OECD Environmental Health and Safety Publications, June 2004.

needed for certain applications. This also leads to DEHP being volatilized and transported in the air. While DEHP has relatively low volatility at ambient temperatures, the volatility changes significantly as temperature rises. Table 11 shows how the vapor pressure of DEHP changes as a function of temperature.<sup>53</sup> DEHP is considered a "medium" volatility plasticizer, yet its vapor pressure increases 10,000-fold when temperature increases from 20°C to 100°C.

Quackenboss<sup>54</sup> devised an equation to estimate the loss of phthalates from thin sheets of PVC as a function of vapor pressure/temperature. At 208°F (98°C) the rate loss of DEHP is estimated at 0.1% per hour. Such elevated temperatures have been reported for dashboards in vehicles and can therefore lead to elevated air concentrations.

Deposition of phthalates onto cooler auto windshields and on dust most likely occurs via the vapor phase at elevated interior car temperatures. Extraordinarily high interior temperatures in vehicles (190°F) and on dashboards (248°F) suggest volatilization and subsequent condensation in cooler areas of cars such as floors and windows. Air concentrations of DEHP in vehicles range from <10,000 to 300,000 ng/m<sup>3</sup> at 77° and 140°F, respectively. For comparison, PVC assembly workplace air contained a range of 10,000-160,000 ng of DEHP/ m<sup>3.55</sup> The highest DEHP level in cars reported were 1,000,000 ng/m<sup>3</sup>. Table 12 shows results of DEHP levels in the air of car interiors under different environmental conditions.<sup>56</sup> These levels exceed air concentration levels recently set by JAMA and TUV.

Global 2000 (an Austrian NGO) recently tested three new cars both in the shade and after heating them

in the sun to 60°C. Overall VOC levels were 4–6 times higher in vehicles in the sun. Average DEHP air concentrations measured over six hours in the vehicles were 340–420 ng/m<sup>3</sup>.<sup>57</sup>

While the levels of DEHP in auto interior air can be significantly higher than in homes or offices, the levels in auto dust are much lower. DEHP is known to react photochemically with hydroxyl radicals in the air, with an estimated half-life of 22.2 hours.<sup>58,59</sup> Photodegradation, with formation of unknown reaction products, may be occurring on slanted automotive windshields at elevated temperatures and to a lesser degree on auto dust that is more directly exposed to solar radiation.

Since adults spend an average of 101 min/day in vehicles,<sup>60</sup> the automobile environment may be a significant source of the daily intake of DEHP and other related chemicals. As shown in Table 12, as the temperature of a vehicle's interior rises, the concentration of DEHP in the air also rises.<sup>61</sup> While no one sits in a vehicle at 140°F, we often enter vehicles that have baked in the sun and have reached temperatures much higher than 77°F.

### Table 12: DEHP Level from Vehicle Interiors

Temperature in a Vehicle Interior	DEHP Levels Measured, ng/m <sup>3</sup>
77°F (or 25°C)	<10,000
140°F (or 60°C)	300,000
Highest documented level of DEHP in vehicles	1,000,000

Source for DEHP concentrations in vehicles: Huber, et.al, 1996

### DISCUSSION OF PBDE RESULTS

OTAL PBDE LEVELS ON WINDshield films are ten times those found on other indoor windows, and auto dust contains up to five times higher levels then those found in house and office dust. Research has shown that work-ing with PBDE containing products, or in contaminated environments such as autos, can lead to elevated exposure. One study found that computer technicians had blood concentrations of deca- and hexa-BDE five times those of hospital cleaners and computer clerks.<sup>62</sup> Assuming inhalation of dust is the primary route of exposure, exposure to PBDEs during a 90minute drive is equivalent to the exposure from 8 hours at work. Occupations requiring workers to spend all or most of their day in a vehicle could result in up to five times the exposure of non-driving occupations.

The absence of deca-BDE in the automobile windshield film samples, and the predominance of the less brominated and more toxic congeners including the banned penta-BDE in the interior samples, also suggests a potentially significant public health issue. Several new studies show that deca-BDE breaks down when exposed to sunlight<sup>63,64,65</sup> and when metabolized by fish.<sup>66</sup> The breakdown products identified include the lower brominated PBDEs that are more toxic and bioaccumulative and are banned by some jurisdictions.

