Short Communication

Exposure to Gasoline Vapour during Offloading of Tankers and Railway Wagons and Biological Multicomponent Monitoring

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The purpose of this study was to measure the exposure of oil depot workers to gasoline vapour components during the offloading of tankers and railway wagons. We also compared the concentrations of airborne benzene, toluene and oxygenates with urinary concentrations of these components or their metabolites at the end of the shift and before the next shift as a means of assessing exposure during work shift. The workers in the offloading operations were chosen for the study because their exposure was expected to be relatively high, and there was no previous literature on the biological monitoring of coincident gasoline components in urine samples from these groups.

In this study, all gasoline was unleaded, and either methyl tert-butyl ether (MTBE) alone or together with methyl tert-amyl ether (MTAE) were used as oxygenates to enhance the octane number and to ensure cleaner exhaust gases. The maximum oxygenate content varied from 12% in reformulated gasoline types to 15% in oxygenated types. In reformulated gasoline the content of aromatic hydrocarbons is also regulated to less than 30% and that of benzene to less than 1%. Several studies on road tanker drivers have described the exposure to gasoline vapour components^{1–3}), and the correlation between air and urine concentrations of gasoline components has been determined for post-shift and pre-next-shift samples of MTBE under field conditions^{2, 3}).

Materials and Methods

The study group consisted of volunteer depot workers ($n=13$) who worked at three coastal depots (eight workers) offloading tankers and two inland depots (five workers) offloading railway wagons in single-shift operations. In the single-shift system, the working time was extended over eight hours until the task of offloading the tanker was finished. Offloading in depots took place in the open

air and the level of exposure depended among other things on the wind direction and velocity. The workers did not use any protective masks. The background information on the study circumstances is shown in Table 1.

Sampling

The concentration of airborne gasoline components during the work shift was measured in personal breathing zone samples collected with passive samplers (Perkin-Elmer ATD-400 sampler tube filled with 150 mg Tenax GR adsorbent, 35/60 mesh). The urine spot samples were collected after the shift and before the next work shift. The urine samples were stored in glass vials with Teflon stoppers and transported cooled to the analytical laboratory.

Analytical and statistical methods

The concentration of airborne aliphatic and alicyclic C3–C11 hydrocarbons, MTBE, MTAE, benzene, toluene, xylenes and trimethyl benzenes were determined in a thermal desorption (Chrompak Purge and Trap Injector) and gas chromatography/ion trap system (GC/MSD Finnigan ITS40 Ultra). Biological monitoring of gasoline was done by determining the concentrations of benzene, toluene, xylenes and trimethyl benzenes, as well as MTBE, MTAE, their metabolites, tertiary butyl alcohol (TBA) and tertiary amyl alcohol (TAA) in urine. The analysis was conducted by solid microphase extraction gas chromatography, with iontrap detection (GC/MSD, Varian 3400 CX, Saturn 2000 ITD).

The results are given as geometric means (GM) with geometric standard deviations (GSD) and arithmetic means with standard deviations (SD). The statistical significance of difference between the offloading groups was derived from the single factor analysis of variance with logarithmic transformed values of the time-weighted average for 8 hours (TWA 8 h). The relationships between the TWA 8 h concentration of a specific compound in the breathing zone (mg/m^3) and the same compound or its metabolite in urine (nmol/l) were expressed by Pearson's product-moment correlation (r).

Results

Benzene, toluene, xylenes, trimethyl benzenes, MTBE and MTAE were identified and quantified from the occupational hygiene samples. The rest of the gasoline components were grouped under the title C3–C11 aliphatic and alicyclic hydrocarbons. The GM, GSD and arithmetic mean $\pm$ SD values for the total gasoline vapour concentration at TWA 8 h were $10.7 \text{ mg}/\text{m}^3$, 2.5 and $16.0 \pm 16.6 \text{ mg}/\text{m}^3$, respectively, during the offloading of tankers. At inland depots during offloading of railway wagons, the corresponding values were $3.77 \text{ mg}/\text{m}^3$, 3.8 and $4.19 \pm 1.75 \text{ mg}/\text{m}^3$. The difference between the groups in exposure levels was significant ($p<0.05$).

