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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

39 1. Introduction

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

46 In Europe, a whole raft of legislation has been adopted in order to minimise population exposure to
47 airborne pollutants such as heavy metals (European Commission (EC), 2015). European air quality
48 directives require member states to establish and maintain a system for monitoring concentrations
49 of heavy metals and other pollutants in ambient outdoor air (EC, 2015). The Air Quality Directive
50 2008/50/EC specifies a target value for ambient concentrations of lead and the Fourth Daughter
51 Directive 2004/107/EC specifies limit values for nickel, arsenic and cadmium. In the UK this
52 monitoring requirement is met by the UK Heavy Metals Air Quality Monitoring Network, operated by
53 the National Physical Laboratory (NPL) on behalf of the Department for the Environment, Food and
54 Rural Affairs (Defra), and from 2016 Defra and the Environment Agency (EA). The network consists of
55 samplers located at 25 different sites around the UK that pump ambient air through cellulose acetate
56 filters and collect the particulate matter (PM₁₀ size fraction). The filters are then sent to the
57 laboratory at NPL, prepared by microwave digestion in acid, then analysed for heavy metals by
58 Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) (Goddard et al., 2015).

59 Beryllium is not one of the metals currently monitored by the UK Heavy Metals Network because
60 there is no existing legislative requirement for it in ambient air. However, the Expert Panel on Air
61 Quality Standards (EPAQS) produced a report for the Department for Environment, Food and Rural
62 Affairs (Defra) (EPAQs, 2008), the purpose of which was to provide guideline levels of priority
63 pollutants, including beryllium, in ambient air ‘at which no or minimal effects on human health are
64 likely to occur’. Beryllium poisoning has been documented in workers handling all insoluble
65 beryllium-containing materials. Short-term, high concentration exposure can result in acute
66 pneumonitis, whereas chronic beryllium disease (CBD) or ‘berylliosis’, a form of interstitial lung
67 disease, can arise after long-term exposure. Both conditions can be fatal. The guideline level given for
68 beryllium in the report was 0.2 ng m⁻³ total particulate in the PM₁₀ size fraction, as an annual average
69 (EPAQs, 2008).

70 The main sources of atmospheric airborne beryllium are anthropogenic: refineries, road traffic,
71 domestic and office heating, power stations and waste incinerators (which may be used for the
72 disposal of electrical items e.g. computers and mobile phones that contain beryllium) (EPAQs 2008).
73 Beryllium is also found in coal, therefore coal-fired power stations and coal slag used as an abrasive
74 in blasting paint will generate airborne beryllium (EPAQs 2008).

75

76 Beryllium is often used in alloys, particularly with copper or nickel, which are used for their high
77 strength and good electrical and thermal conductivities (Beryllium Science and Technology
78 Association, 2016). There are a wide variety of applications for copper-beryllium alloys, including
79 plastic injection and moulding inserts, springs and spring wiring, lightweight structural components
80 for the aerospace and defence industries, non-sparking tools for use in explosive environments,
81 electronic components (relays, switches, connectors), low wear bearings, automotive parts, and
82 telecommunications cables (Materion Corporation, 2015). Nickel-beryllium alloys are used in
83 mechanical and electrical springs that are required to work at high temperatures without deforming.
84 Applications include household oven controls, fire detection equipment, fire suppression sprinkler
85 systems, and in automotive engine and exhaust control systems (Beryllium Science and Technology
86 Association, 2016).

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

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

98 Figure 1 shows the UK emissions of beryllium from 1970 – 2013. In 1970 the total emissions were
99 0.043 kilotonnes, the majority of which was attributable to domestic combustion sources. By 2013,
100 road transport was the main contributory source to total emissions of 0.005 kilotonnes (NAEI, 2016).

