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Exposure Assessment to Trichloroethylene and Perchloroethylene for Workers in the Dry Cleaning Industry

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Abstract Perchloroethylene and trichloroethylene are two particular organochloro compounds, are often used for dry-cleaning. In the present study the excretion of urinary Perchloroethylene and trichloroethylene were evaluated as biomarkers of exposure to these compounds. The mean value of Perchloroethylene in breathing zone and the total Perchloroethylene uptake during the work shift of the three groups of dry-cleaning workers according to the capacity of the dry-cleaning machine (8, 12 and 18 kg) were 31.04, 50.87 and 120.99 mg m^{-3} and 11.46, 22.6 and 41.6 μg L^{-1}, respectively, which were significantly greater than the occupationally nonexposed groups. A good correlation ($r = 0.907$) between the mean values of Perchloroethylene in breathing zone and the urinary concentrations was observed.

Keywords Trichloroethylene · Perchloroethylene · Exposure · Urinary levels

Two particular organochloro compounds, perchloroethylene (PCE) and trichloroethylene (TCE) are often used for dry-cleaning and degreasing. Clothes that have been subjected to commercial dry-cleaning with PCE and TCE were shown to be a source of indoor air pollution from the solvents (NIOSH 1997). The main route for human exposure to PCE and TCE is via inhalation, but the compound is also adsorbed by mouth and skin contact (Aggazzotti et al. 1994). Symptoms that have been reported in persons repeatedly exposed to PCE and TCE vapors are slight-irritation of the mucosa, gastro-intestinal disturbances, alterations of some liver and kidney function parameters or central nervous system malfunctions (Bosco et al. 1987). The workers in dry-cleaning shops, which can be considered to be 'special indoor places', as well as their neighbors are exposed to high concentrations of PCE and TCE (Tovalin-Ahumada and Whitehead 2007). For the assessment of occupational exposure to PCE and TCE the determination of the chlorinated compounds and their metabolites per *se* in blood and in urine was proposed (Poli et al. 2005). PCE and TCE can be eliminated unchanged in exhaled air and urine, a large part can be eliminated as metabolites in urine (Raaschou-Nielsen et al. 2001). PCE and TCE are metabolized by a mixed-function oxidase system to the short-lived epoxide, which facilitates the migration of chloral hydrate, latter is rapidly oxidized to trichloroacetic acid (TCA) or reduced to trichloroethanol (TCOH), which is conjugated to glucuronide or oxidized to TCA (Ertle et al. 1972). TCA in urine is regarded as the best indicator of integrated exposure over the workweek (Csanády et al. 2010). Acute and chronic toxicity of PCE and TCE were the object of several investigations, so we can obtain a good estimation of two kind of exposure by simultaneous measurement of PCE, TCE and TCA in urine. We performed a study on relationship between urine PCE and TCE concentrations (C urine) and air PCE and TCE concentrations (C env) collected at breathing zone of workers in workplace.

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Materials and Methods

Forty healthy men from the city of Tehran, Iran, were enrolled in the study. The study population consisted of 30 Dry-cleaning workers in three groups according the capacity of the dry-cleaning machine (8, 12 and 18 kg) and for the measurement of any background levels originating from other sources such as water and ambient air urine samples were collected from 10 occupationally nonexposed persons in the same districts acted as referents. All of the subjects were men between 27 and 57 (mean 41) years of age and none of them were smokers. Since there may be a significant risk of dermal exposure, so it was requested from dry-cleaning workers to wear plastic gloves during the work shift. Radiello passive samplers (Fondazione S. Maugeri, Padova, Italy) were used for measuring personal exposure to PCE and TCE (Barbieri et al. 2008). After exposure, the chemical substances collected on sorbing cartridges were desorbed into the storing glass tube for about 30 min with 2 mL of carbon disulfide (CS2) low in benzene content and 50 μL of internal standard solution (1 μgL^{-1} CS2 of 1, 2 di-bromopropane). The instrument used for GC–MS analysis was an Agilent (Agilent Technologies, Palo Alto, CA, USA) 6890 plus gas chromatograph equipped with a 5973 mass selective detector quadrupole mass spectrometer. The gas chromatograph was fitted with an HP-5MS column (30 m, 0.25 mm i.d., 0.25 mm film thickness). The instrumental temperatures were as follows: injector temperature, 250°C; initial oven temperature, 45°C (held for 5 min), increased to 90°C at a rate of 5°C min^{-1}, held for 2 min. The inlet was operated in splitless mode. The acquisition mode was SIM. Air concentration (expressed in μg m^{-3}) was calculated using the equation:

