Benzene Exposure During Tunnelling—Using Biological Monitoring to Assess Control Measures and Working Practice

KATE JONES1* and JANE MCCALLUM2

1Health and Safety Laboratory, Harpur Hill, Buxton, SK17 9JN, UK; 2McCallum Safety and Health, 38 Railway Street, Lisburn, Co Antrim, BT28 1XP, UK

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This paper reports the assessment of worker exposure to high levels of benzene (up to 18 p.p.m. 8 h time weighted average, weekly average) during tunnelling on a contaminated land site (former gas works). Although respiratory and personal protection was used, biological monitoring results indicated that workers had urinary S-phenylmercapturic acid levels in excess of that expected following exposure to the UK workplace exposure limit. Factors such as environmental conditions (high temperature and humidity, confined workspace), respiratory and personal equipment providing insufficient protection, human behaviour (removing protective equipment, using mobile phones), and work practices (12-h shifts, too few and too short breaks, lack of drinking water) were identified as contributing to the exposure. A thorough review of control measures and working practice led to significant improvements, resulting in workers’ exposure (as measured by biological monitoring) being kept below the 90th percentile value (8 μmol mol⁻¹ creatinine, 17 μg g⁻¹ creatinine) of data from a good cross section of UK industry (N = 2600) despite the continuing high environmental levels.

Keywords: behaviour; benzene; biological monitoring; contaminated land; personal protective equipment; PPE; S-PMA; tunnelling

INTRODUCTION

The Belfast Sewers Project is a multimillion pound investment to improve and upgrade the wastewater and sewers infrastructure in the city of Belfast. The existing network of 1300 km of sewers was built in Victorian times and is in urgent need of repair and/or replacement. The work is in two parts, the Sewer Rehabilitation Works (which will upgrade 500 sewers) and the Stormwater Management Works. This will involve the construction of a number of new tunnels, the main one of which is a 9.4-km tunnel that is ~4 m in diameter. A number of other tributary tunnels join the main tunnel at various points around the city. This paper reports a study conducted during the construction of the main tunnel.

Initial soil samples taken at the site (a redundant Gas Works) indicated that there could be some risk of pollution once tunnelling began, although this was believed to be low. Soil analysis indicated the presence of various volatile organic compounds with benzene being of greatest concern due to its toxicity and low workplace exposure limit (WEL) [1 p.p.m. 8 h time weighted average (TWA) (HSE, 2007)]. As benzene has a skin notation and control of exposure relied on personal protective equipment (PPE such as gloves and overalls and including respiratory protection, RPE), biological monitoring, in addition to air monitoring, was considered appropriate. S-phenylmercapturic acid (S-PMA) is a sensitive and specific metabolite of benzene. Biological monitoring based on urine analysis of S-PMA is well established and there are biological exposure indices

*Author to whom correspondence should be addressed. Tel: +44 (0)1298 218435; fax: +44 (0)1298 218172; e-mail: kate.jones@hsl.gov.uk

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Baseline sampling was carried out pre-shift on the Monday and post-shift samples were on the following Friday. Two shifts (12-h shifts—day and night) were in operation at the time and a total of 70 workers provided samples. All workers were male with a mean age of 38 years (range 20–64 years). Thirty-one workers (44%) were smokers.

Air monitoring

Personal diffusive samplers were used to measure individual TWA exposures to benzene between April and June (the initial phase of the project).

Urine analysis

Aliquots of urine (2 ml) were acidified with 6 M HCl (200 μl); internal standard (d₇-S-BMA) was added. Samples were then extracted by C18 solid-phase extraction (100 mg/1 ml cartridges). After conditioning with methanol and 10 mM HCl (1 ml of each), the sample was loaded and washed with 10 mM HCl and toluene (1 ml and 250 μl, respectively). The cartridge was dried with nitrogen and S-PMA was eluted with 1 ml dichloromethane (containing 1% acetic acid). The eluate was evaporated to dryness and reconstituted in 100 μl mobile phase (70:30, 20 mM ammonium acetate with 0.1% acetic acid:methanol).

