

# Christmas dinner



*Phthalates and alkylphenols in samples of  
Common carp (Ciprinus carpio L.) from  
4 European countries*

**GREENPEACE**

**Christmas dinner – contaminated**

Phthalates and alkylphenols in samples  
of Common carp (*Ciprinus carpio L.*)  
from 4 European countries

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## Executive summary

The aim of this investigation was to identify the presence and quantify the amount of two groups of chemicals – phthalate esters (or phthalates) and alkylphenols - in samples of carp (*Ciprinus carpio L.*) purchased from a selection of retailers in 4 European countries<sup>1</sup>. Greenpeace commissioned laboratory tests of 12 samples of carp flesh (meat) in total (i.e. 3 from each country). The results confirm widespread presence of phthalates in the samples obtained, as well as more limited evidence for the presence of alkylphenols.

Of particular concern was the presence, and unexpected abundance, of the phthalates DiBP (diisobutyl phthalate), DnBP (di-n-butyl phthalate) and DEHP (bis(2-ethylhexyl)-phthalate) in all samples. This points to another route of human exposure to these known hazardous chemicals, which must be taken into account when assessing the complexity of cumulative exposure from all sources.

Due to the fact that the analyzed samples were obtained by purchase in shops and not directly fished from carp ponds, it is impossible to establish the origin of the contamination with these substances and further research would be needed in this area. However, it was not the aim of the study to distinguish between sources of contamination through the supply chain but simply to determine levels of contamination in the final product at point of sale. The simple fact that these hazardous substances or substances of concern are present in food as it would be purchased and consumed is a matter of great concern.

This latest research, while necessarily limited in scope and sample size, nevertheless contributes both to the otherwise very limited body of evidence on the presence of phthalate esters in fish tissues and to the current legislative debate. In particular, it adds further weight to the argument that legislative measures which attempt merely to place limits on levels of hazardous chemicals in releases from industry, in products or in food can never guarantee a high level of protection for the environment or human health from chemical exposure. The widespread presence of these chemicals in carp tissue demonstrates once again that their ‘adequate control’ is not possible.

The widespread presence of hazardous chemicals is clearly not confined to products nor the environment in its broadest sense. Ultimately these substances are ‘returning’ to humans via a variety of routes including food. The results of these investigations illustrate the need to change the current approach to managing chemicals and to use precautionary principle with the aim of eliminating hazardous chemicals. In order to fulfill this aim two basic elements need to be agreed – sufficient information about the hazardous properties of chemicals must be available and substitution of hazardous chemicals must be mandatory if safer alternatives are available. In this context, these results reinforce the need for legislation that will drive the replacement of hazardous substances with safer alternatives. The current development of new EU legislation on the manufacture and use of chemicals, known as REACH (Registration, Evaluation and Authorisation of Chemicals), provides the opportunity to set out requirements for such substitution as a vital contribution to protecting the public from exposure to hazardous chemicals.

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<sup>1</sup> Austria, Czech Republic, Poland and Slovak Republic

## Introduction.

Due to their widespread use and production, hazardous chemicals are present in many parts of the environment and biota. At the same time we do not have adequate information about most of the chemicals on the market in the EU. This chemical crisis is the result of inadequate government policies towards the management of chemicals to date. In so many aspects of our daily lives, we use and release into the environment, often inadvertently, a wide range of chemicals. The hazards posed by the majority of these substances have never been properly assessed. At the same time, current legislation fails to control exposure even to chemicals that are known to possess hazardous properties, irrespective of whether safer alternatives already exist. As a consequence, from remote, inaccessible regions of the globe to the domestic environment, we find increasing evidence of chemical contamination. Wild animals from the Arctic to the deep sea (Law et al. 2003, Lebeuf et al. 2004, Martin et al. 2004, Rayne et al. 2004, de Boer et al. 1998), rainwater (ter Schure and Larsson 2002, Peters 2003), dust in our homes (Rudel et al. 2003, Santillo et al. 2003a,b), and even our own bodies (WWF 2004, Peters 2004) have all been shown to be polluted with hazardous industrial chemicals. These chemicals are now so ubiquitous that a baby is exposed to industrial chemicals before he or she is even born (Dorey 2003, Peters 2005). Chemicals that persist and build up in our bodies (bioaccumulate), that may be capable of causing cancers or other adverse health effects that may even interfere at a fundamental level with hormone communication systems and their role in development pose unknown consequences for our future (Darnerud 2003, Sharpe and Skakkebaek 2003, Dorey 2003).