$$\text{Conc.}\left(\mu g/m^3\right) = \frac{m(\mu g) \times 10^3}{Q(L/min) \times t(min)}$$

where m = mass of analytes determined in desorbing solvent; Q = uptake rate of substances (59 mL min^{-1} for PCE; 69 mL min^{-1} for TCE); t = exposure time (Radiello Technical Documents (d1 d6) 2010). The study was carried out in May, 2009. Urine samples were collected at the beginning and at the end of the shift. In order to avoid loss of analytes during collection and storage, urine samples (10 ml) were immediately transferred in 20 ml SPME glass vials containing 1 g of NaCl. The samples were shaken and stored at −20°C until analysis.

PCE, TCE and TCA were analyzed using head-space gas chromatography and equipped with single quadrupole mass detection (GC–MS). The sampling procedure involved placing 10 mL of sample into a 20 mL vial containing 1 g NaCl and sealing with a screw-top septum containing cap. The sample was then spiked with a 50 μL of methanol containing 1 μgL^{-1} of 1, 2 di-bromopropane as internal standard. Then, 100 μL of a 0.5 M concentration of the ionpairing agent (TBA–HSO_4), 120 μL of derivatisation reagent (DMS, 1.3 mmol, i.e., high excess) were injected through the septum. The vial was stirred in a Vortex mixer for 3 min, and then placed in a water bath maintained at 60 ± 0.1°C for 15 min to establish phase equilibrium. The vial and SPME holder were clamped into a stand that allowed the vial to be immersed in the water bath only up to the level of the liquid in the vial. The SPME needle was then inserted through the septum into the headspace so as to locate the tip of the exposed fiber approximately 0.5 cm from the top of the liquid; the fiber was allowed to equilibrate for 35 min. The fiber was then retracted, removed from the vial, and placed immediately into the injector of the GC system. The SPME holder was adjusted so that the exposed fiber tip was positioned about halfway (1.5 in.; 1 in. = 2.54 cm) into the GC injector port liner when extended from the protective needle. Injection was accomplished by extending the fiber in the heated inlet for 4.5 min, and the splitter was opened after 3 min. The additional 1.5 min of exposure time in the injector port allowed the fiber to be cleaned of any compounds that were not desorbed in the initial 3 min. Blank samples containing internal standards were analyzed at the beginning and at the end of the sample queue. Triplicates of each sample were extracted by the SPME technique (Rastkari et al. 2011). The instrument used for GC–MS analysis was an Agilent (Agilent Technologies, Palo Alto, CA, USA) 6890 plus gas chromatograph equipped with a 5973 mass selective detector quadrupole mass spectrometer. The gas chromatograph was fitted with an HP-5MS column (30 m, 0.25 mm i.d., 0.25 mm film thickness). The instrumental temperatures were as follows: injector temperature, 250°C; initial oven temperature, 45°C (held for 5 min), increased to 90°C at a rate of 5°C min^{-1}, held for 2 min, then increased to the final temperature 250°C at a rate of 30°C min^{-1}, where it was held for 1 min. The inlet was operated in splitless mode. The temperature of the transfer line was maintained at 290°C. Helium (99.99%) was used as carrier gas at 1 mL min^{-1} (constant flow). The source and quadrupole temperatures were kept at 230 and 150°C, respectively. The electronic beam energy of the mass spectrometer was set at 70 eV. The mass selective detector was operated in electron impact (EI) mode using selected ion monitoring (SIM). The dwell time of each ion was set at 100 ms. The GC conditions were selected to minimize the time of analysis while allowing all the analytes to elute in acquisition groups containing suitable number of ions for monitoring (Table 1). The LOQ values for all compounds were 20 ngL^{-1}. Mean urinary concentrations of PCE, TCE and TCA among four groups (three groups of dry-cleaning workers according the capacity of the dry-

Table 1 Selected ions used for the detection of target analytes by GC–MS in SIM mode

Ion group	Analyte	Time window (min)	Selected ion
1	TCE	2–3	97,130
2	PCE	3.5–4.5	131,166
3	1,2-dibromopropane	7.5–8.5	42,121
4	TCA	11.0–12.0	117,119

cleaning machine (8, 12 and 18 kg) and occupationally nonexposed persons) were analyzed and because the distribution of data might not be normal; the analysis was carried out by means of two statistical procedures: analysis of variance (one way ANOVA) and Kruskal–Wallis test. Results were expressed as mean ± S.D and 95% confidence intervals. The level of significance was set to 0.05 and p values >0.05 were assumed to be nonsignificant.

