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Flame Retardants and Plasticisers on Particulate -in the Modern Computerized Indoor Environment

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Abstract

Large quantities of additives are used as flame retardants and plasticisers in modern electronic goods, such as TV sets, computers and copying machines. The aim of the present study was to investigate some indoor working environments to determine if any flame retardants and plasticizers were present. A new sampling technique for particulate was used successfully. Both neutral and phenolic contaminants were detected in office rooms and a computer hall. The compounds identified were tetrabromobisphenol A, two polybrominated diphenyl ether congeners and nine organophosphate esters, including tris(2-chloro)phosphate and 2-chloropropyl)phosphate. A number of hitherto unidentified environmental contaminants were also indicated. The results indicate a new risk for human exposure to organohalogen compounds.

Introduction

In addition to the traditional environmental contaminants, such as pesticides and industrially applied chemicals as DDT, DDT substitutes and PCB, a vast number of additives to goods and products are manufactured and used in various applications. Additives, e.g. flame retardants, plasticisers, antioxidants, cross-linking agents, colorants, lubricants and flow promoters are produced to modify and protect plastics materials¹. Within each of these groups we may find a large number of chemicals. Several hundred of individual chemicals have been suggested as flame retardants and plasticizers². Among these we have a number of substances that are lipophilic and persistent or semi-persistent - requirements that may lead to their occurrence in the environment. In fact, many of the plasticizers and flame retardants in use, such as chlorinated paraffins (CP), polybrominated diphenyl ethers (PBDEs), phthalates, phosphates and halogenated phenols are detected in the outdoor environment³⁻⁵.

Chemicals used in electronic equipments (TV sets, telephones, computers, fax and copying machines etc.) are potential environmental pollutants, particularly of the indoor environment. The aim of the present study was to screen computerized working environments for flame

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retardants and plasticizers. The work was concentrated to determine substances adsorbed to particles in the indoor environments studied.

Recently the occurrence of organophosphate esters was reported in some common indoor environments⁶. Rather little is known so far about the health effects of organophosphates to humans, but several biological effects are reported in the literature. For instance, tritoyl phosphate and butylated triphenyl phosphate have been shown to be reproductive toxicants⁷⁻⁹. In studies on rats and mice, tri(2-chloroethyl) phosphate has shown neurotoxic and carcinogenic properties¹². Cases of contact allergy to triphenyl phosphate have been reported¹³. The presence of the organophosphate esters was determined by conventional air sampling technique.

In the present study a new sampling device for particulate matter is presented.

Experimental Methods

Chemicals: The following substances were used as references in the analytical work performed: triethyl, tri(n-butyl), tri(2-chloroethyl), tri(2-chloropropyl), triphenyl, tri(2-butoxyethyl), tri(ethylhexyl) and tritoyl phosphate⁶; 2,2',4,4'-tetrabromodiphenyl ether (BDE-47), 2,2',3,4,4'-pentaBDE (BDE 85), 2,2',4,4',5-pentaBDE (BDE-99), 2,2',4,4',6-pentaBDE (BDE-100), 2,2',4,4',5,5'-hexaBDE (BDE-153), 2,2',4,4',5,6'-hexaBDE (BDE-154), 2,2',3,4,4',5',6-heptaBDE (BDE-183)¹⁴⁻¹⁶, numbering system according to Ballschmiter et al¹⁷; Bromkal® 70-5 DE (Chemische Fabrik Kalk GmbH, Germany), 2,4,6-tribromophenol, pentachlorophenol (PCP) and tetrabromobisphenol A (TBBPA) were obtained from Aldrich Chemicals, Germany.

All solvent were of p.a. quality.

Instruments: An ionizer, Air point, with a aluminium collector cup (80 mm in diameter), developed at the Wallenberg Laboratory, Stockholm University, Stockholm, was used to sample airborne particles for one week. The ionizer efficiency was tested in a closed room at rest by measuring the reduction of particles (cat allergen) over time (Figure 1)¹⁷. The room contained 600 particles/cm³ at the start of the experiment.

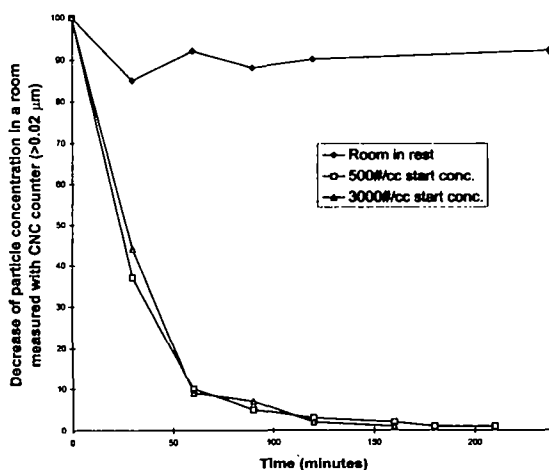


Figure 1. Decrease of particle concentration in a room where the ioniser, Air Point is used, as measured by a CNC counter (particles >0.02 μm)