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Table 1. Demographic, sampling, offloading and meteorological background information on the coastal and inland depots during the study period

	Coastal depots			Inland depots		
	n	Mean	Range	n	Mean	Range
Depots	3			2		
Workers	8			5		
Age (y)		47	30–59		49	40–56
Smokers	4			2		
Duration of shift (h)		13	7.5–17		6.5	6–7.5
Amount of offloaded gasoline (m ³)		3600	2000–6000		650	500–800
Temperature (°C)		15	11–22		13	11–14
Wind (m/s)		4.4	1–7		2.5	0.3–5
Relative humidity (RH%)		85	67–95		91	77–100

Table 2. Characteristics of depot workers' exposure to different gasoline components during offloading of tankers and railway wagons as TWA 8 h (n=13; the quantitation limit of one component is 0.01 mg/m³)

Concentration	GM (mg/m ³)	GSD	Mean (mg/m ³)	SD (mg/m ³)	Range (mg/m ³)
Benzene	0.10	2.4	0.15	0.16	0.02–0.60
Toluene	0.61	2.1	0.77	0.56	0.23–2.44
Xylenes	0.68	1.8	0.81	0.56	0.22–2.70
Trimethyl benzenes	0.50	1.6	0.55	0.27	0.27–1.48
MTBE	0.69	2.7	1.10	1.29	0.15–4.96
MTAE	0.27	3.2	0.54	0.75	0.06–2.60
C3-C11 Aliph. and alicyclic HCs	3.82	3.2	7.46	10.9	0.52–40.4
Total gasoline vapour	7.45	2.5	11.4	14.2	1.50–53.5

For comparison of TWA 8 h values with biological monitoring results, both coastal and inland measurements were combined into one group. The geometric mean of the gasoline vapour concentration of the whole study group (n=13) was 7.45 mg/m³ with GSD 2.5 and the corresponding mean and SD were 11.4 ± 14.2 mg/m³ (range 1.5–53.4 mg/m³). The GM, GSD, arithmetic mean, SD, and range of TWA 8h for benzene, toluene, xylenes, trimethyl benzenes, MTBE, MTAE and aliphatic and alicyclic C3-C11 hydrocarbons are given in Table 2.

As the exposure level during offloading was rather moderate, the concentrations of gasoline components found in urine were also low (Table 3). The concentrations of trimethyl benzenes in urine were below the quantitation limit. In the case of urinary xylenes, eight out of 13 urinary post-shift samples and one pre-shift sample exceeded the quantitation limit. The concentrations of oxygenates and their metabolites, as well as those of benzene and toluene, were detectable both in urine and in the air. The correlation coefficients for airborne and the respective urinary components of gasoline are given in Table 4 for post-shift and pre-next-

shift sampling. For benzene and toluene, grouping was also done according to smoking.

Discussion

Coastal depot workers have a long work shift in tanker offloading once or twice a month. In the inland depots the offloading operation occurs once a week. Tanker drivers are exposed on every workday during onloading and offloading of gasoline. Depot workers encounter situations in which exposure is high, especially during the fixing of pipelines to tankers and wagons, opening and closing of hatches, and during the taking of specimens. The measurements were done during the offloading of tankers and railway wagons without vapour recovery systems. In this study, especially the exposure of inland depot workers to gasoline vapours was lower than expected, and less than half of the drivers' exposure measured in former studies^{2,3}. The technique for handling railway wagons has been changed recently from bottom to top offloading, which causes less leakages and spills. The present results show that the concentrations of gasoline components during the offloading of tankers and

Table 3. Concentrations of gasoline components in urine (U) of the depot workers (n=13) after the work shift (PM) and the next morning (AM)

	Smoking +/-	n	PM				AM			
			Mean nmol/l	SD nmol/l	Median nmol/l	Range nmol/l	Mean nmol/l	SD nmol/l	Median nmol/l	Range nmol/l
U-Benzene	-	7	9	16	<5	<5-46	13	22	<5	<5-63
	+	6	33	24	27	7-65	63	24	59	34-108
U-Toluene	-	7	5	3	<5	<5-11	5	4	<5	<5-12
	+	6	10	5	9	<5-15	5	1	5	<5-7
U-MTBE		13	51	69	36	<5-214	10	15	<5	<5-52
U-MTAE		13	23	26	10	<5-89	<5	3	<5	<5-11
U-TBA		13	216	155	176	10-612	179	88	167	67-407
U-TAA		13	53	64	25	10-218	27	31	10	10-111
U-Xylenes		13	8	<5	8	<5-13	5	<5	5	<5-11
U-Trimethyl benzenes		13	<5	-	<5	<5	<5	-	<5	<5-8

The quantitation limit of single components in urine is 5 nmol/l and half the limit was used for statistical calculations.