There is increasing evidence and concern that the chemicals used in everyday products may pose a threat to human health and environment. Chemicals used as flame-retardants in electronics products such as mobile phones, computers or televisions can contaminate a mother's milk (Lind et al. 2003, Kalantzi et al. 2004). Substances used in the plastic-coated prints sometimes found on children's pyjamas (Greenpeace 2004) are capable of interfering with development, hormone communication and immune system function in animals (Kergosien and Rice 1998, Chitra et al. 2002, Kumasaka et al. 2002, Adeoya-Osiguwa et al. 2003).

As part of an ongoing project, Greenpeace has commissioned independent laboratories to analyse a wide range of consumer products for potentially harmful substances<sup>2</sup>. Greenpeace has also reviewed the actions and policies of a number of consumer goods manufacturers to evaluate their use of, and measures to eliminate, potentially hazardous chemicals from their products. The good news is that a growing number of companies are taking positive and proactive steps to replace such chemicals from a variety of consumer items, ranging from sports shoes and toys to mobile phones, textiles and body care products. The bad news is that many other companies continue to disregard mounting health and environmental concerns over the chemicals added to their products. Information on chemicals used in products and on companies' chemicals policies is published on the Greenpeace products database<sup>3</sup>.

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<sup>2</sup> (see <http://www.greenpeace.org/chemprodreport> and <http://www.greenpeace.org/addproducts>)

<sup>3</sup> (available in English at <http://www.greenpeace.org.uk/Products/Toxics/>, in French at [www.vigitox.org](http://www.vigitox.org), in Dutch at [www.lichaamzondergif.nl](http://www.lichaamzondergif.nl), in Spanish at <http://archivo.greenpeace.org/toxicos/html/home.html> and Czech at <http://www.toxickydomov.cz>)

It is this inaction on the part of the bad companies and continuous production of hazardous chemicals by the chemicals industry that causes the ongoing pollution of the environment and human health. A very recent Greenpeace study documented wide spread contamination of the eels from 10 European countries with brominated flame retardants and PCBs (Santillo et al. 2005).

The European Union is currently deciding on proposals for a substantial new piece of chemicals legislation, known as REACH (Registration, Evaluation and Authorisation of CHemicals). On 17th of November 2005 The European Parliament passed this proposal in the first reading. The Council of Ministers is expected to reach the political agreement during December 2005. In order to protect the environment and public health it is necessary that Council, and later the European Parliament in its second reading, uphold the requirement to substitute hazardous chemicals by replacing them with safer alternatives wherever available, as was recently agreed by the European parliament in its first reading. But it is also important that the lawmakers strengthen the requirements in the registration part of the proposal, i.e. the very basis by which information on the uses and hazards of all chemicals on the market was initially meant to be gathered. This element has so far been substantially weakened, in part through intensive lobbying by industry. Without adequate information about the properties of the chemicals in use it will be very hard to identify the hazardous ones before the full scale of the problems related to them unfolds. Mandatory substitution of hazardous chemicals and requirement for sufficient information in the registration phase are both necessary and must become the key elements of the good chemicals legislation.

## **Analysis of carp samples**

In October 2005 Greenpeace commissioned analysis of 12 samples of Common Carp (*Ciprinus carpio L.*) in the independent laboratories LGC Ltd. in the United Kingdom (LGC 2005). The samples were purchased in the supermarkets and on the markets in 4 Central European countries – Austria, Czech Republic, Poland and Slovak Republic (3 samples per country, see Table 1). The supermarkets, as well the samples, were randomly selected. The laboratories analyzed these samples for presence of various phthalate esters and alkyphenols. The full list of substances analyzed is presented in Table 2.

The analysis showed presence of phthalates in all samples. Alkyphenols were detected in 5 out of 12 samples analyzed (Table 3).

Of the phthalates analyzed, DiBP, DnBP and DEHP were present in all samples. In the case of DiBP, remarkably found at concentrations above 1000 ng.g<sup>-1</sup> (1 ppm) wet weight (ww) in all 12 samples, the highest level measured was 8816 ng.g<sup>-1</sup> (8.8ppm ww) in the sample Poland 2. Samples Austria 3 and Slovakia 1 also contained levels that were significantly higher than the rest of the group, at 5409 and 4884 ng.g<sup>-1</sup> (5.4 and 4.9ppm ww) respectively. DiBP was the most abundant phthalate found in all but one sample (Austria 1).

The consistently high levels of DiBP recorded in the carp tissue are an unexpected feature and one which demands further investigation. Quality control procedures employed by the analysing laboratory confirm the identity of the substance as DiBP and, even allowing for the relative difficulty in quantifying phthalates present as isomeric mixtures, it seems clear that DiBP is a predominant contaminant in the carp muscle tissue sampled.

