Investigation of hazardous chemical discharges from two textile manufacturing facilities, and chemical contamination of nearby canals connecting to the lower Chao Phraya River, Thailand, 2010

Kevin Brigden , Iryna Labunska & David Santillo

Greenpeace Research Laboratories Technical Note 06/2010

Contents

Executive Summary

The Chao Phraya River basin is the largest in Thailand, draining approximately 30% of the country. Along its course this river passes through several cities, including Bangkok, and ultimately flows into the Upper Gulf of Thailand. After passing through Bangkok, and before entering the Gulf, the Chao Phraya flows through Samutprakan Province, to the south east of Bangkok. A number of large canals connect to the Chao Phraya in this Province, an area that houses a wide range of industrial facilities, many of which are situated on the banks of the canals.

This study investigated the presence of hazardous chemicals in wastewaters discharged from two textile manufacturing facilities (Samchai Fabric Co., Ltd. & the Nam Boon Bleaching & Dyeing Factory) to the Samrong canal, as well as in the Samrong canal itself, and in two other nearby canals; the Bangnangkreng and Bangplakod canals.

A total of 11 samples were collected in February and March 2010, including a wastewater sample from each facility, and samples of water and sediment from the three canals. All samples were returned to the Greenpeace Research Laboratories (University of Exeter, UK) for analysis, including quantitative analysis for metals and for a range of volatile organic compounds (VOCs), and qualitative analysis of other, semi-volatile (solvent-extractable) organic compounds.

This study has demonstrated that wastewater discharges from the two textile manufacturing facilities are acting as significant point sources of hazardous substances to the Samrong canal, part of the lower Chao Phraya River basin. Some of the chemicals identified in the wastewater samples are subject to regulations in other countries preventing their use and / or release. These two facilities represent only a small fraction of the total industrial activity in this area, and the river basin as a whole, but nonetheless illustrate what seems likely to be a much wider problem relating to the discharge of industrial wastewaters to the canals linking to the Chao Phraya system.

In addition, water and sediment samples from the Samrong and Bangnangkreng canals, though not Bangplakod canal, were found to be contaminated with a range of toxic metals and hazardous organic pollutants, some of which were also identified in the discharged wastewaters. Levels of chromium, copper, nickel and zinc in Samrong and Bangnangkreng canal sediment samples would exceed thresholds for the characterisation of sediments as "seriously contaminated" in some other countries.

The toxic metals and some of the organic pollutants identified in the canals appear to have sources other than the two facilities investigated. While the precise sources of these additional hazardous substances cannot be determined from the current investigation, it is likely that discharges of wastewaters from the numerous other industrial facilities in the vicinity of the canals are contributing significantly to their chemical contamination.

Key findings from this study can be summarised as follows :-

Samchai Fabric Co. wastewater contained over 150 organic chemicals, including a wide range of established pollutants:-

- Nonyl phenols, well known persistent environmental contaminants that are hormone disrupting chemicals.
- 2-Naphthalenamine (2-naphthylamine), a human carcinogen which is formed from the chemical breakdown of certain dyes.
- Moderate concentrations of copper (289 μg/l), chromium (142 μg/l) and zinc (201 μg/l) though not exceeding Thai effluent standards.

Nam Boon textile factory wastewater contained a wide range of organic pollutants, by far the most abundant of which was tri-iso-butyl phosphate (TiBP), a toxic chemical used in the textile industry.

Samrong canal;-

- Two of the substances identified in the wastewaters, namely nonyl phenols and tri-iso-butyl phosphate (TiBP), were also found in water collected from the Samrong canal.
- High total (dissolved and particulate) concentrations of copper, lead, manganese, nickel and zinc were found at one location, at between 3 and 8 times Thai surface water quality standards (which also specify limits in terms of total, or whole unfiltered water, concentrations). However, dissolved metals made only a small contribution to total concentrations of these metals.
- Sediment from two locations contained high concentrations of metals including zinc, chromium, copper, nickel and lead, with zinc present at up to 30 times typical background levels.

Bangnangkreng canal;-

- Tri-iso-butyl phosphate (TiBP) and nonyl phenols were also present in the water from this canal.
- Total concentrations of copper and nickel, at over 2 times their Thai surface water quality standards, and a high concentration of dissolved nickel (82 μg/l).
- Canal sediment samples were highly contaminated with metals, including the highest concentrations of chromium, copper, nickel and zinc of all samples analysed in this study, with zinc & nickel concentrations at up to 30 and 80 times typical background levels respectively.

Bangplakod canal was largely uncontaminated with metals and organic pollutants**.**

In conclusion, although limited in its scope, this study illustrates the current levels of contamination of these receiving water bodies and highlights the need for more in-depth investigation into the discharge of hazardous chemicals to the Chao Phraya basin, as well as other parts of Thailand.

As part of the development of a more sustainable approach to the management of chemicals and the future protection of water resources within Thailand, a comprehensive understanding of the current use of hazardous substances is required for as wide a range of substances as possible, and of their release to the aquatic and wider environment, making tools such as Pollutant Release and Transfer Registers (PRTR) very important. Furthermore, based on the precautionary principle that prevention is easier and cheaper than cure, this approach should include the setting of zero discharge targets for the most hazardous industrial chemicals used within Thailand, which can then be achieved through the ongoing substitution of hazardous substances with less hazardous or preferably non-hazardous alternatives (the principle of substitution), in order to bring about rapid reductions and ultimate cessation in their discharges, emissions and losses. Such approaches have been developed and are being implemented in other parts of the world, including within the European Union and wider North-East Atlantic (OSPAR) and Baltic (HELCOM) regions.

Introduction

The Chao Phraya River has the largest river basin in Thailand, draining approximately 30% of the country (Molle 2007). Along its course the Chao Phraya flows through several cities, including Bangkok, and ultimately flows into the upper Gulf of Thailand.

This study investigated the presence of hazardous chemicals in three canals that connect to the lower Chao Phraya River in Samutprakan Province, downstream of Bangkok. Numerous industrial facilities are located in the vicinity of the Samrong, Bangnangkreng and Bangplakod canals, many of which discharge wastewaters directly to the canals. A wide range of industrial activities are carried out in these areas, including the manufacturing of textiles, chemicals, steel & plastic products, and metal plating & finishing. This study also investigated the chemical composition of discharged industrial wastewaters to the Samrong canal from two textile manufacturing facilities; Samchai Fabric Co., Ltd. which manufactures a range of fabric and garment products (Samchai 2010), and the Nam Boon Bleaching & Dyeing Factory, which carries out textile finishing as well as bleaching & dyeing processes (ABG 2010).

Sampling program

The areas investigated in this study were visited in February and March 2010, and a total of 11 samples (of wastewaters, canal waters and sediment) were collected. One sample of wastewater was collected from each of the outfalls of the textile factories. In addition, samples of water and sediment were collected from three locations along the Samrong Canal, from two locations along the Bangnangkreng canal, and one location along the Bangplakod canal. All surface water samples were collected from the midpoint of the canals and at medium depth, in accordance with protocols used by the Pollution Control Department (PCD) in relation to surface water quality standards (PCD 2010). Details of the samples collected are presented in the results and discussion section below.

In all cases, samples were collected and stored in pre-cleaned glass bottles that had been rinsed thoroughly with nitric acid and analytical grade pentane in order to remove all heavy metal and organic residues. Wastewater and canal water samples were collected in 1 litre screw-cap bottle for use in the quantitative analysis of metals and qualitative analysis of solvent extractable (semi-volatile) organic compounds. A duplicate sample was collected in a separate 125 ml amber bottle with a ground-glass stopper (filled to leave no headspace) to be analysed for volatile organic chemicals. Sediment samples were collected in 100ml screw-cap bottles. All samples were immediately chilled and kept cool and dark during transit to the Greenpeace Research Laboratories at the University of Exeter in the UK for analysis.

Methodology

A number of different analyses were carried out on the wastewater, canal water and sediment samples. Heavy metal concentrations were determined for all samples by ICP atomic emission spectrometry (AES), following acid digestion and using appropriate certified reference materials in addition to intra-laboratory standards. All water samples contained suspended solids and therefore both the total concentrations in the whole (unfiltered) sample and the concentrations of dissolved forms in a filtered sample were determined separately.

Extractable organic compounds were isolated from each sample and identified as far as possible using gas chromatography and mass spectrometry (GC/MS), following accelerated solvent extraction into a mixture of pentane and acetone for solid samples or solid phase extraction with ethyl acetate, pentane and toluene for wastewater samples. Volatile organic chemicals (VOCs) were identified and quantified in wastewater samples as received (with no pre-treatment) using GC/MS with HeadSpace sample introduction technique. Results for VOCs analysis are reported only for those chemicals which were present in the samples above detection limit. Detailed description of the sample preparation and analytical procedures are presented in the Appendix, including a list of VOCs quantified in the water samples, with limits of detection and quantification (Table 6).

Results and discussion

A summary of the sample details for samples collected from the two textile facility outfalls and locations along the Samrong, Bangnangkreng and Bangplakod canals are presented in Tables 1a & 1b, along with a map showing the three canals and the locations from which samples were collected (Figure 1). A separate enlarged map shows the area from where samples were collected along the Samrong canal (Figure 2).

The results are presented below in two sections, the first for samples from the textile facilities and the Samrong canal on which they are situated, and the second section for the two other canals; Bangnangkreng and Bangplakod.

Background information on certain key pollutants detected during this study is presented in Boxes A-E through the discussion text.

It should be noted that all metals quantified in this study are naturally found at some level in uncontaminated environmental samples, such as sediments and surface waters, though generally at low concentrations. Inputs from point sources such as industrial discharges can, however, result in levels that far exceed natural background concentrations. The following sections focus on those metals found in the various samples at concentrations which are above typical background levels for uncontaminated waters and, therefore, indicative of significant inputs from industrial or other anthropogenic sources.

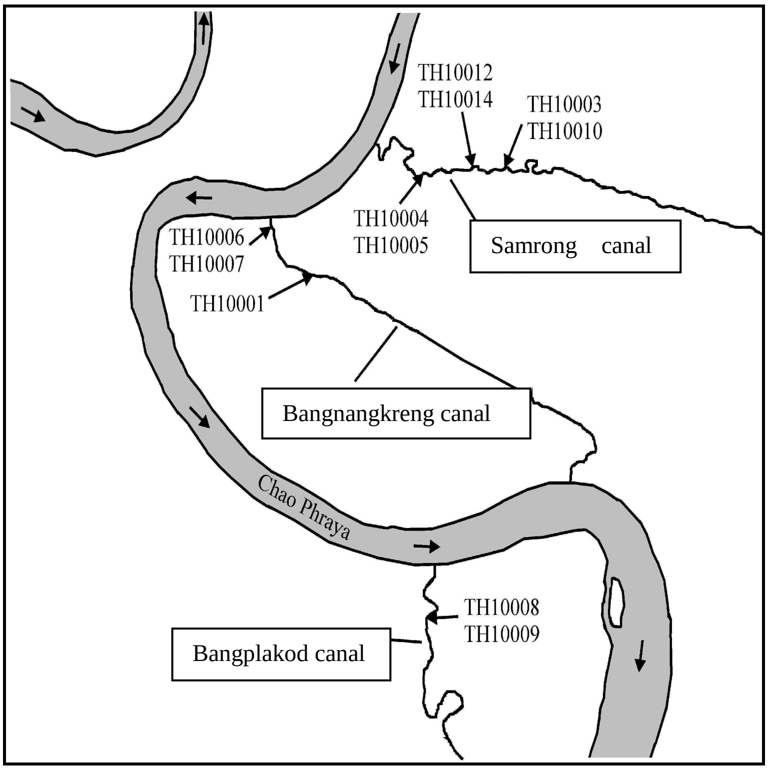

Figure 1. Sketch map of the Samrong, Bangnangkreng & Bangplakod canals, and the Chao Phraya River, Samutprakan Province, Thailand, showing the locations from which samples were collected.

