Determination of beryllium concentrations in UK ambient air

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Abstract

Air quality monitoring of ambient air is essential to minimise the exposure of the general population to toxic substances such as heavy metals, and thus the health risks associated with them. In the UK, ambient air is already monitored under the UK Heavy Metals Monitoring Network for a number of heavy metals, including nickel (Ni), arsenic (As), cadmium (Cd) and lead (Pb) to ensure compliance with legislative limits. However, the UK Expert Panel on Air Quality Standards (EPAQS) has highlighted a need to limit concentrations of beryllium (Be) in air, which is not currently monitored, because of its toxicity. The aim of this work was to analyse airborne particulate matter (PM) sampled onto filter papers from the UK Heavy Metals Monitoring Network for quantitative, trace level beryllium determination and compare the results to the guideline concentration specified by EPAQS. Samples were prepared by microwave acid digestion in a matrix of 2 % sulphuric acid and 14 % nitric acid, verified by the use of Certified Reference Materials (CRMs). The digested samples were then analysed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The filters from the UK Heavy Metals Monitoring Network were tested using this procedure and the average beryllium concentration across the network for the duration of the study period was 7.87 pg m⁻³. The highest site average concentration was 32.0 pg m⁻³ at Scunthorpe Low Santon, which is significantly lower than levels that are thought to cause harm. However the highest levels were observed at sites monitoring industrial point sources, indicating that beryllium is being used and emitted, albeit at very low levels, from these point sources. Comparison with other metals concentrations and data from the UK National Atmospheric Emissions Inventory suggests that current emissions of beryllium may be significantly overestimated.

Keywords: Air quality; heavy metals; beryllium
1. Introduction

Air quality is an area of increasing global concern, as emissions of pollutants, including heavy metals, from anthropogenic sources such as the combustion of fossil fuels for power generation and transport, or processes such as smelting or mining, continue to rise and public awareness of potential health effects improves. Studies conducted by the World Health Organisation (WHO) show the harmful effects of heavy metals exposure to human health (WHO, 2006 and 2012). These typically include, among others, increased risk of cancer and neurotoxic diseases (WHO, 1980 and 1993).

In Europe, a whole raft of legislation has been adopted in order to minimise population exposure to airborne pollutants such as heavy metals (European Commission (EC), 2015). European air quality directives require member states to establish and maintain a system for monitoring concentrations of heavy metals and other pollutants in ambient outdoor air (EC, 2015). The Air Quality Directive 2008/50/EC specifies a target value for ambient concentrations of lead and the Fourth Daughter Directive 2004/107/EC specifies limit values for nickel, arsenic and cadmium. In the UK this monitoring requirement is met by the UK Heavy Metals Air Quality Monitoring Network, operated by the National Physical Laboratory (NPL) on behalf of the Department for the Environment, Food and Rural Affairs (Defra), and from 2016 Defra and the Environment Agency (EA). The network consists of samplers located at 25 different sites around the UK that pump ambient air through cellulose acetate filters and collect the particulate matter (PM$_{10}$ size fraction). The filters are then sent to the laboratory at NPL, prepared by microwave digestion in acid, then analysed for heavy metals by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) (Goddard et al., 2015).

Beryllium is not one of the metals currently monitored by the UK Heavy Metals Network because there is no existing legislative requirement for it in ambient air. However, the Expert Panel on Air Quality Standards (EPAQS) produced a report for the Department for Environment, Food and Rural Affairs (Defra) (EPAQS, 2008), the purpose of which was to provide guideline levels of priority pollutants, including beryllium, in ambient air ‘at which no or minimal effects on human health are likely to occur’. Beryllium poisoning has been documented in workers handling all insoluble beryllium-containing materials. Short-term, high concentration exposure can result in acute pneumonitis, whereas chronic beryllium disease (CBD) or ‘berylliosis’, a form of interstitial lung disease, can arise after long-term exposure. Both conditions can be fatal. The guideline level given for beryllium in the report was 0.2 ng m$^{-3}$ total particulate in the PM$_{10}$ size fraction, as an annual average (EPAQS, 2008).

The main sources of atmospheric airborne beryllium are anthropogenic: refineries, road traffic, domestic and office heating, power stations and waste incinerators (which may be used for the disposal of electrical items e.g. computers and mobile phones that contain beryllium) (EPAQS 2008). Beryllium is also found in coal, therefore coal-fired power stations and coal slag used as an abrasive in blasting paint will generate airborne beryllium (EPAQS 2008).
Beryllium is often used in alloys, particularly with copper or nickel, which are used for their high strength and good electrical and thermal conductivities (Beryllium Science and Technology Association, 2016). There are a wide variety of applications for copper-beryllium alloys, including plastic injection and moulding inserts, springs and spring wiring, lightweight structural components for the aerospace and defence industries, non-sparking tools for use in explosive environments, electronic components (relays, switches, connectors), low wear bearings, automotive parts, and telecommunications cables (Materion Corporation, 2015). Nickel-beryllium alloys are used in mechanical and electrical springs that are required to work at high temperatures without deforming. Applications include household oven controls, fire detection equipment, fire suppression sprinkler systems, and in automotive engine and exhaust control systems (Beryllium Science and Technology Association, 2016).