Table 4. Relationship between the concentrations of urinary gasoline components or their metabolites (nmol/l) collected after the work shift hours (PM) and the next morning (AM), and the breathing zone concentrations of the same components (TWA 8 h, mg/m³) expressed as Pearson's correlation coefficient (r)

Compound	Smoking +/-	n	Correlation coefficient (r)	
			PM	AM
Benzene	-	7	0.981	0.983
	+	6	0.321	0.141
Toluene	-	7	0.823	0.166
	+	6	0.653	0.433
Xylenes		13	0.411	0.495
Trimethyl benzenes		13	0.455	0.245
MTBE		13	0.830	0.437
TBA		13	0.526	0.836
MTAE		13	0.960	0.955
TAA		13	0.967	0.990

railway tank wagons were considerably below the current occupational exposure limits⁴⁾.

Biological monitoring of exposure to gasoline by analysing relevant components in the urine is an feasible approach to the estimation of exposure to different gasoline blends. The correlation coefficients for airborne and urinary parameters should exceed 0.532 so that the linear regression is acceptable at less than a 5% risk level⁵⁾. Urinary benzene and toluene determinations after working hours have been advocated by several research groups⁶⁻⁹⁾ to monitor even low exposure to these solvents. The relation to corresponding solvent exposure in nonsmokers has been good for benzene, $r=0.76-0.97^{6-7)}$,

but smoking significantly disturbs this relationship (smokers: $r=0.559^{6)}$. In this study the exposure of non-smokers to benzene, with one exception, was very low when measured both in air and in urine. For this non-smoker, low benzene exposure (0.6 mg/m³, TWA 8 h) could be estimated also with biological samples (46 nmol/l; post shift value). On the whole, benzene levels in the air were higher for smokers than for non-smokers, but their relation to urinary benzene was not good due to the interfering exposure from smoking. From blood samples, the exposure of non-smokers to benzene can be estimated as less than 3 mg/m³, and for toluene it is assumed to be about the same (1 ppm=3.8 mg/m³)⁷⁾. The benzene and toluene levels in this study were all under 3 mg/m³, and most of them much less. When these compounds were analysed in urine, a difference in sensitivity can be seen. Toluene, which scarcely dissolves in water phase (urine), gives a lower response in detection than benzene, even though the toluene concentrations in the air were higher. Nevertheless, the relationship of the exposure of non-smokers to toluene in the post-shift measurement was rather good ($r=0.82$, $n=7$) as also reported in an Italian study (0.76, $n=63$)⁶⁾. The relationship in higher toluene exposure (30-600 mg/m³) according to Monster has been excellent ($r=0.94$)⁸⁾. One phenomenon, which has no explanation, was the high benzene and toluene morning values of some non-smokers. It seems that there has been exposure from an unknown source after the working day.

The levels of urinary xylenes and trimethyl benzenes in this study were below or just above the detection limit and therefore the estimation of exposure to gasoline with these components is not reliable as can be seen from the correlation coefficients for airborne and urinary concentrations, $r=0.245-0.455$, in Table 4.

MTBE and TAME or their metabolites, TBA and TAA,

in urine have also been reported as indicators of exposure^{2,3)}. Regardless of the low component levels of oxygenates and their metabolites in urine and in air, the correlations between these two measurements were mainly good. Rapidly excreted urinary MTBE after working hours (PM) showed a high correlation ($r=0.83$), and the slowly eliminating tert-butyl alcohol (TBA) a poor correlation ($r=0.53$) with the exposure. The situation was reversed in the (AM) samples for MTBE ($r=0.44$) and TBA ($r=0.84$). MTAE and tert-amyl alcohol (TAA) in urine gave excellent correlations both after working hours and the next morning ($r=0.96$ – 0.99). For the assessment of exposure to gasoline blends in which oxygenates constitute a certain percentage, the sum of urinary ethers (MTBE+MTAE, PM) can be used as an indicator of a day's exposure, whereas the sum of urinary alcohols (TBA+TAA, AM) allows the monitoring of repeated exposures as well.

Biological monitoring of several urinary components offers a reliable tool to estimate exposure to different gasoline blends as seen with oxygenates and their metabolites even at very low breathing zone concentrations. The estimation is also reasonably good with post-shift urinary benzene and toluene of non-smokers. As a means of assessing exposure to gasoline blends, multicomponent analysis of post-shift urine is useful, as it also takes into account rapidly excreting small aromatics. Repeated exposure is also revealed in the analysis of metabolites of the oxygenates, TBA and TAA in pre-shift samples.

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