Hazardous Chemicals in PVC Flooring

A report compiled for the Healthy Flooring Network by
Michelle Allsopp, David Santillo and Paul Johnston
Greenpeace Research Laboratories
Universisty of Exeter
EX4 4PS

Greenpeace Research Laboratories Technical Note
N: 14/00, November 29th 2000

Abstract
This study investigated the composition of PVC flooring with respect to certain chemical additives, namely phthalate plasticisers and organotins. The study included analysis of five PVC flooring samples that were available for retail in the UK. Samples were found to contain high levels of several organotin compounds, in particular DBT (37.7 to 569 ppm) and TBT (128 to 17,940 ppb). Two phthalates were also detected at high concentrations. Diisononyl phthalate (DINP) was found in all samples at levels ranging from 4.7 to 15.8% by weight and butyl benzyl phthalate (BBP) was present in three samples at levels from 1.6 to 5.0%.

These finding are of concern in relation to the presence of hazardous substances in consumer products, their potential release to the environment and, in turn, their potential impacts on the environment and human health. Phthalates and organotins are hazardous chemicals. Organotins cause toxicity to the immune system in laboratory animals whilst phthalates exhibit a wide range of toxicity's. The use of PVC flooring and other household furnishings has generated concern recently after it was hypothesised that the release to air and particulates of the phthalate plasticiser di(2-ethylhexyl) phthalate (DEHP), present in PVC interior surfaces, may increase the risk of childhood asthma. Another study linked exposure to PVC floors in the home with increases in bronchial obstruction in children, possibly caused by plasticisers. In respect of the known and suspected toxicity's of phthalates and organotins and their possible impacts on human health, the results of this study are of great concern.

INTRODUCTION

PVC (polyvinyl chloride, or vinyl) is currently a very widely used plastic with many applications including flooring, furniture, window frames, pipes and short-life packaging. The use of PVC has increased greatly during recent decades and consumption is predicted to increase still further in the future (see van der Naald and Thorpe 1998). PVC is always formulated with a range of additives to enhance its properties (Ehrig 1992). Additives for PVC have included hazardous substances such as lead, cadmium, organotins and phthalate plasticisers. The use of such additives has generated concern regarding environmental contamination and human health, in part, because of potential leaching of these additives from PVC products. For instance, children's toys made from soft PVC have been shown to contain 10-40% by weight of phthalate plasticisers (Stringer *et al.* 2000), and an emergency ban has been ordered by the European Union since December 1999 on the use of certain phthalates in toys designed to be chewed by children of under three years old (Official Journal of the European Communities 1999). A permanent ban is under discussion. In addition to concerns about chemical additives in PVC, there are also concerns about contamination of the environment by hazardous chemicals during the production of PVC (Stringer 1998), and the serious waste problems posed by the now perpetually growing mountain of PVC waste (van der Naald and Thorpe 1998).

The present study was undertaken as part of a wider study on the identification of hazardous chemicals as additives in carpets and PVC flooring. The intention of the present study was to identify and quantify levels of chemical additives in PVC flooring, specifically, phthalates and organotins. PVC is commonly used for the production of flooring for homes because it provides inexpensive, easy to clean surfaces and is especially practical in kitchens, bathrooms and children's playrooms and bedrooms (see Jaakkola *et al.* 1999). PVC flooring is constructed from soft PVC that has been plasticised to make it flexible. The most commonly used plasticisers for manufacturing soft PVC are phthalates (phthalate esters). Historically, di-ethylhexyl phthalate (DEHP) has been the most commonly used phthalate but and more recently there appears to be increased market use of di-isononyl phthalate (DINP) (Stringer 2000). Phthalates do not bind to PVC chemically, but are present as freely mobile and leachable components of the plastic matrix. Consequently phthalates are gradually lost from PVC over time by volatilisation to the air (Cadogan *et al.* 1993). It is however not possible to measure directly the amount of phthalates emitted from PVC flooring to air using currently available technologies (Friedberg and Karlsson 1993, Howick 1996). Moreover, the results of such studies will always be strongly influenced by the particular conditions employed. Phthalates have a high affinity for particles and a recent study in Norway showed that as well as vaporising to air, these chemicals were also present in suspended particles in air and in sedimented dust samples from homes (Oie *et al.* 1997). The study demonstrated that phthalates migrated from PVC flooring to sedimented house dust. For PVC floors, washing has also been shown to release phthalates into the water (Moller *et al.* 1996).