Samrong canal & two textile manufacturing factories

Two samples of wastewater were collected from separate outfalls discharging industrial wastewaters into the Samrong canal. One wastewater sample (TH10010) was collected from the outfall of the Samchai Fabric Co. factory (from a channel carrying wastewater from a discharge pipe to the canal), and the second (TH10012) from the outfall of the Nam Boon textile factory. In addition, samples of water and sediment were collected from the Samrong canal in the vicinity of the two textile factories. These included a sample of water from the canal close to the outfall of the Nam Boon textile factory (TH10014), a sample of sediment from the canal adjacent to the Samchai Fabric Co. factory (TH10003), as well as a sample of both canal water (TH10004) and sediment (TH10005) from a location close to where this canal joins the Chao Phraya river, adjacent to the Aditya Brila group chemical factory.

The results for the organic and heavy metals analyses of the samples associated with the Samrong channel are presented in Table 2a.

Sample	Type	Description
TH10010	wastewater	Samchai Fabric Co. factory; channel between discharge pipe and Samrong canal
TH10003	sediment	Samrong canal, adjacent to Samchai Fabric Co. factory (TH10010); furthest from Chao Phraya
TH10012	wastewater	Nam Boon textile factory discharge pipe to the Samrong canal
TH10014	canal water	Samrong canal, adjacent to Nam Boon textile factory (TH10012)
TH10004	canal water	Samrong canal, adjacent to the Aitya Brila Group chemical factory; closest to Chao Phraya
TH10005	sediment	Samrong canal, (as TH10004)

Table 1a. Description of samples associated with the Samchai Fabric Co. and Nam Boon textile manufacturing factories, and the Samrong canal, Samutprakan Province, Thailand, 2010

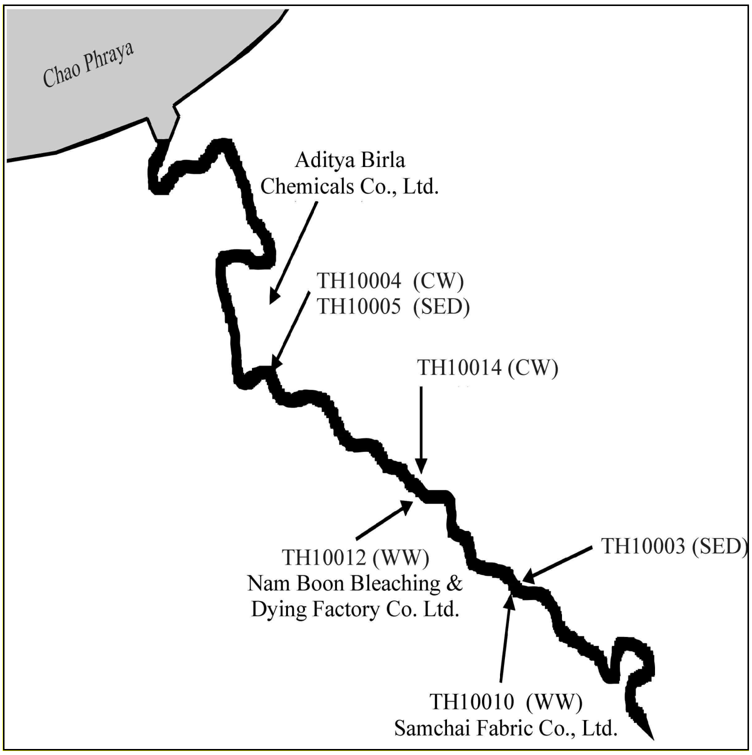

Figure 2. Enlarged sketch map of the Samrong canal, Samutprakan, Thailand, showing the locations from which samples were collected. WW - wastewater, CW – canal water, SED - sediment

Wastewaters

Wastewater from the Samchai Fabric Co. factory (TH10010), which was dark green in appearance, had the highest load of organic compounds among the samples investigated in this study. 154 organic compounds were isolated from this sample, of which 81 (52%) have been identified to a high degree of reliability. This sample contained a high number of aliphatic hydrocarbons (27 compounds), together with aromatic hydrocarbons, including polycyclic aromatic hydrocarbons (PAHs) (naphthalene and its three derivatives), nitrogen-containing compounds (two indene derivatives), branched alkyl benzenes (17 compounds) and sulphur. Taken together, such chemical groups suggest contamination with oil or other petrochemical products. This wastewater sample also contained a range of the industrial detergent derivatives alkylphenols, including 20 isomers of nonyl phenol, well known persistent environmental contaminants with hormone-disrupting properties. More information on alkylphenols is presented in Box A.

Additionally, the Samchai Fabric Co. wastewater (TH10010) contained 2-naphthalenamine, also known as 2-naphthylamine (2NA), a known human carcinogen (DHHS 2005). 2NA has uses as an intermediate in the dye industry (Rossoff 2002), and can be formed as a breakdown product of some azo dyes (Pinheiro *et al.* 2004). Additional information on 2NA is presented in Box B. Clearly, wastewater from the Samchai Fabric Co. factory is a point source of the carcinogenic compound 2-naphthylamine, and appropriate actions should be taken to prevent further release of this dangerous substance into receiving waters and to the wider environment.

Location	Samchai Fabric Co.			Nam Boon textile				closest to Chao Phraya		
Sample	TH10010		TH10003	TH10012		TH10014		TH10004		TH10005
Type	waste water		canal	waste water		canal water		canal water		canal
	total	diss	sediment	total	diss	total	diss	total	diss	sediment
METAL	(µg/l)	(µg/l)	(mg/kg)	(µg/l)	(µg/l)	(µg/l)	(µg/l)	(µg/l)	(µg/l)	(mg/kg)
Antimony	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20
Arsenic	<50	<50	33	<50	<50	<50	<50	85	<50	18
Barium	369	113	514	307	205	85	63	722	64	255
Cadmium	<5	<5	<1	<5	<5	<5	<5	<5	<5	<1
Chromium	142	100	634	<20	<20	86	<20	1380	<20	493
Chromium (VI)	<50	<50	-	<50	<50	<50	<50	<50	<50	-
Cobalt	<20	<20	20	<20	<20	<20	<20	<20	<20	20
Copper	289	196	295	31	29	23	<20	511	<20	199
Lead	<50	<50	83	<50	<50	<50	<50	198	<50	70
Manganese	275	60	831	400	394	303	259	2620	630	635
Mercury	<2	<2	0.8	<2	<2	<2	<2	<2	<2	0.6
Nickel	<20	<20	265	<20	<20	110	31	797	<20	221
Selenium	<200	<200	<30	<200	<200	<200	<200	<200	<200	<30
Thallium	<200	<200	<10	<200	<200	<200	<200	<200	<200	<10
Vanadium	<20	<20	50	<20	<20	<20	<20	177	<20	60
Zinc	201	64	2940	92	63	329	11	4640	<10	1430
pH	8		-	7		7		8		-
Organic compound isolated	154		12	79		32		14		6
Number reliably identified (% of total)	81 (53%)		5 (42%)	27 (34%)		17 (53%)		6 (43%)		3 (50%)
Tri-iso-butyl phosphate				1		1		1		
Aliphatic hydrocarbons	27		4	18		1		2		3
PAHs & derivatives	4		1							
Alkyl benzenes	17							3		
Nonyl phenols	20					11				
Other alkyl phenols	8									
Indene derivatives	2									
2-Naphthalenamine	1									
Sulfur, mol. (S8)	1									
Terpenoids				3		4				
Bis(2-ethylhexyl) maleate				1						
Chloroform*				1						
Other compounds	1			3						

Table 2a. Organic chemicals identified, and concentrations of metals and metalloids, in samples of canal water, sediment and discharged wastewaters associated with the Samrong canal, Thailand, 2010. Concentrations of metals in wastewater and canal water samples are reported in µg/l, both as total concentrations in the whole (unfiltered) sample and separately as (diss)olved concentrations in filtered samples. Concentrations of metals in sediments are reported as mg/kg dry weight. * - Chloroform was detected at a concentration of 31 µg/l.

Box A. Alkyl phenols and their ethoxylates

Alkylphenols (APs), which includes **octyl phenols (OP)** and **nonyl phenols (NP)** are non-halogenated chemicals manufactured almost exclusively to produce alkylphenol ethoxylates (APEs), a group of non-ionic surfactants. The most widely used APEs are nonylphenol ethoxylates (NPEs) and, to a lesser extent, octylphenol ethoxylates (OPEs). Once released to the environment, APEs can degrade back to APs, which are persistent, bioaccumulative and toxic to aquatic life. NPEs have been used as surfactants, emulsifiers, dispersants and/or wetting agents in a variety of industrial and consumer applications including the manufacture of textiles, the largest share in industrial and institutional cleaning products (detergents), with smaller amounts used as emulsifiers, textile and leather finishers and as components of pesticides and other agricultural products and water-based paints (OSPAR 2001, Guenther *et al.* 2002). OPEs are reported to have had a similar range of uses to NPEs, although fewer reliable data are available for this group.

Both APEs and APs (especially nonylphenol and its derivatives) are widely distributed in fresh and marine waters and, in particular, sediments, in which these persistent compounds accumulate (see e.g. Fu *et al.* 2008, Shue *et al.* 2009, David *et al.* 2009). Because of their releases to water, APEs and APs are also common components of sewage effluents and sludge (Micic & Hofmann 2009, Ying *et al.* 2009, Yu *et al.* 2009), including that applied to land. NP has been detected in rain and snow in Europe (Fries & Püttmann 2004, Peters *et al.* 2008), while residues of both NP and OP have been reported as contaminants in house dust (Butte & Heinzow 2002, Rudel *et al.* 2003) and indoor air (Rudel *et al.* 2003, Saito *et al.* 2004). Research into levels in wildlife remains limited, although there have been reports of significant levels in both invertebrates and fish in the vicinity of sites of manufacture and/or use of APEs and close to sewer outfalls (Lye *et al.* 1999, Rice *et al.* 2003, Mayer *et al.* 2007). Both NP and OP are known to accumulate in the tissues of fish and other organisms, and to biomagnify through the food chain (OSPAR 2001). Basheer *et al.* (2004) identified alkylphenols as common contaminants of seafood from Singapore. More recently, the presence of alkylphenols as contaminants in human tissues has also been reported (Lopez-Espinosa *et al.* 2008).

The most widely recognised hazard associated with APs (both NP and OP) is undoubtedly their estrogenic activity, i.e. their ability to mimic natural estrogen hormones. This can lead to altered sexual development in some organisms, most notably the feminisation of fish (Jobling *et al.* 1995, 1996). Atienzar *et al.* (2002) described direct effects of NP on DNA structure and function in barnacle larvae, a mechanism which may be responsible for the hormone disruption effects seen in whole organisms. In rodents, exposure to OP caused adverse effects on male and female reproductive systems, including lower sperm production and increased sperm abnormalities (Blake *et al.* 2004). Chitra *et al.* (2002) and Adeoya-Osiguwa *et al.* (2003) describe effects on mammalian sperm function, while DNA damage in human lymphocytes has also been documented (Harreus *et al.* 2002), although the significance of these findings has been challenged by some. Impacts on immune system cells *in vitro* have also been described (Iwata *et al.* 2004).