To our knowledge, this is the first study to quantify residues of DiBP in fish muscle tissue. As such, comparison of the high levels found here with previous studies is simply not possible. Given the levels found, however, it would clearly be valuable to extend studies of this compound to other specimens and, indeed, other species in order to determine if accumulation of this compound is a reproducible phenomenon.

This study does not give insight, nor attempt to give insight, into potential sources of DiBP (or, indeed, the other phthalates detected). DiBP has similar physicochemical properties to DnBP and, according to industry sources, is used in similar applications. In comparison to DnBP, however, the toxicity and environmental fate of DiBP appear to have been very poorly researched. Whether there is any specific and substantial source of DiBP exposure in the carp-growing industry, or in materials commonly used in preparing carp for sale, is not currently known but deserves further investigation.

DnBP was commonly the second most abundant phthalate present. Three samples contained levels of this compound slightly above 1000 ng.g<sup>-1</sup> (1ppm ww), namely Austria 3, Poland 1 and Slovakia 1. The remaining nine samples contained levels in the range 260 to 640 ng.g<sup>-1</sup> (0.26-0.64 ppm ww).

The only other phthalate detected in all 12 samples was the widely used, and more commonly recognized environmental contaminant, DEHP. The highest level was found in sample Austria 3 (834 ng.g<sup>-1</sup> wet weight, or 0.83ppm ww) and the second highest in sample Poland 3 (503 ng.g<sup>-1</sup> wet weight, or 0.5ppm ww). Levels in other samples fell between 75 and 285 ng.g<sup>-1</sup> (0.075-0.28ppm ww).

Both DnBP, also known simply as DBP, and DEHP are classified as toxic for reproduction: category 2 under Directive 2003/36/EC amending, for the 25th time, Council Directive 76/769/EEC (CONSLEG 2004). These same phthalates were banned in 2003 for use in cosmetics products by Directive 2003/15/EC. This ban took effect in March 2005. The evidence for adverse impacts on early development of mammals, especially reproductive development, is extensive for both these phthalates, and has been reaffirmed by several recent studies. For further details, see the Annex1.

After a temporary EU-wide ban on the use of certain phthalates in children's toys and childcare articles had been renewed numerous times, the European Parliament finally decided on a permanent ban on the use of DEHP, DBP and BBP in all toys and childcare articles in July 2005. The not yet published Directive also prohibits the use of the phthalates DINP, DIDP and DnOP in toys and childcare articles that can be put in the mouth whether or not they are intended for this use (EP 2005).

With respect to the other phthalates included in this study, diethyl phthalate or DEP (used extensively as a carrier solvent and alcohol denaturant in cosmetics and other personal care products (Greenpeace 2005)) was identified above the detection limit in

11 out of 12 samples, while diisononyl phthalate or DINP (commonly used as a plasticizer in soft PVC products) was present in 5 out of 12 samples, with levels in sample Austria 3 (8912 ng.g<sup>-1</sup> wet weight, or 8.9ppm ww) far exceeding those in the other samples. Incidentally, this was also the highest level of any single phthalate measured in this study. Dimethyl phthalate or DMP was also detected in 5 samples analyzed.

Concentrations of certain other phthalate esters, especially the commonly used and encountered DEHP, have recently been determined in other fish species. Ost recently, for example, Vethaak *et al.* (2005) reported levels of DEP, DBP (DnBP) and DEHP in muscle of bream (*Abramis brama*) caught in Dutch waters of 22-231, 20-147 and 70-1503 ng g<sup>-1</sup> wet weight respectively. Median values were higher for carp in the current study than in the bream studied by Vethaak *et al.* (2005) for DBP (531 compared to 44 ng g<sup>-1</sup>), somewhat lower for DEP (58 compared to 111 ng g<sup>-1</sup>) and of a similar order for DEHP (184 compared to 153 ng g<sup>-1</sup>). Levels in muscle tissue of flounder (*Platichthys flesus*) analysed by Vethaak *et al.* (2005) were generally far lower (medians 7.8 ng g<sup>-1</sup> for DBP, 34 ng g<sup>-1</sup> for DEP and 64 ng g<sup>-1</sup> for DEHP). Whether these differences primarily reflect differences in sources and pathways of exposure in the fish from Dutch waters compared to the carp, or species-specific patterns of accumulation of phthalate esters, remains to be determined through future research.

The alkylphenols were detected far less frequently in the analyzed samples compared to phthalates, though this was due in part to the relatively high detection limits achievable (generally greater than 100 ng g<sup>-1</sup>, or 0.1ppm ww). 4-nonylphenol was detected in 4 out of 12 samples, with the highest concentration measured in sample Slovakia 1 (145 ng.g<sup>-1</sup> wet weight, or 0.14ppm ww). 4-n-octylphenol was identified above the detection limit in only one sample, namely Austria 1, despite the lower detection limits achievable for this compound.