The highest ambient air levels of beryllium have been recorded near factories where beryllium is processed or beryllium-containing products are manufactured (EPAQs 2008). Eisenbud et al. (1949), found that within 212 m of a beryllium processing plant in Loraine, Ohio, USA, concentrations of beryllium were measured as high as 460 ng m\(^{-3}\), falling to 30 ng m\(^{-3}\) a mile (1.61 km) away. In Czechoslovakia, ambient concentrations of up to 17 ng m\(^{-3}\) beryllium were measured in a town located near two power plants burning coal with a high beryllium content (Bencko et al., 1980).

A study at a roadside location in Birmingham, UK (Harrison et al., 2003) monitored daily concentrations of metals, including beryllium, in various particle size fractions. The mean beryllium concentration found in PM\(_{10}\) was 0.05 ng m\(^{-3}\), with individual results ranging from 0.01 – 0.15 ng m\(^{-3}\) – approaching the 0.2 ng m\(^{-3}\) limit recommended by EPAQs (EPAQS, 2008). To the best of the authors’ knowledge, this is the only example of actual measurements of beryllium in UK ambient air to date.

Figure 1 shows the UK emissions of beryllium from 1970 – 2013. In 1970 the total emissions were 0.043 kilotonnes, the majority of which was attributable to domestic combustion sources. By 2013, road transport was the main contributory source to total emissions of 0.005 kilotonnes (NAEI, 2016).
The aim of this work is to analyse filter samples from the UK Heavy Metals Air Quality Monitoring Network for the concentration of beryllium in PM$_{10}$, to establish levels across the UK in relation to the EPAQs guideline level of 0.2 ng m$^{-3}$.

In terms of analytical methodology, microwave assisted digestion using acids provides a fast and efficient preparation technique for environmental samples requiring trace metals analysis that today is considered routine (Sandroni, V. et al., 2003). Heating in closed vessel systems results in an increase in pressure as the digestion acids evaporate and gases are produced by the decomposing sample matter, thus increasing the boiling point of the reagents and aiding the rapid breakdown of the sample matrix (Lamble and Hill, 1998). There are a number of digestion procedures documented for beryllium in workplace air sampled onto filters in the literature (Ashley et al., 2005), (Brisson et al., 2006) and (Oatts, 2012) on which the method in this paper was based. Instrumental analysis by ICP-MS is a well-established technique for the determination of ultra-trace levels of metals, including beryllium (Harrison et al., 2003), (Ashley et al., 2005), so was employed in this study to analyse the digested filter samples.

2. Experimental section

Figure 1: UK beryllium emissions 1970 – 2013 (NAEI, 2016).
2.1 Test samples

Certified reference materials (CRMs) were chosen that most closely resembled the network samples (PM on filters) in terms of sample media. The CRMs measured were NIST SRM 1944, a mixture of marine sediment collected near urban areas in New York and New Jersey purchased from NIST (National Institute of Standards and Technology, USA) and ‘Be from BeO on Filter Media’, produced by High Purity Standards (HPS), USA, purchased from Greyhound Chromatography. This material consists of mixed cellulose ester filters (37 mm diameter, 0.8 µm pores) spiked with a stock solution prepared from NIST SRM 1877 (beryllium oxide (BeO) powder, prepared from high fired BeO).

The filter samples tested were sourced from the UK Heavy Metals Monitoring Network. The network filter samples consist of PM$_{10}$ from ambient air sampled onto cellulose ester filters (47 mm diameter, 0.8 µm pores, purchased from Pall Corporation). From each monitoring site, three to five months’ worth of filters were tested, sampled between March and July 2016. As concentrations of heavy metals in ambient air are not subject to significant seasonal variation (Goddard et al., 2015), concentrations measured over this substantial proportion of the year should yield average concentrations strongly indicative of an annual average.

2.2 Sample preparation

Samples were prepared by microwave acid digestion (Anton Paar Multiwave 3000). Sub-samples of the reference material NIST 1944 were accurately weighed on a calibrated balance (Sartorius LA230S, resolution 0.1 mg). The ‘Be from BeO on Filter Media’ reference material filters were digested directly as whole filters. The network filter samples were cut into accurate portions using a template and ceramic scissors. The sub-samples were then transferred to microwave vessels and the acid mixtures added. From each monitoring site, three to five months’ worth of filters were tested.