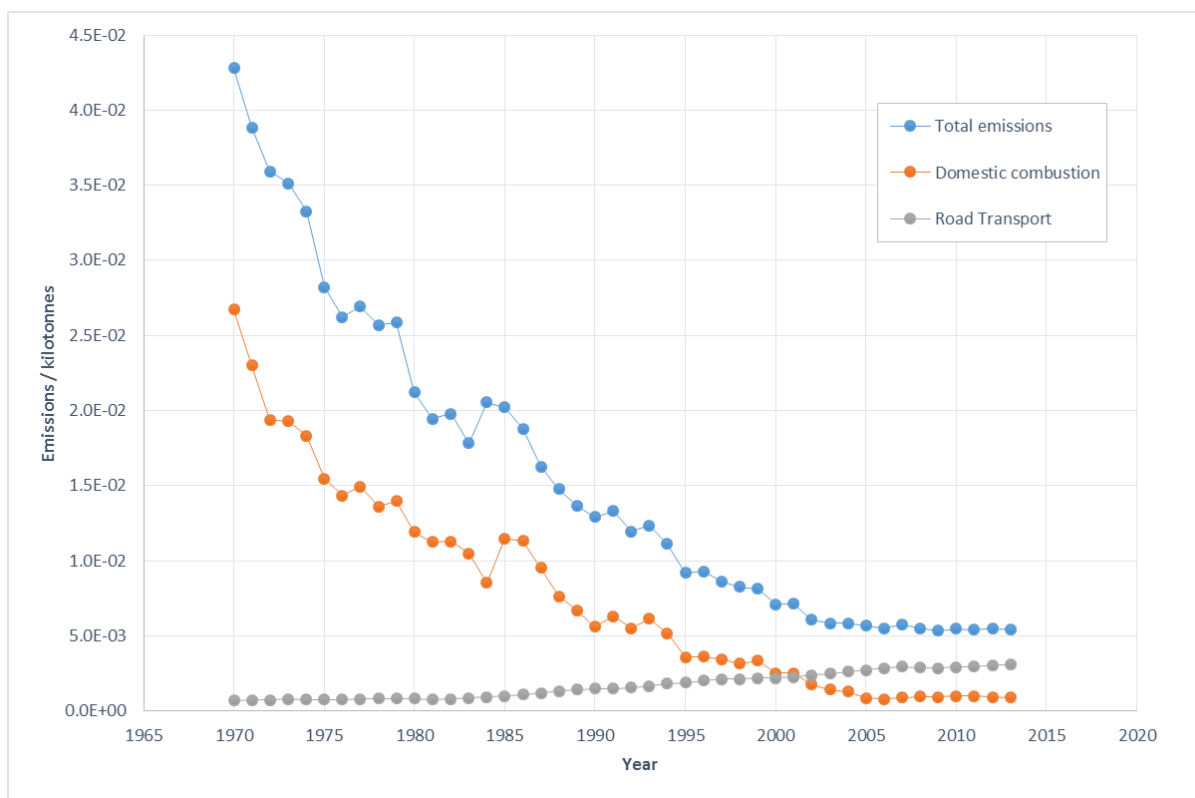


Figure 1: UK beryllium emissions 1970 – 2013 (NAEI, 2016).

101
102
103

104 The aim of this work is to analyse filter samples from the UK Heavy Metals Air Quality Monitoring
105 Network for the concentration of beryllium in PM₁₀, to establish levels across the UK in relation to the
106 EPAQs guideline level of 0.2 ng m⁻³.

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

118 2. Experimental section

119

120 2.1 Test samples

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

128 The filter samples tested were sourced from the UK Heavy Metals Monitoring Network. The network
129 filter samples consist of PM₁₀ from ambient air sampled onto cellulose ester filters (47 mm diameter,
130 0.8 μm pores, purchased from Pall Corporation). From each monitoring site, three to five months'
131 worth of filters were tested, sampled between March and July 2016. As concentrations of heavy
132 metals in ambient air are not subject to significant seasonal variation (Goddard et al., 2015),
133 concentrations measured over this substantial proportion of the year should yield average
134 concentrations strongly indicative of an annual average.

135

136 2.2 Sample preparation

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

143 The microwave program heated the samples to 220 °C for 60 minutes at up to 1400 W. The acids
144 used were 95 % H₂SO₄ (1 ml) and 70 % HNO₃ (10 ml) resulting in a matrix of 2 % H₂SO₄, 14 % HNO₃, as
145 recommended in studies by Ashley et al (2005), Brisson et al. (2006) and Oatts (2012). All
146 concentrated acids used were Analytical Reagent grade purchased from Fisher Scientific. Once
147 cooled, the digested solutions were transferred to a centrifuge tube and made up to 50 g in purified
148 water (18 M Ω quality, Elga Purelab Flex 2). The digested solutions of NIST 1944 were filtered prior to
149 analysis to remove particulate content. Cellulose filter papers of 90 mm diameter and 5-13 μm pores
150 (Fisher Scientific) were used.

151

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

154

155 2.3 ICP-MS analysis

156

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

159 A quality assurance (QA) solution containing a mid-range concentration of beryllium was repeatedly
160 analysed throughout the analytical sequence. The responses were plotted and the equation of the
161 polynomial line fitted was used to correct the responses of the calibration standards and samples for
162 drift, as in previous work (Brown et al., 2008). The stock beryllium solution, Be 1000 $\mu\text{g ml}^{-1}$, was
163 sourced from Metlab Supplies.

164 The ICP-MS was calibrated by direct analysis of external calibration standards containing known
165 concentrations of beryllium, traceable to the NIST SRM 3100 series of mono-elemental solutions
166 (stock solution, Be 1000 $\mu\text{g ml}^{-1}$, sourced from Metlab Supplies). Calibration curves were generated
167 from the measured responses of the calibration standards and used to interpolate the sample
168 concentrations using NPL's XLGenline software which performs generalised least squares regression
169 (Smith, 2010). The calibration range encompassed the measured sample concentrations. The
170 calibration standards were prepared in a matrix of 2 % H_2SO_4 , 14 % HNO_3 . All measurements were
171 blank corrected with the appropriate matrix blank.

172

173 2.4 Water soluble beryllium

174 Metals such as beryllium pose a significant health risk to humans and ecosystems if they are present
175 in a water soluble form, as they are more easily absorbed into biological systems (Williams et al.,
176 2000). However, insoluble or low-solubility beryllium containing particles that are inhaled can be
177 transferred to the lymph nodes or pulmonary intersitium, where they can be retained for many years
178 until they are slowly solubilized, resulting in adverse health effects (Maier, 2002).