Human exposure to phthalates in the indoor and outdoor environment occurs via background contamination of air, food and water. Of these, by far the greatest exposure has been estimated to occur via food intake (0.25 mg per day or >90%) (US ATSDR 1997). Nevertheless, a recent study on exposure via air in the indoor environment concluded that exposure through this route was greater than previously assumed because of the presence of phthalates in suspended particles in the air and in house dust (Oie *et al.* 1997). Human exposure to phthalates may also occur from direct contact with PVC products, for instance, skin contact with the surface of floors and, in the case of young children, chewing of soft PVC toys (CSTEE 1998). A recent study in the USA that investigated levels of phthalate metabolites (breakdown products) in urine concluded that human exposure to phthalates was greater than previously assumed (Blount *et al.* 2000). Studies on laboratory animals have shown that phthalates exhibit a wide range of toxic effects (KEMI 1994, US ATSDR 1997). In humans, data on health effects are mainly limited to a few studies on occupational exposure to phthalates and impacts on health. However, one recent study (Oie *et al.* 1997) hypothesised that exposure to the phthalate DEHP in the home, especially from inhalation of particulate matter containing DEHP, may increase the risk of inflammation of the lung airways and as a consequence, increase the risk of asthma. The hypothesis was partly formed on the basis of previous research evidence that mono (2-ethylhexyl) phthalate (MEHP), which is the major breakdown product of DEHP, was found to induce bronchial hypersensitivity in rats, and that pre-term human infants exposed to PVC respiratory tubing systems had a higher risk of bronchial asthma. Recently, a further study in Norway indicated that PVC flooring may increase the risk of bronchial obstruction in young children (Jaakkola *et al.* 1999). Exposure to phthalate plasticisers from surface materials in the home was hypothesised to be the causal agent.

Regarding organotins, these compounds have been used for a variety of applications following their discovery and initial use as a moth repellent in the 1920's (Moore *et al.* 1991). Organotins, specifically tributyltin (TBT), has been used on a worldwide basis as an antifouling agent in paints for boats and ships. Organotins are also used as heat stabilisers in PVC and as biocides in industry and agriculture. It has recently been reported that the major use of organotins is for the heat stabilisation of PVC which represents about two-thirds of the global consumption of these compounds (Sadiki and Williams 1999). Both butyltins and octyltins have been used. The latter group of compounds were specifically developed in an attempt to overcome toxicity problems of the generally toxic butyltins (Matthews 1996). Studies on laboratory rodents have shown that TBT is toxic to the immune system (see e.g. Kergosien and Rice 1998). As a consequence of its use in paint for marine shipping, TBT has caused major reproductive problems some species of shellfish and in some instances has been related to massive populations declines (Gibbs 1988, 1993, Bryan *et al.* 1986, 1987). This has led to national restrictions on its use for shipping and more recently to a decision for a global phase out for this use by 2008 adopted under the International Maritime Organisation Assembly Resolution A.895(21). Concern has also been expressed about the level of intake of TBT from consumption of contaminated fish and shellfish (Belfroid *et al.* 2000). A recent study in Germany raised concern about the presence of comparatively high levels of TBT and other organotins in PVC flooring (Oeko-Test 2000). Research on organotins has suggested that they leach from PVC under laboratory simulated landfill conditions (Mersiowsky *et al.*1999) and from PVC water pipes to water (Sadiki and Williams 1999).

The intention of the present study was to provide information on the quantity and type of phthalates and organotins in five PVC flooring samples that were purchased in the UK. The study was undertaken to provide empirical data on the chemical composition of PVC flooring. It was not intended to generate data for calculating potential leaching rates of phthalates and organotins from PVC flooring, or for calculating potential doses that individuals may take from exposure to PVC flooring in the home and potential consequences for human health.

METHODS

Samples

Five different samples of PVC flooring for analysis (NGP009, NGP010, NGP011, NGP012, NGP013) were purchased from various retail suppliers in the UK (see table 1).