The microwave program heated the samples to 220°C for 60 minutes at up to 1400 W. The acids used were 95 % H$_2$SO$_4$ (1 ml) and 70 % HNO$_3$ (10 ml) resulting in a matrix of 2 % H$_2$SO$_4$, 14 % HNO$_3$, as recommended in studies by Ashley et al (2005), Brisson et al. (2006) and Oatts (2012). All concentrated acids used were Analytical Reagent grade purchased from Fisher Scientific. Once cooled, the digested solutions were transferred to a centrifuge tube and made up to 50 g in purified water (18 MΩ quality, Elga Purelab Flex 2). The digested solutions of NIST 1944 were filtered prior to analysis to remove particulate content. Cellulose filter papers of 90 mm diameter and 5-13 µm pores (Fisher Scientific) were used.

The final solutions were then analysed for beryllium content using a PerkinElmer Elan 9000 ICP-MS. Liquid argon (99.9999 % purity) was supplied by BOC Gases for the plasma gas.

2.3 ICP-MS analysis
The ICP-MS was optimised prior to analysis to ensure sufficient sensitivity and minimal oxide/doubly charged ion formation.

A quality assurance (QA) solution containing a mid-range concentration of beryllium was repeatedly analysed throughout the analytical sequence. The responses were plotted and the equation of the polynomial line fitted was used to correct the responses of the calibration standards and samples for drift, as in previous work (Brown et al., 2008). The stock beryllium solution, Be 1000 µg ml⁻¹, was sourced from Metlab Supplies.

The ICP-MS was calibrated by direct analysis of external calibration standards containing known concentrations of beryllium, traceable to the NIST SRM 3100 series of mono-elemental solutions (stock solution, Be 1000 µg ml⁻¹, sourced from Metlab Supplies). Calibration curves were generated from the measured responses of the calibration standards and used to interpolate the sample concentrations using NPL’s XLGenline software which performs generalised least squares regression (Smith, 2010). The calibration range encompassed the measured sample concentrations. The calibration standards were prepared in a matrix of 2 % H₂SO₄, 14 % HNO₃. All measurements were blank corrected with the appropriate matrix blank.

2.4 Water soluble beryllium

Metals such as beryllium pose a significant health risk to humans and ecosystems if they are present in a water soluble form, as they are more easily absorbed into biological systems (Williams et al., 2000). However, insoluble or low-solubility beryllium containing particles that are inhaled can be transferred to the lymph nodes or pulmonary interstitium, where they can be retained for many years until they are slowly solubilized, resulting in adverse health effects (Maier, 2002).

A selection of the UK Heavy Metals Network filters tested for total beryllium were also analysed to obtain indicative concentrations of water soluble beryllium species. The filters were selected from across the range of total beryllium concentrations measured initially.

Filters were cut accurately into portions using a template and ceramic scissors as before. The portions for each sample were placed in a 50 mL centrifuge tube and 10 mL purified water (18.2 MΩ, Elga Purelab Flex 2) was added. The solutions were then sonicated for 30 minutes at 50-60 Hz (Fisherbrand S-Series Ultrasonic Cleaner).

After sonication, the filter and any dislodged particulate matter were removed from the sample solution by filtration. The initial filtration was carried out using a 90 mm diameter cellulose filter paper, pore size 5-13 µm (Fisher Scientific). The filtrate was then made up to 50 g with 2 % H₂SO₄, 14 % HNO₃ acid matrix. The resulting solutions still contained some particulate matter, so they were filtered again through 25 mm polypropylene membrane syringe filters, pore size 0.2 µm (VWR...
International). These solutions were then analysed by ICP-MS and the data processed in the same way as the acid digests for total beryllium.

3. Results and Discussion

3.1 Certified reference materials (CRMs)

The recoveries reported in Table 1 were obtained with the microwave program specified in section 2.2, using a 2 % H$_2$SO$_4$, 14 % HNO$_3$ acid matrix.

<table>
<thead>
<tr>
<th>Replicate</th>
<th>Recovery % NIST SRM 1944 (1.6 ± 0.3 mg/kg *)</th>
<th>Recovery % Be from BeO on Filter Media (0.050 ± 0.001 µg/filter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>92.3 ± 10.2</td>
<td>103.9 ± 7.6</td>
</tr>
<tr>
<td>2</td>
<td>86.4 ± 9.3</td>
<td>106.4 ± 6.5</td>
</tr>
<tr>
<td>3</td>
<td>84.1 ± 8.1</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>90.7 ± 8.6</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 1: Recoveries of NIST 1944 and Filter CRMs (with certified/reference values in brackets) digested in 2 % H$_2$SO$_4$, 14 % HNO$_3$. The recovery uncertainties are quoted to $k=2$.

* denotes the beryllium mass fraction in NIST 1944 is supplied as a reference value only.
3.2 Limits of Detection and Quantitation

Sixteen blank filters were analysed prior to any network filter samples. The resulting concentrations were used to calculate the Limits of Detection and Quantitation (LOD and LOQ).