Table 13 shows the percentage of light transmission of different types of auto glass.<sup>67</sup> The table also shows the approximate time needed to reach a level of exposure (5 Joules per cm<sup>2</sup>) that could trigger rashes in photosensitive occupants. While this level does not directly correlate with photolytic breakdown of deca-BDE, it does illustrate how rapidly high UV exposure can occur in vehicles. Deca has been shown to be very short-lived under direct UV exposure.

Assuming that deca-BDE is breaking down into penta-BDE and other types of breakdown products in car interiors, this not only suggests potential health risks from the exposure, but also underscores the need for automobile industry and government action that would



promote a prompt phase-out of deca-BDE use in auto interiors and perhaps in other products.

Despite opposition from some member states, the European Parliament and leading electronic industries, the European Commission (EC) decided in October 2005 to delay a deca-BDE ban set to take effect July 2006. In early January, the Danish government sued the EC over its failure to ban deca. Yet, leading companies such as Dell, Apple, and Sony have already invested in alternatives. And our findings, supporting the hypothesis that the unbanned deca-BDEs can break down into forms that are associated with health effects in animal studies, contradicts the reasoning of the European Commission.

### Table 13: Percentage of Light Transmissionof Different Types of Automotive Glass

	Average Transmission Percentage	
Type of Glass	Over UV range 315–400 nm	Approximate time for 5 J cm <sup>2</sup>
Nonlaminated: clear	62.8	30 min
Nonlaminated: light green	35.7	1 hour
Laminated: clear	9.7	3 hour
Laminated: green	9.0	3 hour

### ALTERNATIVES TO DECA-BDES AND PHTHALATES

### N MOVING TO SAFER ALTERNATIVES to phthalates and PBDEs automakers have three options to pursue:

- 1. re-design the auto interior to eliminate the need for the chemical
- 2. select an alternative material or product that does not require the chemical
- 3. substitute an alternative chemical

Table 14 illustrates the application of this substitution approach in two examples: the use of DEHP in PVC and the use of deca-BDE in textiles. Specific substitution options for PBDEs and phthalates are discussed below.

### **PBDEs and Deca**

The Lowell Center for Sustainable Production, at the University of Massachusetts, has evaluated alternatives to deca-BDEs in textiles, the chief application of these compounds in automobiles. Examining alternatives ranging from the use of inherently fire-resistant materials to chemical deca-BDE substitutes, the Center concluded: "While there is no single replacement for deca-BDE for textiles, the multitude of options on the market make it clear that viable market ready approaches exist."<sup>68</sup>

According to the Lowell Center recommendations, the basic strategies for halogen-free fire retardation in automotive seating applications are:



- use of substitutes, such as phosphonic acid or tetrakis (hydroxy-methyl phosphonium salt compound with urea);
- 2. use of more fire-resistant fibers, such as melamine, polyaramides, glass, nylon, wool, leather etc.;
- 3. reduction of fuel load, i.e. no foams;
- 4. enhancement of fire barrier between foam and fabric.

The Danish EPA reports that producers have succeeded in replacing brominated BFRs in textiles with compounds based on phosphorus, nitrogen, and zirconium, all in a price range similar to that of deca and

Substitution Options	DEHP	Deca-BDE (in Textiles)
Re-design product to eliminate need for chemical/function	no good examples	Eliminate foam use or use barrier technology to protect foam from flames
Eliminate chemical through material selection	Replace PVC with alternative materials that do not use plasticizers, including plastics such as Thermoplastic Polyolefins (TPOs) and Polyurethanes	Use inherently flame resistant mateirals
Substitute with another chemical	Use alternative plasticizers, including adipates, citrates, and trimellitates	Use alternative flame retardants, including phosphorous alternatives

#### **Table 14: Examples of Substitution Options**

fulfilling fire safety standards in the transportation industry. In Denmark, PBDEs have been totally phased out in flexible foams used in automotive seats and lamination of textiles. Alternatives used are chlorinated phosphate esters, halogen-free additives containing ammonium polyphosphates, and reactive phosphorus polyols.