Table 1. List of PVC Flooring Samples

Sample Number	Sample Brand
NGP009	Marley Floors. The Tile Collection, Cushioned tiles 5 010 941 207 609
NGP010	B & Q plc. Vinyl tiles. Item no. 24408486 Batch no. 0294
NGP011	Gerflor Limited. Classical collection, Rembrandt with roctop surface, 181 R
NGP012	Armstrong. Rhinofloor, Diamond with Rhinogloss, 30806
NGP013	Forbo Nairn. Cushionflor, Ultima, Gemini, 35128

Phthalates

Analysis of phthalates was carried out by the Laboratory of the Government Chemist, Teddington, Middlesex, UK, using a UKAS accredited method, LGC SOP OTH/C1-0015 (details provided on request). The above PVC flooring samples were analysed for six phthalates, as listed by the EU Scientific Committee on Toxicity, Ecotoxicity and the Environment (CSTEE), (Di-isononyl phthalate (DINP), Di-ethylhexyl phthalate (DEHP), Di-n-octyl phthalate (DnOP), Di-butyl phthalate (DBP), Di-isodecyl phthalate (DIDP), Butyl Benzyl

Phthalate (BBP). The limit of detection for all phthalate compounds tested for was ≤ 0.05 % by weight. Also tentatively identified was diheptyl phthalate which was co-extracted with the other phthalates.

Organotins

Organotin analysis was carried out by GALAB, D-21502 Geesthacht, Germany, using an accredited method (details available on request). The PVC flooring samples were analysed for organotins (monobutyltin (MBT), dibutyltin (DBT), tributyltin (TBT), tetrabutyltin, monooctyltin, dioctyltin, tricyclohexyltin and triphenyltin). The limit of determination was 0.3 μg/kg, limit of detection 0.1 μg/kg, measurement uncertainty 10-20% and recovery 75-100%.

RESULTS

Results of the analysis of 5 PVC flooring samples for phthalates and organotins are presented in tables 2 and 3 respectively. With regard to phthalates, DINP was found in all of the samples and BBP was present in three out of the five samples. Given the hazardous nature of these compounds the levels of DINP and BBP found in the samples are clearly of concern. Diheptyl phthalate was also detectable in 3 of the samples. All other phthalates that were analysed, including DEHP, were below the detection limit.

Several organotins were identified as components of all the PVC flooring samples. Dibutlytin (DBT) compounds are the most commonly used organotin stabilisers in PVC (see Matthews 1996). It was not surprising, therefore that DBT was found to be present at the greatest concentrations (range 37,700 to 569,000 ppb or 37.7 to 560 ppm).. Levels of TBT were also high (2,730 to 17,940 ppb) in four out of the five samples. The TBT concentrations in the PVC flooring samples were similar to those reported by in a recent study on 16 samples of PVC flooring from Germany (range, not detectable to 3520 ppb) (Oeko-Test 2000), with the exception of sample NGP009, for which the concentration (17,940 ppb) was nearly an order of magnitude higher than samples previously tested in Germany.

Table 2. Percentage Concentration by Weight of Phthalates in Samples of PVC Flooring

Phthalate (%m/m)	**Sample NGP009**	**Sample NGP010**	**Sample NGP011**	**Sample NGP012**	**Sample NGP013**
Di-isononyl phthalate (DINP)	8.26	4.7	14.3	15.8	7.4
Bis ethylhexyl phthalate (DEHP)	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05
Di-n-octyl phthalate (DnOP)	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05
Di-butyl phthalate (DBP)	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05
Di-isodecyl phthalate	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05

(DIDP)					
Butyl Benzyl Phthalate (BBP)	≤ 0.05	≤ 0.05	4.0	1.6	5.0
Compounds tentatively identified: Diheptyl phthalate (DHP)	-	-	√	√	√