## Accept the risk or take precautions?

Carp sold on the markets in the Central Europe are predominantly originating from aquaculture ponds which have a centuries-long tradition in this region. Large ponds in which these carp and other fishes are farmed belong in some parts of the region to the traditional countryside and are part of the cultural heritage. They are quite isolated from the large river bodies. Prior to the actual placing on the market the living carp are placed for a certain period into artificial basins to clean them of sediment and suppress the muddy taste of their flesh.

Due to the fact that the analyzed samples were obtained by purchase in shops and not directly fished from these ponds, it is impossible to establish the origin of the contamination with these substances and further research would be needed in this area. For example, the possibility cannot be excluded that materials used in the preparation of carp for sale, storage and handling by the retailer and final packaging for the consumer may have contributed to the levels of phthalates found in the final tissue samples analysed in this study. However, it was not the aim of the study to distinguish between sources of contamination through the supply chain but simply to

determine levels of contamination in the final product at point of sale. The simple fact that these hazardous substances or substances of concern are present in food as it would be purchased and consumed is a matter of great concern.

The widespread presence of hazardous chemicals is clearly not confined to products nor the environment in its broadest sense. Ultimately these substances are ‘returning’ to humans via a variety of routes including food (but also including direct exposure to consumer products, to contaminated air and dust in the indoor environment, etc.) (see e.g. Santillo et al. 2003a,b). This latest research, while necessarily limited in scope and sample size, nevertheless contributes both to the otherwise very limited body of evidence on the presence of phthalate esters in fish tissues and to the current legislative debate. In particular, it adds further weight to the argument that legislative measures which attempt merely to place limits on levels of hazardous chemicals in releases from industry, in products or in food can never guarantee a high level of protection for the environment or human health from chemical exposure. The widespread presence of these chemicals in carp tissue demonstrates once again that their ‘adequate control’ is not possible. There is a clear need for precautionary action, and specifically a need to eliminate hazardous chemicals by substituting them with safer alternatives.

The definitive health risks of any particular chemical substance are always difficult, if not impossible, to quantify, and though they may take many years to complete, standard risk assessments are often highly subjective or even inconclusive. The assumptions used and judgments made in reaching conclusions regarding risks to the environment or human health are rarely communicated beyond technical papers, despite the importance of these aspects to the interpretation of conclusions drawn and the degree of uncertainty that underlies them. Moreover, risk assessment starts from the position that some level of exposure to a chemical, even one showing intrinsically hazardous properties, is ultimately ‘acceptable’ and can be managed. Given the added complexities resulting from the fact that we are exposed not to individual chemicals, but chemical mixtures and that there are commonly many different sources of each chemical in our daily lives, it is clear that traditional narrow risk assessment techniques are unlikely to provide adequate protection.

A more precautionary approach to the evaluation and control of chemicals is urgently required.

## **The way forward**

This research showed the wide presence of hazardous and potentially hazardous chemicals in samples of common carp (*Ciprinus carpio L.*) from 4 European countries. There are no known legislative limits on the content of phthalates and alkylphenols in carp or in fish tissue generally. Nevertheless, given the levels detected here, consumption of carp has the potential to make a significant contribution to overall exposure to phthalates from all sources.

The solution lies in the good overarching chemicals legislation that would set to provide sufficient information about produced and used chemicals and eliminate hazardous ones.

REACH, the proposed EU chemicals reform, has the potential to set in motion an authorisation process that would require the phase out and substitution of hazardous chemicals, in particular ‘substances of very high concern’ which display properties that may harm our health and environment. This includes chemicals that are persistent, bioaccumulative and toxic (PBT) and those that are very persistent and very bioaccumulative (vPvB), chemicals that have the potential to cause cancer, reproductive damage or give rise to genetic mutations (CMR) and chemicals that can affect the hormonal system (endocrine disruptors). While it remains to be seen whether phthalates and alkylphenols will ultimately be officially identified as “chemicals of very high concern” under REACH and thus undergo the authorization process (or whether, in fact, their use will be largely prohibited in future under the Restrictions component of REACH), the emerging evidence of hazardous properties clearly gives grounds for their consideration. It is also necessary that the final legislation contains the requirement to provide sufficient information about the properties of the chemicals in order to establish the hazards they might pose.

The REACH proposal, published by the EU Commission in October 2003, has suffered from intensive lobbying by industry. The proposed regulation contains a loophole that would authorize the continued use of a ‘substance of very high concern’ even if a safer alternative were available.

Greenpeace believes that for REACH to protect us from exposure to harmful chemicals, an authorisation for the use of ‘chemicals of very high concern’ should be refused unless no safer alternatives are available and the use is essential to society. This is the principle of substitution.

