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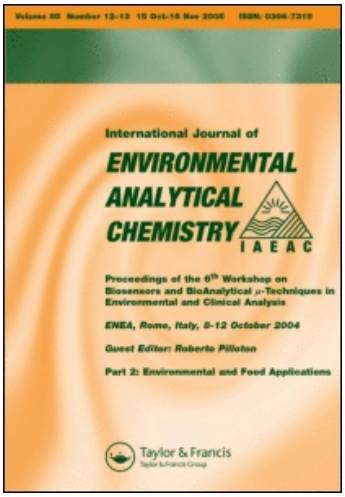

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Biomonitoring of alkylphenols exposure for textile and housekeeping workers

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4-Nonylphenols (NP), 4-*tert*-ocytylphenols (OP), and 2,4-di-*tert*-butylphenols (BP) are ubiquitous in daily foodstuffs. These alkylphenols are widely used in industry, and NP and OP are endocrine disruptors. This study involved biomonitoring of the alkylphenols in plasma and urine from textile and housekeeping workers. The objective was to measure the internal level of alkylphenols and clarify the occupational exposure of alkylphenols for these two working groups. Forty textile workers and 33 housekeeping workers were recruited in this study. Urine and plasma samples were enzymatic deconjugation, followed by cleanup with solid-phase extraction. After extraction, the samples were analysed with reverse-phase high-performance liquid chromatography coupled with fluorescence detection. The method was validated with the recovery and reproducibility test. The measurement results demonstrated apparent occupational exposure, since the urinary alkylphenols were significantly higher in the end-of-shift samples, 42.06 ± 46.63 ng/mL, than in the preshift samples, 23.50 ± 17.34 ng/mL, for the textile exposed workers. Meanwhile, the three kinds of alkylphenols were commonly detected in the biological samples. The plasma concentrations were higher than the urine concentrations. The average plasma concentrations of NP, OP, and BP were 53.21 ± 49.74, 16.02 ± 2.81, and 25.83 ± 7.10 ng/g for the housekeeping workers and 6.25 ± 4.83, 6.52 ± 8.67, and 6.47 ± 13.34 ng/mL in urine, respectively. The results of this study suggest that multiple exposure routes, including dietary intake, inhalation, and skin absorption, might contribute to the internal alkylphenol dose. The potential adverse effects caused by exposure of occupational workers is concerned.

Keywords: Biomonitoring; Nonylphenols; Endocrine disruptor

1. Introduction

Alkylphenol polyethoxylates (APEOs), which were introduced in the 1940s, are the second largest group of commercially produced nonionic surfactants. Annual global production of APEOs is approximately 650 000 tons [1]. APEOs are widely used, not only in detergents, but also in paints, herbicides, pesticides, and numerous other formulated products. APEOs with eight to 12 ethoxylate groups are commonly

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used, and nonylphenol polyethoxylates (NPEOs) represent about 80% of APEOs, while octylphenol polyethoxylates (OPEOs) make up most of the remaining 20% [2]. The use of NPEOs has been banned or restricted in many European countries because of growing concern about their toxicity to aquatic organisms of the degradation products, such as nonylphenols and octylphenols. Soto *et al.* [3] found that nonylphenol elicited both cell proliferation and receptor induction in human oestrogen-sensitive MCF7 breast tumour cells [3]. Moreover, White *et al.* [2] also showed that some alkylphenols are oestrogenic in fish, birds, and mammals [2]. These environmental oestrogenic chemicals may cause precocious sexual development [4]; recently, these chemicals have been hypothesized to account for the growing frequency of infertility and related disorders of the male reproductive system in humans [5].

