WWF DETOX CAMPAIGN

Factsheet

Chain of Contamination: The Food Link

Organotin compounds – incl. butyltins (TBT) and octyltins

Background

Organotin compounds (OTCs) are man-made chemical compounds, based on a hydrocarbon structure combined with tin. The most well known organotin is tributyltin (TBT), used widely in marine antifoulant paints to prevent the growth of organisms such as barnacles on the hull of ships. Other organotins include the mono- and dibutyltins (MBT, DBT), octyltins (monooctyltin, MOT and dioctyltin, DOT) and mono-, di- and tri- phenyltins (MPT, DPT, TPT). Organotins have many applications, which include use as stabilisers in PVC, catalysts in chemical reactions, glass coatings, agricultural pesticides, biocides in marine antifoulant paints and wood treatments and preservatives (Batt, 2006) and in anti-odour/anti-fungal treatments for textiles and textile polymers (Greenpeace, 2003b, Peters, 2006). The five major commercial applications (biocides, PVC stabilizers, catalysts, agrochemicals and glass coatings) account for approximately 20, 000 tons of tin consumption per year (Batt, 2006).

TBT is now an omnipresent global contaminant. Extensive use in antifouling paints on watercraft led to the widespread distribution of TBT (and its breakdown products DBT and MBT) in the global marine and freshwater environment, in water, sediment and biota (wildlife species) (de Brito et al., 2002, Ciesielski et al., 2004, Connelly, et al., 2001, Elgethun et al., 2000, Kannan et al., 1996, 1999a, Lee et al., 2006, 2005, Strand & Jacobsen, 2005, Sudaryanto et al., 2004, Ueno et al., 2004). TBT has even been found in marine sediments in Antarctica (Negri, et al., 2004). The persistence of some organotin compounds means that they remain in sediments, particularly anoxic (without oxygen) sediments, for long periods of time e.g. the half-life of TBT in deep sediment has been estimated to be approximately 87+/-17 years (Viglino et al., 2004). “Hot spots” of particularly high levels of TBT in water, sediment and biota are normally associated with commercial ports, harbours, shipyards, shipping lanes, marinas and the like (Alzieu, 2000, Shim et al., 2002, Smith et al., 2006), although the situation is slowly improving following legislation banning the use of TBT in antifoulant paints (see below). Dredging activities can, however, resuspend previously buried residues of TBT back in to the water column, creating localised pollution in such areas (Canellas-Bolta et al., 2005).

The damaging environmental effects of organotins released from antifoulant paints first came to light in the late 1970’s and early-mid 1980’s, with two regional case histories in particular demonstrating the extent of the impacts – the collapse of oyster fisheries in Arcachon Bay, France and the phenomenon of “imposex” (the development of male sexual characteristics) in female marine snails from UK coastal waters, which led to widespread population declines (Santillo, et al., 2001).

At the end of the 1970’s widespread reproductive failures decimated populations of the commercially important Pacific oyster (*Crassostrea gigas*) in Arcachon Bay in France, but it took until the early 1980’s until a causal agent was identified (Santillo et al., 2001). High levels of TBT in the waters of the bay were found to have impaired reproduction (by inhibiting embryogenesis and larval development) and causing shell deformities in the osyters (Alzieu et al., 1986, Alzieu, 2000, Ruiz et al., 1996). Similar impacts were seen in *C.gigas* from UK coasts (Waldock et al., 1987, Waldock & Thain, 1983, Thain & Waldock, 1986). Restrictions (see below) on the use of TBT as a biocide TBT has since reduced ambient water concentrations, allowing oyster populations to recover (Alzieu, 2000).