The instrumental LOD was calculated as three times the standard deviation of the filter blank concentrations (pg g\(^{-1}\)). This value was then corrected for the mass of sample solution, filter sub-sampling and a typical volume of air sampled to give the method LOD (pg m\(^{-3}\)):

Calculation of the method LOD:

\[
LOD_m = \frac{LOD_I \cdot m_{SS}}{V_{air} F_p}
\]

- LOD\(_m\) = method LOD in (pg m\(^{-3}\));
- LOD\(_I\) = instrumental LOD in (pg g\(^{-1}\));
- m\(_{SS}\) = mass of sample solution (g);
- F\(_p\) = filter portion (i.e. 1, as whole filters were used for this test);
- V\(_{air}\) = a typical volume of sampled air (m\(^3\)) (i.e. 168 m\(^3\) for a typical weekly sample collected at 16.7 L min\(^{-1}\)).

The instrumental LOQ was calculated in a similar fashion, but multiplying the standard deviation of the filter blank concentrations by a factor of ten, then substituting the instrumental LOQ into the equation above to obtain the overall method LOQ. See Table 2 below for the instrumental (ICP-MS) and overall method LODs and LOQs calculated.

<table>
<thead>
<tr>
<th></th>
<th>Instrumental pg g(^{-1})</th>
<th>Overall Method pg m(^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>LOD</td>
<td>3.46</td>
<td>1.13</td>
</tr>
<tr>
<td>LOQ</td>
<td>11.54</td>
<td>3.78</td>
</tr>
</tbody>
</table>

**Table 2**: Instrumental and Overall Method Limits of Detection and Quantitation (LOD and LOQ)
3.3 UK Heavy Metals Monitoring Network filter samples

Metals network filter samples from every site on the UK Heavy Metals Network (see Fig. 2) were tested for beryllium (Be) content. The network site composition shown in Fig. 2 was correct for the sampling period in 2015.

**Figure 2:** Locations and classifications of monitoring sites on the UK Heavy Metals Network (Goddard et al., 2015).
The monitoring sites are classified according to their location in terms of description of the surrounding area and immediate proximity to pollution emission sources as specified in Council Directive 2008/50/EC and UK guidelines (Defra, 2015).