At least one auto manufacturer, Volvo, claims it produces a PBDE-free automobile, and others claim they have eliminated PBDEs from a variety of applications.<sup>69</sup> Volvo Group (the original parent company of Volvo), which produces trucks and buses, has also banned the use of three phthalates, including DEHP.<sup>70</sup> Volvo Group has also placed all brominated flame retardants on its "grey list" signifying that their use shall be limited.<sup>71</sup>

Ford reports that it has eliminated PBDEs, including deca, from interior components that customers may come into contact with.<sup>72</sup>

A number of manufacturers have eliminated PBDEs from non-automobile uses. These include Apple, Epson, IBM, and some Hewlett-Packard products; as well as Panasonic cell phones, fax machines and conventional phones. Ericsson, a manufacturer of cell phones and other electronics, has eliminated deca-BDE from its products and has found cost-effective alternatives. Other companies like IKEA are requesting PBDE-free polyurethane foam from their suppliers.<sup>73</sup> Toshiba replaced toxic flame-retardants in casings for electronic parts by switching to a non-flammable type of plastic that didn't need any chemical additives.<sup>74</sup>

### **Phthalates**

The simplest strategy to avoid phthalates in automobiles and homes is to replace PVC-based materials with non-toxic plastic alternatives and/or natural fibers. PVC plastic is under increasing competition from the thermoplastic polyolefins (TPOs), which are easier to recycle, and polyurethanes. With the European Union and Japanese governments requiring automakers to recycle greater percentages of their autos, the recyclability of plastics is also of growing concern.

TPOs, which include polypropylene and polyethylene, have been among the fastest growing materials in the auto industry. In the last 10 years, TPO use has risen about 10% per year through replacement of polyurethanes, PVC, and thermoplastic elastomers (TPE) for exterior bumper fascias, air dams, step pads, body-side trim, and underbody parts. Most of these conventional exterior applications have converted to TPO. Yet, growth will remain rapid, as TPO increasingly wins roles for body parts like fenders, doors, quarter panels, interior energy-management, and instrument panels.<sup>75</sup>

Their low-cost, toughness, ductility, and ease of recycling make TPOs the preferred plastic for automakers. "Instrument panels exemplify how the push to cut costs and ease of recycling favors TPO. Using a TPO skin with glass-reinforced PP [polypropylene] structural carriers and TPO molded-in-color panels provides an economical solution based on a single polymer. Already, over 20 PP/TPO instrument panels are scheduled for future vehicles, led by Japanese polymer technology."<sup>76</sup>

Polyurethanes are used in seats, head rests, steering wheels, instrument panels, door panels, and headliners. Polyurethane foam has been the dominant plastic in interiors because of its use in seating and headliners.<sup>77</sup> Polyurethane manufacturers are seeking to expand the market share by introducing new products, called polyurethane elastomer "skins", for use in automotive interiors. BASF, for example, recently introduced Elastoskin, which is used in instrument panels and interior door panels on "top-of-the-line cars such as the Buick Park Avenue, Oldsmobile Aurora and Cadillac CTS."<sup>78</sup> Polyurethanes, however, are not being recycled in the U.S.<sup>79</sup>

If PVC usage cannot be avoided, phthalate plasticizers should be replaced with available alternatives such as trimellitates, aliphatic dibasic esters, phosphates, benzoates, citrate esters, polymeric plasticizers, sulfonic acid, and chloroparaffins. Of these, three main types of plasticizers have been proposed for replacing phthalates:<sup>80</sup>

- 1. Adipates
- 2. Citrates
- 3. Trimellitates

Higher price is currently the biggest barrier to substitution. Adipates, trimellitates, and citrates cost about 50%, 100%, and 140% more than phthalates, respectively.

In Europe the substitute plasticizer of choice appears to be DINP (diisononyl phthalate). EU risk assessment procedures have not identified any negative environmental impacts of DINP.

In the auto sector, the Japanese Auto Manufacturers Association (JAMA) recently announced a voluntary agreement of its members to reduce air concentrations in vehicles of a number of chemicals, including phthalates. In Europe an independent certification organization (TUV Rheinland Group) has established a standard for an allergy-free automobile interior. European Ford's Focus C-Max was the first vehicle certified to this standard and Ford is looking to certify additional vehicles in the future.