Ding *et al.* [7] reported that NPE-type residues in Taiwanese rivers and sediments were higher than in other countries, owing to the deficient municipal wastewater treatment in Taiwan [6–9]. The authors also found 0.2–21% levels of NPEOs in 41% of 90 household detergents [10]. NPnEOs are used extensively in emulsifying, dispersing, wetting, and foaming agents in various industries in Taiwan. Lu found nonylphenols and 2,4-di-*tert*-butylphenol (BP) to be ubiquitous in foodstuffs [11]. BP is added as an antioxidant in plastic manufacture. Accordingly, Taiwanese people might be exposed to significant levels of alkylphenols. Moreover, industrial workers using APEOs may be exposed to even higher levels of alkylphenols because of additional occupational exposure. NPEOs serve as nonionic surfactants in the textile-manufacture process. They can be scouring agents and also dyeing auxiliaries. Meanwhile, the aforementioned high detection rate of NPEOs in household detergents may result in the high exposure level of housekeeping workers who are frequently using detergents in professional cleaning work. Bisphenol A (BPA) was sometimes measured in reports dealing with xeno-oestrogens [12–14]. BPA is the monomer of polycarbonate and epoxy resin and is used as an antioxidant or stabilizer in polyvinyl chloride [13]. It was reported endogenously through a metabolic transformation in the body of workers occupationally exposed to bisphenol A diglycidyl ether (BADGE). Hanaoka *et al.* [12] found that the concentrations of urinary BPA were higher in workers using epoxy resin and who sprayed BADGE [12]. According to the authors, BPA may disrupt secretion of gonadotrophic hormones in men. The present study measured three alkylphenols, including NP, OP, and BP, because of concerns about health effects as well as the ubiquity in the environment of Taiwan.

Muller *et al.* [15] studied the pharmacokinetic behaviour of NP in humans [15]. They found that parent and conjugated NP can be measured in both urine and blood samples by using gas chromatography/mass spectrometry. Inoue *et al.* [16] employed a high-performance liquid chromatograph with a multi-electrode electrochemical coulometric-array detector to measure NP and OP in human plasma [16]. Tsuda *et al.* [18] measured NP and other alkylphenols in fish and shellfish by high-performance liquid chromatograph with a fluorescence detector [14]. Despite growing concern about the oestrogenic effects of some alkylphenols, reports relating to internal levels in humans are rare. This study aimed to determine the internal dose of two occupational groups, textile and housekeeping industry workers. Urine and plasma specimens were collected and analysed. From the observations of workers, inferences can be made regarding the possibility of occupational exposure, and internal levels in workers can be clarified.

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2. Experimental

2.1. *Study subjects*

This study involved 40 textile workers (24 male and 16 female) and 33 housekeeping workers (16 male and 17 female). All participants gave their written informed consent. A self-administered questionnaire was used to record subject data, including sex, age, job classification, occupational history, and diet. The textile company produces dyed fabric. NPEOs are important textile agents and serve as nonionic surfactants for washing fabrics during the dyeing procedure. Twenty-seven workers were classified as the exposed group, being directly engaged in fabric dyeing, while eight office workers served as the control group. The remaining five workers were unable to be classified. The two groups were working in the same building except that the control group comprised clerks and did not come into direct contact with surfactant. The housekeeping workers performed professional building cleaning. These workers generally used various household detergents and performed floor, wall, window, and facility cleaning or washing. These workers used various detergents, such as heavy-duty bathroom cleaners, window and floor cleaners, and so on. All of these workers claimed to wear protective gloves always while working and to wash their hands before eating.

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2.2. *Sampling strategies*

All textile workers provided preshift and end-of-shift urine samples, and the preshift urine and blood samples for housekeeping workers were collected simultaneously. End-of-shift urine samples for housekeeping workers could not be collected. The preshift samples were collected after 2 h of work, while the end-of-shift samples were collected after 7–8 h of work. All urine samples were collected in glass containers, chill-transported to the laboratory, then stored at $-20^{\circ}C$ until analysis. Blood was obtained by venous puncture using glass tubes containing EDTA as the anticoagulant and immediately chill-transported to the laboratory. Plasma was fractionated by centrifugation at 1800 rpm for 15 min and kept frozen until analysis.

2.3. *Alkylphenol measurements*

2.3.1. Reagents. Acetic acid, acetonitrile, ammonium acetate, ammonium solution, hydrochloric acid, methanol, 2,4-di-*tert*-butylphenol (BP, purity, 98%), β-glucuronidase/arylsulfatase (5.2 U/mL/2.1 U/mL) were all purchased from Merck (Darmstadt, Germany) and were of analytical grade. Meanwhile, 4-nonylphenol (*p*-isomers, >85%) and 4-*tert*-octylphenol (>90%) were purchased from Fluka (USA).