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

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

186 After sonication, the filter and any dislodged particulate matter were removed from the sample
187 solution by filtration. The initial filtration was carried out using a 90 mm diameter cellulose filter
188 paper, pore size 5-13 μm (Fisher Scientific). The filtrate was then made up to 50 g with 2 % H_2SO_4 , 14
189 % HNO_3 acid matrix. The resulting solutions still contained some particulate matter, so they were
190 filtered again through 25 mm polypropylene membrane syringe filters, pore size 0.2 μm (VWR

191 International). These solutions were then analysed by ICP-MS and the data processed in the same
192 way as the acid digests for total beryllium.

193

194 3. Results and Discussion

195

196 3.1 Certified reference materials (CRMs)

197

198 The recoveries reported in Table 1 were obtained with the microwave program specified in section
199 2.2, using a 2 % H₂SO₄, 14 % HNO₃ acid matrix.

200

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

201 **Table 1:** Recoveries of NIST 1944 and Filter CRMs (with certified/reference values in brackets)
202 digested in 2 % H₂SO₄, 14 % HNO₃. The recovery uncertainties are quoted to *k*=2.

203 * denotes the beryllium mass fraction in NIST 1944 is supplied as a reference value only.

204

205

206 3.2 Limits of Detection and Quantitation

207

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

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

213 Calculation of the method LOD:

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

214

215 LOD_m = method LOD in (pg m⁻³);

216 LOD_I = instrumental LOD in (pg g⁻¹);

217 m_{SS} = mass of sample solution (g);

218 F_p = filter portion (i.e. 1, as whole filters were used for this test);

219 V_{air} = a typical volume of sampled air (m³) (i.e. 168 m³ for a typical weekly sample collected at 16.7 L
220 min⁻¹).

221

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

226

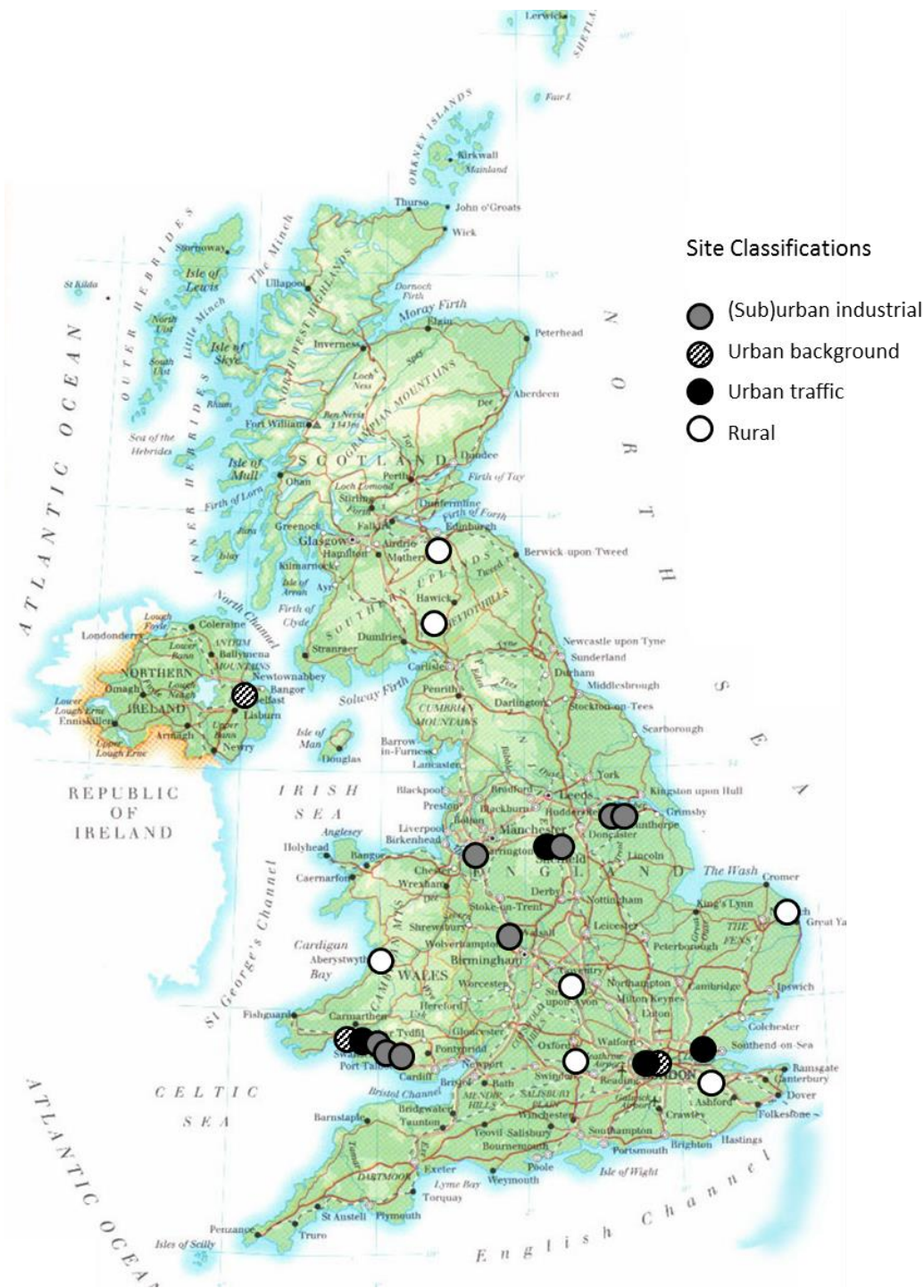
	Instrumental pg g⁻¹	Overall Method pg m⁻³
LOD	3.46	1.13
LOQ	11.54	3.78