Although the European Parliament in its first reading of the REACH proposal supported the demand for mandatory substitution of hazardous chemicals, it is now up to the Council of Ministers to support this demand.

Some companies are responding to increasing consumer awareness of synthetic chemicals in products and are setting in place policies to phase out and replace certain harmful chemicals. Such companies prove that an innovative approach, leading to a new generation of safer products, can equally lead to commercial success. But without the sufficient information about the properties of the chemicals available these companies will have very hard task in identifying all the hazardous chemicals and even proper safer alternatives. Furthermore, voluntary agreements and commitments are not enough to drive innovation “across the board” and the green solutions necessary to ensure environmental and consumer protection from hazardous chemicals. REACH needs to provide the legally binding structures to implement a chemicals policy based on precaution and driving innovation.

The challenge now is for elected representatives and government ministers to strengthen REACH and thus to protect us from hazardous chemicals in everyday life.

## TABLES

**Table 1.**

Sample	Country of origin	Date of purchase	Place of purchase
Austria 1	Austria	8.10.2005	Nordsee, Vienna
Austria 2	Austria	8.10.2005	Hella Gruber, Vienna
Austria 3	Austria	8.10.2005	Billa Corso, Vienna
Czech Republic 1	n/a	6.10.2005	Tesco, Prague
Czech Republic 2	n/a	6.10.2005	Delvita, prague
Czech Republic 3	n/a	6.10.2005	Carrefour, Prague
Poland 1	Poland	10.10.2005	Carrefour, Warsaw *
Poland 2	Poland	10.10.2005	Carrefour, Warsaw *
Poland 3	Poland	10.10.2005	Auchan, Warsaw
Slovakia 1	Slovakia	9.10.2005	Carrefour, Bratislava
Slovakia 2	Slovakia	9.10.2005	Tesco, Bratislava
Slovakia 3	Slovakia	9.10.2005	Metro, Ivanka pri Dunaji

\* according to the information provided by the retailer during the purchase the samples originated from 2 different sources

**Table 2.**

Name	Abbreviation
Di-methylphthalate	DMP
Di-ethylphthalate	DEP
Di-n-propylphthalate	DPP
Di-isobutylphthalate	DiBP
Di-n-butylphthalate	DnBP
Butylbenzylphthalate	BuBzP
Di-2-ethylhexylphthalate	DEHP
Di-isononylphthalate	DINP
Di-n-Octylphthalate	DOP
Di-isodecylphthalate	DiDP
4-(1,1,3,3-tert-methylbutyl)phenol	4TMBP
4-n-Octylphenol	4nOP
4-Nonylphenol	4NP

**Table 3.**

ng/g (wet weight)	DMP	DEP	DPP	DiBP	DnBP	BuBzP	DEHP	DOP	DINP *	DiDP *	4TMBP	4OP	4NP *
Austria 1	<12.6	52.3	<12.6	2668.0	561.2	<12.6	285.8	<12.6	8912.5	<126.1	<12.6	14.0	<126.1
Austria 2	11.9	72.4	<11.7	2757.5	637.9	<11.7	131.1	<11.7	<117.2	<117.2	<11.7	<11.7	119.9
Austria 3	<12.1	59.0	<12.1	5409.7	1046.1	<12.1	834.4	<12.1	<121.5	<121.5	<12.1	<12.1	124.8
Czech Republic 1	<10.5	57.1	<10.5	2913.0	451.7	<10.5	96.6	<10.5	<104.8	<104.8	<10.5	<10.5	<104.8
Czech Republic 2	10.2	59.5	<10.1	1566.4	442.1	<10.1	182.1	<10.1	204.1	<100.5	<10.1	<10.1	<100.5
Czech Republic 3	<12.3	58.7	<12.3	2037.3	452.7	<12.3	208.1	<12.3	<122.6	<122.6	<12.3	<12.3	<122.6
Poland 1	21.8	81.7	<12.5	2071.3	1018.9	<12.5	186.8	<12.5	179.8	<124.8	<12.5	<12.5	<124.8
Poland 2	<13.8	<13.8	<13.8	8816.1	622.3	<13.8	114.5	<13.8	<138.0	<138.0	<13.8	<13.8	<138.0
Poland 3	12.8	51.0	<11.4	1746.6	501.8	<11.4	503.0	<11.4	<114.2	<114.2	<11.4	<11.4	<114.2
Slovakia 1	<12.9	82.6	<12.9	4884.8	1077.7	<12.9	213.4	<12.9	<129.1	<129.1	<12.9	<12.9	145.4
Slovakia 2	10.3	48.0	<9.1	2827.7	423.8	<9.1	102.6	<9.1	199.8	<90.9	<9.1	<9.1	<90.9
Slovakia 3	<7.6	34.5	<7.6	1001.9	261.7	<7.6	75.9	<7.6	179.0	107.3	<7.6	<7.6	89.1

\* Three analytes, (nonylphenol, di-isononylphthalate and di-isodecylphthalate) have multiple isomers and an inherent lower response. The lowest calibration standard for these compounds was at the 250ng mL<sup>-1</sup> level.