Around the same time, following earlier observations of the appearance of a penis in female dogwhelks (*Nucella lapillus*) from Plymouth Sound, UK (which increased in prevalence with proximity to the harbour) (Blaber, 1970), research revealed imposex in *N.lapillus* occurring widely throughout the coastal waters of the southern UK (Bryan et al., 1986). This phenomenon was linked with exposure to high levels of TBT in coastal waters and is due to the androgenic properties of TBT i.e. TBT acts like a male hormone. Symptoms of TBT exposure in these invertebrates includes the development of male sexual characteristics e.g. a penis and vas deferens (imposex) by females (Bailey & Davies, 1988a, b,) leading to widespread population declines (Vos et al., 2000). Again, recovery in some populations has been observed following the ban on the use of TBT based paints on vessels (Birchenough et al., 2002, Miller et al., 1999). Imposex has been observed in many other species of molluscs (e.g. ten Hallers-Tjabbes et al., 2003, Santos et al., 2004) and it is reported that over 150 species of prosobranch gastropods (snails) worldwide have now been affected by TBT (and TPT) (Matthiessen et al., 1999).

TBT also affects higher animals where currently concerns are particularly focussed on its effects on the immune system. It has been detected in fish, birds, otters, seals, sharks, porpoises and whales (Guruge et al., 1996, Iwata, et al., 1995, Law et al., 1998, Lee et al., 2005, Kannan et al., 1996, 1999a, Tanabe et al., 1998).

Following the finding that TBT was severely impacting shellfish populations, bans on the use of organotin antifoulants were introduced in the EU, US and Japan in the 1980s for small vessels (<25m), and have been followed by a convention adopted by the International Maritime Organisation (IMO) prohibiting the application of organotin antifoulants on all vessels and offshore installations from January 2003 and requiring they are removed (or covered by a barrier to prevent their leaching) by January 2008 (ENDS Report, 2001, IMO, 2001). The convention will enter into force 12 months after 25 States representing 25% of the world's merchant shipping tonnage have ratified it (IMO, 2001). Currently 16 states representing 17,27% of the world's merchant shipping tonnage have ratified the convention and WWF is urging other countries to do so. In addition to the IMO convention, the EU has taken its own action on TBT. The European regulation 782/2003 entered in force in 2003, banning TBT in new ship coatings (EU, 2003). Under this law, from 2008 ships carrying an active TBT based paint will no longer be allowed to enter European harbours.

Organotins have also been found in air (Boraiko et al., 2004), household dust (Fromme et al., 2005, Greenpeace, 2003a), soil (Marcic et al., 2006), sewage and sewage sludge (Chau et al., 1992, Fent, 1996) and landfill leachate (Mersiowsky et al., 2001). Compared to the marine species, information on the presence of organotins in terrestrial species and humans is much more limited. MBT, DBT and TBT have however been found in the liver of humans in Denmark and Japan (Nielsen & Strand, 2002, Takahashi et al., 1999), in the blood of humans in the US (Kannan et al., 1999b) and in dogs and monkeys (Takahashi et al., 1999).

Major uses

There are five major types of applications for organotins – as biocides, PVC stabilisers, catalysts, agrochemicals and glass coatings (Batt, 2006). However, it should be noted that uses of the tri-substituted organotins (TBT, TPT) and uses of the mono and disubstituted organotins (MBT, DBT, MOT, DBT) do not overlap. For example mono and di compounds are not suitable for use as biocides and tri-substituted compounds are not suitable as stabilisers for PVC (Batt, 2006, Dobson et al., 2005).

Thus, mono- and diorganotins (MBT, DBT) are used extensively as heat stabilizers for processing polyvinyl chloride (PVC). The primary purpose of these tin stabilizers is to reduce the polymer backbone degradation of the PVC. (Batt, 2006, RPA, 2005). The main applications for tin stabilizers are building products, such as pipe and fittings, and siding and profiles (windows, etc.), packaging, and flexible PVC (e.g. wall-coverings, flooring) (Batt, 2006, Greenpeace, 2003a, Sadiki & Williams, 1999). MOT and DOT are used as PVC stabilisers for food contact materials (Batt, 2006, Greenpeace, 2003b, Kawamura et al., 2000, RPA, 2005). It is estimated that between 12 to 13K tons of tin are used annually in tin stabilizers worldwide (Batt, 2006).