More than 10 years ago, the Ministerial Meeting under the OSPAR Convention agreed on the target of cessation of discharges, emissions and losses of hazardous substances to the marine environment of the north-east Atlantic by 2020, and included NP/NPEs on the first list of chemicals for priority action towards this target (OSPAR 1998). Since then, NP has been included as a “priority hazardous substance” under the European Union (EU) Water Framework Directive, such that action to prevent releases to water within 20 years will be required throughout Europe (EU 2001). On 16 December 2008, the Water Framework Directive was amended by the EU Directive 2008/105/EC laying down environmental quality standards (EQS) in the field of water policy (EU 2008). Both nonylphenol and octylphenol have been designated as a “priority substance" by this Directive, which aims to combat the pollution of surface waters by 33 priority chemical substances. Already, however, the widely recognised environmental hazards presented by AP/APEs have led to some long-standing restrictions on use in many countries. Of particular note in the European context is the Recommendation agreed by the Paris Commission (now part of the OSPAR Commission) in 1992, which required the phase-out of NPEs from domestic cleaning agents by 1995, and industrial cleaning agents by the year 2000 (PARCOM 1992). However, the precise extent to which this measure was effective is unclear.

The EU risk assessment for nonylphenol identified significant risks to the aquatic environment, to the soil and to higher organisms through secondary poisoning arising through numerous uses of NPEs (EU 2002b). According to Directive 2003/53/EC, as of January 2005 products containing greater than 0.1% NP or NPEs may no longer be placed on the market within Europe, with some minor exceptions principally for “closed-loop” industrial systems (EU 2003). At the same time, very little information exists regarding the ongoing uses of OP and its derivatives in consumer products and, as a consequence, our direct exposure to them.

Box B. 2-Naphthalenamine (2NA)

2-Naphthalenamine, also known as 2-naphthylamine (2NA), is classified by the International Agency for Research on Cancer (IARC) as a human carcinogen based on sufficient evidence of carcinogenicity in humans (DHHS 2005). This chemical, either alone or present as an impurity in other compounds, has been shown to cause bladder cancer in exposed workers. There is also sufficient evidence for the carcinogenicity of 2NA in experimental animals. When administered orally, it has been shown to cause malignant bladder tumours in hamsters, dogs, and rhesus monkeys and liver tumours in mice; bladder tumours also were observed in rats at a low incidence. Commercial manufacture and use of 2NA was banned in the USA in the early 1970s. 2NA has known uses as an intermediate in the dye industry and as an antioxidant in the rubber industry (Rossoff 2002). It can also be formed as a breakdown product of some azo dyes (Pinheiro *et al.* 2004). Within Europe, the use of azo dyes in textile and leather articles which may come into direct and prolonged contact with the human skin or oral cavity, and which could breakdown to carcinogenic aromatic amines, , including 2NA, are prohibited from use (EU 2002a).

Following the implementation of this directive, the Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers (ETAD) has advised to its members to cease the use of azo dyes that may release comparable concentrations of the banned amines from textile articles within the European Union (ETAD 2008).

For the other wastewater sample (TH10012), collected from the Nam Boon textile factory outfall that discharges via a concealed pipe into the Samrong channel, a smaller number of organic compounds were isolated (79 compounds) compared to the Samchai Fabric wastewater (TH10010), with only 27 of those (34%) being reliably identified. The range of organic compounds detected in this sample was different from that found in the wastewater sample collected from the Samchai Fabric factory (TH10010), other than the fact that aliphatic hydrocarbons were present in both samples. Among other organic compounds detected in the Nam Boon wastewater (TH10012) were tri-iso-butyl phosphate (TiBP), bis(2-ethylhexyl) maleate and chloroform. Chloroform, present in this sample at a concentration of 31µg/l, was the only chlorinated volatile organic compound (VOC) that was detected in the wastewaters analysed in the current study. Sample TH10012 also contained three compounds belonging to a class of terpenoids, naturally occurring compounds that could be isolated from plants, some of which (e.g. sitosterols) are used in a fabric softening compositions (Hofer *et al.* 2002).

TiBP was by far the most abundant organic compound among those identified in the Nam Boon wastewater (TH10012). This chemical belongs to a family of trialkyl phosphate esters that are widely used in various industrial processes. Due to its properties of being a very strong wetting agent and very strong polar solvent, TiBP is used in the textile industry. It is clear that Nam Boon textile factory uses this chemical in its technological processes and discharges wastewater containing residues of this chemical directly to the Samrong canal. As a result, a significant amount of TiBP may be entering the Samrong canal over time, and be transported *via* the surface waters of the Chao Phraya system over long distances as this chemical is quite soluble in water. More information of TiBP is presented in Box C.

Box C. Tributyl phosphate esters

Tributyl phosphate (TBP) may exist in two isomeric forms: tri-n-butyl phosphate (TnBP) and tri-iso-butyl phosphate (TiBP). TnBP is manufactured by the reaction of butanol with phosphorus oxychloride. It is used as a solvent for cellulose esters, lacquers, and natural gums, as a primary plasticiser in the manufacture of plastics, textile and vinyl resins, as a metal extractant, as a base stock in the formulation of fire-resistant aircraft hydraulic fluids, as a flame retardant, and as an antifoaming agent. TnBP is also an important extractant in nuclear fuel processing (Dodi & Verda 2001; Lamouroux *et al.* 2000).

TiBP is mainly used as an antifoaming agent in various aqueous systems where it has the ability to both destroy the foam and act as a foam inhibitor. It is also used in the production of solutions of synthetic resins and natural rubber. In both cellulose based plastics and synthetic resins, it is used as a flame-retarding plasticizer. Other uses of TiBP include application as a pasting agent for pigment pastes, as an important component in the manufacture of hydraulic fluids for aircraft, and as a very strong wetting agent and very strong polar solvent in the textile industry and in the field of adhesives.

TBP is continuously lost to the air and aquatic environment during its various uses. The biodegradation of TBP is moderate or slow depending on the ratio of TBP to active biomass. This involves stepwise enzymatic hydrolysis to orthophosphate and butanol, which subsequently undergoes further degradation. TiBP has been found frequently in air (Isetun *et al.* 2004), in surface water near sewage treatment plants discharges (Andersen *et al.* 2004), in sediments (García-López *et al.* 2009), in fish and in liver samples from seabirds (Evenset *et al.* 2009).

TBP toxicity has primarily been investigated for aquatic organisms and rodents. It has also been shown that TBP is toxic to selected protozoa species (Bowen *et al.* 2006). The inhibitory concentrations (EC_0, EC_{50}, EC_{100}) of TBP for the multiplication of unicellular algae, protozoa, and bacteria have been estimated to lie within the range of 3.2-100 mg/litre (WHO 1991). The acute toxicity to fish (LC_{50}) ranges from 4.2 to 11.8 mg/litre. TBP increases the drying rate of plant leaves, which results in rapid and complete inhibition of leaf respiration. TBP is reported to be slightly teratogenic at high dose levels. Administration of TBP to male mice was associated with an increased incidence of benign liver tumors (hepatocellular adenomas) and an increase in liver weights for male and female mice (Auletta *et al.* 1998). Only limited data exist on the toxic effect of TBP on humans. In an *in vitro* study, TBP has been reported to have a slight inhibitory effect on human plasma cholinesterase (WHO 1991). Also, both TnBP and TiBP are classified as skin irritants (Rudnick 2006).

Bis(2-ethylhexyl) maleate (also known as dioctyl maleate), detected in sample TH10012, has various applications including as an intermediate for organic synthesis, and as an emollient in various skin and hair care products such as cleansers, moisturizers, sunscreens, eye shadows, hair relaxers and hair styling products. In industry, it is also used as a plasticizer in emulsion-type paints, papers, textile coating, adhesives and oil additives (Chan & Wakelin 2006). It is also used in surfactants and wetting agents. It has been shown that bis(2-ethylhexyl) maleate can cause allergic contact dermatitis following application in a moisturizer (Chan & Wakelin 2006).

Chloroform, also known as trichloromethane, is a well known chlorinated solvent and toxic contaminant which may enter the environment with wastewaters from a number of industrial processes involving the use of this chemical. In the case of textile manufacture, chloroform may be used as a solvent during the application of soluble polymers (Foitzik *et al.* 2006). However, chloroform can also be generated as a by-product during water disinfection using chlorine-containing compounds (Oxenford 1996), a source which cannot be ruled out in this instance. Chloroform has been specified by the International Agency for Research on Cancer in the Group 2B as possibly carcinogenic to humans (IARC 1998). Studies have shown that the main target organs for animal carcinogenicity from chloroform are the liver, kidney and/or intestine (Dunnick & Melnik 1993, Snyder & Andews 1996, Chiu *et al.* 1996). Chloroform is also identified as a priority pollutant under the EU Water Framework Directive (EU 2000), with a proposed Annual Average Environmental Quality Standard (AA-EQS) for internal surface waters of 2.5 µg/l (EC 2006). Although the concentration recorded in the wastewater at the time of sampling was more than 10 times above this standard, it is important to note both that the standard applies in Europe to the quality of receiving waters rather than quality of discharges and that it is not possible to extrapolate from a single sample to estimate an annual average. Nonetheless, the fact that this effluent discharge is a point source of such pollutants indicates the importance of careful monitoring to ensure EQS are not exceeded and, as far as possible, to eliminate such discharges.

Finally, the Nam Boon wastewater (TH10012) contained a number of organic compounds which could not be identified to any degree of reliability. However, some of these compounds have shown mass-spectra fragmentation characteristic for a number of different isomeric compounds, indicating the diversity and complexity of the wastewaters discharged from this facility.

The Samchai Fabric wastewater (TH10010) contained concentrations of copper (total 289 µg/l, dissolved 196 µg/l), chromium (total 142 µg/l, dissolved 100 µg/l), and to a lesser extent zinc (total 201 µg/l, dissolved 64 µg/l), all above levels typically found in uncontaminated surface waters. The Nam Boon wastewater (TH10012) contained lower levels of these metals, with copper (total 31 µg/l, dissolved 29 µg/l) and zinc (total 92 µg/l, dissolved 63 µg/l) above typical background concentrations. Background concentrations of dissolved copper and chromium in uncontaminated surface waters are typically below 10 µg/l, and often far lower, while those of zinc are generally below 50 µg/l (ATSDR 2004, ATSDR 2005a, ATSDR 2008, Comber *et al.* 2008, Kruawal *et al.* 2005).

For both wastewater samples, the concentrations of all quantified metals were below their respective Thai industrial effluent standards, which define maximum levels for total concentrations in the whole sample, including copper (2000 µg/l), chromium (750 µg/l) and zinc (5000 µg/l) (MSTE 1996).

Copper and chromium compounds have known uses in textile manufacturing, particularly for dyeing processes (IPPC 2003), and copper has previously been reported in some dye plant effluents (Sharma *et al.* 2007). Many aquatic organisms are highly sensitive to copper, particularly when it is present in dissolved forms, and impacts can occur at very low concentrations (ATSDR 2004, Bryan & Langston 1992, Sandahl *et al.* 2007). More information on key metals is presented in Boxes D & E.