Analysis was by negative ion electrospray liquid chromatography-tandem mass spectrometry using an Applied Biosystems 3200 Triple Quad mass spectrometer with a Shimadzu HPLC system. Injections (10 μl) were made onto a 150 × 2 mm Synergi 4 μ Hydro-RP 80A column (Phenomenex) using a flow rate of 0.2 ml min⁻¹. A gradient elution was used from 70% 20 mM ammonium acetate with 0.1% acetic acid (30% methanol) to 95% methanol (5% 20 mM ammonium acetate with 0.1% acetic acid) from 1 to 5 min. Samples were then extracted by C18 solid-phase extraction (100 mg/1 ml cartridges). After conditioning with methanol and 10 mM HCl (1 ml) and reconstituted in mobile phase containing 1% acetic acid:methanol.

A curtain gas of 10 p.s.i. was used with auxillary gases of 45 and 35 p.s.i.; the collision cell had a pressure of 5 p.s.i. Lens voltage for S-PMA were as follows: −25 V (DP), −3.5 V (entrance potential), −14 V (CEP), −18 V (CE), and −2 V (CXP). The multiple reaction mode transitions monitored were 238→109 for S-PMA and 259→130 for the internal standard. The method was linear (least squares regression) to 500 nmol l⁻¹ with a quantification limit of 10 nmol l⁻¹ (detection limit 2 nmol l⁻¹, 3 x signal:noise). The inter-assay coefficient of variation was 13% at 200 nmol l⁻¹.

Creatinine was determined in all urine samples using a Cobas Mira (ABX France) and an automated alkaline picrate method (Bonsnes and TH, 1945).
The coefficient of variation for within-day analysis was 1.5% and for between-day analysis was 3% at 6 mM.

RESULTS

Personal air monitoring showed that weekly average 8 h TWA results for benzene rose from less than 0.6 p.p.m. in April to between 2.4 and 18 p.p.m. in May and June, significantly exceeding the UK WEL of 1 p.p.m. (8 h TWA).

Initial biological monitoring results for the first few weeks showed little change with ~75% of samples within the background range. However, during early May, the weather became very warm and the temperature within the tunnel increased significantly as work progressed. Air monitoring showed an increase in benzene exposure levels at this time. The men were complaining about the heat and were sweating profusely inside their suits. This was particularly problematic for the men using the TBM at the front of the tunnel and a small number exhibited signs of what was believed to be heat stress/dehydration. Additional bottled water was made available at this time, but the next series of biological monitoring results showed significant benzene exposure with 20% of samples exceeding the urinary S-PMA equivalent of the UK WEL as described in the Introduction (Fig. 1). There were statistically highly significant differences in the urinary S-PMA results between the different job categories (Kruskall–Wallis, P < 0.001). Four of the job categories (fitter, miner, pit boss, and TBM driver) all had mean exposures in excess of this UK WEL ‘equivalent’ (Table 1) and maximum S-PMA levels at this time reached more than 10 times this UK WEL ‘equivalent’ [239 μmol mol\(^{-1}\) creatinine, 90th percentile was 26.9 μmol mol\(^{-1}\) creatinine (57 μg g\(^{-1}\) creatinine)]. On investigation, it was found that due to the heat and the need to drink water more frequently, workers had been removing their PPE in the tunnel during work, when leaving the tunnel at break times, and at the end of their shifts. Some also reported taking off their respirators to answer their mobile phones.

As a result of these elevated S-PMA levels, a decision was taken to stop work immediately until control of exposure could be improved. This resulted in a week’s shutdown with no mining being undertaken. During this time, a chiller was added to the ventilation system to improve working comfort and thus improve PPE compliance. HSE Northern Ireland was informed and meetings were held with the Site Inspector and a Medical Inspector.

After the shutdown, PPE was upgraded to include chemical suits with a protection factor of 40 (Scotts Micro Chem 3000 professional disposable suit with double zips and cuffs), Scott Tornado T25 Chemical hoods with forced air ventilation, and three carbon filters for all workers in the tunnel, rubber gauntlets, and wellington boots. Half-masks were made available to the other workers at the pit top and bottom.

In addition, changes were made to working practice including the replacement of suits, filters, and gloves after each meal break; provision of additional bottled water; introducing shorter working time between breaks and a third shift to reduce the men’s exposure time (3 × 8-h shifts from 2 × 12-h shifts). Any worker with an elevated biological monitoring test result was interviewed by the Health and Safety Manager and asked about specific behaviours, breakdowns or non-compliance regarding PPE, or if they could recall any incident that could explain the result. The occupational health nurse spoke to each of the groups about the health risks and the importance of wearing PPE correctly, highlighting the need for prompt reporting of any system failures or health effects. Each worker was also spoken to individually to explain their own biological monitoring results and to answer any specific queries or concerns. There were regular reminders of the importance of PPE compliance at pre-shift briefings and toolbox talks and additional, non-operational, supervision was introduced to carry out regular air monitoring and enforce PPE compliance where necessary.