227 **Table 2:** Instrumental and Overall Method Limits of Detection and Quantitation (LOD and LOQ)

228

229 3.3 UK Heavy Metals Monitoring Network filter samples

230
231 Metals network filter samples from every site on the UK Heavy Metals Network (see Fig. 2) were
232 tested for beryllium (Be) content. The network site composition shown in Fig. 2 was correct for the
233 sampling period in 2015.



234
235 **Figure 2:** Locations and classifications of monitoring sites on the UK Heavy Metals Network
236 (Goddard et al., 2015).
237

238 The monitoring sites are classified according to their location in terms of description of the
239 surrounding area and immediate proximity to pollution emission sources as specified in Council
240 Directive 2008/50/EC and UK guidelines (Defra, 2015).

241 From each monitoring site, three to five months' worth of filters were tested. The average ambient
242 concentrations of beryllium measured at all the sites are shown in Table 3.
243

Site Number	Site Name	Site Classification	Average beryllium concentration pg m ⁻³	Uncertainty (k=2) pg m ⁻³	Relative Uncertainty (%)
59	ICI Weston Point	(Sub)urban Industrial	5.99	1.53	26
69	Bilston Lane, Walsall	(Sub)urban Industrial	17.6	3.38	19
104	Port Talbot	(Sub)urban Industrial	19.0	1.81	10
106	Scunthorpe Town	(Sub)urban Industrial	11.1	1.52	14
107	Scunthorpe Low Santon	(Sub)urban Industrial	32.0	2.38	7
113	Pontardawe Tawe Terrace	(Sub)urban Industrial	3.95	2.64	67
117	Sheffield Tinsley	(Sub)urban Industrial	9.32	2.93	31
118 [#]	Sandvik Neath	(Sub)urban Industrial	7.81	2.63	34
201 [#]	Pontardawe Leisure Centre	(Sub)urban Industrial	8.85	2.97	34
62	London Westminster	Urban Background	7.25	1.38	19