Box D. Metals

Chromium (Cr) is primarily used in the metallurgical industry (in stainless steel and other alloys), as well as in various industrial processes including leather tanning and certain textile processes (ATSDR 2008, IPPC 2003). Hexavalent chromium compounds are used in metal finishing (chrome plating), in wood preservatives and as corrosion inhibitors (ATSDR 2008). Chromium normally exists in the environment in trivalent Cr(III) forms, which generally have very low solubility in water and tend to rapidly precipitate or adsorb onto suspended particles and bottom sediments. Hexavalent Cr(VI) forms can exist, though far less frequently, and these compounds are usually converted rapidly to trivalent Cr(III) compounds by reducing compounds. Hexavalent forms tend to be readily soluble in water and therefore can be highly mobile in aquatic environments (ATSDR 2008, DeLaune *et al.* 1998, Lin 2002). Uncontaminated surface water typically contains less than 10 µg/l of chromium, and concentrations in uncontaminated freshwater sediments are typically below 100 mg/kg (ATSDR 2008, Salomons & Forstner 1984). Chromium (III) is an essential nutrient for animals and plants, though large doses may be harmful. In contrast, hexavalent chromium is highly toxic even at low concentrations, including for many aquatic organisms (Baral *et al.* 2006). Hexavalent chromium compounds are also corrosive, and in humans allergic skin reactions readily occur following exposure, independent of dose (ATSDR 2008). Furthermore, hexavalent chromium is a known human carcinogen under some circumstances (IARC 1990).

Copper (Cu) is a widely used metal, primarily as a pure metal or as part of mixtures (alloys) with other metals, though there are also many other uses of copper compounds, including within metal finishing processes and textile manufacture, including dyeing processes (IPPC 2003). The manufacture of plumbing materials is one of the main uses of main uses of copper metal and alloys, in part due to the malleability and thermal conductivity of copper (ATSDR 2004). Levels of copper in the environment are typically quite low, commonly less than 50 mg/kg in uncontaminated freshwater sediments (ATSDR 2004). Background concentration of dissolved copper in uncontaminated surface waters can vary significantly, but levels are typically below 10 µg/l, and often far lower (ATSDR 2004, Comber *et al.* 2008). Copper is an important element for humans and animals in low doses. However, expose to high levels of bioavailable copper can lead to bioaccumulation and toxic effects (ATSDR 2004). Releases of copper to aquatic systems are of particular concern as many aquatic organisms are extremely sensitive to copper, particularly in soluble forms which are generally far more bioavailable and toxic to a wide range of aquatic plants and animals (ATSDR 2004, Adams & Chapman 2006), with some effects occurring even at very low concentrations (Sandahl *et al.* 2007).

Lead is a metal that is found naturally in the environment, though usually at very low concentrations unless at locations affected by inputs from human activities. Uncontaminated freshwater sediments typically contain less than 30 mg/kg of lead (ATSDR 2007). Leads has no known biochemical or nutritional function and is highly toxic to humans as well as many animals and plants (ATSDR 2007, Adams & Chapman 2006, WHO 1989). Levels can build up in the body through repeated exposure and have irreversible effects on the nervous system, which is of particular concern for the developing nervous system in young humans, with impacts occurring even at very low levels of exposure. Other effects include damage to the blood system, and impacts on the kidneys and on reproduction (ATSDR 2004, Jusko *et al.* 2008, Sanders *et al.* 2009). Some studies have indicated that there may be no safe level of exposure, particularly in the developing central nervous system in humans (Canfield *et al.* 2003).

Nickel as a metal and its alloys, as well as nickel compounds, have many industrial uses, including in metal plating, the manufacture of plumbing and electronic devices, in catalysts, batteries, pigments and ceramics (ATSDR 2005b, DHHS 2005). Levels of nickel in the environment are typically low, with uncontaminated freshwater sediments generally containing below 60 mg/kg nickel. Concentrations in uncontaminated surface waters are typically below 20 µg/l (Alloway 1990, ATSDR 2005b, Salomons & Forstner 1984). Although nickel bound to sediments and soils is generally persistent, water-soluble nickel compounds can be quite mobile. Very small amounts of nickel are essential for normal growth and reproduction in most animals and plants, and this is most likely also true for humans (ATSDR 2005b). However, toxic and carcinogenic effects can result from exposure to higher concentrations for a wide range of life forms, including gastrointestinal and cardiac effects (ATSDR 2005b, Cempel & Nikel 2006). In humans, a significant proportion of the population (2-5%)

are also nickel sensitive, and effects can occur in sensitised individuals at far lower concentrations (ATSDR 2005b). For some aquatic organisms, impacts can occur at very low nickel concentrations (Deleebeeck *et al.* 2008). Furthermore, some nickel compounds have been classified as carcinogenic to humans, and there is also evidence of carcinogenicity in animals (DHHS 2005, IARC 1990).

Zinc (Zn) and its compounds have numerous industrial uses. As a metal, zinc is primarily used as a protective coating of iron and steel and other metals/alloys, particularly through galvanizing, including in the manufacture of plumbing materials and electronic devices. Zinc compounds also have numerous uses, including in paints and pigments, batteries and catalysts (ATSDR 2005a). Levels of zinc are generally quite low in the environment; with levels typically below 100 mg/kg in uncontaminated freshwater sediments, while levels in uncontaminated surface waters are typically below 50 µg/l (ATSDR 2005, Salomons & Forstner 1984). Zinc is an essential nutrient for humans and animals, however exposure to high concentrations of bioavailable zinc can result in significant bioaccumulation with possible toxic effects, including for aquatic organisms (Adams & Chapman 2006, ATSDR 2005a). Symptoms of high doses in humans include pancreatic damage, anaemia and gastrointestinal distress, with similar effects also reported for animals (ATSDR 2005a, IPCS 2001).

Canal samples

Both samples of surface water from the Samrong canal, that collected by the Nam Boon outfall (TH10014) and that collected closer to the Chao Phraya (TH10004), contained TiBP, though as expected at lower abundance than it was detected in the Nam Boon wastewater itself (TH10012). However, the fact that this chemical was detected in both directions from the identified point source (discharge from Nam Boon textile factory, sample TH10012) suggests that contaminants released with the wastewaters may be spreading through the canal system. At the same time, canal water sample TH10014 also contained 11 isomers of nonyl phenol, isomers of which were also detected (at even higher number) in the wastewater discharged to the Samrong canal from the other factory sampled in this study, Samchai Fabric Co. (TH10010). Again, the abundance of nonyl phenols in the canal water TH10014 was lower than it was detected in the wastewater sample TH10010. Thus, migration of these chemicals along the channel may indicate wider pollution of the investigated area with other contaminants discharged with the wastewater from textile factories located along Samrong canal. As there are numerous other industrial facilities located along the banks of the canal in this area, it is possible that there are other sources of these chemicals than the two specifically sampled in this study. Nonetheless, both the Nam Boon and Samchai Fabric Co. factories are clearly contributing to the overall burden of pollution.

Water collected from the Samrong canal adjacent to the Nam Boon factory (TH10014) was largely uncontaminated with metals, with only nickel at a notably elevated level. The dissolved nickel concentration (31 µg/l) was above background concentrations for uncontaminated surface waters, which are typically below 20 µg/l (ATSDR 2005b, Salomons & Forstner 1984). Although few data are available on metal concentrations in the lower Chao Phraya river basin, one recent study found dissolved nickel at 4 µg/l for the Chao Phraya River upstream of Bangkok (Kruawal *et al.* 2005).

Box E. Metal threshold levels for effluents and surface waters / sediments

Effluent standards and surface water quality standards

The table below presents Thai standards for total concentrations of certain metals in industrial effluents and surface waters, along with the highest levels found in this study for discharged wastewaters and surface waters, as well as local background surface water concentrations for the Chao Phraya River.

Metal (total concentration, µg/l)	Chromium	Copper	lead	Manganese	Nickel	Zinc
Highest value, this study;						
Wastewater (value, sample #)	142 (#10)	289 (#10)	<20 (all)	400 (#12)	<20 (all)	201 (#10)
Canal water (value, sample #)	1380 (#04)	511 (#04)	198 (#04)	2620(#04)	797 (#04)	4640 (#04)
Industrial effluent standard (a)	1000	2000	200	5000	1000	5000
Surface water quality standard (b)	50**	100	50	1000	100	1000
Local background surface water (c)	2.3	2.5	3.7	100	5	370

*Table E1. Highest total metal concentrations found in this study (#xx refers to TH100xx), with industrial effluent and surface water quality standards, and local background surface water concentrations; (a) MSTE (1996), (b) NEB 1994 **-hexavalent chromium only, (c) REO 2010*

Examples of contaminated sediments threshold levels

Standards that define thresholds for maximum acceptable levels of metals in river sediments have not been defined in Thailand. As a result, certain thresholds from other countries are presented below for comparison with the highest levels found in this study, including threshold levels for seriously contaminated sediments in the Netherlands (NMHSPE 2000), and levels defined by the National Oceanic and Atmospheric Administration (NOAA) of America, above which adverse biological effects would usually be expected to be observed in aquatic organisms (Long & Morgan 1990).

Metal (mg/kg)	Chromium	Copper	Lead	Nickel	Zinc
Highest concentration, this study	1030 (TH10007)	355 (TH10007)	209 (TH10001)	4760 (TH10007)	2960 (TH10007)
Dutch threshold (a)	380	190	530	210	720
NOAA level (b)	145	390	110	50	270

Table E2. Certain contaminated sediments threshold levels set in other countries, compared with the highest sediment concentrations found in this study for key metals. All values in mg/kg dry weight. (a) NMHSPE 2000, (b) Long & Morgan 1990

Thai surface water quality standards specify limits for total metal concentrations in whole water samples (PCD 2010). The level of total nickel in the canal water (110 µg/l) was just above the Thai surface water quality standard for nickel (100 µg/l) (NEB 1994). In contrast, a 2010 report recorded a background total nickel concentration of 5 µg/l for the Chao Phraya, upstream of Bangkok (REO 2010). Other more stringent surface water quality standards for dissolved metal concentrations exist in other countries, including the European Union (EU) environmental quality standards (EQS) which are defined for certain hazardous substances in inland surface waters, with the aim of achieving good surface water chemical status. The level of dissolved nickel in the canal water (31 µg/l) was higher than the EU annual average EQS of 20 µg/l (EC 2008, see Box E), though again it must be noted that the figure from the current study is a single point measurement.

The canal water (TH10004) collected closer to the Chao Phraya River, adjacent to a chemical factory, contained similar concentrations of dissolved metals to those in TH10014 with, in this case, only the dissolved manganese concentration (630 µg/l) above typical uncontaminated surface water concentrations (typically below 200 µg/l, and often far lower; Barceloux 1999). A recent study of dissolved metals in the lower Chao Phraya basin reported dissolved manganese at 130 µg/l (Kruawal *et al.* 2005).

However, far higher total concentrations (both dissolved forms and those bound to suspended particulates) were found for many metals in whole (unfiltered) water samples, including those that were present at high levels in both sediment samples from this canal. The total concentrations of copper, lead, manganese, nickel and zinc in TH10004 exceeded their Thai surface water quality standards by between 3 and 8 times (see Box E for details; PCD 2010).

This canal water sample (TH10004) visually contained a very high level of suspended solids. Although this sample was collected from the midpoint of the canals and at medium depth, in accordance with protocols used by the PCD (PCD 2010), it is possible that the level of suspended solids, as well as the high total water levels of many metals (many of which were also present at high levels in the canal sediments), is due to localised resuspension of sediment from the bottom of the canal into the water body.