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Sampling of organophosphates were also performed with a personal sampling equipment, which has previously been described⁶. The sampler holder was made of anodised aluminium. A 25 mm binder free A/E borosilicate glass fibre filter (Gelman Sciences Inc., Ann Arbor, MI, USA), and two 15x15mm cylindrical polyurethane foam (PUF) plugs (Specialplast AB, Gillinge, Sweden) were used to trap the particulate and the semi-volatile associated fractions, respectively. Air was pumped through the sampler using a battery-operated personal sampler pump (224-PCXR7, SKC Inc., Eighty Four, PA, USA). The flow rate was set to 3.0 L/min and samples were collected during 700 min, yielding a total air volume of 2.1 m³.

Gas chromatography with nitrogen/phosphorus selective detection was performed as described by Carlsson et al⁶ for analysis of phosphate esters. All other analysis were performed on a Varian 3400 gas chromatograph (Varian, Walnut Creek, CA, USA), equipped with a split/splitless injector and an electron capture detector. A DB-5 fused silica column (30 m, 0.25 mm, 0.25µm phase thickness, was used for all analyses.

Samples and sample preparations: Samples were collected in official working environments, offices and a computer hall at a school according to the information in Table 1. All rooms tested contained at least one computer. Blank samples were analysed together with each sample.

The particles were removed from the sampling cup by wet wiping with purified glass wool dipped in dichloromethane. The solvent volume was reduced to 200 µl, n-hexane (4.0 ml) was added and the procedure was repeated once. The compounds in the sample, dissolved in hexane (4.0 ml), was partitioned to potassium hydroxide (0.5 M in 50% ethanol, 2.0 ml). The hexane phase was transferred to another tube and the water phase was shaken once more with hexane. The hexane phase represents the neutral fraction. Any phenolic compounds were isolated from the aqueous phase by adding dilute hydrochloric acid (2 M, 1.0 ml) after which hexane: methyl *tert*-butyl ether (1:1, 4.0 ml) was added. The organic phase was removed and the solvent volume reduced to 200 µl. The samples were treated with diazomethane. Both the neutral phase and the phenolic phase compounds were treated with conc. sulfuric acid. The hexane phases were analysed by GC for persistent compounds and compared to the reference compounds used (c.f. above).

Regarding the samples collected with personal sampler, the filters and polyurethane foam plugs (PUFs) were extracted using ultrasonication in dichloromethane for 2x20 minutes, as described earlier⁶.

Results and Discussion

The environmental contaminants were identified by comparison to standard substances. The working environments studied are described and the compounds detected on the particles analysed from these rooms are given in Table 1. It is notable that both tetrabromobisphenol A (TBBPA) and the PBDEs are present in the rooms and even though no quantifications yet can be made by this technique it is possible to make some semi-quantitative statements. Thus TBBPA is present in the highest amount in the computer hall. It is obvious that the interest for TBBPA as an environmental contaminant has been of little interest since very limited data has been published on its presence in the environment (for a review see ref 19). Almost 20 years ago a report showed that TBBPA was present in air at a company producing organobromine compounds²⁰. Thereafter TBBPA has occasionally been reported to be present in sediments and water but not in biota¹⁹. TBBPA is produced in large quantities (annual production exceeds

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Table 1. Sample origin, equipment in the rooms and particulate content of organic pollutants.

Room number	Room type	Phenolic type compounds	PBDEs	Organo-phosphates
R-I	Computer hall, with x personal computers	TBBPA	BDE-47 BDE-99	NA
R-II	Office with one PC and a printer, 6 m ² , located downtown Stockholm	TBBPA	BDE-47 BDE-99	NA
R-III	Secretaries office at a university department, 15 m ² , 2 PC, 1 fax	TBBPA	BDE-47 BDE-99	NA
R-IV	Office, Stockholm University, 15 m ² , 1 PC, 1 printer,	TBBPA	BDE-47 BDE-99	NA
R-V	Office at National Institute for Working Life, 7.5 m ² , 1 PC.	NA	NA	9 organo-phosphate compounds, see Experimental

NA = not analysed

60.000 tonnes)¹⁹. This fact plus the detection of TBBPA in human plasma among the general population is intriguing²¹ and call for further studies of TBBPA in environmental samples.

The presence of PBDEs in the air particulate is also interesting showing that these compounds are leaking into the indoor environment from electronic devices. The PBDEs are well-known environmental contaminants and also present in human blood²¹. The PBDE congeners detected on the particulate are the dominating PBDE congeners in the environment.