Results and Discussion

Table 2 shows the results of environmental measurements (mg m^{-3}) in the three groups of dry-cleaning workers and occupationally nonexposed persons during a day work shift. The mean value for exposure to PCE in breathing zone of the three groups of dry-cleaning workers according to the capacity of the dry-cleaning machine (8, 12 and 18 kg) were 31.04, 50.87 and 120.99 mg m^{-3}, respectively, which were significantly greater than the occupationally nonexposed groups but below the 1999 ACGIH TLV(TWA) (170 mg m^{-3}) (ACGIH 1999). Although nonparametric statistical tests show significant differences between the mean value of TCE concentration in breathing zone of dry-cleaning workers and occupationally non exposed persons, the results of parametric test (ANOVA) were not statistically significant. This phenomenon may be due to the huge variation of data within each group (Mean and SD of each group are given in Table 2); although a positive trend in the TCE concentration in breathing zone by increasing the capacity was observed.

The results of the mean urinary concentration of PCE, TCE and TCA (μg L^{-1}) in the three groups of dry-cleaning workers and occupationally nonexposed persons in two different samples collected: before starting work and at the end of the shift are shown in Table 3. The mean PCE and TCE concentrations in dry-cleaning workers were significantly greater than the occupationally nonexposed group. The total PCE uptake during the work shift in the three groups of dry-cleaning workers according to the capacity of the dry-cleaning machine (8, 12 and 18 kg) were calculated to be on average 11.46, 22.6 and 41.6 μg L^{-1}, respectively. The concentration of PCE increased during the day for all three groups of dry-cleaning workers. The increase is more marked among workers who work with dry-cleaning machine with 18 kg capacity. As can be seen in Table 2, excretion of TCA in dry-cleaning workers were significantly higher than occupationally non exposed group ($p < 0.001$) and its urinary concentration was approximately constant during one work shift. In order to search the relationship between PCE in the air of workplace (C_{env}) and that in urine (C_{urine}), a regression analysis was performed. The result is shown in Fig. 1. Two groups of data were regressed well, $C_{urine} = 3.0794 + 0.5141 \times C_{env}$; $r = 0.907$; $p < 0.0001$.

TCE and PCE have been widely used in many industries since the Second World War, mainly because of their degreasing properties and non-flammable character. The toxic effects of TCE and PCE on the human nervous system have been known for some time. Exposure to TCE and PCE has induced cancer in the liver, kidney and other organs in experimental animals (Raaschou-Nielsen et al. 2001). Environmental exposure to TCE is mainly via the atmosphere, while the contribution from exposure to drinking water and foodstuffs is negligible (Vedrina-Dragojev and Vedrina-Dragojevi 1997). The aim of this study was to monitor the degree of chronic and acute exposure to PCE and TCE of dry-cleaning workers through the evaluation of breathing zone and urinary concentrations. The dry cleaning workers were chosen for the study because their exposure was expected to be relatively high and there were few reports in literature about biological and environmental monitoring of PCE and TCE in urine samples from these groups. Previous studies indicated that PCE in blood is a preferred biological index for monitoring PCE exposures (Furuki et al. 2000; Lauwerys et al. 1983), but urine is a preferable biological sample to blood, as sample collection does not require an invasive blood drawing, not always well accepted by study subjects. In general the advantage of using unmetabolized compounds as biomarkers is that the urinary concentration of the unmetabolized substance is less influenced by inter individual metabolic differences than the urinary disposition of corresponding metabolites. However, due to the similar significance of unmetabolized chemicals in blood and urine as biomarkers of exposure (Fustinoni et al. 2000), and also since there is good correlation between C_{env} and C_{urine}, for the assessment of exposure to PCE and TCE, the urinary concentrations of PCE and TCE after the 1 day shift were chosen as an indicator of a day's (acute) exposure, where as the urinary concentration of PCE and TCE before the 1 day shift allows the monitoring of repeated (chronic) exposure. As the results indicated, a significant difference was observed in PCE concentrations in both pre and post-shift samples among job categories ($p < 0.05$ by ANOVA and Kruskal–Wallis test). The mean PCE concentrations in exposed workers (dry cleaning workers) were significantly