The range of organic compounds identified in sediment collected from the canal adjacent to the Samchai Fabric Co. factory (TH10003) was not very high, with only 12 compounds isolated, 5 of which were identified to a high degree of reliability (4 linear aliphatic hydrocarbons, plus the trans-isomer of decahydronaphtahlene). Decahydronaphthalene (also known as decalin or bicyclo[4.4.0]decane) has uses as an industrial solvent in some resins and fuel additives. Decalin is a toxic compound which primarily affects the developing kidney (Zeliger 2008). Possible sources of this chemical in the sediment sample TH10004 should be further investigated.

This sediment (TH10003) also contained high concentrations of zinc, as well as chromium, copper, nickel and lead. The concentrations of these metals exceeded their typical background levels in sediments (Alloway 1990, ATSDR 2004, ATSDR 2005a&b, ATSDR 2007a&b, Salomons & Forstner 1984) by approximately 30 times (zinc), 6 times (chromium & copper) and 3-4 times (arsenic, nickel and lead) respectively. Recent data for local background levels of these metals in the lower Chao Phraya basin could not be found.

A second canal sediment (TH10005), collected closer to the Chao Phraya River at the same location as canal water sample (TH10004), had a very similar profile of metal contamination to that found in the sediment collected adjacent to the Samchai Fabric Co. factory (TH10003), though with somewhat lower metals concentrations being found in TH10005. The metals present at above background levels reflected those found at high concentrations in suspended (particulate, not dissolved) forms in canal water from the same location (TH10004). Only 6 organic compounds were isolated from this sample (TH10005), 3 of which were identified as linear aliphatic hydrocarbons.

Maximum acceptable levels of metals in freshwater sediments have not been defined in Thailand. However, comparison with relevant thresholds from other countries highlights the high levels of many metals in this canal. For both sediment samples from the Samrong canal, the concentrations of chromium, copper, nickel and particularly zinc exceeded threshold levels for seriously contaminated sediments in the Netherlands (NMHSPE 2000), and levels defined by the National Oceanic and Atmospheric Administration (NOAA) of America, above which adverse biological effects have been usually observed in aquatic organisms (Long & Morgan 1990, see Box E for details).

Bangnangkreng & Bangplakod canals

Three samples were collected from the Bangnangkreng canal, from a section of the canal close to steel and textile manufacturing factories (Table 1b). A sample of canal water (TH10006) and canal sediment (TH10007) were collected from a location close to a sluice gate which connects the Bangnangkreng canal and the Chao Phraya river (see Figure 1). One further sample of sediment (TH10001) was collected from the Bangnangkreng canal further from its junction with the Chao Phraya River.

Two further samples were collected from the separate Bangplakod canal. Both the canal water (TH10008) and sediment (TH10009) were collected from the same location, in a section of the canal close to industrial facilities, including a steel manufacturing factory and a feather (bleaching) factory.

Sample	Type	Description
TH10001	sediment	Bangnangkreng canal, furthest from the sluice gate, close to steel and textile factories
TH10006	canal water	Bangnangkreng canal, close to the water gate
TH10007	sediment	Bangnangkreng canal, (as TH10006)
TH10008	canal water	Bangplakod canal, close to steel and feather bleaching factories
TH10009	sediment	Bangplakod canal, (as TH10008)

Table 1b. Description of samples collected from the Bangnangkreng and Bangplakod canals, Thailand, 2010

Results

The data from the analyses are summarised in Table 2b. Water sample TH10006 collected from the Bangnangkreng canal contained the highest number of organic chemicals (40 compounds) among all canal water samples investigated in this study. Of the 24 organic compounds (60%) were identified to a high degree of reliability and included linear aliphatic hydrocarbons, alkylated benzenes, 11 isomers of nonyl phenol, benzenemethanol and TiBP. It is necessary to note that, although analysed only qualitatively in the current study, the apparent abundance of TiBP in this sample was very high and comparable to that recorded in the wastewater sample TH10012 (discharge from the Nam Boon textile factory into the Samrong channel). Again, similarly to wastewater sample TH10010 (discharged from the Samchai Fabric Co. factory), canal water sample TH10006 showed the presence of estrogenic nonyl phenols. These findings suggest that the canal water close to the sluice gate connecting the Bangnangkreng canal and the Chao Phraya river is affected by wastewater discharged from a textile factory located in close proximity to the sampling point, but which was not investigated in this study. Moreover, it is possible to speculate that TiBP was liberally discharged at this location such that, even with dilution in the canal water, its presence was highly conspicuous. Figure 3 shows chromatograms obtained for the Bangnangkreng canal water sample (TH10006, left) and for the wastewater sample from the Nam Boon textile factory (TH10012, right); the TiBP peak is by far the most prominent in both cases.

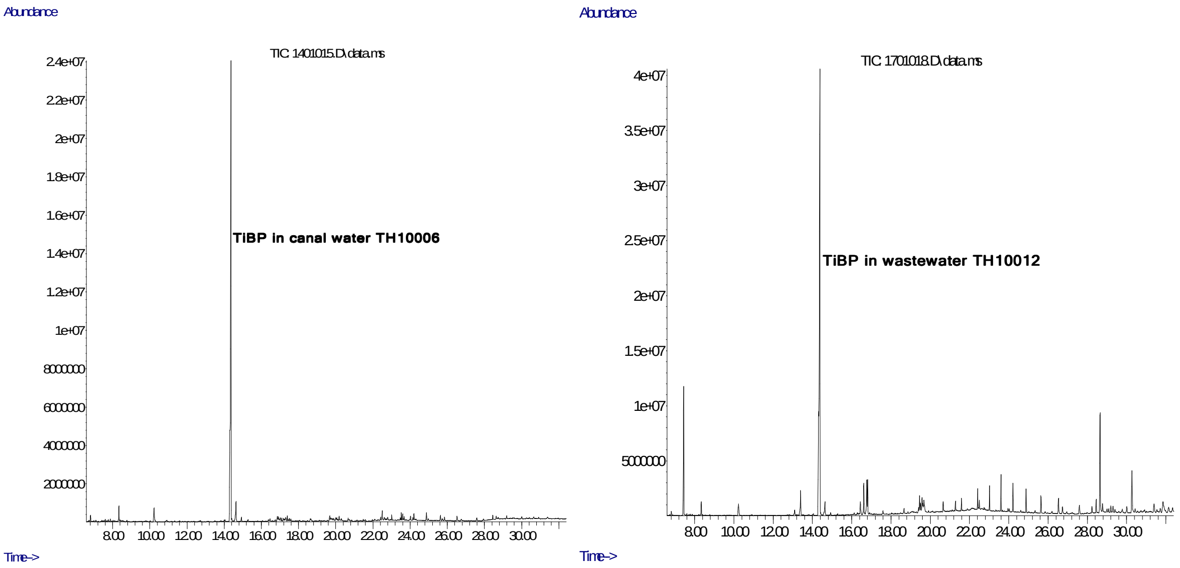

Figure 3. Chromatograms of Bangnangkreng canal water sample TH10006 (left) and wastewater sample from the Nam Boon textile factory TH10012 (right).

Benzenemethanol, also known as benzyl alcohol, which was detected in the sample TH10006, is a natural component of some plants. However, it has some industrial uses including as food flavoring agent, textile dye additive and as a solvent (EU 2002c).

The sample of water from the Bangnangkreng canal (TH10006) contained dissolved nickel at 82 µg/l, a concentration above levels that are usually found in uncontaminated surface waters, which typically contain below 20 µg/l dissolved nickel (ATSDR 2005b, Salomons & Forstner 1984). A background dissolved nickel concentration of 3 µg/l has been reported for the Chao Phraya upstream of Bangkok (Kruawal *et al.* 2005). Though not applicable in Thailand, the dissolved nickel concentration in this sample would exceed the annual average surface water standard of the European Union (20 µg/l, EC 2008). This canal water (TH10006) contained higher values for total concentrations of some metals, most notably copper (205 µg/l) and nickel (233 µg/l), both at over 2 times their Thai surface water quality standards of 100 µg/l (NEB 1994). This indicates that the canal water is contaminated with nickel and copper, although these metals are predominantly bound to suspended particulates rather than in dissolved forms (see Boxes D & E for more detail).

The sediment sample collected from the same location (TH10007) contained the highest concentrations of chromium, copper, nickel and zinc found in all sediments samples analysed in this study, with the high levels of nickel and copper reflecting the high concentrations found in the canal water at this location (TH10006). The level of nickel in the sediment was approximately 80 times higher than concentrations expected for uncontaminated river sediment (Alloway 1990, ATSDR 2005b), while the concentrations of copper, chromium and zinc in the sample exceeded their typical background levels by 7, 10 and 30 times respectively (ATSDR 2004, Salomons & Forstner 1984, ATSDR 2005a). The sediment also contained somewhat elevated levels of arsenic and lead, at approximately 2-3 times above usual background levels (ATSDR 2007a&b). Organic compounds detected in this sediment sample (TH10007) were mainly represented by linear aliphatic hydrocarbons (22 compounds), three polycyclic aromatic hydrocarbons, and one branched alkyl benzene. These organic compounds may indicate contamination by oil or other petrochemicals, though the presence of naturally occurring aliphatic hydrocarbons cannot be ruled out.

Location	Bangnangkreng				Bangplakod		
	by sluice gate			middle			
Sample	TH10006		TH10007	TH10001	TH10008		TH10009
Type	canal water		canal sediment	canal sediment	canal water		canal sediment
	total	diss			total	diss	
METAL	(µg/l)	(µg/l)	(mg/kg)	(mg/kg)	(µg/l)	(µg/l)	(mg/kg)
Antimony	<20	<20	<20	<20	<20	<20	<20
Arsenic	69	<50	30	<10	<50	<50	<10
Barium	66	59	334	255	80	63	149
Cadmium	<5	<5	<1	<1	<5	<5	<1
Chromium	52	<20	1030	220	21	<20	118
Chromium (VI)	<50	<50	-	-	<50	<50	-
Cobalt	<20	<20	19	19	<20	<20	18
Copper	205	<20	355	131	<20	<20	51
Lead	<50	<50	126	209	<50	<50	29
Manganese	170	31	853	641	595	177	1890
Mercury	<2	<2	0.4	0.5	<2	<2	0.3
Nickel	233	82	4760	114	<20	<20	42
Selenium	<200	<200	<30	<30	<200	<200	<30
Thallium	<200	<200	<10	<10	<200	<200	<10
Vanadium	<20	<20	39	76	<20	<20	63
Zinc	105	<10	2960	1790	41	<10	190
pH	8		-	-	7		-
Organic compound isolated	40		51	11	14		8
No. reliably identified (% of total)	24 (60%)		26 (52%)	4 (36%)	none		1 (13%)
Tri-iso-butyl phosphate	1						
Aliphatic hydrocarbons	9		22	4			1
PAHs & derivatives			3				
Alkyl benzenes	2		1				
Nonyl phenols	11						
Other compounds	1						

Table 2b. Organic chemicals identified, and concentrations of metals and metalloids, in samples of canal water and sediment associated with the Bangnangkreng and Bangplakod canals, Thailand, 2010. Concentrations of metals in canal water samples are reported in µg/l, both as total concentrations in the whole (unfiltered) sample and separately as (diss)olved concentrations in filtered samples. Concentrations of metals in sediments are reported as mg/kg dry weight.