Table 3. Concentration of Organotin Compounds (μg/kg) in Samples of PVC Flooring

Organotin (μg/kg)	Sample NGP009	Sample NGP010	Sample NGP011	Sample NGP012	Sample NGP013
Monobutyltin	5,300	1,620	48,800	330	2620
Dibutyltin	569,000	37,700	200,000	107,000	351,000
Tributyltin	17,940	128	4,390	2,730	5,100
Tetrabutyltin	12,300	138	5,770	1,440	4,350
Monooctyltin	120	980	400	<50	54
Dioctyltin	110	10,200	2,120	990	1,560
Tricyclohexyl -tin	<50	<50	<50	<50	<50
Triphenyltin	<50	<50	<50	<50	<50

Discussion

In this study, five different samples of PVC flooring purchased in the UK were analysed for phthalates and organotins. Even though the number of samples was small, some general trends were apparent. DINP was the predominant phthalate found and DBT was the organotin which was found at the highest concentrations in the PVC flooring samples. Monobutyltin, TBT, tetrabutyltin and dioctyltin were also found as chemical components in all samples, while monooctyltin was found at somewhat lower concentrations. Tricyclohexyltin and triphenyltin were below the limit of detection in all samples.

Regarding phthalates, DEHP has generally been recognised as the most commonly used phthalate plasticiser for PVC, at least until recently, and Blount *et al.* (2000) noted that DEHP and DINP are the phthalate esters produced in the largest quantities. In the current study, DINP, a mixture of 30 or more isomers of dinonyl phthalate, was found in all samples in quantities ranging from 4.7 to 15.8% by weight, whereas DEHP was below the limit of detection. The use of DINP in PVC flooring rather than DEHP may reflect a market shift away from DEHP towards the use of the much more poorly characterised isomeric phthalates. This shift may be a consequence of serious concerns relating to suspected reproductive toxicity and other hazards associated with DEHP (CSTEE 1998, Stringer *et al.* 2000). However, a shift to using DINP instead of DEHP should give no room for complacency because even though DINP has been not been studied as extensively as DEHP, it has also been shown to exhibit a range of toxic effects in laboratory animals. Therefore there is little reason to assume that it presents less of a potential hazard than DEHP.

BBP was found in samples NGP011, NGP012 and NGP013 at concentrations of 4.0, 1.6 and 5%. Given the high toxicity of BBP, it was not expected that this phthalate would be found as a plasticiser in PVC flooring. This phthalate has been shown to have teratogenic, reproductive and developmental effects in laboratory animals (see Blount *et al.* 2000). It has also been shown to have endocrine-disrupting properties in offspring of rats that were exposed to the chemical during gestation. Male offspring had significant decreases in sperm count as well as other reproductive abnormalities at an exposure dose which approached levels to which humans are exposed to in everyday life (Sharpe *et al.* 1995). Although two other studies could not repeat these results and the reasons for these inconsistencies are not clear, the authors remain confident of the validity of the original results (Sharpe *et al.* 1998). A study was undertaken recently in the US which investigated human exposure to phthalates (Blount *et al.* 2000). The study reported the presence of metabolites (breakdown products) of several phthalates in urine of nearly 300 individuals from the general population. It concluded that phthalate exposure is both higher and more common than previously expected, especially for BBP, DEP, and DBP. The authors noted that this was of concern given the reproductive and developmental toxicity of these chemicals in laboratory animals.

The presence and quantity of DINP and BBP found in PVC flooring in the present study is of concern given the potential toxicity of these compounds and their ability to leach from PVC potentially resulting in human exposure. It is of particular concern with respect to the health of children. According to Oie *et al.* (1997) small children are subject to the highest exposure risk from phthalate plasticisers used in surfaces in the home due to having a volume of respiration, per kg body weight, twice as large as adults and spending much time indoors. In addition, young children have a breathing zone close to the floor and this potentially increases their exposure (Jaakola *et al.* 1999). A study in Norway recently reported a higher incidence of bronchial obstruction among children living in homes with PVC flooring compared to children living in homes with wood or parquet floors. The link between exposure to PVC flooring and bronchial obstruction was suggested to possibly due to exposure to plasticisers (Jaakola *et al.* 1999). On this note, the use of PVC flooring in the home is of obvious concern.

The present study identified several organotin compounds as additives in PVC flooring samples. It was not an unexpected result to find organotins in PVC flooring, particularly DBT, since it is known that these chemicals are used as stabilisers in PVC plastic. However, the concentrations of some organotins in the flooring samples, most notably DBT and TBT, may be considered to be high. This is of concern given the immunotoxicity of these compounds.