From each monitoring site, three to five months’ worth of filters were tested. The average ambient concentrations of beryllium measured at all the sites are shown in Table 3.
<table>
<thead>
<tr>
<th>Site Number</th>
<th>Site Name</th>
<th>Site Classification</th>
<th>Average beryllium concentration pg m⁻³</th>
<th>Uncertainty (k=2) pg m⁻³</th>
<th>Relative Uncertainty (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>59</td>
<td>ICI Weston Point</td>
<td>(Sub)urban Industrial</td>
<td>5.99</td>
<td>1.53</td>
<td>26</td>
</tr>
<tr>
<td>69</td>
<td>Bilston Lane, Walsall</td>
<td>(Sub)urban Industrial</td>
<td>17.6</td>
<td>3.38</td>
<td>19</td>
</tr>
<tr>
<td>104</td>
<td>Port Talbot</td>
<td>(Sub)urban Industrial</td>
<td>19.0</td>
<td>1.81</td>
<td>10</td>
</tr>
<tr>
<td>106</td>
<td>Scunthorpe Town</td>
<td>(Sub)urban Industrial</td>
<td>11.1</td>
<td>1.52</td>
<td>14</td>
</tr>
<tr>
<td>107</td>
<td>Scunthorpe Low Santon</td>
<td>(Sub)urban Industrial</td>
<td>32.0</td>
<td>2.38</td>
<td>7</td>
</tr>
<tr>
<td>113</td>
<td>Pontardawe Tawe Terrace</td>
<td>(Sub)urban Industrial</td>
<td>3.95</td>
<td>2.64</td>
<td>67</td>
</tr>
<tr>
<td>117</td>
<td>Sheffield Tinsley</td>
<td>(Sub)urban Industrial</td>
<td>9.32</td>
<td>2.93</td>
<td>31</td>
</tr>
<tr>
<td>118#</td>
<td>Sandvik Neath</td>
<td>(Sub)urban Industrial</td>
<td>7.81</td>
<td>2.63</td>
<td>34</td>
</tr>
<tr>
<td>201#</td>
<td>Pontardawe Leisure Centre</td>
<td>(Sub)urban Industrial</td>
<td>8.85</td>
<td>2.97</td>
<td>34</td>
</tr>
<tr>
<td>62</td>
<td>London Westminster</td>
<td>Urban Background</td>
<td>7.25</td>
<td>1.38</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>Location</td>
<td>Environment Type</td>
<td>Ambient Concentration (μg/m³)</td>
<td>Standard Deviation (μg/m³)</td>
<td>Sample Size</td>
</tr>
<tr>
<td>---</td>
<td>---------------------------</td>
<td>--------------------</td>
<td>-------------------------------</td>
<td>---------------------------</td>
<td>-------------</td>
</tr>
<tr>
<td>100</td>
<td>Swansea Coedgwilym</td>
<td>Urban Background</td>
<td>7.31</td>
<td>2.79</td>
<td>38</td>
</tr>
<tr>
<td>103</td>
<td>Belfast Centre</td>
<td>Urban Background</td>
<td>3.91</td>
<td>1.25</td>
<td>32</td>
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<tr>
<td>110</td>
<td>Chadwell St. Mary</td>
<td>Urban Background</td>
<td>7.43</td>
<td>1.61</td>
<td>22</td>
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<tr>
<td>119</td>
<td>Sheffield Devonshire Green</td>
<td>Urban Background</td>
<td>6.65</td>
<td>1.54</td>
<td>23</td>
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<tr>
<td>101</td>
<td>Swansea Morriston</td>
<td>Urban Traffic</td>
<td>7.26</td>
<td>2.72</td>
<td>38</td>
</tr>
<tr>
<td>114</td>
<td>London Marylebone Road</td>
<td>Urban Traffic</td>
<td>8.77</td>
<td>1.87</td>
<td>21</td>
</tr>
<tr>
<td>115</td>
<td>Pontardawe Brecon Road</td>
<td>Industrial Suburban</td>
<td>3.71*</td>
<td>2.40</td>
<td>65</td>
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<tr>
<td>65</td>
<td>Eskdalemuir</td>
<td>Rural</td>
<td>2.52*</td>
<td>1.39</td>
<td>55</td>
</tr>
<tr>
<td>202</td>
<td>Auchencorth Moss</td>
<td>Rural</td>
<td>2.55*</td>
<td>1.45</td>
<td>57</td>
</tr>
<tr>
<td>203</td>
<td>Yarner Wood</td>
<td>Rural</td>
<td>3.57*</td>
<td>1.43</td>
<td>40</td>
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<tr>
<td>204</td>
<td>Cwmystwyth</td>
<td>Rural</td>
<td>3.03*</td>
<td>1.40</td>
<td>46</td>
</tr>
<tr>
<td>205</td>
<td>Harwell</td>
<td>Rural</td>
<td>4.21</td>
<td>1.48</td>
<td>35</td>
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<tr>
<td>206</td>
<td>Heigham Holmes</td>
<td>Rural</td>
<td>4.42</td>
<td>1.50</td>
<td>34</td>
</tr>
<tr>
<td>208</td>
<td>Detling</td>
<td>Rural</td>
<td>3.81</td>
<td>1.44</td>
<td>38</td>
</tr>
<tr>
<td>209</td>
<td>Fenny Compton</td>
<td>Rural</td>
<td>4.92</td>
<td>1.24</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td><strong>Network Average</strong></td>
<td></td>
<td><strong>7.87</strong></td>
<td><strong>1.95</strong></td>
<td><strong>33</strong></td>
</tr>
</tbody>
</table>

**Table 3**: Average ambient concentrations of beryllium based on analysis of 3-5 months’ worth of filters at each network monitoring site.
The sites at Sandvik, Neath and Pontardawe Leisure Centre are operated independently of the network by Neath Port Talbot County Borough Council.

* Denotes concentrations < Limit of Quantitation (LOQ = 3.78 pg m$^{-3}$). All concentrations were above the Limit of Detection (LOD = 1.13 pg m$^{-3}$).
Distinct differences can be seen between results from sites of different classifications, see Fig. 3.

**Figure 3:** Ambient concentrations of beryllium at each network monitoring site with site classifications indicated.
It is clear from Fig. 3 that the highest concentrations of beryllium were found at sites in the Urban Industrial classification. These sites are located in urban areas exposed to industrial point sources (Goddard et al., 2015). The difference between beryllium levels observed at Urban Industrial sites and sites of other classifications suggests that some of the industrial point sources are producing incrementally higher emissions of beryllium than in purely urban locations. Road traffic contributes a significant source of beryllium emissions from combustion of DERV (diesel oil for road vehicles) from cars, LGVs and HGVs (NAEI, 2016), and is used in automotive components (Beryllium Science and Technology Association, 2016) which explains why the levels at Urban Traffic sites are higher than levels at Rural sites. The only Industrial Suburban site, Pontardawe Brecon Rd., is located downwind of a point source, hence the levels slightly above the Rural baseline. As would be expected, the lowest concentrations of beryllium were measured at Rural sites.

The five Urban Industrial sites showing the highest average beryllium ambient concentrations were: Scunthorpe Low Santon (32.0 pg m\(^{-3}\)), Port Talbot (19.0 pg m\(^{-3}\)); Bilston Lane, Walsall (17.6 pg m\(^{-3}\)); Scunthorpe Town (11.1 pg m\(^{-3}\)) and Sheffield Tinsley (9.32 pg m\(^{-3}\)).