2.3.2. Standard solutions. Stock solutions (10 000 mg/L) of NP, OP, and BP were prepared separately in methanol. A mixture of stock standard solution (1000 mg/L) was obtained by diluting the above-mentioned three solutions with methanol. Working standard solutions were then prepared daily by diluting the stock mixture solution to appropriate concentrations.

2.4. *Instrumentation*

A Millipore water purification device (Millipore, Bedford, MA) was used to supply ultrapure water. All water was prepared freshly before use and gathered in a glass

container. A Hitachi (Tokyo) LC system was used for the analysis. This system comprised a model L-6200 intelligent pump, a model L-7200 auto-sampler, a model F-4010 fluorescence detector, a model L-6100 interface for linking the detector, and model D-6000 data management software. The software was run on a Copam computer (Taiwan) for online recording of the output.

2.5. *Sample pretreatment*

2.5.1. Plasma samples. Plasma samples were homogenized using a model XL 2020 sonicator (USA) for 10 min. One gram (Precisa, 40SM-200A, Switzerland) of homogenized plasma was placed in a beaker and diluted with 5 mL of pure water. The pH values of the diluted samples were then adjusted to 5.5 (Hanna model 8520, Italy) with acetic acid, and then 1 mL of 1 M ammonium acetate solution (pH 5.3) and 125 μL β-glucuronidase/arylsulfatase were added. The mixture was incubated for 15 h at 37°C in a shaker bath (Kodman, USA) and then acidified to pH 3 using hydrochloric acid.

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2.5.2. Urine samples. Ten millilitres of urine sample was pretreated using identical procedures to those used for plasma, except that sonication was not carried out.

2.6. *Sample cleanup*

Following enzymatic deconjugation, samples were cleaned up with Varian PH solid-phase extraction (SPE) cartridges. SPE cartridges were inserted with 2 cm of silanized glasswool and washed with 20 mL of methanol. After conditioning the cartridges with 3 mL of pure water adjusted to pH 3.0 using 1.0 M HCl, the deconjugated samples were passed through. The sample application was followed by washing with 5 mL of pure water, and then the adsorbed compounds on the cartridge were eluted with 3 mL of methanol. The condition and elution were processed under the vacuum manifold. To extend the HPLC lifespan, all samples were filtered through a 5-μm PTFE membrane filter (Titin, USA).

2.7. *Analytical conditions*

The reverse-phase column was a Luna C18-A (150 × 4.6 mm i.d., 5-μm particle size, (Phenomenex, USA) column. The isocratic mobile phase was a mixture of acetonitrile : water (75 : 25, v/v), and the flow rate was 1.0 mL/min. The fluorescent detector was operated with an excitation wavelength of 275 nm and an emission wavelength of 300 nm. The samples were injected in quantities of 50 μL.

2.8. *Recovery, reproducibility, and detection limits*

The recovery of the analytes for urine and plasma samples was determined by the spike method. Samples containing undetectable analytes were homogeneously mixed and separated into two portions. These two portions were treated with identical procedures, except for the addition of a known amount of NP, OP, and BP to one portion. Following deconjugation, cleanup and chromatographic measurement, the recovery was calculated by comparing the concentrations obtained and the added known

amount of the analyte. The added amounts of analytes in the spiking experiments were 80, 160, 320, 800, and 1600 ng.

Reproducibility was determined by sample measurements at the five spiked concentrations for duplicate tests. The between-day precision was evaluated by assessing the duplicate tests on six separate occasions. The coefficient of variation (CV) for each analyte was calculated based on the standard deviation of the arithmetic mean of the CV at each concentration. The detection limit of the analytical method, DL, was determined by spiking the lowest concentrations, C, detectable after sample pretreatment and cleanup. The determination was repeated five times. The threefold standard deviation of response, $3SD$, and the mean values for the response, $\overline{X}$, were calculated [17]. The detection limit was obtained by