PVC plastic is known to contain many different chemical additives. In the present study, a number of organotins and phthalate plasticisers were identified in PVC flooring samples, but these chemicals will not be the only additives present. Other hazardous chemicals such as chlorinated paraffins will most likely also be present in some cases. Given the potential toxicity of additives in PVC plastic to human health and to the environment, the future of this plastic is highly questionable. Indeed, decisions have already been made by national governments of Sweden (Swedish government Environmental Bill, adopted April 28th 1999) and Denmark (Strategy on PVC, June 1999) which involve restrictions on PVC. At the international level, legislation under the auspices of the OSPAR Convention is in place with regard to the phase out of all hazardous chemicals, including organotins and certain phthalates. This agreement to phase out all hazardous chemicals by the year 2020 was undertaken by 15 states of the North East Atlantic Region and the European Commission. As a first step towards implementation of the agreement, OSPAR also agreed in 1998 on a “List of Chemicals for Priority Action” (the

Priority List). The list includes organotins and the phthalates DBP and DEHP. It was agreed that chemicals on the priority list required urgent action to address their discharges, emissions, and losses by 2003. For the organotins, the priority action has focused on the main sources of organotins, that is TBT in shipping and triphenyltin in agricultural use (PRAM 2000).

Conclusions

In conclusion, hazardous chemical additives, phthalates and organotins, were identified in five samples of PVC flooring purchased in the UK. These chemicals have the potential to leach into the environment from flooring resulting, in turn, in human exposure. This is of concern given potential effects on health of these compounds. Measures have already been agreed at international and national levels to phase out the use of certain phthalates and organotins on the basis of concerns for human health and the environment. The presence of these hazardous substances in PVC flooring highlights an important product sector which will need urgent attention in this regard. Moreover, given that the use of hazardous additives in PVC is seemingly unavoidable, and their leaching inevitable, the use of PVC for such applications must be questioned.

References

Belfroid, A.C., Purperhart, M. & Ariese, F. (2000). Organotin levels in seafood. Marine Pollution Bulletin 40 (3): 226-232.

Blount B.C., Silva M.J., Caudill S.P., Needham L.L., Pirkle J.L., Sampson E.J., Lucier G.W., Jackson R.J. and Brock J.W. (2000). Levels of seven urinary phthalate metabolites in a human reference population. Environmental Health Perspectives 108 (10): 979-982.

Bryan, G.W., Gibbs, P.E., Hummerstone, L.G. & Burt, G.R. (1986) The decline of the gastropod *Nucella lapillus* around south-west England: evidence for the effect of tributyltin from antifouling paints. Journal of the Marine Biological Association U.K. 66: 611-640.

Bryan, G.W., Gibbs, P.E., Hummerstone, L.G. & Burt, G.R. (1987). Copper, zinc and organotin as long-term factors governing the distribution of organisms in the Fal estuary in southwest England. Estuaries 10(3): 208-219.

Cadogan D.F., Papez M., Poppe A.C., Pugh D.M. and Scheubel J. (1993). An assessment of the release, occurrence and possible effects of plasticisers in the environment. PVC 93. The Future.

CSTEE (1998). Scientific Committee on Toxicity, Ecotoxicity and the Environment (CSTEE). Opinion on: Phthalate migration from soft PVC toys and child-care articles – Data made available since 16th June 1998. Opinion expressed at the 6th CSTEE plenary meeting. Brussels, 26/27 November 1998.

Ehrig R.J. (Ed.) (1992). Plastics recycling. Products and Processes. Munich: Hanser Publishers, 289 pp.

Friedberg M. and Karlsson R. (1993). Low emission PVC - Floorings and Indoor Air Quality. In: PVC 93: The Future. The Institute of Materials PVC Group of the Polymer Industry Division. 27-29 April 1993, Brighton Metropole Hotel, Brighton, UK.

Gibbs, P.E., Pascoe, P.L. & Burt, G.R. (1988). Sex change in the female dog-whelk, *Nucella lapillus*, induced by tributyltin from antifouling paints. Journal of the Marine Biological Association U.K. 68: 715-731.