Honda also indicates it has "developed and implemented PVC-free technologies for interior and exterior parts such as trim, sealants and adhesives, including sash tape, sunroof drain hose, washer tube, window molding, weather strip, door molding roof molding, floor mat, seat

### Industry Initiatives to Reduce Phthalate Exposure in Auto Interiors

The Japanese Automobile Manufacturers Association (JAMA) has vowed to reduce the presence of volatile organic chemicals in cars typically associated with "new car smell." As JAMA notes, VOCs are viewed as "one of the reasons behind the sick house dilemma," and possibly harming human respiratory health.

One of the VOCs targeted by JAMA is Di-2ethylhexyl phthalate or DEHP, which we found at highest levels in our study sampling. JAMA has set a voluntary maximum standard of 7.6 parts per billion in the air of car interiors. The standard, consistent with a recommendation from the Japanese Ministry of Health, Labor and Welfare, will take effect in model year 2007 for all automobiles manufactured and sold in Japan.

In a second initiative, the TUV Rheinland Group in Cologne, an industry body controlling and approving quality standards of industrial and consumer products, has established an "Allergy-Free" certificate for automobile interiors. The certificate has importance even for car owners and passengers who do not have allergies. As Motor Trend magazine reported, "an important part of the TUV tests consisted of extensively analyzing passenger compartment air quality and thereby examining the concentration of organic substances such as formaldehyde, phenols, phthalates, or solvents."<sup>83</sup>

The TUV standard for total phthalates in vehicle interiors is 30 micrograms per cubic meter. At least one domestic U.S. manufacturer has already obtained a TUV allergy-free certificate: Ford for its Focus C-MAX. It is clearly possible for automakers to comply with the standard by refraining from the use of PVC plastics or other materials requiring phthalate additives.



covering, and change lever boot." Honda efforts have targeted the "... elimination or reduction of materials (such as PVC) that have high chlorine content."<sup>81</sup>

Among automakers, Toyota appears to be making the most progress towards a comprehensive sustainable plastics program. In a previous Ecology Center report, *Moving Toward Sustainable Plastics*, Toyota was recognized for setting clear, comprehensive and measurable goals for sustainable plastics, and committing to reducing its use of PVC.<sup>82</sup>

### Recommendations

This study strongly supports the continued phase-out of PBDEs and new government initiatives that target deca-BDE for phase-out at the earliest possible date. It should also spur automakers to make greater efforts to pursue sustainable plastics that do not require the addition of toxic phthalates in car interiors. The presence of PBDEs and phthalates in automobile interiors, when coupled with the many other sources of exposure to these compounds in daily life, is both troubling and unnecessary when alternatives exist for many applications and are already in use by some automakers.

Fortunately, car owners can also take some direct actions to minimize any health risks from PBDEs in car interiors. Some of these actions will also reduce risks associated with the other interior car pollutants. Because high temperatures in car interiors appear to contribute to the breakdown of deca-BDE into compounds that studies demonstrate pose significant health risks, actions

### **Deca-BDE: The Controversy (Like the Chemical) Persists**

Although the European Commission in October 2005 exempted deca-BDE from restrictions imposed by European Union hazardous substance legislation for electronic equipment, concern about its environmental and human health impact continues to grow.

The Commission found that for deca-BDE "there is no need for measures to reduce the risks for consumers beyond those that are being applied already" despite mounting evidence that the compound breaks down into more toxic forms. Shortly after the European Commission decision, Sweden signaled its intention to move ahead of the EU with a national regulation banning deca-BDE in new products.

Saying that legal action in the European Court of Justice would be considered against the deca-BDE exemption, the chair of the European Parliament's environment committee, Karl-Heinz Florenz said, "It has been our assumption that deca-BDE would be explicitly banned." Had the exemption not been granted, a European ban on deca-BDE in new products would have taken effect in July 2006. In early January 2005, the Danish government announced that it is taking legal action against the European Commission for its decision.

Deca-BDE has also been exempted from state-level bans in Michigan and other states despite the fact that:

to reduce or prevent such high temperatures can contribute to reduced health risks.

Specific recommendations include:

### **FOR MANUFACTURERS**

• Manufacturers should reduce the risk to vehicle occupants and take voluntary action to phase out PBDEs and phthalates in their automobiles, especially auto interiors. As an interim step, North American automakers should also voluntarily comply with recent Japanese and European initiatives that would limit hazardous air pollutant levels in auto interiors.