$$\mathrm{DL} = C \times \overline{X}/3SD.$$

3. Results

3.1. *Analytical methods*

Table 1 lists the detection characteristics of NP, OP, and BP, and figure 1 shows the respective chromatogram for the NP, OP, and BP in the standard solution, real plasma, and urine sample. The detection limits for NP, OP, and BP in plasma were 0.36, 0.48, and 1.05 ng/g and 1.60, 1.16 and 1.28 ng/mL for the urine samples, respectively. The recoveries of NP, OP, and BP for the plasma samples were 114.66 ± 7.84, 107.99 ± 8.31, and $108.73 \pm 6.04\%$ and 83.64 ± 7.50, 84.14 ± 7.29 and $76.43 \pm 6.35\%$ for the urine samples, respectively. The coefficients of variation were all below 10%. Table 2 lists the details.

3.2. *Application to human samples*

3.2.1. Blood samples. NP, OP, and BP were detected in all plasma samples for the housekeeping workers. The NP concentrations ranged from 12.06 to 284.74, with the highest average concentration of 53.21 ± 49.74 ng/g occurring for NP, followed by BP and OP (table 3); OP ranged from 12.68 to 23.85 ng/g and from 12.90 to 49.11 ng/g for BP.

No significant differences existed between alkylphenols levels and subject characteristics, including gender, age, job classification, occupational history, and dietary pattern for the housekeeping workers.

Table 1. Detection characteristics of NP, OP, and BP.

Compound	Retention time (min)	$\mathrm{RSD_{RT}}$ (%)[a]	Detection limit in plasma (ng/g)	Detection limit in urine (ng/mL)	Linear range (μg/L)	r
NP	9.22 ± 0.03[b] (9.17–9.29)[c]	0.01	0.36	1.60	5 ~ 385	0.9995
OP	6.43 ± 0.02 (6.39–6.47)	0.02	0.48	1.16	5 ~ 385	0.9998
BP	7.37 ± 0.02 (7.33–7.43)	0.08	1.05	1.28	5 ~ 385	0.9999

[a]The relative standard deviation within a series of replicate analyses ($n = 6$) of retention time; [b]Mean $\pm$ SD. [c]Min–max.

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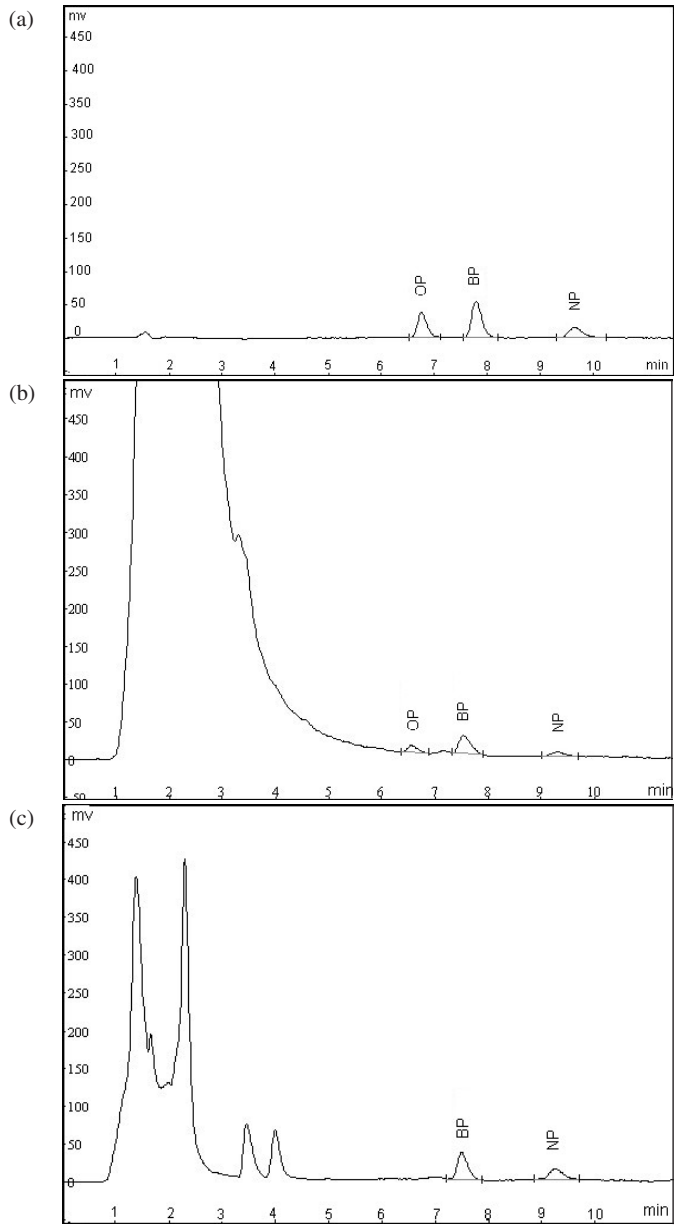