The second sediment sample from the Bangnangkreng canal (TH10001), collected further away from the Chao Phraya River in the vicinity of steel and textile manufacturing factories, contained the same metals above usual background levels as sample TH10007, though to a lesser extent (particularly in the case of nickel). The concentrations of lead and zinc were 7 and 18 times higher than concentrations of these metals expected for uncontaminated river sediment, while the concentrations of chromium, copper and nickel were all approximately 2 times higher than their respective usual background levels (ATSDR 2004, Salomons & Forstner 1984, ATSDR 2005b, ATSDR 2007). The only organic compounds detected in sediment sample TH10001 were four linear aliphatic hydrocarbons, which might be of natural origin.

As was the case for the Samrong canal sediment, the concentrations of some metals in the Bangnangkreng canal sediments were above relevant contaminated sediment thresholds from other countries, particularly for nickel, but also for chromium, copper and zinc. See Box E for details.

For the sediment sample from the Bangnangkreng canal that was most contaminated with metals, TH10007, the concentrations were only slightly higher than those found in one of the sediment samples collected from the Samrong canal (TH10003), with the exception of the considerably higher level of nickel.

Bangplakod canal

The sample of canal water from the Bangplakod canal (TH10008) did not contain any of the quantified metals at levels above those typically found in uncontaminated surface waters. None of the organic compounds isolated from this sample have been identified, possibly due to their presence in the sample at very low levels.

Similarly, the associated sediment from the Bangplakod canal at the same location (TH10009) was largely uncontaminated with metals, although this sample did contain manganese and zinc at concentrations slightly higher than typical background levels for these metals in uncontaminated freshwater sediments (ATSDR 2005a, ATSDR 2008, Cooper 1984). Again, the loading of organic chemicals in this sample was very low, with only one compound reliably identified as eicosane, a linear aliphatic hydrocarbon.

Conclusions

This study has demonstrated the release of hazardous chemicals within industrial wastewaters discharged from two textile manufacturing facilities located on the banks of the Samrong canal which connects to the lower Chao Phraya River in Thailand. Amongst the chemicals identified in the wastewaters are substances that are subject to regulations in other countries preventing their use and / or release. The release of hazardous chemicals from these facilities is contributing to the contamination of the Samrong canal with hazardous chemicals.

The Samrong canal, and the nearby Bangnangkreng canal (though not the Bangplakod) are currently contaminated with a range of toxic metals and hazardous organic pollutants, although discharged wastewaters from the two textile facilities do not appear to be contributing to the presence of some of the toxic metals and organic pollutants identified in the canal samples. With numerous industrial facilities operating along the banks of the three canals, the precise sources of these additional hazardous substances cannot be determined from the current investigation. However, the current and historic discharges of contaminated industrial wastewaters from the numerous other industrial facilities in the vicinity of the canals to the canals are likely to contribute significantly to their chemical contamination.

This study did not attempt to investigate all sources of hazardous chemicals to the Chao Phraya River basin. The three canals investigated in this study represent only a fraction of the areas within the Chao Phraya basin where industrial facilities are located, particularly for the lower section. These canals, however, are likely to provide examples of what might also be happening elsewhere, highlighting what is likely to be a broader problem relating to the discharge of industrial wastewaters to the Chao Phraya River and to canals linking to it.

Although limited in its scope, this study illustrates the current levels of contamination of the three receiving water bodies, and highlights the need for more in-depth investigation into the discharge of hazardous chemicals to the Chao Phraya River basin, as well as other parts of Thailand.

The development of a more sustainable approach to the management of chemicals and the future protection of water resources within Thailand will require a comprehensive understanding of the current use of hazardous substances for as wide a range of substances as possible, and of their release to the aquatic and wider environment, making tools such as Pollutant Release and Transfer Registers (PRTR) very important. At an early stage, such an approach, based on the precautionary principle that prevention is easier and cheaper than cure, needs to include the setting of zero discharge targets for the most hazardous industrial chemicals used within Thailand, which can then be achieved through the ongoing substitution of hazardous substances with less hazardous or preferably non-hazardous alternatives (the principle of substitution) in order to bring about rapid reductions and ultimate cessation in their discharges, emissions and losses . Such approaches have been developed and are being implemented in other parts of the world, including within the European Union and wider North-East Atlantic (OSPAR) and Baltic (HELCOM) regions.

References

ABG (2010) Asian Buyer Guide website. www.asianbuyersguide.com/company/nam-boon-bleaching-and-dyeing-factory-co-ltd-38038.html

Adams, W.J. & Chapman, P.M. (2006) Assessing the hazard of metals and inorganic metal substances in aquatic and terrestrial systems. ISBN: 1420044400. CRC Press

Adeoya-Osiguwa, S.A., Markoulaki, S., Pocock, V., Milligan, S.R. & Fraser, L.R. (2003) 17-beta-estradiol and environmental estrogens significantly effect mammalian sperm function. Human Reproduction 18(1): 100-107

Alloway, B.J. (1990). Heavy metals in soils. John Wiley and Sons, Inc. New York, ISBN 0470215984

Andresen, J. A.,. Grundmann, A & Bester, K. (2004**)** Organophosphorus flame retardants and plasticisers in surface waters. Science of The Total Environment 332(1-3): 155-166

Atienzar, F.A., Billinghurst, Z. & Depledge, M.H. (2002) 4-n-nonylphenol and 17-beta-estradiol may induce common DNA effects in developing barnacle larvae. Environmental Pollution 120(3) 735-738

ATSDR (2004) Toxicological profile for copper, United States Public Health Service, Agency for Toxic Substances and Disease Registry, September 2004

ATSDR (2005a) Toxicological profile for zinc, United States Public Health Service, Agency for Toxic Substances and Disease Registry, August 2005

ATSDR (2005b) Toxicological profile for nickel. Agency for Toxic Substances and Disease Registry, US Public Health Service, August 2005

ATSDR (2007a) Toxicological profile for lead, United States Public Health Service, Agency for Toxic Substances and Disease Registry, August 2007

ATSDR (2007b) Toxicological profile for arsenic, United States Public Health Service, Agency for Toxic Substances and Disease Registry, August 2007

ATSDR (2008) Toxicological profile for chromium, United States Public Health Service, Agency for Toxic Substances and Disease Registry, September 2008

Auletta, C.S., Kotkoskie, L.A., Saulog, T. & Richter, W.R. (1998) A dietary oncogenicity study of tributyl phosphate in the CD-1 mouse. Toxicology 128 (2): 135-141

Baral, A., Engelken, R., Stephens, W., Farris, J. & Hannigan, R. (2006) Evaluation of aquatic toxicities of chromium and chromium-containing effluents in reference to chromium electroplating industries. Archives of Environmental Contamination and Toxicology 50(4): 496-502

Barceloux, D.G. (1999) Manganese. Clinical Toxicology 37(2): 293-307

Basheer C., Lee H.K & Tan K.S. (2004) Endocrine disrupting alkylphenols and bisphenol-A in coastal waters and supermarket seafood from Singapore. Marine Pollution Bulletin 48(11-12): 1145-1167

Blake C.A., Boockfor F.R., Nair-Menon J.U., Millette C.F., Raychoudhury S.S. and McCoy G.L. (2004) Effects of 4-*tert*-octylphenol given in drinking water for 4 months on the male reproductive system of Fischer 344 rats. Reproductive Toxicology 18(1): 43-51

Bowen, K.R., Flanagan, K.B., Acree Jr., W.E. & Abraham, M.H. (2006) Correlating toxicities of organic compounds to select protozoa using the Abraham model. Science of The Total Environment 369 (1-3): 109-118

Bryan, G.W. & Langston, W.J. (1992). Bioavailability, accumulation and effects of heavy metals in sediments with special reference to United Kingdom estuaries: a review. Environmental Pollution 76: 89-131

Butte, W. & Heinzow, B. (2002) Pollutants in house dust as indicators of indoor contamination. Reviews in Environmental Contamination and Toxicology 175: 1-46

Canfield, R.L., Henderson, C.R., Cory-Slechta, D.A., Cox, C., Jusko, T.A., Lanphear, B.P. (2003) Intellectual impairment in children with blood lead concentrations below 10 mu g per deciliter. New England Journal of Medicine 348(16): 1517-1526

Cempel, M., Nikel, G. (2006) Nickel: A review of its sources and environmental toxicology. Source: Polish Journal of Environmental Studies 15(3): 375-382

Chan, I. & Walkelin, S.H. (2006) Allergic contact dermatitis from dioctyl maleate in a moisturizer. Contact dermatitis 55(4): 250

Chitra, K.C., Latchoumycandane, C. & Mathur, P.P. (2002) Effect of nonylphenol on the antioxidant system in epididymal sperm of rats. Archives of Toxicology 76(9): 545-551

Chiu, N., Orme-Zavaleta, J., Chiu, A., Chen, C., DeAngelo, A., Brattin, W. & Blancato, J. (1996) Characterization of cancer risk associated with exposure to chloroform. Environmental Carcinogenesis & Ecotoxicology Reviews. Journal of Environmental Science and Health C14(2): 81-104

Comber, S.D.W., Merrington, G., Sturdy, L., Delbeke, K., van Assche, F. (2008) Copper and zinc water quality standards under the EU Water Framework Directive: The use of a tiered approach to estimate the levels of failure. Science of the Total Environment 403(1-3): 12-22

Cooper W.C. (1984) The health implications of increased manganese in the environment resulting from the combustion of fuel additives: a review of the literature. Journal of Toxicology and Environ Health 14(1): 23–46

David, A., Fenet, H. & Gomez, E. (2009) Alkylphenols in marine environments: Distribution monitoring strategies and detection considerations. Marine Pollution Bulletin 58(7): 953-960

DeLaune, R.D., Patrick, W.H. & Guo, T. (1998) The redox-pH chemistry of chromium in water and sediment. In Allen, H.E., Garrison, A.W., Luther, G.W., eds, Metals in Surface Waters. Ann Arbor, USA. ISBN:1575040875: 262 pp.