Organotins including MBT, DBT, DOT are used as catalysts to speed up chemical reactions, especially polymerization, and MBT is also the predominant organotin used in glass coating processes (Batt, 2006, ENDS Report, 2000, RPA, 2005).

The biocidal properties of tributyltins were utilised in antifoulant paints for ships, boats and marine installations, but TBT based paints are now banned for these uses (see above). TBTs are also used for industrial wood treatment and preservatives, and in the US in industrial cooling tower water to control slime, algae, and fungi (although use is declining as organotin compounds are replaced in these applications) (Batt, 2006). TPT compounds are used as pesticides for crop protection, primarily as fungicides (which kill or inhibit the growth of fungi) and acaracides (which kill mites and ticks) (Batt, 2006).

TBT is also used as an antifungal agent in consumer products, such as carpets and textiles (Allsopp et al., 2000, 2001) and can be used to prevent odours and mildew in clothing (Greenpeace, 2003b, Peters, 2006). Organotins are (or have been) also used in consumer products such as nappies (where they were found as contaminants from manufacture), toys, baking papers, beach balls, non-allergenic pillows, cycling shorts, athletes foot spray, shoe insoles and PVC prints on clothing e.g. T-shirts (ENDS Report, 2003, 2000, RPA, 2005).

Despite the distinction in uses outlined above, within a commercial organotin product there can be related substances present (either included intentionally or as impurities). For example, even in mono- and di-substituted commercial products used as PVC stabilisers, there can be a small fraction of tri-substituted compounds (Dobson et al., 2005).

How do organotins get into the environment (and food chain)?

The major input of TBT into the marine environment is through its use as a biocide. TBT can leach into seawater from the hulls of ships coated with TBT-based antifoulant marine paints, particularly in area of high shipping activity such as ports, marinas and shipyards (see above). Although its use is now banned, inputs into the aquatic environment via this route are likely continue in countries or regions not in compliance with the ban, or from old or disused vessels or installations. In addition to direct leaching from hulls, dry docks (where the hulls of ships are cleaned by sandblasting) and wastewater treatment plants (where organotin compounds may be discharged in the effluent) also represent potentially important sources to the marine environment. TBT can bond to suspended material and is deposited in sediments, and depending on the conditions, is degraded to DBT or MBT (see above), but dredging activities may resuspend organotins bound in sediments back into the water column (Canellas-Bolta et al., 2005). The relative persistence of organotins and their accumulation in sediments means they are available for uptake by fish and shellfish, particularly benthic (“bottom-living”) organisms associated with sediment (EFSA, 2004, FSA, 2005) and have been found in marine organisms from around the world (see above). Concentrations of contaminants of fish and shellfish can vary with the type of shellfish, the geographical location and the spawning period (FSA, 2005).

The manufacture, industrial use and application to consumer products of organotin compounds can result in their release to air, soil and water (RPA, 2005). The application of sewage sludge to agricultural land (Fent, 1996) might also be an input to the terrestrial environment. The use of TBT biocides on treated wood may also result in significant inputs to the local soil environment (RPA, 2005). Disposal to landfill of waste materials and consumer products containing organotins can result in their presence in landfill leachate (Mersiowsky et al., 2001), which can make its way to groundwater and eventually riverine, estuarine and marine environments.

How are people exposed to organotins?

The most significant route of human exposure to organotins, particularly TBT, is dietary – specifically through the consumption of contaminated fish and shellfish (EFSA, 2004, FSA, 2005, EC SCOOP, 2003). Research indicates that organotins are absorbed from the gastrointestinal tract in humans (EFSA, 2004, FSA, 2005) and for the general population, bivalve molluscs (e.g. mussels, clams) seem to be the major source of organotins, followed by fish (both marine and freshwater) and then crustaceans/processed fish products (EC SCOOP, 2003). The use of MOT and DOT as stabilisers in PVC food packaging is another potential route of exposure (RPA, 2005), given the propensity of organotins to migrate from these materials.