Gibbs, P.E. (1993). A male genital defect in the dog-whelk, *Nucella lapillus* (Neogastropoda), favouring survival in a TBT-polluted area. Journal of the Marine Biological Association U.K. 73: 667-678.

Hardell L., Ohlson C-G. and Fredrikson M. (1997). Occupational exposure to polyvinyl chloride as a risk factor for testicular cancer evaluated in a case control study. International Journal of Cancer 73: 828-830.

Howick C. (1996). Emissions from PVC materials - What is the current situation? In: PVC 1996 New Perspectives. The Institute of Materials PVC Committee. 23-25 April Metropole Hotel, Brighton, UK.

Jaakkola J.J., Oie L. Nafstad P., Botten G., Samuelsen S.O. and Magnus P. (1999). Interior surface materials in the home and the development of bronchial obstruction in young children in Oslo, Norway. American Journal of Public Health 89 (2): 188-191.

Kemi Report (1994). Phthalic acid esters used as plastic additives: The Swedish National Chemicals Inspectorate, Report 12/94. ISSN 0284-1185.

Kergosien D.H. and Rice C.D. (1998). Macrophage secretory function is enhanced by low doses of tributyltin-oxide (TBTO), but not tributyltin-chloride (TBTCl). Arc. Environ. Contam. Toxicol. 34: 223-228.

MAFF (1996). Ministry of Agriculture, Fisheries and Food. Phthalates in Food. Food surveillance Information Sheet Number 82, March 1996.

Matthews G (1996). PVC. Production, Properties and Uses. The Institute of Materials. ISBN 0 901716 59 6.

Mersiowsky I., Stegmann I., Ejlertsson J. and Svensson B. (1999). Long-term behaviour of PVC Products under soil-buried landfill conditions. Final Report of the Research Project. TUHH. 2nd revised edition.

Moller S., Larsen J., Jelnes J.E., Faegemann H., Ottosen L.M. and Knudsen F.E. (1996). Environmental aspects of PVC. Publ: Danish Environmental Protection Agency, Environmental Project No. 313. 110pp.

Moore, D.W., Dillon, T.M. & Suedel, B.C. (1991). Chronic toxicity of tributyltin to the marine polychaete worm, *Neanthes arenaceodentata*. Aquatic Toxicology 21: 181-198.

Official Journal of the European Communities (1999). Commission Decision of 7 December 1999. OJ L 315/46 9.12.1999.

Oie L., Hersoug L-S., Madsen J.O. (1997). Residential exposure to plasticisers and its possible role in the pathogenesis of asthma. Environmental Health Perspectives 105 (9): 972-978.

PRAM (2000). OSPAR Programmes and Measures Committee (PRAM). Draft OSPAR background document on organic tin compounds. Presented by the Netherlands. PRAM 00/3/8-E. Calais: 10-14 April, 2000.

Sadiki A-I. and Williams D.T. (1999). A study on organotin levels in Canadian drinking water distributed through PVC pipes. Chemosphere 38 (7): 1541-1548.

Sharpe R.M., Fisher J.S., Millar M.M., Jobling S. and Sumpter J. (1995). Gestational and lactational exposure of rats to xenoestrogens results in reduced testicular size and sperm count production. Environmental Health Perspectives 103 (12): 1136-1143.

Sharpe R.M., Turner K.J. and Sumpter J.P. (1998). Endocrine disruptors and testis development. Environmental Health Perspectives 106 (5): A220-A221.

Stringer R. and Temuge T. (1998). The Dark Side of Petkim. Greenpeace 1998.

Stringer R., Labunska I., Santillo D., Johnston P., Siddorn J and Stephenson A. (2000). Concentration of phthalate esters and identification of other additives in PVC children's toys. Environmental Science and Pollution Research 7 (1): 27-36.

US ATSDR (1997). (Agency for Toxic Substances and Disease Registry, US Public Health Service). Toxicological Profiles. CRC Press Inc.

van der Naald W. and Thorpe B.G. (1998). PVC Plastic: A looming waste crisis. Greenpeace International. ISBN 90-73361-44-3.