Figure 1. Typical chromatograms of (a) NP, OP, and BP standard solution ($100\,ng\,mL^{-1}$), (b) urine, and (c) plasma sample.

3.3. *Urine samples*

3.3.1. Housekeeping workers. The urinary NP, OP, and BP concentrations ranged from n.d. (not determined) to 36.67, n.d. to 71.52 and n.d. to 24.61 ng/mL, respectively, for the housekeeping workers. One, five, and one sample contained NP, OP, and BP below the detection limit. The average NP, OP, and BP concentrations were

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Table 2. Percentage recovery and precision of alkylphenols in human biological samples (%).

Compound	Plasma			Urine		
	Recovery	Coefficient of variation		Recovery	Coefficient of variation	
		Within-day[a]	Between-day[b]		Within-day	Between-day
NP	114.66 ± 7.84[c]	5.36 ± 0.01	6.86 ± 2.85	83.64 ± 7.50	4.42 ± 1.85	7.04 ± 2.15
OP	107.99 ± 8.31	4.36 ± 0.01	7.76 ± 2.02	84.14 ± 7.29	5.12 ± 2.33	7.76 ± 1.68
BP	108.73 ± 6.04	3.94 ± 0.04	7.62 ± 0.05	76.43 ± 6.35	3.59 ± 1.15	7.51 ± 2.02

[a]$N = 6$; [b]$N = 30$; [c]Mean ± *SD*.

6.25 ± 4.83, 6.52 ± 8.67, and 6.47 ± 13.34 ng/mL. The urinary NP, OP, and BP levels were lower than those of the plasma samples (table 3). No subject characteristics correlated significantly with the urinary levels of the three compounds.

3.3.2. Textile workers. The preshift urinary NP, OP, and BP for the 40 textile workers ranged from n.d. to 71.93, n.d. to 7.02, n.d. to 35.72 ng/mL, respectively. The detection rates were 90, 50 and 97.5%, respectively. The average NP, OP, and BP concentrations were 21.18 ± 17.88, 1.41 ± 1.73, and 10.41 ± 5.29 ng/mL. The end-of-shift urinary NP levels (37.97 ± 45.93 ng/mL) were significantly higher than the preshift levels. Slightly raised end-of-shift levels also appeared for OP and BP, but there was no statistically significant difference.

This study further classified the textile workers based on their self-reporting job title. Twenty-seven workers (exposed group) were found to have significantly higher NP levels than the eight workers (control group), namely 42.06 ± 46.63 *vs.* 24.16 ± 26.22 ng/mL for their end-of-shift urine samples (table 3). However, the two groups did not differ significantly for the preshift samples. Meanwhile, the NP levels for the end-of-shift samples from the exposed group were significantly higher than those of the preshift group (42.06 ± 46.63 *vs.* 23.50 ± 17.34); no significant difference was observed between the end-of-shift and preshift NP levels for the control group (table 3). Other comparisons by gender, years of employment, and use of protective equipment did not differ significantly in urinary NP levels. Figure 2 illustrates the distribution of the urinary NP, OP, and BP concentrations, which were grouped as textile (preshift), textile (end-of-shift), and housekeeping.

3.4. *Subject description*

Regarding dietary pattern, 20 housekeeping workers did not have preferable dietary habits, and 11 preferred a meat diet; one was a vegetarian, and one liked to eat seafood. The subject ages were distributed from 21 to 59 years, with an average of 41.9 years. The subjects had a relatively short duration of working in their current jobs, and the average number of working years was 2.80 ± 3.54. The subjects all came into contact with detergent, but generally used protective gloves according to the report.