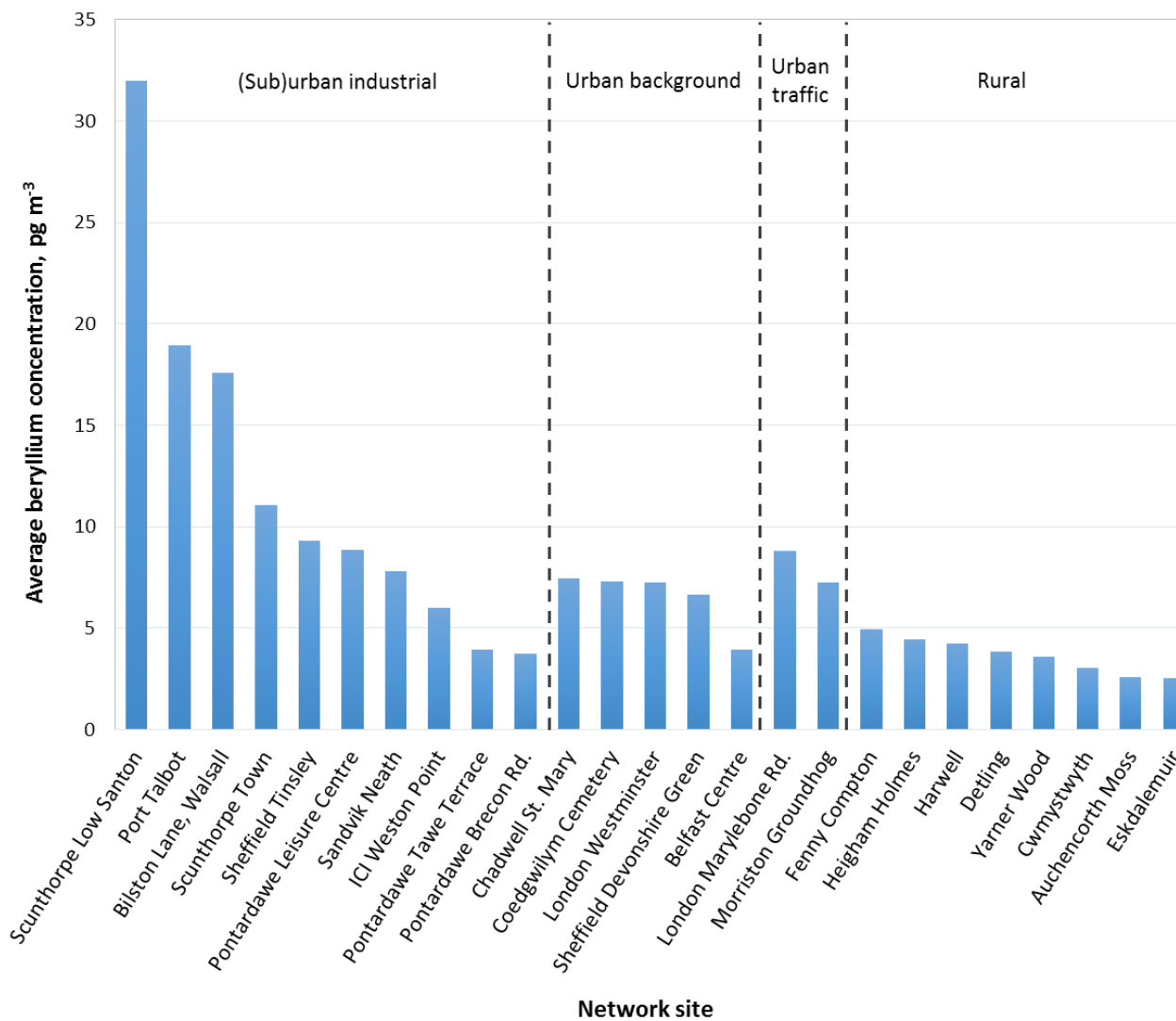
100	Swansea Coedgwilym	Urban Background	7.31	2.79	38
103	Belfast Centre	Urban Background	3.91	1.25	32
110	Chadwell St. Mary	Urban Background	7.43	1.61	22
119	Sheffield Devonshire Green	Urban Background	6.65	1.54	23
101	Swansea Morriston	Urban Traffic	7.26	2.72	38
114	London Marylebone Road	Urban Traffic	8.77	1.87	21
115	Pontardawe Brecon Road	Industrial Suburban	3.71*	2.40	65
65	Eskdalemuir	Rural	2.52*	1.39	55
202	Auchencorth Moss	Rural	2.55*	1.45	57
203	Yarner Wood	Rural	3.57*	1.43	40
204	Cwmystwyth	Rural	3.03*	1.40	46
205	Harwell	Rural	4.21	1.48	35
206	Heigham Holmes	Rural	4.42	1.50	34
208	Detling	Rural	3.81	1.44	38
209	Fenny Compton	Rural	4.92	1.24	25
Network Average			7.87	1.95	33

245

Table 3: Average ambient concentrations of beryllium based on analysis of 3 -5 months' worth of filters at each network monitoring site.

246 # The sites at Sandvik, Neath and Pontardawe Leisure Centre are operated independently of the network by Neath Port Talbot County Borough Council.
247 * 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).
248

249 Distinct differences can be seen between results from sites of different classifications, see Fig. 3.



250
251

Figure 3: Ambient concentrations of beryllium at each network monitoring site with site classifications indicated.

252
253 It is clear from Fig. 3 that the highest concentrations of beryllium were found at sites in the Urban
254 Industrial classification. These sites are located in urban areas exposed to industrial point sources
255 (Goddard et al., 2015). The difference between beryllium levels observed at Urban Industrial sites
256 and sites of other classifications suggests that some of the industrial point sources are producing
257 incrementally higher emissions of beryllium than in purely urban locations. Road traffic contributes a
258 significant source of beryllium emissions from combustion of DERV (diesel oil for road vehicles) from
259 cars, LGVs and HGVs (NAEI, 2016), and is used in automotive components (Beryllium Science and
260 Technology Association, 2016) which explains why the levels at Urban Traffic sites are higher than
261 levels at Rural sites. The only Industrial Suburban site, Pontardawe Brecon Rd., is located downwind
262 of a point source, hence the levels slightly above the Rural baseline. As would be expected, the
263 lowest concentrations of beryllium were measured at Rural sites.

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

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

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

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

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

282 While the levels found at these sites are the highest observed in this study, the averages are still
283 significantly below the EPAQs guideline level of 0.2 ng m⁻³ (EPAQs, 2008). The averages at all

284 stations are an order of magnitude below the EPAQs guidelines with the exception of Scunthorpe
 285 Low Santon, where the average is six times less than the guideline.