The point source for the Port Talbot, Scunthorpe Town and Low Santon sites is Tata Steel, a steel production company (Tata Steel Europe Ltd, 2016). Tata Steel produces structural components for use in the automotive industry, a known area of application for beryllium metal (Materion Corporation, 2015).

The point source for the site at Bilston Lane, Walsall is Brookside Metals, a company listed as producing gunmetal, brass, bronze and other copper alloy ingots (Brookside Metals, 2016). The measured concentrations suggest that the site may produce beryllium alloys such as copper-beryllium or nickel-beryllium.

The Sheffield Tinsley site is located downwind of the Outokumpu plant which produces stainless steel (Outokumpu, 2016). The levels observed suggest the plant may be involved in processing beryllium alloys, or producing components containing beryllium.

Of the two Urban traffic sites, the highest beryllium concentration was observed at London Marylebone Road (8.77 pg m\(^{-3}\)). The most likely source for sites in this classification is road traffic, in particular for beryllium emissions, combustion of DERV (diesel oil for road vehicles) from cars, LGVs and HGVs (NAEI, 2016).

While the levels found at these sites are the highest observed in this study, the averages are still significantly below the EPAQs guideline level of 0.2 ng m\(^{-3}\) (EPAQs, 2008). The averages at all
stations are an order of magnitude below the EPAQs guidelines with the exception of Scunthorpe Low Santon, where the average is six times less than the guideline.

To summarise the overall influence of site classification on the beryllium concentrations measured, Table 4 shows the average incremental concentration increases between the site classifications in ascending order.

<table>
<thead>
<tr>
<th>Site Classification</th>
<th>Average beryllium concentration / pg m$^3$</th>
<th>Approximate increment according to site type / pg m$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rural</td>
<td>3.6</td>
<td>-</td>
</tr>
<tr>
<td>Urban Background</td>
<td>6.5</td>
<td>2.9</td>
</tr>
<tr>
<td>Urban Traffic</td>
<td>8.0</td>
<td>1.5</td>
</tr>
<tr>
<td>(Sub)urban Industrial</td>
<td>11.9*</td>
<td>3.9*</td>
</tr>
</tbody>
</table>

Table 4: Showing the average incremental changes observed between sites in different site classifications. *The concentrations measured in (Sub)urban industrial locations varied significantly, from 3.71 pg m$^3$ (comparable to rural sites) – 32.0 pg m$^3$. Therefore the incremental change from concentrations found at Urban Traffic sites ranged considerably.

The incremental concentration increases were calculated as shown below:

$$[Be]^{UB} - [Be]^R = I^{R:UB}$$

Where:

$$[Be]^{UB} = \text{average beryllium concentration found at urban background sites}$$

$$[Be]^R = \text{average beryllium concentration found at rural sites}$$

$$I^{R:UB} = \text{approximate incremental increase in beryllium concentration from rural to urban background sites}$$

The increments for the other site classifications were calculated in the same way.
Correlation of Beryllium with other metals

The network samples are analysed for the following suite of heavy metals to meet the reporting requirements of the Heavy Metals Network: vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), selenium (Se), cadmium (Cd) and lead (Pb) (Goddard et al., 2015). The beryllium results obtained for the network samples were compared to the results measured for the other metals to see if there were any correlations that could suggest shared point sources. The datasets had outliers removed using Grubbs’ test for statistical outliers (Grubbs, 1969) before the correlations were calculated.

The highest correlation found using the whole dataset (outliers removed), although still not particularly strong, was between the beryllium and lead results, giving an $R^2$ of 0.5043 (see Fig. 4). Other high correlations were with manganese: 0.4653 and vanadium: 0.3911.

None of the calculated correlations are particularly high, but the scatter plot indicates a clear relationship with lead. The lowest correlation was between beryllium and nickel, $R^2$: 0.0008. In terms of associations with similar point sources, beryllium, manganese and lead are all emitted by the combustion of coal from industrial and domestic sources (NAEI, 2016). A significant proportion of beryllium and vanadium emissions are attributed to road transport combustion of DERV (NAEI, 2016). By comparison, none of these sources are associated with significant emissions of nickel.

At the two Scunthorpe monitoring sites, Scunthorpe Town and Scunthorpe Low Santon, a strong correlation was observed between beryllium and iron, $R^2$: 0.9706, see Figure 5 below.
The strength of this correlation should be viewed with caution, as it is only based on eight data points. Both Scunthorpe sites monitor the point source at Tata Steel, an iron and steelmaking production company (Tata Steel Europe Ltd, 2016). The four highest points were measured at Scunthorpe Low Santon, which is located nominally downwind of the point source (Goddard et al., 2015). Beryllium emissions from iron and steelmaking processes comprise only 0.1% of total UK emissions (NAEI, 2016), but locally this still produces significant beryllium concentrations.