### **FOR GOVERNMENT**

• Congress and/or the states should encourage rapid action to phase out the use of these toxic chemicals by

- Some of the highest levels of deca-BDE in the world have been found in the blood and breast milk of U.S. citizens, raising concern about the health of nursing infants;
- Deca-BDE has been shown to cause developmental neurological effects in laboratory animals;
- Deca-BDE has been found in top predators worldwide, including Arctic birds;
- The Scientific Committee on Health and Environmental Risks (SCHER), physicians and professors who serve an advisory role within the European Commission, "strongly" urged further risk reduction measures for deca-BDE in light of evidence that it breaks down into highly toxic compounds.

The U.S. has over 250 million pounds of deca-BDE in use and a comparable amount is believed to persist in landfills and contaminated sediments. "When you live in the country with the highest levels of these chemicals in body tissue and breast milk, what happens in Europe can directly influence our exposure to deca," said Laurie Valeriano of the Washington Toxics Coalition.

Despite its deca-BDE exemption, the European Commission did support further testing and research on levels and effects of deca-BDE.

requiring phase-out timelines and providing research and technical assistance to vehicle manufacturers for assessment and development of alternatives. Voluntary industry efforts should also be given public recognition.

### **FOR VEHICLE OCCUPANTS**

- Car owners should park in shaded areas or garages whenever possible.
- Car owners should consider purchasing sunscreens to help reflect solar radiation to reduce interior car temperatures.
- Whenever weather conditions permit, car owners returning to their cars after parking should open windows to permit ventilation of chemicals accumulated in the interior of cars.

### APPENDIX 1: EXPERIMENTAL SECTION: SAMPLE COLLECTION

### Dust

The dust samples were collected with a canister type vacuum cleaner (Miele Model S247i) and a fresh vacuum filter bag. Dust samples from cars were collected outside of a local car wash, with free car washes provided to owners of privately owned vehicles in exchange for participating in the study. Vacuum cleaning of the carpets and seat cushions took approximately ten minutes. For the field blank, a new filter bag filled with 100 grams of acid-washed sand was used to run ambient air for 10 minutes. No measurable amounts of brominated flame retardants were detected in the blank. Ten grams of each of the homogenized dust and sand were subjected to extraction and further analysis.

### Film

Window wipe samples were collected from the inside of the front windshields of 111 vehicles. Privately owned vehicles were solicited to participate in the study as they arrived at a local household recycling center. Utilizing the Vehicle Identification Number (VIN) system, the location of manufacture (country) for each vehicle sampled was recorded. Separate composites were collected for Honda and Toyota vehicles depending whether the vehicle was manufactured in the US or Japan. Between six and ten vehicles from each manufacturer were grouped for each composite. The study attempted to include only vehicles produced between 2000 and 2005. Vehicles which had windows cleaned within the last two weeks were not sampled. A variety of parameters, including ambient air temperature, vehicle age, and curb weight, were also recorded.

A cardboard template with an opening of  $0.2 \text{ m}^2$ (60 x 33.33 cm) was placed over the outside of the windshield designating the area to be wiped. The template allowed 3–4 inches between the sampling area and the edge of the windshield. A similar approach was used for obtaining wipe samples from the exterior of vehicle windows. Windows were sampled by vigorously wiping the glass surface with a laboratory Kimwipe (12 x 12 inches) that was wetted with HPLC grade isopropanol (IPA). N-DEX brand nitrile gloves were used to perform the collection of the samples. The wetted wipes were stored in capped glass jars at  $32^{\circ}$ F prior to analysis. A field blank containing ten IPA wetted Kimwipes (corresponding to a total of 2 m2 of wiped area) was also collected.

### Extraction

Dust and film samples were collected into pre-cleaned glass jars with Teflon-lined caps. After collection, samples were stored in the dark at 4°C during and after receipt at the laboratory. Extraction of samples was performed within 14 days of collection. Sample extracts were stored in the dark at 4°C, and analyzed within 40 days of extraction. PBDEs were analyzed using a modified EPA 8270 method developed by Ann Arbor Technical Services (ATS). The method was validated by ATS with detection and quantitation using both ECD and MS/MS following the validation procedures as specified by USEPA.