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

Site Classification	Average beryllium concentration / pg m^{-3}	Approximate increment according to site type / pg m^{-3}
Rural	3.6	-
Urban Background	6.5	2.9
Urban Traffic	8.0	1.5
(Sub)urban Industrial	11.9*	3.9*

289 **Table 4:** Showing the average incremental changes observed between sites in different site
 290 classifications. *The concentrations measured in (Sub)urban industrial locations varied significantly,
 291 from 3.71 pg m^{-3} (comparable to rural sites) – 32.0 pg m^{-3} . Therefore the incremental change from
 292 concentrations found at Urban Traffic sites ranged considerably.
 293

294 The incremental concentration increases were calculated as shown below:

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

295 Where:

296 $[Be]^{UB}$ = average beryllium concentration found at urban background sites

297 $[Be]^R$ = average beryllium concentration found at rural sites

298 $I^{R:UB}$ = approximate incremental increase in beryllium concentration from rural to urban background
 299 sites

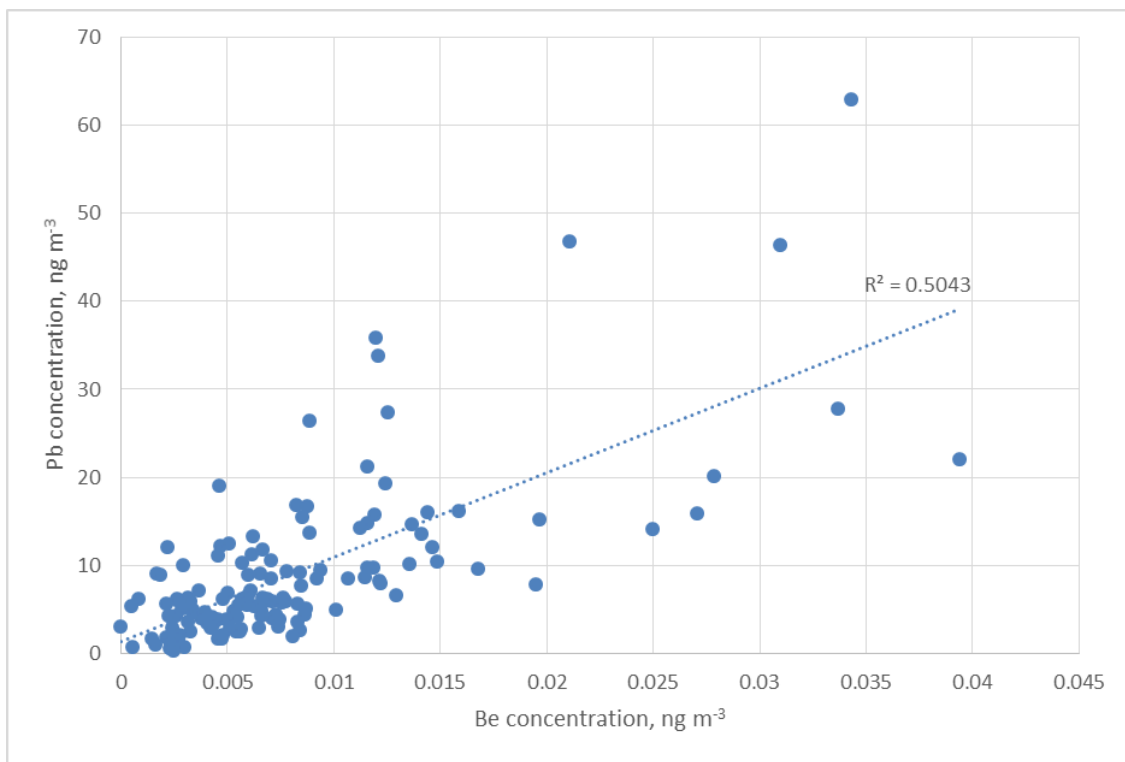
300 The increments for the other site classifications were calculated in the same way.

301

302 3.4 Correlation of Beryllium with other metals

303 The network samples are analysed for the following suite of heavy metals to meet the reporting
304 requirements of the Heavy Metals Network: vanadium (V), chromium (Cr), manganese (Mn), iron (Fe)
305 cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), selenium (Se), cadmium (Cd) and lead (Pb)
306 (Goddard et al., 2015). The beryllium results obtained for the network samples were compared to the
307 results measured for the other metals to see if there were any correlations that could suggest shared
308 point sources. The datasets had outliers removed using Grubbs' test for statistical outliers (Grubbs,
309 1969) before the correlations were calculated.