The current-job duration was much longer for the textile workers, with an average of 15 years. The ages of this group of subjects ranged from 21 to 67 years, with an average of 41.2 ± 5.9 years. Most of the exposed group also used protective gloves and masks.

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Table 3. Internal alkylphenols levels for the housekeeping and textile workers.

			NP		OP		BP	
		n	Preshift	End-of-shift	Preshift	End-of-shift	Preshift	End-of-shift
Housekeeping	Urine[a]	29	6.25 ± 4.83	–	6.52 ± 8.67	–	6.47 ± 13.34	–
	Plasma[b]	33	53.21 ± 49.74	–	16.02 ± 2.81	–	25.83 ± 7.10	–
Textile	Exposed group	27	23.50 ± 17.34	42.06 ± 46.63*	2.70 ± 1.70	3.40 ± 13.50	10.41 ± 4.84	13.86 ± 15.42
(Urine only)	Control group	8	17.21 ± 15.22	24.16 ± 26.22	2.09 ± 2.50	3.74 ± 5.07	3.63 ± 9.10	14.21 ± 8.52*

[a]Unit for urine: ng/mL; [b]Unit for plasma: ng/g; *$p < 0.05$; the differences between 42.06 ± 46.63 and 23.50 ± 17.43; 42.06 ± 46.63 and 24.16 ± 26.22; 14.21 ± 8.52 and 3.63 ± 9.10.

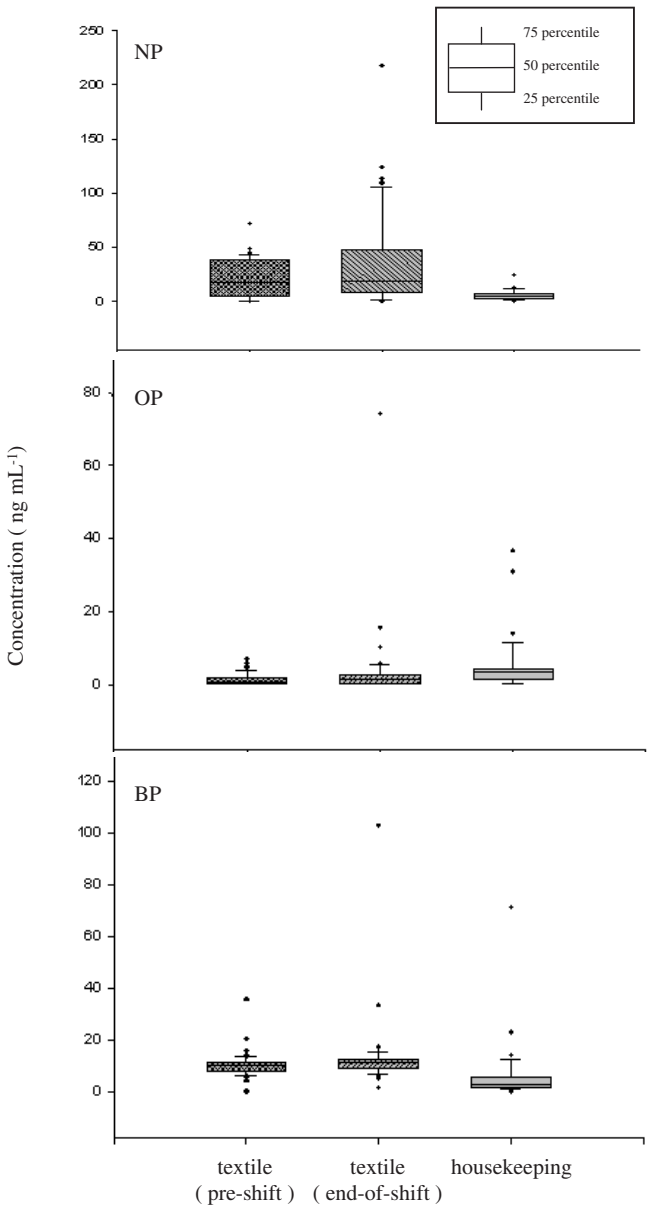

Figure 2. Concentrations of urinary NP, OP, and BP for textile and housekeeping workers.