3.5 Comparison of observed beryllium concentrations with emissions data

A previous study (Brown, 2010) compared annual estimated emissions published on the NAEI website with measured levels of heavy metals in ambient air reported for the UK Heavy Metals Network by performing a generalized least squares regression analysis of measured concentrations of seven metals against their respective estimated emissions. This involved a large dataset with both concentration and emission values from 1980 – 2007. Measured concentrations in ng m⁻³ were plotted against emissions in Megagrams (Mg) for each metal, and the resulting slope gave an indication of the sensitivities of ambient concentrations to emissions. The study concluded that metals mainly emitted from diffuse sources (so would be observed at many network monitoring sites), e.g. transport, showed the highest sensitivities of ambient concentrations to emissions. Lead was calculated as the most sensitive to changes in emissions with a slope of 0.16. As the majority of monitoring sites have historically been located near roads, the reduction in emissions from leaded petrol will have had a significant impact on the measured ambient concentrations. Of the metals tested, chromium was calculated as the least sensitive to changes in emissions, with a slope of
0.0054. This was considered to be because the annual average concentrations were dominated by emissions from a single point source, measured at just one monitoring site (Brown, 2010). Vanadium was the next least sensitive with a slope of 0.015, and appeared to be an outlier when the proportion of estimated transport-related emissions were plotted against the emission sensitivity ratio for each metal. Vanadium had the second highest percentage of estimated transport emissions, yet the second lowest emission sensitivity ratio. The study found that the NAEI had revised historical vanadium emissions estimates downwards, which suggests overestimation of vanadium emissions had previously been a problem (Brown, 2010).

For the current study, the median beryllium concentration in ng m\(^{-3}\) was ratioed against the total UK beryllium emissions value in Megagrams (Mg) reported on the NAEI website (NAEI, 2016) for the year 2013 (the latest year for which data is available at time of publishing). The resulting ratio was:

\[
\frac{0.0067 \text{ ng m}^{-3}}{5.4106 \text{ Mg}} = 0.0012 \text{ ng m}^{-3}\text{Mg}^{-1}
\]

This value is less than that calculated for chromium and vanadium in the previous study (Brown, 2010), so could imply that measured ambient beryllium concentrations are relatively insensitive to changes in emissions, indicating a higher proportion of emissions from industrial point sources. However, according to the NAEI (2016), DERV from road traffic constitutes the largest single contributory source of beryllium emissions. This contradiction may indicate a similar issue to that observed with vanadium in the previous study, of an overestimation of beryllium emissions, particularly from transport sources. In support of this, Figure 2 shows that beryllium concentrations were significantly higher at sites monitoring industrial point sources than diffuse traffic sources.

To draw more definitive conclusions a larger dataset of concentration: emission ratios over a longer time period would clearly be preferable, but as the only available concentrations from which to calculate a ratio were from the present study, that was a limiting factor. Nonetheless, the amount of sub-data contributing to the single ratio calculated is substantial, which gives confidence that the value generated is suitable for comparison with the ratios calculated in the previous study (Brown, 2010).

### 3.6 Water soluble beryllium

A selection of the UK Heavy Metals Network filters tested for total beryllium were also tested for indicative levels of water soluble beryllium species.

The indicative results obtained for water soluble beryllium are shown in Figure 6, along with the total beryllium measured for the same sample for comparison. The sample IDs are in the format of: Site number – Year sampled – Batch period of year sampled – Number of filters in batch. (Filters are sampled weekly, then batched together into four-weekly batches for digestion and analysis. A year is divided into 13 four weekly periods.)
Figure 6: Concentrations of water soluble and total beryllium in selected network samples. The Limit of Quantitation (LOQ) = 3.78 pg m$^{-3}$. The Limit of Detection (LOD) = 1.13 pg m$^{-3}$.

All the water soluble beryllium results were below either the LOQ or both the LOQ and LOD. On this basis it would seem that there are no significant levels of water soluble beryllium present in the samples tested. However there does appear to be a correlation between concentrations of water soluble and total beryllium. Of the samples containing significant concentrations of total beryllium (i.e. above the LOQ), the highest proportion of water soluble beryllium as a percentage of total beryllium was 30.9 % in sample 106-2015-7-4. To draw any definitive conclusions a larger selection of samples should be tested.

4. Conclusions

The aim of this work was to provide an overview of outdoor beryllium levels in the UK. This involved sample preparation by acid digestion and subsequent ICP-MS analysis of airborne particulate matter (PM) sampled onto filter papers from the UK Heavy Metals Monitoring Network for the determination of trace level beryllium. The data produced was analysed to look for any relationship between observed levels and site location, and to compare the levels measured with a guideline level of 0.2 ng m$^{-3}$ published by the Expert Panel on Air Quality Standards (EPAQS, 2008).
An average beryllium concentration obtained from filter batches sampled over the sampling period was ascertained for each monitoring site on the network. All concentrations were significantly below the EPAQs guideline level of 0.2 ng m\(^{-3}\). The average concentration across the network for the duration of the study period was 7.87 pg m\(^{-3}\). The maximum average site concentration observed was 32.0 pg m\(^{-3}\) (0.032 ng m\(^{-3}\)) at Scunthorpe Low Santon.