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## ANNEX 1

# PHTHALATES

**Around ninety percent of the total quantity of phthalates produced in Europe are used as softeners in PVC products like toys, rain clothing, floor covering, vinyl wallpaper and electrical cables. Other applications include use in paints, glues, printing inks and cosmetics.**

### PRODUCTION AND USE

Despite its recognized toxicity, DEHP is undoubtedly still the most commonly used plasticizer in PVC plastics. Other widely used phthalates are DINP and DIDP. DBP and DEP are more volatile and are primarily used as plasticisers in specialist polymer dispersions, as gelling agents and as solvents or fixatives in cosmetics and other personal care products (Santillo *et al.* 2003). DEP is used in a wide range of personal care products as a solvent and vehicle for fragrances and other cosmetic ingredients. Another application of DEP is to render the alcohol used in cosmetics unfit to drink (SCCNFP 2003).

In Western Europe about one million tonnes of phthalates are produced each year, of which approximately 900,000 tonnes are used to plasticize PVC (polyvinyl chloride). DEHP alone accounts for about 30% of the volume produced (ECPI 2005).

### ENVIRONMENTAL DISTRIBUTION

As a result of their high production volume and widespread use, phthalates have become among the most ubiquitous man-made chemicals in the global environment (Santillo *et al.* 2003). They do not easily biodegrade and can, in some cases, accumulate in the environment and in organisms. In a TNO study commissioned by Greenpeace Netherlands in 2003, the phthalates DEHP and DINP were measured in significant concentrations in rainwater (Peters 2003).

Since DEP is an ingredient of perfumes and other personal care products it appears that inhalation of DEP may be a significant route of exposure (Adibi 2003). Absorption through the skin is also likely to be a contributory factor. Scientists found high concentrations of phthalate breakdown products in women's urine, to which the use of nail varnish and perfume may have made a significant contribution (Blount *et al.* 2000). Small children may have a higher exposure to phthalates than adults via toys, household furnishings and floor coverings. In a urine study in the USA, the highest concentrations of metabolites for a number of phthalates were found in the urine of children aged between 6 and 11 (CDC 2003). Hospital patients may be exposed through the use of PVC in medical equipment. The phthalate DEHP in PVC blood and infusion bags has been shown to leach into the blood (Rubin *et al.* Schiffer 1976).

Overall, despite the recognition that our exposure to phthalates is commonplace, precise information on the significance of different sources and their contribution to overall exposure remains limited (Latini 2005).

## EFFECTS

A variety of adverse effects have been attributed to phthalate exposure in laboratory studies, while increasing epidemiological evidence suggests links between exposure and effects even in humans detectable at population level. Historically, most interest centred on impacts of phthalate esters on the liver and kidney as target organs, and on carcinogenicity as the endpoint of primary concern. It has been known for some time, for example, that long-term exposure of rats to the phthalate DINP led to increases in liver and kidney weight (CSTEE 1998). Furthermore, exposure to DEHP has been linked to liver cancer in rodents (Seo *et al.* 2004). In the last decade, however, attention has shifted to the observed ability of many phthalate esters to interfere at fundamental level with development in young animals, especially development of the reproductive system, possibly mediated through disruption of hormone systems. What has also become clear is that much of the toxicity observed can be attributed not to the parent diester compounds themselves, but to their primary monoester breakdown products which are formed rapidly in the body.

Several phthalates, e.g. DEHP, DBP and BzBP, or at least their monoester metabolites, appear to have an anti-androgenic effect. Exposure during pregnancy can affect the development of the testicles and sperm production (Park *et al.* 2002, Ema *et al.* 2002, Miyawaki 2002, Mylchreest *et al.* 2002). One study reported that girls with early breast development (6 months - 8 years) often had phthalates in their blood serum in much higher concentrations than their age contemporaries in the control group (Colon *et al.* 2000).

DEP has generally been considered to have a low overall toxicity, but newly emerging evidence raises significant concerns regarding its safety. DEP is rapidly metabolized in the human body to its monoester form (MEP), which has been reported at up to thirty times higher concentrations in human urine than metabolites of any other phthalate ester (Duty *et al.* 2003). The highest levels were found in women, possibly reflecting differences in frequency of use of personal care products (Silva *et al.* 2004).