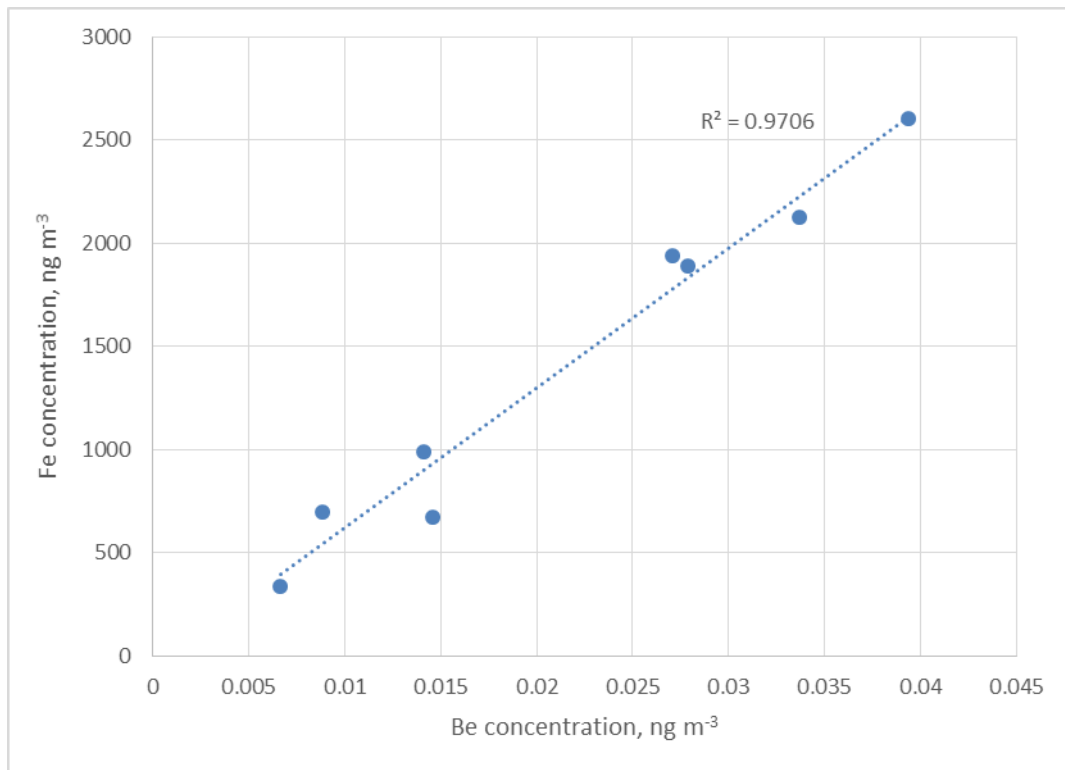
310 The highest correlation found using the whole dataset (outliers removed), although still not
311 particularly strong, was between the beryllium and lead results, giving an R^2 of 0.5043 (see Fig. 4).
312 Other high correlations were with manganese: 0.4653 and vanadium: 0.3911.



313
314 **Figure 4:** Correlation of results for beryllium (Be) and lead (Pb) measured in network samples.

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

321 At the two Scunthorpe monitoring sites, Scunthorpe Town and Scunthorpe Low Santon, a strong
322 correlation was observed between beryllium and iron, R^2 : 0.9706, see Figure 5 below.



323
324

Figure 5: Correlation of results for beryllium (Be) and iron (Fe) measured at the Scunthorpe sites.

325 The strength of this correlation should be viewed with caution, as it is only based on eight data
 326 points. Both Scunthorpe sites monitor the point source at Tata Steel, an iron and steelmaking
 327 production company (Tata Steel Europe Ltd, 2016). The four highest points were measured at
 328 Scunthorpe Low Santon, which is located nominally downwind of the point source (Goddard et al.,
 329 2015). Beryllium emissions from iron and steelmaking processes comprise only 0.1 % of total UK
 330 emissions (NAEI, 2016), but locally this still produces significant beryllium concentrations.

331

332 [3.5 Comparison of observed beryllium concentrations with emissions data](#)

333 A previous study (Brown, 2010) compared annual estimated emissions published on the NAEI
 334 website with measured levels of heavy metals in ambient air reported for the UK Heavy Metals
 335 Network by performing a generalized least squares regression analysis of measured concentrations of
 336 seven metals against their respective estimated emissions. This involved a large dataset with both
 337 concentration and emission values from 1980 – 2007. Measured concentrations in ng m⁻³ were
 338 plotted against emissions in Megagrams (Mg) for each metal, and the resulting slope gave an
 339 indication of the sensitivities of ambient concentrations to emissions. The study concluded that
 340 metals mainly emitted from diffuse sources (so would be observed at many network monitoring
 341 sites), e.g. transport, showed the highest sensitivities of ambient concentrations to emissions. Lead
 342 was calculated as the most sensitive to changes in emissions with a slope of 0.16. As the majority of
 343 monitoring sites have historically been located near roads, the reduction in emissions from leaded
 344 petrol will have had a significant impact on the measured ambient concentrations. Of the metals
 345 tested, chromium was calculated as the least sensitive to changes in emissions, with a slope of

346 0.0054. This was considered to be because the annual average concentrations were dominated by
347 emissions from a single point source, measured at just one monitoring site (Brown, 2010). Vanadium
348 was the next least sensitive with a slope of 0.015, and appeared to be an outlier when the proportion
349 of estimated transport-related emissions were plotted against the emission sensitivity ratio for each
350 metal. Vanadium had the second highest percentage of estimated transport emissions, yet the
351 second lowest emission sensitivity ratio. The study found that the NAEI had revised historical
352 vanadium emissions estimates downwards, which suggests overestimation of vanadium emissions
353 had previously been a problem (Brown, 2010).

354 For the current study, the median beryllium concentration in ng m^{-3} was ratioed against the total UK
355 beryllium emissions value in Megagrams (Mg) reported on the NAEI website (NAEI, 2016) for the year
356 2013 (the latest year for which data is available at time of publishing). The resulting ratio was:

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

357 This value is less than that calculated for chromium and vanadium in the previous study (Brown,
358 2010), so could imply that measured ambient beryllium concentrations are relatively insensitive to
359 changes in emissions, indicating a higher proportion of emissions from industrial point sources.
360 However, according to the NAEI (2016), DERV from road traffic constitutes the largest single
361 contributory source of beryllium emissions. This contradiction may indicate a similar issue to that
362 observed with vanadium in the previous study, of an overestimation of beryllium emissions,
363 particularly from transport sources. In support of this, Figure 2 shows that beryllium concentrations
364 were significantly higher at sites monitoring industrial point sources than diffuse traffic sources.