Deleebeeck, N.M., De Schamphelaere, K.A., Janssen, C.R. (2008) A novel method for predicting chronic nickel bioavailability and toxicity to daphnia magna in artificial and natural waters. Environmental Toxicology and Chemistry 27(10): 2097–2107

DHHS (2005) 11th Report on carcinogens. U.S. Department of Health and Human Service. National Toxicology Program. January 31, 2005. http://ntp.niehs.nih.gov/ntp/roc/eleventh/profiles/s117naph.pdf (accessed 25.05.10)

Dodi, A. & Verda, G. (2001) Improved determination of tributyl phosphate degradation products (mono- and dibutyl phosphates) by ion chromatography. Journal of Chromatography A 920**:** 275-281

Dunnick, J.K & Melnik, R.L. (1993) Assessment of the carcinogenic potential of chlorinated water: experimental studies of chlorine, chloramine and trihalomethanes. Journal of the National Cancer Institute 85(10): 818-823

EC (2006) Proposal for a Directive of the European Parliament and of the Council on environmental quality standards in the field of water policy and amending Directive 2000/60/EC, European Commission COM(2006) 397 final, Brussels, 17.7.2006

EC (2008) Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council. http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:32008L0105:EN:NOT

Environment, No. 3, B.E. 2539. Presented by the Pollution Control Department, Ministry of Natural

ETAD (2008) ETAD Information Notice No. 6 available from: http://www.etad.com/documents/Downloads/publications/notice_no_6_rev_2008.pdf (accessed 15th June 2010)

EU (2000) Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for the Community action in the field of water policy. Official Journal L327, 22/12/2000: 1-72

EU (2001) Decision No 2455/2001/EC Of The European Parliament And Of The Council Of 20 November 2001 Establishing The List Of Priority Substances In The Field Of Water Policy And Amending Directive 2000/60/EC, Official Journal L 249 , 17/09/2002: 27-30

EU (2002a) Directive 2002/61/EC of the European Parliament and of the Council relating to restrictions on the marketing and use of certain dangerous substances and preparations (azo colourants) of 19 July 2002 amending for the nineteenth time Council Directive 76/769/EEC relating to restrictions on the marketing and use of certain dangerous substances and preparations (azocolourants). OJ L243: 215-218

EU (2002b) European Union Risk Assessment Report: 4-nonylphenol (branched) and nonylphenol, Luxembourg: Office for Official Publications of the European Communities, 2002 http://ecb.jrc.it/documents/existing-chemicals/risk_assessment/report/4-nonylphenol_nonylphenolreport017.pdf

EU (2002c) Opinion of the Scientific Committee on Food on Benzyl Alcohol. European Commission, Health & Consumer Protection Directorate-General, Directorate C - Scientific Opinions. SCF/CS/ADD/FLAV/78 Final, (expressed on 24 September 2002), http://ec.europa.eu/food/fs/sc/scf/out138_en.pdf (accessed on 16.06.10)

EU (2003) Directive 2003/53/EC Of The European Parliament And Of The Council Of 18 June 2003 Amending For The 26th Time Council Directive 76/769/EEC Relating To restrictions on the marketing and use of certain dangerous substances and preparations (nonylphenol, nonylphenol ethoxylate and cement) http://europa.eu.int/eur-lex/pri/en/oj/dat/2003/l_178/l_17820030717en00240027.pdf

EU (2008) Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council. Official Journal of the European Union L 348:84-97

Evenset, A., Leknes, H., Christensen, G.N., Warner, N., Remberger, M. & Gabrielsen, G.W. (2009) Screening of new contaminants in samples from the Norwegian Arctic. Norwegian Pollution Control Authority SPFOreport: 1049/2009 TA-2510/2009, ISBN 978-82-449-0065-2. http://npweb.npolar.no/portal/filearchive/newContaminants2009.pdf (accessed 16.06.10)

Foitzik, R.C., Kaynak, A. & Pfeffer, F.M. (2006) Application of soluble poly(3-alkylpyrrole) polymers on textiles. Synthetic Metals 156 (7-8):637-642

Fries E. & Püttmann W. (2004). Occurrence of 4-nonylphenol in rain and snow. Atmospheric Environment 38(13): 2013-2016

Fu, M.Z., Li, Z.Y. & Gao, H.W. (2007) Distribution characteristics of nonylphenol in Jiaozhou Bay of Qingdao and its adjacent rivers. Chemosphere 69: 1009-1016

García-López, M., Rodríguez, I.,. Cela, R, Kroening, K.K. & Caruso, J.A (2009) Determination of organophosphate flame retardants and plasticizers in sediment samples using microwave-assisted extraction and gas chromatography with inductively coupled plasma mass spectrometry**.** Talanta 79(3): 824-829

Guenther, K., Heinke, V., Thiele, B., Kleist, E., Prast, H. & Raecker, T. (2002) Endocrine disrupting nonylphenols are ubiquitous in food. Environmental Science and Technology 36(8): 1676-1680

Harreus, U.A., Wallner, B.C., Kastenbauer, E.R. & Kleinsasser, N.H. (2002) Genotoxicity and cytotoxicity of 4-nonylphenol ethoxylate on lymphocytes as assessed by the COMET assay. International Journal of Environmental Analytical Chemistry 82(6): 395-401

Hofer, U., Kaufmann, W. & Rembold, M (2002) Composition for treatment textiles. US patent 6398982

IARC (1990) Nickel and certain nickel compounds. In: International Agency for Research on Cancer (IARC) monographs on the evaluation of the carcinogenic risk of chemicals to humans. Volume 49; Chromium, Nickel and Welding. ISBN 9283212495

IARC (1998) Overall evaluation of carcinogenicity: an updating of IARC Monographs Volumes 1 to 42. Chloroform. Supplement 7, p.152

International Agency for Research on Cancer, IARC (1990) Chromium. In International Agency for Research on Cancer (IARC) monograph; Chromium, Nickel and Welding. IARC monograph, Vol. 49, 677pp. ISBN 9283212495

IPCS (2001) Zinc, Environmental Health Criteria, No. 221, International Programme on Chemical Safety, UNEP/ILO/WHO, ISBN 9241572213

IPPC (2003) Reference document on best available techniques for the textiles industry, Integrated Pollution Prevention and Control (IPPC), July 2003. http://eippcb.jrc.ec.europa.eu/reference/brefdownload/download_TXT.cfm

Isetun, S., Nilsson, U. & Colmsjo, A. (2004) Evaluation of solid-phase microextraction with PDMS for air sampling of gaseous organophosphate flame-retardants and plasticizers. Analytical and Bioanalytical Chemistry 380: 319–324

Iwata M., Eshima Y., Kagechika H. & Miyaura H. (2004).The endocrine disruptors nonylphenol and octylphenol exert direct effects on T cells to suppress Th1 development and enhance Th2 development. Immunology Letters 94(1-2): 135-139

Jobling, S., Reynolds, T., White, R., Parker, M.G. & Sumpter, J.P. (1995) A variety of environmentally persistent chemicals, including some phthalate plasticizers, are weakly estrogenic. Environmental Health Perspectives 103(6): 582-587

Jobling, S., Sheahan, D., Osborne, J.A., Matthiessen, P. & Sumpter, J.P. (1996) Inhibition of testicular growth in rainbow trout (*Oncorhynchus mykiss*) exposed to estrogenic alkylphenolic chemicals. Environmental Toxicology and Chemistry 15(2): 194-202

Jusko, T.A., Henderson Jr., C.R., Lanphear, B.P., Cory-Slechta, D.A., Parsons, P.J., R.L. Canfield (2008) Blood lead concentrations < 10 μg/dL and child intelligence at 6 years of age. Environmental Health Perspectives 116(2): 243-248

Kruawal, K., Sacher, F., Werner, A., Muller, J., Knepper, T.P. (2005) Chemical water quality in Thailand and its impacts on the drinking water production in Thailand. Science of the Total Environment 340: 57– 70

Lamouroux, C., Virelizier, H., Moulin, C., Tabet, J.C. & Jankowski, C.K. (2000) Direct Determination of Dibutyl and Monobutyl Phosphate in a Tributyl Phosphate/Nitric Aqueous-Phase System by Electrospray Mass Spectrometry. Analytical Chemistry 72 (6): 1186–1191

Lin C-J. (2002) The chemical transformations of chromium in natural waters - A model study. Water air and soil pollution 139 (1-4): 137-158

Lopez-Espinosa, M. J., Freire, C., Arrebola, J. P., Navea, N., Taoufiki, J., Fernandez, M. F., Ballesteros, O., Prada, R. & Olea, N. (2009) Nonylphenol and octylphenol in adipose tissue of women in Southern Spain. Chemosphere 76(6): 847-852

Lye, C.M., Frid, C.L.J., Gill, M.E., Cooper, D.W. & Jones, D.M. (1999) Estrogenic alkylphenols in fish tissues, sediments, and waters from the UK Tyne and Tees estuaries. Environmental Science & Technology 33(7): 1009-1014

Mayer, T., Bennie, D., Rosa, F., Palabrica, V., Rekas, G., Schachtschneider, J. & Marvin, C. (2008) Dispersal of Contaminants from Municipal Discharges as Evidenced from Sedimentary Records in a Great Lakes Coastal Wetland, Cootes Paradise, Ontario. Journal of Great Lakes Research 34(3): 544-558

Micic, V. & Hofmann, T. (2009) Occurrence and behaviour of selected hydrophobic alkylphenolic compounds in the Danube River. Environmental Pollution 157(10): 2759-2768

Molle, F. (2007) Scales and power in river basin management: the Chao Phraya River in Thailand. The Geographical Journal 173(4): 358–373

MSTE (1996) Industrial Effluent Standards, notification of the Ministry of Science, Technology and

NEB (1994) Surface water quality standards, notification of the National Environmental Board, No. 8, B.E. 2537, issued under the Enhancement and Conservation of National Environmental Quality Act B.E.2535 (1992), published in the Royal Government Gazette, Vol. 111, Part 16, dated February 24, B.E.2537; www.pcd.go.th/info_serv/en_reg_std_water05.html

OSPAR (1998) OSPAR Strategy with Regard to Hazardous Substances, OSPAR Convention for the Protection of the Marine Environment of the North-East Atlantic, OSPAR 98/14/1 Annex 34

OSPAR (2001) Nonylphenol/nonylphenolethoxylates, OSPAR Priority Subtances Series, OSPAR Convention for the Protection of the Marine Environment of the North-East Atlantic, OSPAR Commission, London, ISBN 0-946956-79-0: 18 pp.

Oxenford, J.L. (1996) Disinfection by-products: current practices and future directions. In: Disinfection by-products in water treatment: the chemistry of their formation and control. Minear, R.A. & Amy G.A. [Ed] CRC Press, Inc. ISBN 1-56670-136-8: 3-16

PARCOM (1992) PARCOM Recommendation 92/8 on nonylphenol-ethoxylates, OSPAR Convention for the Protection of the Marine Environment of the North-East Atlantic, OSPAR Commission, London: 1 p.

PCD (2010) Pollution Control Department, personal communication with the director of Industrial Wastewater Pollution department, June 2010

Peters, R.J.B., Beeltje, H. & van Delft, R.J. (2008) Xeno-estrogenic compounds in precipitation. Journal of Environmental Monitoring 10: 760-769

Pinheiro, H. M., Touraud, E. & Thomas, O. (2004) Aromatic amines from azo dye reduction: status review with emphasis on direct UV spectrophotometric detection in textile industry wastewaters. Dyes and Pigments 61(2):121-139

REO (2010) Water Quality Monitoring and analysis of Water Surface Report 1/2010, 35 p., Regional Environment Office (REO), 6 Nonthaburi Province

Resources and Environment; www.pcd.go.th/info_serv/en_reg_std_water04.html

Rice, C.P., Schmitz-Afonso, I., Loyo-Rosales, J.E., Link, E., Thoma, R., Fay, L., Altfater, D. & Camp, M.J. (2003) Alkylphenol and alkylphenol-ethoxylates in carp, water, and sediment from the Cuyahoga River, Ohio. Environmental Science & Technology 37(17): 3747-3754

Rossoff, I.S. (2002) Encyclopedia of clinical toxicology. A comprehensive guide and reference to the toxicology of prescription and OTC drugs, chemicals, herbals, plants, fungi, marine life, reptiles, and insect venoms, food ingredients, clothing and environmental toxins. The Parthenon Publishing Group, USA. ISBN 1-84214-101-5. 1507pp.