Changes to the DNA of human sperm cells were found to be more prevalent in individuals who also show high levels of MEP in their urine (15); further studies are necessary to determine if there is a causal relationship. Other research has identified a possible link between exposure to two phthalate metabolites, namely MEP and MBP (monobutyl phthalate), measured in urine samples and restricted lung function in adult men (Hoppin *et al.* 2004). A recent study found an association between male genital development and some phthalate metabolites, including MEP and MBP. These findings support the hypothesis that prenatal phthalate exposure at environmental levels can adversely affect male reproductive development in humans (Swan *et al.* 2005).

In addition to its known reproductive toxicity, DBP is also classified within the EU as “very toxic to aquatic organisms”. Recent studies have confirmed that DBP, following conversion in the body to MBP, can interact directly with enzyme systems in mammals involved in steroid and lipid metabolism (Wyde *et al.* 2005) and that even short-term prenatal exposure to MBP can lead to long-term developmental impacts after birth (Kremer *et al.* 2005, Kai *et al.* 2005). Irreversible impacts on the mammary glands in male rats have also been reported (Lee *et al.* 2004). Fennell *et al.* (2004) recently confirmed that MBP can cross the placenta and is detectable, either as MBP or as further metabolites in amniotic fluid.

The other phthalate recognized as a reproductive toxin, namely DEHP (again primarily as its primary metabolite MEHP), was shown by Awal *et al.* (2005) to cause very rapid onset of damage (after only a few hours) in the developing testes of young guinea pigs. In addition, Voss *et al.* (2005) have recently highlighted previously unidentified risks of testicular cancer following lifetime exposures to DEHP.

### EXISTING CONTROLS

In 1998, the OSPAR Commission agreed on the target of cessation of discharges, emissions and losses of all hazardous substances to the marine environment by 2020. DBP and DEHP were included on the first list of chemicals for priority action towards achieving this target (OSPAR 1998). The use of phthalates in soft PVC children's toys has been an issue of major concern, because children can ingest these softeners by sucking and biting on the toys. At the end of 1999 the EU unanimously agreed to a three-month ban of certain phthalates in toys, which could be put in the mouth and in childcare articles for the under-threes. This ban was repeatedly extended and was therefore actually in place for years.

In July 2005 the European Parliament decided to a permanent ban on the use of DEHP, DBP and BBP in all toys and childcare articles. The EP also agreed to ban the phthalates DINP, DIDP and DNOP in toys and childcare articles that can be put in the mouth whether or not they are intended for this use (EP 2005).

Bis(2-Methoxyethyl) phthalate (since 1999), DEHP and DBP (since 2003) are also classified as Toxic for reproduction: category 2 under directive 76/769/EEC (CONSLEG 2004). These same phthalates were therefore banned for use in cosmetics products by directive 2003/15/EC amending the cosmetics directive 76/768/EEC (EC 2003).

The new European chemicals legislation REACH is expected to come into force in 2006. If regulators show willing it would provide an excellent opportunity to phase out other uses of these chemicals.

### ALTERNATIVES

Phthalates are mainly used in PVC. The best solution is to replace PVC products with other materials: linoleum, tiles, wood or carpet on the floor instead of vinyl. The majority of alternatives are widely available. Electricity cables made from polypropylene (PP) function just as well as PVC. Alternatives for soft PVC toys are toys made of less harmful plastics or cloth toys. PVC-free and DEHP-free alternatives are available for almost every use of PVC in the health care setting. DEP could be replaced as an alcohol denaturant or its use abolished.

**BBZP:** butyl benzyl phthalate - **DEHP:** di-(2-ethylhexyl) phthalate – **DEP:** diethyl phthalate - **DIBP:** di-iso-butyl phthalate - **DIDP:** di-iso-decyl phthalate - **DINP:** di-iso-nonyl phthalate – **DMP:** dimethyl phthalate – **DOP:** di-n-octyl phthalate – **DBP:** di-n-butyl phthalate - **DCHP:** diphenyl phthalate

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## ALKYLPHENOLS

*Alkyphenols (APs) are non-halogenated chemicals, a major proportion of which are manufactured to produce alkylphenol ethoxylates (APEs), a group of non-ionic surfactants.*

### PRODUCTION AND USE

Commonly used alkylphenol compounds include nonylphenols (NPs) and octylphenols (OPs), and their ethoxylates, particularly nonylphenol ethoxylates (NPEs). NPEs were extensively used as additives in plastics and as surface active ingredients in industrial detergents and emulsifiers. They were used in textile and carpet cleaning and as emulsifiers in solvents and are still used in some agricultural pesticides. A small proportion has been used in other products, for example as ingredients in personal care products and possibly in glues and sealants, though information is extremely scarce (OSPAR 2001).