4. Discussion

Gas chromatography and high-performance liquid chromatography coupled with various detectors have been used to determine alkylphenols in biological samples, including gas chromatography–mass spectrometry (GC–MS) [18–21], liquid chromatography–mass spectrometry (LC–MS) with online preparation [22], high-performance liquid chromatography with multi-electrode electrochemical coulometric-array

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detector [16], and capillary electrophoresis [19,23]. However, alkylphenol exposure in humans has not been studied, except for a few studies conducted by Inoue *et al.* [16] exploring the internal dose of NP and OP in limited subjects [16,21,22]. Kawaguchi *et al.* [21] found humans to have a very low level of free NP and OP [21]. In estimating daily alkylphenol intake, Müller *et al.* reported that the oral intake of NP by nonoccupationally exposed humans was below 0.16 mg per day [24]. Inoue *et al.* [16] stated that NP did not pose an oestrogenic health risk to individuals with non-occupational exposure [25]. To our knowledge, no previous studies have examined the occupational exposure of alkylphenols. The detection levels of NP, OP, and BP in plasma and urine samples in this study are of a higher concentration than those of previously reported studies [21,22,26]. This indicates a significant exposure via the occupational environment. The exposed group of textile workers might be exposed to surfactants by inhalation, ingestion, and contact with skin during work, while the control group of the same company was exposed to a less degree via inhalation of airborne particles, since the latter would have working in the same building with the control group. NP in water had been reported to escape into the air [27]. The background contamination may raise the measured concentrations, but it has been thoroughly investigated during the development of analytical methods in this study. We found that a significant contamination of NP came from the use of plastic vessels during sampling, transportation, storage, and pretreatment processes. In this study, the background levels were reduced to a level as low as possible by (1) excluding the plastic materials throughout the sample handling processes and (2) conducting background correction for each batch of measurement. A blank sample (pure water) was treated identically with the real samples in the whole processes.

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This study adopted the sample cleanup procedure of Inoue [16] as well as the enzymatic deconjugation of Müller [15], with some modifications. The modifications include: (1) inserting silanized glass wool into the solid-phase extraction cartridges to avoid clogging the sample in the cartridges and thus improving recovery; (2) before sample application, washing the cartridge with 20 mL of methanol to remove trace NP contamination; (3) sonicating the plasma sample before enzymatic deconjugation to homogenize the matrix and improve recovery precision. The detection limits of this modified method were comparable with those of the method of Inoue *et al.* [16]. However, the recoveries and relative standard deviation of this method were better than those of the method of Inoue *et al.* [16]. Meanwhile, the NP, OP, and BP were fully separated and detected with a high sensitivity using the Luna C18 column and spectrofluorimetric detection at 275/300 nm.

Alkylphenols were reported as contaminants not only in food, but also in air samples [28]. We were concerned with occupationally exposed workers encountering multiple routes of contamination, especially in Taiwan, for several reasons: (1) household detergents are reported to contain a wide range of NPEOs, which are widely used in industries [10]; (2) plastic products are intensively used in Taiwan, and NP and BP are added to improve the properties of such products [13]; and (3) alkylphenols are detected in daily foodstuffs. This study employed HPLC with fluorescence detection for measurement. The fluorescence detector has a higher sensitivity than the UV detector for measuring trace amounts of alkylphenols in human biological samples.

Inoue *et al.* [16] reported no detectable OP and NP before deglucuronidation for 10 healthy volunteers [22]. Following deglucuronidation, trace amounts of urinary NP were detected in only one subject. No urinary OP was detected, even after

deglucuronidation. However, urinary NP was found to be up to 110 ng/mL and 16 ng/mL following intake of NP in meals estimated above 35 μg and below 35 μg, respectively [22]. The present study found a high detection rate of NP, OP, and BP for the two occupational groups. The detection rate of NP exceeded that of OP, and was even higher for BP. The significant increase in postwork NP levels for the exposed group of textile workers, but not for the control group, indicated occupational exposure. Meanwhile, the exposure was more intensive for the textile workers than for the housekeeping workers, because the NP levels of the former significantly exceeded those of the latter.