Rudel R.A., Camann D.E., Spengler J.D., Korn L.R. & Brody J.G. (2003) Phthalates, alkylphenols, pesticides, polybrominated diphenyl ethers, and other endocrine-disrupting compounds in indoor air and dust. Environmental Science and Technology 37(20): 4543-4553

Rudnick, L.R. (2006) Synthetics, mineral oils, and bio-based lubricants: **chemistry and technology.** CRC Press, 2006. p.96

Saito I., Onuki A. & Seto H. (2004). Indoor air pollution by alkylphenols in Tokyo. Indoor Air 14(5): 325-332

Salomons, W. & Forstner, U. (1984) Metals in the hydrocycle. Springer-Verlag, Berlin, Heidelberg, New York, Tokyo, ISBN 3540127550

Samchai (2010) www.bangkokcompanies.com/Thailand_Companies/S31/samchai.htm

Sandahl, J.F., Baldwin, D.H., Jenkins, J.J., Scholz, N. (2007) A sensory system at the interface between urban stormwater runoff and salmon survival. Environmental Science & Technology 41(8): 2998-3004

Sanders, T., Liu, Y., Buchner, V., Tchounwou, P.B. (2009) Neurotoxic effects and biomarkers of lead exposure: a review. Reviews on Environmental Health 24(1): 15-45

Sharma, K.P, Sharma, S., Sharma, S., Singh, P.K., Kumar, S., Grover, R., & Sharma, P.K. (2007) A comparative study on characterization of textile wastewaters (untreated and treated) toxicity by chemical and biological tests. Chemosphere 69 (1): 48-54

Shue, M.F., Chen, F.A., Kuo, Y.T. & Chen, T.C. (2009) Nonylphenol concentration and estrogenic activity in Kaoping River and its tributaries, Taiwan. Water Science & Technology 59(10): 2055-2063

Snyder, R. & Andews, L.S. (1996) Toxic effects of solvents and vapours. In: Casarett and Doull's Toxicology: The Basic Science of Poisons. Fifth Edition. Klaasen, C.D, Amdur, M.O. & Doull, J. [Ed]. Mc-Graw-Hill, ISBN 0-07-105476-6, pp.737-772

WHO (1991) Tri-n-butyl phosphate. Environmental Health Criteria 112. World Health Organization, Geneva, 1991. http://www.inchem.org/documents/ehc/ehc/ehc112.htm (accessed 16.06.10)

WHO, World Health Organisation (1989) Lead; environmental aspects. Environmental Health Criteria 85. ISBN 9241542853

Ying, G.G., Kookana, R.S., Kumar, A. & Mortimer, M. (2009) Occurrence and implications of estrogens and xenoestrogens in sewage effluents and receiving waters from South East Queensland. Science of the Total Environment 407(18): 5147-5155

Yu, Y., Zhai, H., Hou, S. & Sun, H. (2009) Nonylphenol ethoxylates and their metabolites in sewage treatment plants and rivers of Tianjin, China. Chemosphere 77(1): 1-7

Zeliger, H.I (2008) 31 – Kidneys. In: Human Toxicology of Chemical Mixtures. Toxic consequences Beyond the impact of One-Component Product and Environmental Exposures. William Andrew Inc. Published by Elsevier Inc.: 507-513

Appendix 1. Analytical methodology

Analysis for Volatile Organic Compounds (VOCs)

Method

VOCs were analysed using an Agilent 6890 gas chromatograph with an Rtx-624 column (30m, 0.25mm ID, 1.4µm film thickness) connected to an Agilent 7694 Headspace Sampler and linked to an Agilent 5973N MSD operated in EI mode. The GC oven temperature program included an initial temperature of 35^0C (held for 4min), rising to 55^0C at 5^0C/min, and then to 210^0C at 15^0C/min. The carrier gas was helium, supplied at 1ml/min. From each sample, three 10ml portions were sub-sampled into 20ml headspace vials. One sub-sample was analysed with the GC-MS in total ion monitoring (SCAN) mode to identify as many of the volatile organic compounds present as possible. Identification of compounds was carried out by matching spectra against the Wiley7N Library, employing expert judgment in order to avoid misidentifications. The two remaining sub-samples were then used for duplicate quantitative analysis for those halogenated (chlorinated, brominated and mixed) VOCs which had been detected in the samples through screening. Quantification was performed in Selective Ion Monitoring (SIM) mode using a 5 point external calibration method. Halogenated VOCs quantified in the water samples with limits of detection and quantification are presented in Table 6.

Quality control

Standard deviation (SD), relative standard deviation (RSD) and limits of detection (LOD) were calculated using data from the analysis of seven replicates of a standard mixture of commonly occurring VOCs, containing 1ppb of each analyte. Limits of quantification (LOQ) were determined as the lowest concentration in the linear regression used for quantification. A number of blanks of laboratory air capped at the time that sub-sampling had taken place were also analysed, alongside samples of the ultra pure reagent water which was used for the preparation of standard calibration solutions. The initial calibration curve for each compound of interest was verified immediately prior to sample analysis by analysing a calibration standard at a concentration near the midpoint concentration for the calibration range of the GC-MS.

Compound	**LOQ, µg/l**	**LOD, µg/l**	**SD, µg/l**	**RSD, %**	**r^2**
Chloroform	0.3	0.3	0.05	4.5	0.999
Bromoform	0.5	0.4	0.06	6.6	0.999
Ethene, dichloro-	0.4	0.4	0.06	5.6	1.000
Ethene, 1,2-dichloro-, cis- *	1.0	1.0	0.20	10.1	0.999
Ethene, trichloro-	0.4	0.4	0.06	7.1	0.999
Ethene, tetrachloro-	0.3	0.3	0.05	5.1	0.999
Ethane, 1,1,1-trichloro-	0.3	0.3	0.05	4.3	0.999
Ethane, 1,2-dichloro-*	1.0	1.0	0.21	9.4	1.000
Ethane, 1,1,2,2-tetrachloro-	0.2	0.2	0.04	6.1	1.000
Methane, bromodichloro-*	0.5	0.5	0.09	3.7	0.997
Methane, dibromochloro-	0.5	0.2	0.03	3.9	0.999
Methane, dichloro-	0.2	0.2	0.03	4.3	0.999
Methane, tetrachloro-	0.3	0.3	0.05	3.9	0.999

Table 6. Standard deviation (SD), relative standard deviation (RSD) and limit of detection (LOD) were calculated using concentration of the seven replicas of the standard mixture containing 1ppb of each analyte. Limit of quantification (LOQ) is the lowest concentration in the linear regression (r^2 – corresponding correlation coefficient) used for quantification. - 2ppb of analyte was used.*

Analysis for extractable organic compounds

Preparation

20 µg of deuterated naphthalene was added as an Internal Standard (IS) to each portion of sample that was subject to extraction. For sediment samples, approximately 10 g of each sample (wet weight) was extracted employing Accelerated Solvent Extraction (ASE) technique using Dionex ASE-350 with a mixture of pentane and acetone 3:1, at a temperature of 100^{o}C. Water samples (500ml) were prepared using solid phase extraction technique with Dionex AutoTrace workstation, eluting solvents were ethyl acetate followed by a mixture of pentane and toluene 95:5. Obtained extracts were concentrated to a volume of 3ml with a stream of clean nitrogen and cleaned up prior to analysis.

Clean-up procedures were the same for the crude extracts from both aqueous and sediment samples. Each extract was shaken with 3ml isopropyl alcohol and 3ml TBA-reagent (mixture of 3% tetrabutylammonium hydrogen sulphate and 20% sodium sulphite in deionised water) and left to stand until the aqueous and organic phases had separated. The pentane phase was collected and eluted through a Florisil column, using a 95:5 pentane:toluene mixed eluent, and the cleaned extract concentrated to a final volume of 1ml as before. 20 µg of bromonaphthalene was added to each extract as a second IS prior to GC-MS analysis.

Analysis

For the total organic compounds screening, samples were analysed using an Agilent 5890 Series II GC with Restek Rtx-XLB column (30m, 0.25mm ID, 0.25 µm film thickness) linked to an Agilent 5972 MSD operated in EI mode and interfaced with an Agilent Enhanced Chem Station data system. The GC oven temperature program employed was as follows: an initial temperature of 35^{0}C, held for 2 minutes, raised to 260^{0}C at 10^{0}C/min, then to 320^{0}C at 6^{0}C/min (held for 8min). The carrier gas was helium, supplied at 1ml/min. Identification of compounds was carried out by matching spectra against both the Wiley 7N and Pesticides Libraries, using expert judgment as necessary in order to avoid misidentifications. Additionally, both the spectra and retention times of compounds isolated from the samples were matched against those obtained during GC-MS analysis of standard mixtures containing a range of chlorinated benzenes, phenols and pesticides, polychlorinated biphenyls (PCBs), phthalates, polycyclic aromatic hydrocarbons (PAHs) and aliphatic hydrocarbons.

Quality control

A number of extraction and solvent blanks were also analysed to ensure the detection of any possible contamination resulting from sample handling in the laboratory.

Analysis for metals and metalloids

Preparation

A representative portion of each sediment sample was air dried to constant weight, homogenised, sieved through a 2mm mesh and then ground to a powder using a pestle and mortar. Approximately 0.5g of each sample was digested with 2 ml concentrated hydrochloric acid and 8 ml concentrated nitric acid, firstly overnight at room temperature, then using microwave-assisted digestion with a CEM MARS Xpress system, with a temperature ramp to 180^{o}C over 15 minutes followed by holding at 180^{o}C for a further 15 minutes. Following cooling, digests were filtered and made up to 50ml with deionised water. For water samples, to obtain total concentrations, a representative portion of each whole sample was acidified by the addition of concentrated nitric acid to give a final concentration of 10% v/v. In addition, a portion of each whole sample was filtered and then acidified in the same way. 50 ml of each acidified sample was digested firstly overnight at room temperature, then using microwave-assisted digestion with a CEM MARS Xpress system, with a temperature ramp to 180^{o}C over 15 minutes followed by holding at 180^{o}C for a further 15 minutes. Cooled digests were filtered and made up to 50 ml with deionised water.

Analysis

Prepared sample digests were analysed by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) using a Varian MPX Simultaneous Spectrometer. Multi-element standards at concentrations of 0.5, 1.0, 2.5 and 10 mg/l respectively, and matrix matched to the samples, were used for instrument calibration. Any sample exceeding the calibration range was diluted accordingly, in duplicate, and re-analysed. Analysis of the mercury content in the samples was carried out separately. Mercury (Hg) was determined using cold vapour generation ICP-AES. Ionic mercury, Hg (II), was reduced to elemental mercury, Hg (0), through reaction of the sample with sodium borohydride (0.6% w/v), sodium hydroxide (0.5% w/v) and hydrochloric acid (10 molar). The elemental mercury vapour was carried in a stream of argon into the spectrometer. Two calibration standards were prepared, at 10 µg/l and 100 µg/l, matrix matched to the samples.

Quality control

For sediment samples, two samples were prepared in duplicate and analysed to verify method reproducibility, along with an identically prepared blank. To check the method efficiency, certified reference material (CRM) samples were prepared in an identical manner; GBW07311, stream sediment certified by the China National Analysis Centre for Iron and Steel, Beijing, China, and LGC6187, leachable metals in river sediment certified by the Laboratory of the Government Chemist, UK.

For water samples, three whole samples and four filtered samples were prepared in duplicate and analysed to verify method reproducibility, along with a blank sample (10% v/v nitric acid in deionised water), and a mixed metal quality control solution of 4 mg/ l, other than mercury at 80 µg/l. All control samples were prepared in an identical manor to the samples.

Calibration of the ICP-AES was validated by the use of quality control standards at 8 mg/l and 0.8 mg/l (sediment samples) or 4 mg/l and 0.4 mg/l (water samples) prepared in an identical manner but from different reagent stocks to the instrument calibration standards. For cold vapour generation mercury analysis, the calibration was validated using two quality control standards (10 µg/l and 80 µg/l), prepared internally from different reagent stock.

Further details of the methods employed can be provided on request.