In Europe it is thought that for most of their former uses APEs have now been replaced by alcohol ethoxylates, which appear to have a much more favourable environmental profile. Other NP derivatives have been used as antioxidants in some plastics (Guenther *et al.* 2002), although the scale of such uses has not been reported.

### ENVIRONMENTAL DISTRIBUTION

Both APEs and APs are widely distributed in fresh and marine waters, accumulating in particular in sediments, in which these persistent compounds accumulate. Because of releases to water, APEs and APs have also been common components of sewage sludge, including sludge used on the land.

Research into levels in wildlife remains very limited. There have been reports of significant levels in fish and aquatic birds downstream from sites where APEs are manufactured and/or used. Both NPs and OPs are known to accumulate in the tissues of fish and other organisms and to biomagnify through the food chain (OSPAR 2001).

Recent research demonstrated the widespread presence of NPs in a variety of foods in Germany (Guenther *et al.* 2002). Little is known about the extent and consequences of direct exposure from use in consumer products. Both NP and OP residues have been found in house dust (Santillo *et al.* 2003). A Greenpeace study (2003) showed that NPs were ubiquitously present in rainwater, perhaps reflecting continued use of NPEs at that time. OPs were found in a limited number of rainwater samples (Peters 2003).

### EFFECTS

The main hazards associated with APEs result from their partial degradation to shorter-chain ethoxylates and to the parent APs themselves, both of which are toxic to aquatic organisms. The EU risk assessment for NPs identified significant risks to the aquatic environment and to the soil through the then current uses of NPEs, but also to higher organisms resulting from the accumulation of NPs through the food chain (OSPAR 2001). With respect to human exposure through use in consumer products, the CSTE (2001) observed 'a serious lack of measured data for NP'.

The most widely recognised hazard associated with APs is their ability to mimic natural oestrogen hormones, which has been shown to alter sexual development in some organisms, for example the feminisation of fish. This is thought to have contributed significantly to the widespread changes in sexual development and fertility among fish in UK rivers (Jobling *et al.* 2002). Exposure of male rainbow trout (*Oncorhynchus mykiss*) to four different alkylphenolic chemicals caused synthesis of vitellogenin in male fish (a process normally dependent on the fish's natural oestrogen hormones and therefore predominant in females), as

well as inhibition of testicular growth (Jobling *et al.* 1996). In laboratory experiments with the freshwater snail (*Marisa cornuarietis*) and marine snail (*Nucella lapillus*), it induced a complex syndrome of alterations referred to as “superfemales” (Oehlmann *et al.* 2000).

Research with mice has shown that NPs have an effect on the male sex organs, the quality of sperm and the fertility of parents and descendants (Kyselova *et al.* 2003). Studies with mice also showed that NPs can increase the levels of certain antibodies and messenger chemicals, which are themselves implicated in allergic reactions (Lee *et al.* 2003).

APs can cross the placenta and have been found in the umbilical cords of babies (Takada *et al.* 1999) and NPs are found in breast milk (Guenther *et al.* 2002). Hazards to human health remain unclear, although recent studies describe effects on mammalian sperm function (Adeoya-Osiguwa *et al.* 2003, Chitra *et al.* 2002), while DNA damage in human lymphocytes has also recently been documented (Harreus *et al.* 2002). Preliminary studies show that NPs may disrupt the human immune system by adversely affecting groups of white blood cells.

## EXISTING CONTROLS

In 1992 parties to the Ospar Convention decided to phase out NPEs in cleaning agents, starting with use in household products (PARCOM 1992). In 1998 the OSPAR Commission agreed on the target of cessation of discharges, emissions and losses of all hazardous substances to the marine environment by 2020. NPs/NPEs were included on the first list of chemicals for priority action towards achieving this target (OSPAR 1998). NPs have also been included as a ‘priority hazardous substance’ under the EU Water Framework Directive (EC 2001). A decision on the prioritisation of OPs/OPEs under this Directive is still under consideration. According to Directive 2003/53/EC, as of January 2005 products containing more than 0.1% NPs or NPEs may no longer be placed on the market within Europe, with some minor exceptions, principally for ‘closed loop’ industrial systems (EC 2003).

Very little specific information exists regarding the scale and diversity of use of NPs and their derivatives in consumer products up to that date and, consequently, regarding our exposure to them over the years. Furthermore, it is also difficult to establish the extent to which OPs and other alkylphenols and their derivatives remain in use within Europe. The new European chemicals policy – REACH – is expected to come into force in 2006. This could further restrict the production and use of environmentally harmful chemical substances such as APs.

## ALTERNATIVES

APEs can be substituted by other substances, for example alcohol ethoxylates, though direct substitution may be complex in some situations.

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