PBDEs were extracted using methylene chloride and acetone in a pressurized fluid extraction device. The extract was partitioned on Florisil<sup>™</sup> to separate PBDE congeners from interfering compounds. The concentrated extract was injected into a gas chromatograph to separate the individual congeners. PBDEs were detected using an electron capture detector. The method detection limit for PBDEs was 0.004 µg/g dry mass for all PBDEs except BDE-209. The method detection limit for BDE-209 was 0.01 µg/g.

### **Quality Control**

Replicate spike and recovery experiments were carried out concurrently with the dust and film samples for all 11 PBDEs and representative semi-volatiles. Mean percent recoveries were within control limits, ranging from 62% to 100% for all PBDEs except BDE-28. BDE-28 recovery was slightly outside of the control limit with a percent recovery of 46%. The relative range (percent difference) between the 2 replicate QA samples was within control limits, with an average of 4% difference. BDE-118 was used as a surrogate on all samples. Percent recoveries ranged from 70% to 185%. The mean percent recoveries for representative semivolatiles (Acenapthene, 1,4-Dichlorobenzene, 2,4-Dinitrotoluene, N-nitroso-di-n-propylamine, Pyrene and 1,2,4-Trichlorobenzene) were within control limits, ranging from 70% to 87%. The relative range between the 2 replicates averaged 13% and ranged from 8% to 25%. Nitrobenzene and Terphenyl were used as surrogates on all samples. Percent recoveries were within control limits, ranging from 65% to 103%. No corrections to the reported data have been made for these recoveries.

### **Field Blank**

A field blank containing ten IPA wetted Kimwipes (corresponding to a total of 2 m<sup>2</sup> of wiped area) was collected. Background levels in  $\mu g/m^2$  were subtracted from the results of the composite samples taking into account varying sample sizes for each composite.

### APPENDIX 2: PBDES AND PHTHALATES ANALYZED

Names and Congeners of PBDEs Tested in This Study	
Congener Number	Congener
BDE-28	2,4,4'-Tri-BDE
BDE-47	2, 2', 4, 4'-Tetra-BDE
BDE-66	2,3', 4,4'-Tetra-BDE
BDE-77	3,3',4,4'-Tetra-BDE
BDE-85	2,2',3,4,4'-Penta-BDE
BDE-99	2, 3', 4, 4', 5-Penta-BDE
BDE-100	2, 3', 4, 4', 6-Penta-BDE
BDE-138	2,2',3,4,4',5'-Hexa-BDE
BDE-153	2, 2', 4, 4', 5, 5'-Hexa-BDE
BDE-154	2, 2', 4, 4', 5, 6'-Hexa-BDE
BDE-209	2, 2', 3, 3', 4, 4', 5, 5', 6, 6'-Deca-BDE

Names of Phthalates Analyzed		
Di (2	e-ethylhexyl) phthalate (DEHP)	
B	utyl benzyl phthalate (BBP)	
D	i-isobutyl phthalate (DIBP)	
	Di-octyl phthalate (DOP)	
C	Di-n-butyl phthalate (DBP)	
D	i-n-octyl phthalate (DNOP)	
	Diethyl phthalate (DEP)	
[	Dimethyl phthalate (DMP)	

### APPENDIX 3: AUTOMOBILE INDOOR AIR QUALITY STANDARDS

JAMA Standard		
Substance Name	Indoor Concentration Guideline Value,* µg/m³	
Formaldehyde	100	
Toluene	260	
Xylene	870	
Paradichlorobenzene	240	
Ethyl benzene	3800	
Styrene	220	
Cholorpyrifos	1 / (0.1 children)	
Di-n-butyl phthalate	220	
Di-2-ethylhexyl phthalate	330	
Tetradecane	220	
Diazinon	0.29	
Acetaldehyde	48	
Fernobucard	33	

TUV Standard		
Substance/Class	Limit Value w/out air exchange, µg/m³	
Formaldehyde	60	
BTEX (except benzene)	200	
Benzene	5	
Styrene	30	
Halogenated hydrocarbons	10	
Esters and Ketones	200	
Aldehydes (except Formaldehyde)	50	
Alcohols	50	
Glycol-ethers-esters	100	
Nitrosamines	1	
Amines	50	
Phenoles	20	
Phthalates	30	

### **JAMA Testing Methods**

Concentration level measurements are according to the "Vehicle Cabin VOC Testing Methods (Passenger Cars)" adopted by JAMA.