Once these improvements in control measures and working practice had been introduced, work resumed with at least weekly biological monitoring. Following these improvements, a dramatic reduction in S-PMA levels was seen (Fig. 2), with only three results out of 432 (0.7%) exceeding the UK WEL.
One worker, with persistent elevated S-PMA levels (despite evidence of his compliance being reported by others and his own claims that he had complied with all the necessary controls), was removed from the tunnel.

**DISCUSSION**

This case study illustrates the value of biological monitoring in situations where control of exposure primarily relies on RPE and other PPE. It also highlights the impact of working conditions and working practice on workers’ exposure. Although air monitoring had identified ‘hot spots’ of contamination, the intermittent nature of these pockets of benzene contamination and the extensive use of PPE meant that it was not sufficient to assess the risk of exposure. Biological monitoring was able to give an integrated measurement of actual systemic exposure (despite the PPE) and highlight issues with both the PPE and its use. As well instances of removing PPE while still in contaminated areas, it is possible that some exposure was due to dermal absorption of vapours penetrating the initial suits. Dermal absorption of vapours has previously been demonstrated, particularly in hot and humid conditions (Jones et al., 2003). Absorption of benzene has also been suspected (Colman and Coleman, 2006) from contaminated overalls; changing of overalls more frequently led to reduced S-PMA levels.

This case study also draws attention to the potential problems of contaminated land (the main shaft was dug out on the site of a disused gas works) and tunnelling. The Health and Safety Laboratory have previously dealt with a similar incident where extremely high benzene exposures were occurring during tunnelling of contaminated land (HSL, unpublished data). Again, 21% of samples exceeded the urinary S-PMA equivalent of the UK WEL, with the maximum exposure over 100 times this UK WEL equivalent (3379 μmol mol⁻¹ creatinine, 7117 μg g⁻¹ creatinine), demonstrating that very high exposures can occur in these situations despite the high level of PPE usually provided. These exposures are likely to be exacerbated by hot and humid conditions and the contained environment. A study of oil shale mineworkers (Sorensen et al., 2004) showed that underground workers had higher levels of S-PMA than surface workers and that there was a significant increase in S-PMA throughout the working week in underground workers but not in surface workers. Davidoff et al. (1998) also studied

### Table 1. Urinary S-PMA levels for workers by job category in the 5 weeks from the middle of May, leading to the shutdown

<table>
<thead>
<tr>
<th>Job</th>
<th>N (workers)</th>
<th>N (samples)</th>
<th>Mean (SD) S-PMA, range μmol mol⁻¹ creatinine</th>
<th>% samples &gt; UK WEL equivalenta</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBM driver</td>
<td>4</td>
<td>13</td>
<td>45.1 (29.3), 13.4–99.2</td>
<td>77</td>
</tr>
<tr>
<td>Miner</td>
<td>5</td>
<td>22</td>
<td>32.4 (32.6), 0.1–113.4</td>
<td>55</td>
</tr>
<tr>
<td>Pit boss</td>
<td>3</td>
<td>14</td>
<td>24.0 (19.0), 0.1–66.2</td>
<td>50</td>
</tr>
<tr>
<td>Fitter</td>
<td>6</td>
<td>11</td>
<td>42.9 (75.5), 2.2–238.5</td>
<td>36</td>
</tr>
<tr>
<td>Belt man</td>
<td>3</td>
<td>14</td>
<td>18.2 (22.7), 0.1–73.2</td>
<td>21</td>
</tr>
<tr>
<td>Loco driver</td>
<td>7</td>
<td>30</td>
<td>14.6 (29.8), 0.1–157.9</td>
<td>20</td>
</tr>
<tr>
<td>Electrician</td>
<td>5</td>
<td>18</td>
<td>16.1 (32.2), 0.1–140.5</td>
<td>11</td>
</tr>
<tr>
<td>Pit bottom</td>
<td>7</td>
<td>31</td>
<td>12.1 (21.3), 0.1–121.2</td>
<td>10</td>
</tr>
<tr>
<td>Pit top</td>
<td>14</td>
<td>46</td>
<td>5.8 (7.0), 0.1–27.9</td>
<td>7</td>
</tr>
<tr>
<td>Grouter</td>
<td>4</td>
<td>16</td>
<td>7.0 (10.4), 0.1–41.1</td>
<td>6</td>
</tr>
<tr>
<td>Shift engineer</td>
<td>8</td>
<td>20</td>
<td>6.7 (7.4), 0.1–29.4</td>
<td>5</td>
</tr>
<tr>
<td>Manager</td>
<td>4</td>
<td>13</td>
<td>4.3 (6.6), 0.1–19.4</td>
<td>0</td>
</tr>
</tbody>
</table>