In the pharmacokinetic study carried out by Müller *et al.* [15,24] on NP in humans, the half-life of NP in blood and the bioavailability (determined from oral and intravenous AUCs) were found to be 2–3 h and 20%, respectively [15]. The authors also demonstrated that only 10% of the applied dose is excreted in urine. Therefore, the urinary NP was much lower than that in blood. The present study revealed that the NP, OP, and BP concentrations in plasma were higher than those in urine. This agrees with Müller's report [15]. The latter analysed blood concentrations of parent NP and NP resulting from cleavage of the glucuronide and sulphate conjugates after intravenous application to a human volunteer. This showed that the concentrations of parent NP arising from cleavage of conjugates are of the same order of magnitude as parent NP, and the amount of NP present in the form of conjugates after oral administration was much higher (two orders of magnitude) than that seen after intravenous administration. Inoue also found a significant increase in urinary NP in exposed volunteers after deglucuronidation of urine sample [22]. Thibaut *et al.* [29,30] found conjugated NP in urine and bile of rainbow trout, and confirmed the structure of NP-glucuronide by electrospray ionization/mass spectrometry [29,30]. The present study thus analysed both parent and conjugated forms of alkylphenols. The increase in NP after work confirmed its short half-life. The higher NP levels of preshift urine for the exposed textile workers compared with the control group might result from the dietary intake of breakfast and occupational exposure before urine collection. Although we requested workers to collect preshift urine, some collections had not been completed until 1–2 h of work. This study suggests first morning void be collected to reflect the baseline levels before work. The occupational exposure route may include ingestion, skin absorption, and inhalation.

Dietary intake may be vital in daily alkylphenol exposure. Urinary NP levels are changed after eating, and control of foods and drinks in the subjects studied is needed. However, it was very difficult to get employers and workers to cooperate, and so in this study, a uniform diet was not provided during the sampling period. Besides contamination of basic foods themselves, levels of alkylphenols in meals may be further increased through food processing, including detergent residues in food vessels and plastic food-wrapping materials [31]. The internal dose background level for Taiwanese people should be considered owing to the intensive use of plastic and lack of regulations regarding the content of household detergent.

BP and OP were also detected in several foodstuffs. Lu analysed NP, OP, BP, NP1EO, and NP2EO in 20 foods, and found that NP had the highest detection rate and concentrations, followed by BP, OP, NP2EO, and NP1EO [11]. The ubiquity of NP and BP in daily food was surprising. This ubiquity may result in the high detection rate of NP and BP in the biological samples. The reason for the elevated end-of-shift

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urinary BP needs to be clarified. However, the authors cannot exclude contributions from lunchtime meals.

A comparison of alkylphenol levels in plasma and urine samples from housekeeping workers reveals much higher levels in the former than in the latter. Thus, the textile workers may have even higher levels of NP in plasma. The relatively higher plasma NP compared with OP and BP, while comparable for the three in the preshift urine samples for the housekeeping workers, implies exposure from breakfast intake as well as the workplace. NP1EO and NP2EO were also analysed for certain samples. Neither plasma nor urine contained NP1EO and NP2EO (data not shown). Urinary and plasma NP might originate from the metabolism of NPEOs or free-form NP. The latter are putative residues of the reaction of alkyphenol and ethoxylates.

Urinary creatinine was measured to ascertain the comparability of urine concentrations between pre- and end-of-shift samples. In order to exclude any bias from creatinine measurement, alkyphenol concentrations are reported in nanograms per liter of urine in this study.

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5. Conclusions

This study confirms the occupational NP exposure for the textile workers. Both textile and housekeeping workers are intensive users of detergents containing NPEOs. However, urinary NP levels of the former are much higher than for the latter, owing to differences in how the detergent is manipulated. The frequent detection of NP, OP, and BP in biological samples suggests significant dietary intakes, which accords with the findings of ubiquitous alkylphenols in foodstuffs by Lu [11].

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