While the ambient beryllium concentrations were low, there were still noticeable links between concentrations and site classification and location. The highest concentrations were observed at sites in the (Sub)urban Industrial classification. The top five concentrations were found at Scunthorpe Low Santon, Port Talbot; Bilston Lane, Walsall, Scunthorpe Town; and Sheffield Tinsley. All these sites are located to monitor specific industrial point sources of emissions that are known to use or produce metals or metal alloys (Goddard et al, 2015). Such industries have known applications for beryllium (Brookside Metals, 2016), so are most likely to be the sources of the elevated beryllium levels.

Concentrations of heavy metals in ambient air are not considered subject to significant seasonal variation (Goddard et al., 2015), therefore the average concentrations measured over the sampling period of three to five months should be considered strongly indicative of an annual average. Even so, it would be beneficial for potential future studies to analyse filters sampled over a longer time period to give greater confidence in the conclusions drawn and establish any longer-term trends.

The network site locations are chosen to be representative of site classification specifications (Goddard et al, 2015), not because high concentrations of beryllium are expected there. It is possible that a site located to monitor a confirmed source of beryllium emissions would yield higher concentrations than those observed from the existing network sites. Additionally, only two Urban traffic sites are included in the network site configuration. As road transport is known to contribute to a significant proportion of beryllium emissions (NAEI, 2016), and the roadside study in Birmingham, UK (Harrison et al., 2003) found daily concentrations from 0.01 – 0.15 ng m\(^{-3}\) (EPAQS, 2008), further monitoring at roadside locations would be advantageous to gain a better understanding of levels of beryllium emissions from transport.

The beryllium levels measured in the network samples were compared to levels of the other metals reported in the same samples to meet the requirements of the Heavy Metals Network, to ascertain if there were any correlations that could suggest shared point sources. The highest correlations found were with lead, manganese and vanadium (using the whole dataset) and iron (at the two Scunthorpe sites, monitoring the Tata iron and steelworks). Beryllium, manganese and lead are all emitted by the combustion of coal from industrial and domestic sources (NAEI, 2016). A significant proportion of beryllium and vanadium emissions are attributed to road transport combustion of DERV (diesel oil for road vehicles) from cars, LGVs and HGVs (NAEI, 2016). Beryllium emissions from iron and steelmaking processes comprise only 0.1 % of total UK emissions (NAEI, 2016), but locally this still produces significant beryllium concentrations.
The median beryllium concentration observed in this study was compared to estimated beryllium emissions (NAEI, 2016), to gain an insight into the nature of emissions sources. The ratio of concentrations: emissions yielded a value indicative of industrial point sources contributing the largest proportion of emissions. However the NAEI suggests the largest emission of beryllium are from diffuse traffic sources. Similarly to previous observations for vanadium (Brown, 2010) this indicates that emissions of beryllium may be overestimated by the NAEI, probably by at least an order of magnitude. These observations should only be considered indicative, as the only available concentrations from which to calculate a ratio were from the present study.

A selection of the UK Heavy Metals Network filters tested for total beryllium were also tested for water soluble beryllium species, as these are more easily absorbed into biological systems and therefore pose a significant health risk to humans and ecosystems (Williams et al., 2000). Conversely, insoluble or low-solubility beryllium containing particles that are inhaled can also cause adverse health effects as they are slowly solubilized over the course of many years (Maier, 2002).

All the water soluble beryllium results were below either the LOQ or both the LOQ and LOD, so on that basis it seems that no significant levels of water soluble beryllium were present in the samples tested. A correlation between concentrations of water soluble and total beryllium was apparent. Of the samples containing significant concentrations of total beryllium, the highest proportion of water soluble beryllium as a percentage of total beryllium was 30.9 %. To draw any definitive conclusions a larger selection of samples should be tested.

Overall, the low beryllium concentrations measured at the network sites gives reassurance that beryllium emissions are not likely to pose a significant problem for UK ambient air quality, even though the highest levels were measured at sites monitoring industrial point sources, suggesting a strong possibility that beryllium is being used at these facilities. Targeted monitoring at confirmed industrial point sources (especially coal-fired power stations) and roadside locations would be advantageous to establish potential hot-spots of beryllium emissions that would not have been apparent at the existing network sites.
Acknowledgements

The funding of the Heavy Metals air quality networks by the UK Department for Environment, Food and Rural Affairs, and the Optical, Gas and Particle Metrology Programme within the UK National Measurement System by the UK Department for Business, Innovation and Skills are gratefully acknowledged.
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