#### Summary

- Pre-measurement conditions: Standard condition, ventilating for 30 minutes with doors and windows open.
- (2) Concentration measurements with vehicle closed (Formaldehyde): Close all doors and windows, use radiating lamps to heat vehicle in an airtight state, controlling cabin temperature at 40°C. Maintain this condition for 4.5 hours, then sample cabin air for 30 minutes.
- (3) Concentration measurements when driving (Toluene, etc.): After sampling, start the engine (air-conditioner operation) and sample cabin air for 15 minutes in that state.

### APPENDIX 4: WINDSHIELD WIPE SAMPLE VEHICLES

2001 BMW 525 2002 BMW 330 CI 2003 BMW 330 I 2003 BMW 330 Xi 2001 BMW 530 I 2001 BMW X5 1998 BMW 540i 2000 Chrysler Cherokee Classic 2000 Chrysler Dodge Caravan 2001 Chrysler Dodge Stratus 2002 Chrysler Intrepid 2002 Chrysler Jeep Cherokee 2003 Chrysler Liberty 2002 Chrysler Town and Country 2003 Chrysler Town and Country 2004 Chrysler Town and Country 2005 Chrysler Town and Country 2004 Ford Escape 2005 Ford Escape 2003 Ford Explorer 2003 Ford Explorer 2003 Ford Explorer Sport Trac 2002 Ford F-150 2000 Ford F-150 XL 2004 Ford Freestar 2000 Ford Ranger 2000 Ford Taurus 2002 GM Buick Rendevous 2001 GM Chevy Venture 2003 GM Monte Carlo 2003 GM Pontiac Vibe 2003 GM Pontiac Vibe 2004 GM Saturn Vue 2004 GM Silverado 2002 GM Silverado Z71 2003 GM Trailblazer 2003 GM Trailblazer 2003 Honda Import Civic Hybrid 2000 Honda Import CR-V 2001 Honda Import CR-V 2001 Honda Import CR-V 2002 Honda Import CR-V 2004 Honda Import CR-V 2004 Honda Import CR-V 2001 Honda Import Insight 2003 Honda USA Accord EX 2002 Honda USA Civic EX 2000 Honda USA Civic LX 2001 Honda USA Civic LX 2002 Honda USA Civic LX 2003 Honda USA Civic LX 2001 Honda USA Odyssey 2004 Honda USA Odyssey 2003 Honda USA Pilot 2004 Honda USA Pilot

2001 Hyundai Elantra 2004 Hyundai Kia - Rio Cinco 2004 Hyundai Kia - Sedona 2004 Hyundai Santa Fe 2002 Hyundai Sonata LXV6 2004 Hyundai XG 350L 1995 Mercedes C 220 2001 Mercedes C 240 2003 Mercedes C 240 2003 Mercedes C 240 2003 Mercedes C 320 1999 Mercedes E 320 2000 Mercedes E 320 2000 Mercedes E 320 2001 Subaru Forester 2001 Subaru Forester 2001 Subaru Forester 2002 Subaru Forester 2002 Subaru Forester 2002 Subaru Forester 2004 Toyota Import Lexus LS430 2001 Toyota Import Lexus RX300 2001 Toyota Import Prius 2001 Toyota Import Prius 2005 Toyota Import Prius 2004 Toyota Import Rav-4 2004 Toyota Import Scion xA 2004 Toyota Import Scion xB 2003 Toyota USA Camry 2004 Toyota USA Camry 2002 Toyota USA Corolla 2002 Toyota USA Corolla 2000 Toyota USA Sienna 2002 Toyota USA Sienna 2002 Toyota USA Sienna 2003 Toyota USA Sienna 2004 Toyota USA Sienna 2004 Toyota USA Tacoma 2000 Volvo Cross Country 2000 Volvo S 40 2002 Volvo S 80 2003 Volvo S60 2005 Volvo V 50 2001 Volvo V 70 2002 Volvo V 70 2004 Volvo V70 2005 Volvo XC 70 2004 Volvo XC 90 2001 VW Audi A4 2001 VW Audi A6 2001 VW Jetta 2001 VW Jetta 2000 VW Passat 2000 VW Passat 2001 VW Passat 2003 VW Passat

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