Nine organophosphates were detected and identified in air samples from an office room. Several phthalates were also detected, but were not further analysed in this study. Among the organophosphate esters are two isomers of tributyl phosphate, tri(2-chloroethyl) phosphate, three isomers of tri(chloropropyl) phosphate, triphenyl phosphate, tri(2-butoxyethyl) phosphate and tri(2-ethylhexyl)phosphate. Sampling was performed using both the ionizer and conventional sampling technique pumping air through a glass fibre filter and two polyurethane foam (PUF) plugs. A method for quantification of organophosphates with the former technique has so far not been developed. Therefore this was made using the conventional method. At a sampling flow rate of 3L/min, the organophosphates could only be detected in the particulate phase, i.e. on the filter. The most abundant organophosphates in the office were the butylated and the chlorinated phosphates, occurring at 10-50 ng/m. Concentrations have previously been determined in outdoor air⁶. Only sub-nanograms of the organophosphates could be detected. This strengthens the assumption that the main sources of this type of compounds originate from inside the office building.

Using the new ionizing sampler, the same organophosphate compounds were detected. However, the phosphates with the lowest molecular weights occurred in higher relative concentration when compared to the conventional sampling technique. The ionizing sampling device is assumed to collect particles, and not volatiles. This do further indicate that the

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organophosphates occur associated to particulate matter in the air. Why the lower molecular weight species occur in higher relative amount has to be further investigated.

One of the esters, triphenyl phosphate, was found to originate exclusively from the computer. In the absence of the computer, this compound could not be detected in the air samples. The concentration level was significantly higher in the presence of a new computer, compared to an

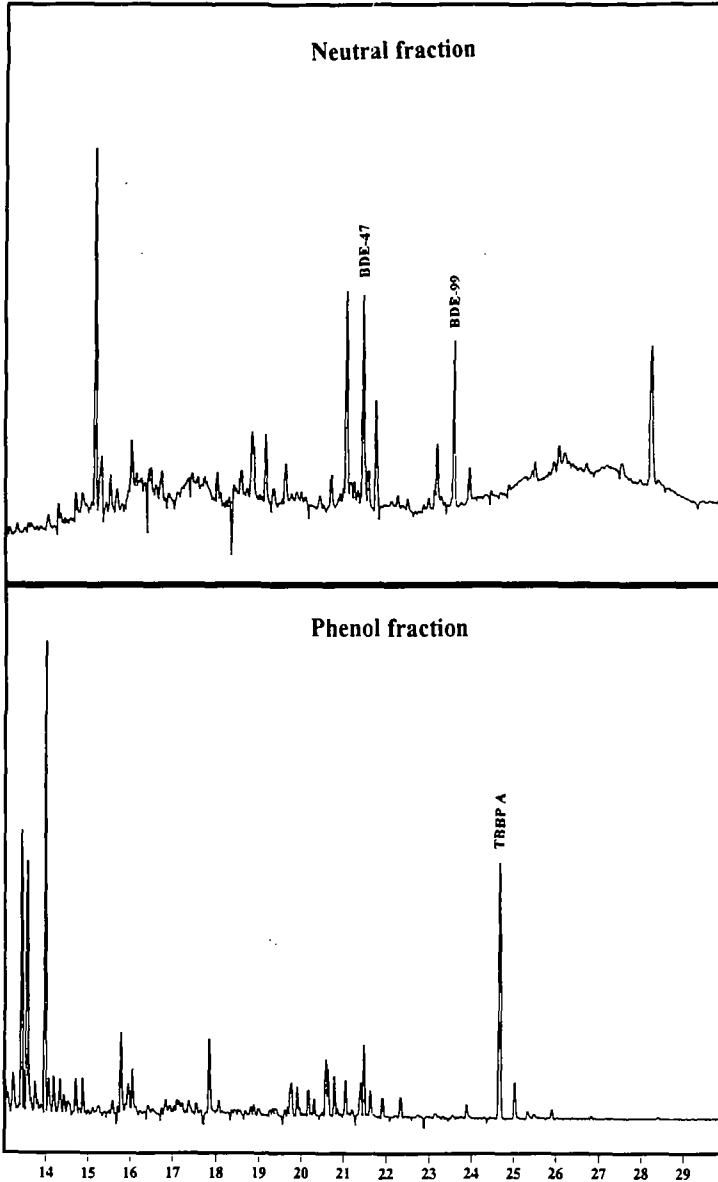


Figure 2. Gas chromatogram (ECD) of neutral compounds (upper chromatogram) and derivatised (methylated) phenolic compounds (lower chromatogram) in particulate matter from a computer hall in Stockholm.

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older. The computer also emitted a higher concentration of triphenyl phosphate when switched on. The emission is of great interest, since this compound have shown contact allergy properties. This may be one contributing cause to the reported cases of skin problems related to VDU (Visual Display Unit) work.

An additional number of organic compounds are present in indoor air from some of the rooms investigated. Thus, a general chromatographic picture is seen that indicate the presence of chlorinated paraffins (Figure 2, upper) and a cluster of unidentified compounds are shown in the chromatogram of methylated phenolic compounds (Figure 2, lower chromatogram); both chromatograms from a sample from room R-I.

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