Organotins in food

Food item(s)	Reference(s)	Comments
Shellfish (mussels, clams, cockles, oysters, winkles, scallops and razor shells).	Food Standards Agency UK (October 2005). Survey of organotins in shellfish. Food Survey Information Sheet 81/05 http://www.food.gov.uk/science/surveillance/	Analysis of MBT, DBT and TBT in 125 shellfish samples from commercial UK shellfish beds and 44 retail samples. TBT detected in 49 samples, DBT in 18, MBT in 8. Highest level of TBT and total organotins in mussels.
Fish and shellfish (Marine/freshwater fish, crustaceans, molluscs, processed/canned fish).	EC (European Commission) SCOOP (2003). "Assessment of the dietary exposure to organotin compounds of the population of the EU member states". October 2003	Analysis of fish (marine and freshwater), crustaceans, molluscs, processed and canned fish from Belgium, Denmark, France, Germany, Greece, Italy, The Netherlands and Norway for 6 organotins TBT, DBT MBT, TPT, DPT, MPT. Highest levels of TBT and derivatives found in bivalve molluscs. Crustaceans and canned/processed fish groups present the lowest levels of OTC.
Seafood	Zhou et al., (2001). J Agric Food Chem., 49(9), pp4287-91.	Analysis of TBT, DBT and MBT in commercial seafood products collected from seven Chinese cities. Butyltins found in all samples, and were stable during cooking or processing.
Wine* and beer	Azenha & Vasconcelos (2002). J Agric Food Chem., 50(9), pp2713-6. Forsyth et al., (1994). Food Addit Contam., 11(3), pp343-50. Forsyth et al., (1992). Food Addit Contam., 9(2), pp161-9.	Analysis of butyltin compounds in Portuguese wines. Survey of organotin compounds (MBT, DBT,TBT) in blended wines. Determination of butyltin, cyclohexyltin and phenyltin compounds in beers and wines.
General foods (beans, fruit, vegetables, fish, meat, potatoes, sugar, beverages, alcohol, eggs, milk and corn)	Qunfang et al., (2004). Food Addit Contam., 21(12), pp1162-7.	Analysis of butyltin compounds in 12 types of foods collected in China. Low levels (ng/g) of butyltin compounds detected in some samples.

Table 1: Organotin compounds in food items – examples from the literature

* Agglomerated cork stoppers have been identified as a source of organotin (butyltin) compounds in wine (Jiang et al., 2004).

A number of other exposure routes have also been investigated in a recent risk assessment on human exposure to organotins (RPA, 2005), carried out in response to concerns expressed by the Committee on Toxicity, Ecotoxicity and the Environment (CSTEE) over previous risk assessments (CSTEE 2003, ENDS Report, 2003, 2004). These include direct exposure via the environment in the proximity of certain production/processing facilities, inhalation of indoor air and dust, via drinking water supplied by PVC piping, and dermal (skin) exposure and inhalation exposure through the use of various consumer products impregnated with or containing organotins such as treated insoles, pillows and clothing, PVC products, female hygiene products, nappies, and clothing with PVC prints (RPA, 2005). Consistent with these findings is the identification of indoor air and dust as a potential human exposure route (Fromme et al., 2005, Greenpeace, 2003a).

What health effects are associated with exposure to organotins?