a21 μmol mol⁻¹ creatinine (44 μg g⁻¹ creatinine) based on correlation reported by (DFG, 2009). 1 μmol S-PMA mol⁻¹ creatinine equates to ~2.1 μg g⁻¹ creatinine.
workers exposed to high levels of benzene as a result of excavating a subway tunnel under a former gasoline station (no biological monitoring was conducted). Certainly, the exposures seen in the two UK tunnelling examples are far higher than in other industries in the UK (oil and gas, steel, coke works, chemical processing, etc.) where only about 3% of results (N = 2600, data from this study not included) exceed the UK WEL equivalent (HSL, unpublished data). Based on these data from a wide range of industry, the 90th percentile value for urinary S-PMA of 8 µmol mol\(^{-1}\) creatinine (17 µg g\(^{-1}\) creatinine) could be suggested as an action level above which controls should be investigated.

It is well known that smokers exhibit higher urinary levels of S-PMA than non-smokers in the general population and it has previously been stated (Maestri et al., 2005) that smoking status needs to be considered where low-level occupational exposures to benzene are expected. In the study reported here, there was no significant difference between smokers and non-smokers for the initial work [smokers: mean 7.3 µmol mol\(^{-1}\) creatinine (15.4 µg g\(^{-1}\) creatinine), SD = 16.9 µmol mol\(^{-1}\) creatinine, n = 361; non-smokers: mean 5.4 µmol mol\(^{-1}\) creatinine (11.4 µg g\(^{-1}\) creatinine), SD = 16.9 µmol mol\(^{-1}\) creatinine, n = 488; t-test \(P = 0.1057\)] due to the high exposures. However after the improvements, which reduced the exposures considerably, smoking status did become significant [smokers: mean 2.6 µmol mol\(^{-1}\) creatinine (5.4 µg g\(^{-1}\) creatinine), SD = 4.4 µmol mol\(^{-1}\) creatinine, n = 121; non-smokers: mean 1.4 µmol mol\(^{-1}\) creatinine (2.9 µg g\(^{-1}\) creatinine), SD = 2 µmol mol\(^{-1}\) creatinine, n = 153; t-test \(P = 0.0029\)]. Although some workers were still demonstrably occupationally exposed, mean results were now within the general population levels [smokers <10.2 µg g\(^{-1}\) creatinine (4.8 µmol mol\(^{-1}\) creatinine, n = 134); non-smokers <4.0 µg g\(^{-1}\) creatinine (1.9 µmol mol\(^{-1}\) creatinine, n = 102) (Maestri et al., 2005)]. Similar levels have also been reported in the UK (Aston et al., 2002).

The thorough review of control measures and working practice in light of the elevated biological monitoring results in this study led to significant improvements in the protection factors of PPE supplied, compliance with correct PPE use, and the working environment. These improvements resulted in significant reductions in actual worker exposure to benzene [95% of S-PMA results below the proposed action level, 90th percentile was 5.4 µmol mol\(^{-1}\) creatinine (11 µg g\(^{-1}\) creatinine)] despite continuing contamination, demonstrating that working safely in high ambient benzene concentrations in a hot, humid, confined environment is possible but that means of monitoring the efficacy of controls (and their use) is vital. Biological monitoring is a valuable tool in monitoring such exposures where control is highly reliant on PPE and skin absorption may also be an issue. A 90th percentile value for SPMA of 8 µmol mol\(^{-1}\) creatinine (17 µg g\(^{-1}\) creatinine) is indicative of current UK industry practice.

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