Table 2 The mean value (SD) for exposure of PCE and TCE in breathing zone

	Sample size (n)	Capacity of the dry-cleaning machine	PCE (mg m^{-3})	TCE (mg m^{-3})
Dry-cleaning workers	10	8	31.04 (13.73)	1.56 (0.68)
	10	12	50.87 (16.74)	1.75 (0.74)
	10	18	120.99 (20.28)	2.40 (0.63)
Occupationally non exposed persons	10	–	5.25 (2.26)	0.98 (0.46)
p value*	–	–	<0.001	0.062
p value**	–	–	<0.001	<0.001

* One-way ANOVA

** Kruskal–Wallis test

Table 3 Mean urinary concentration (SD) of PCE, TCE and TCA in four groups before starting work shift and at the end of work shift

	Sample size (n)	Capacity of the dry-cleaning machine	PCE (μg/L)		TCE (μg/L)		TCA (μg/L)	
			Before	After	Before	After	Before	After
Dry-cleaning workers	10	8	6.58 (2.49)	18.04 (7.28)	2.38 (1.06)	4.46 (1.39)	4.17 (1.73)	4.04 (1.70)
	10	12	14.17 (4.40)	36.77 (12.45)	5.53 (2.25)	11.31 (3.62)	10.32 (3.58)	10.41 (3.50)
	10	18	21.95 (6.85)	63.55 (13.80)	8.18 (2.42)	4.46 (1.39)	12.69 (3.46)	12.72 (3.36)
Occupationally non exposed persons	10	–	0.35 (0.15)	0.34 (0.18)	0.31 (0.14)	0.29 (0.18)	0.26 (0.16)	0.24 (0.14)
p value*	–	–	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
p value**	–	–	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001

* One-way ANOVA

** Kruskal–Wallis test

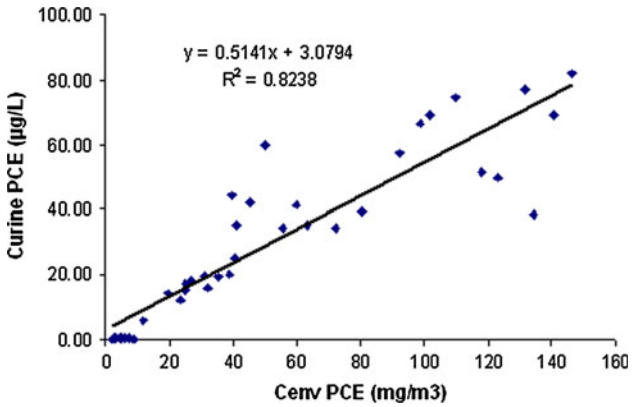

Fig. 1 *Scatter diagram* relating the time—weighted average of environmental concentration (in the breathing zone) (C_{env}) and the urinary concentration (C_{urine}) of PCE

greater than that of occupationally nonexposed group. Since PCE is the major part of the solvent which is used in dry cleaning processes in Iran, airborne PCE usually occurs at higher concentrations than TCE. In accordance, the concentrations of TCE detected in urine of the workers were clearly lower than the parallel PCE concentrations. Since there may be a significant risk of dermal exposure, so it was requested from workers to wear plastic gloves during the work shift, so no significant skin exposure occurred during the study. Airborne PCE levels of dry-cleaning shops were similar to the ones asserted in the literature (Bayaa et al. 1998). The urinary PCE levels detected in this study was more than those were obtained for Italian dry cleaning workers (Poli et al. 2005); whereas it is much lower than levels which are reported for Koreans workers (Jang et al. 1993). TCA in urine is regarded as the best indicator of integrated exposure over the workweek (Csanády et al. 2010) but, TCA in urine is not specific to PCE exposure. Trichloroethylene (TCE) and 1.1.1 trichloroethane also metabolize to TCA. In addition TCA is a byproduct of chlorinating drinking water (Legay et al. 2010); also different metabolizing capacities may play a role in the differences in urinary TCA concentrations among different persons. So it seems that in estimation of workers' exposure with biological samples, according to this study, analysis of the concentration of PCE detected before and/after the work shift seems to give the most reliable estimation of chronic and acute exposure. Analysis of the acidic metabolite TCA in urine was not reliable enough for exposure estimation. The concentrations of

TCA found in this study correspond well with those found in other studies (Raaschou-Nielsen et al. 2001). In conclusion, from the results of this pilot study it seems that indoor air in dry-cleaning shops is in an acceptable condition but it should be remembered that little is known about the effects to human health of chronic exposure to 'low' doses of PCE (or TCE) (Bayaa et al. 1998).

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