The toxic effects of organotins were first documented in the marine environment and the effects of TBT from antifoulant paints on invertebrates (molluscs) have been described above. The main concerns regarding the exposure of mammalian species, including humans, to butyltin compounds (MBT, DBT, TBT) are focussed on their potential for immunotoxicity (effects on the immune system), hepatotoxicity (liver), neurotoxicity (nervous system) and developmental toxicity (Snoeij et al., 1987). The effects of long term human exposure to organotins at environmentally realistic levels is unknown, but even in the absence of definitive studies, the available information on mammalian toxicity, derived largely from animal and *in vitro* research (see below) suggest there are potential risks from exposure to organotins, particularly for young children (RPA, 2005). To quote a recent risk assessment - "Aggregating the various exposure routes…suggests that the overall exposure for 70% of young child consumers will exceed the group TDI, while the 'typical' (median) 8kg child consumer is exposed to about 160% of the TDI. Although arguments can be advanced that there are uncertainties within each of the associated sets of calculations, it would appear that the risks associated with the extensive and varied use of organotins cannot be readily dismissed as negligible". (RPA, 2005)

Butyltin compounds, in particular DBT, have been shown to induce thymus atrophy in the rat (Pieters, 1994), the thymus being a crucial organ in the immune system, responsible for T-cell production. Butyltins have been shown *in vitro* to significantly inhibit the function of human natural killer (NK) lymphocytes, which are a primary immune defence against tumour and virally infected cells in humans (Whalen et al., 1999, 2002). A study on lymphocytes from marine mammals (porpoises, bottlenose dolphins, a seal, a sea-lion) and humans has shown that butyltins (in combination with polychlorinated biphenyls) suppressed the immune response in these cells, which the authors suggest could "pose a serious threat to the immune functions in free-ranging marine mammals and humans" (Nakata et al., 2002).

Rodent studies have shown butyltins, particularly DBT, to be toxic to the liver and pancreas (Merkord et al., 2001, Ueno, et al., 2003a, b) and to induce various developmental effects such as decreased foetal weight and increased incidence of malformations following *in utero* exposure (Ema et al., 1995, 1996, Ema & Harazono, 2001). Research also suggests TBT exposure may disrupt thyroid hormone homeostasis, influencing development of the foetus during pregnancy (Adeeko et al., 2003). DBT has also been shown to be a potent developmental neurotoxicant both *in vitro* and *in vivo*, significantly inhibiting neurite (nerve cell) growth and causing cell death in specific areas of the brain (neocortex and hippocampus) of postnatal day 38 rat offspring (Jenkins et al., 2004), and inducing apoptosis (cell death) in brain cells (from the cerebellum) (Mundy & Freudenrich, 2006).

Other effects of organtin exposure have also been reported, for example in studies in mice, tributyltin (TBT) chloride induces the differentiation of adipocytes (fat cells) *in vitro*, increases adipose (fat) mass *in vivo*, promotes adipogenesis (fat formation) and lipogenic pathways *in vivo* and *in utero* exposure to TBT leads to increased fat accumulation in newborn mice (Grun et al., 2006). The authors postulate that "developmental or chronic lifetime exposure to organotins may therefore act as a chemical stressor for obesity and related disorders". TBT has also been shown to be toxic to the developing testes (Kumasaka et al., 2002). Exposure of premature mice to TBT damaged the Sertoli cells in the developing testes, resulting in reduced sperm counts.

How can exposure to organotins be reduced?

As exposure to organotins is primarily through the consumption of shellfish and fish, it is worth following the advice of the UK Food Standards Agency (FSA) with regards to the frequency of fish consumption and the types of fish and shellfish that should be consumed. Details of FSA analysis of shellfish for organotins (and other chemicals) can be found here - http://www.food.gov.uk/science/surveillance/.

Avoidance of PVC in the home should help to minimise the amount of organotin stabilisers present in household air and dust. Similarly, exposure may be reduced by avoiding "antifungal" treated clothing and footwear, although if this is part of a recommended strategy to treat a fungal infection some antifungal treatment should be maintained for articles of clothing that cannot be washed at higher temperatures to destroy the residual fungus.

Further information

http://www.greenpeace.org/international/campaigns/toxics
http://www.checnet.org/HealtheHouse/home/index.asp
http://www.ortepa.org/

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