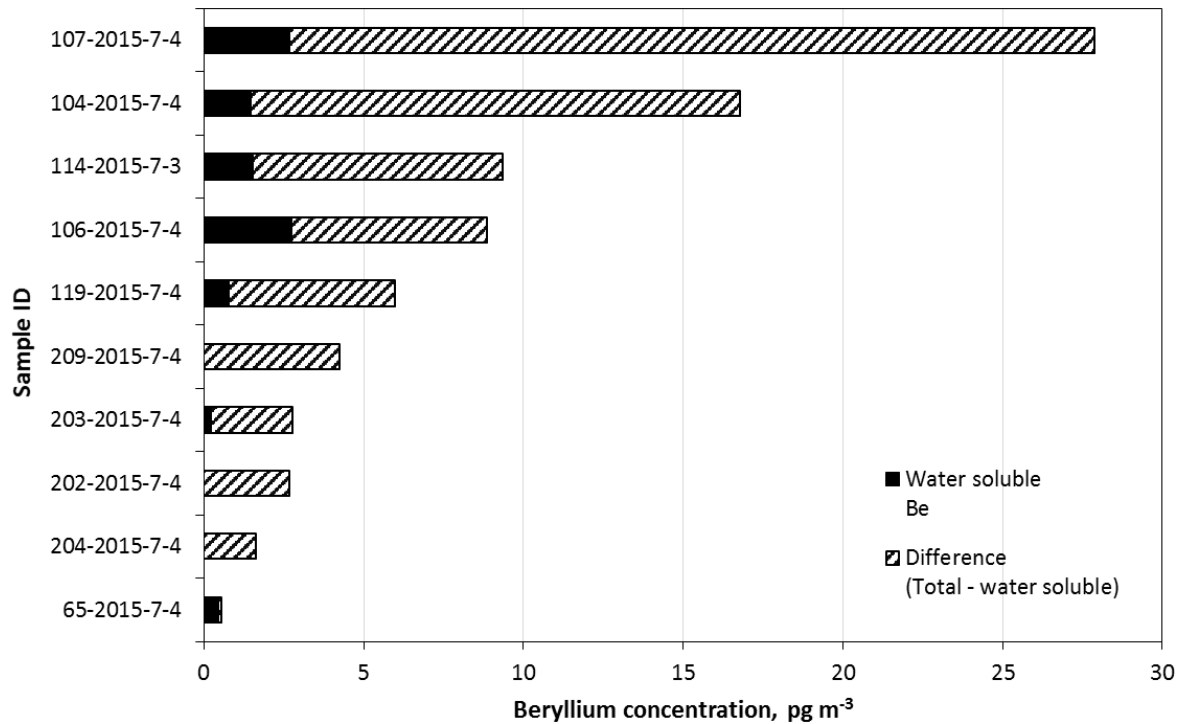
365 To draw more definitive conclusions a larger dataset of concentration: emission ratios over a longer
366 time period would clearly be preferable, but as the only available concentrations from which to
367 calculate a ratio were from the present study, that was a limiting factor. Nonetheless, the amount of
368 sub-data contributing to the single ratio calculated is substantial, which gives confidence that the
369 value generated is suitable for comparison with the ratios calculated in the previous study (Brown,
370 2010).

371

372 3.6 Water soluble beryllium

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

375 The indicative results obtained for water soluble beryllium are shown in Figure 6, along with the total
376 beryllium measured for the same sample for comparison. The sample IDs are in the format of: Site
377 number – Year sampled – Batch period of year sampled – Number of filters in batch. (Filters are
378 sampled weekly, then batched together into four-weekly batches for digestion and analysis. A year is
379 divided into 13 four weekly periods.)



380
381
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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.

384

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

392

393 4. Conclusions

394 The aim of this work was to provide an overview of outdoor beryllium levels in the UK. This involved
395 sample preparation by acid digestion and subsequent ICP-MS analysis of airborne particulate matter
396 (PM) sampled onto filter papers from the UK Heavy Metals Monitoring Network for the
397 determination of trace level beryllium. The data produced was analysed to look for any relationship
398 between observed levels and site location, and to compare the levels measured with a guideline level
399 of 0.2 ng m⁻³ published by the Expert Panel on Air Quality Standards (EPAQS, 2008).

400 An average beryllium concentration obtained from filter batches sampled over the sampling period
401 was ascertained for each monitoring site on the network. All concentrations were significantly below
402 the EPAQs guideline level of 0.2 ng m^{-3} . The average concentration across the network for the
403 duration of the study period was 7.87 pg m^{-3} . The maximum average site concentration observed was
404 32.0 pg m^{-3} (0.032 ng m^{-3}) at Scunthorpe Low Santon.

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

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

417 The network site locations are chosen to be representative of site classification specifications
418 (Goddard et al, 2015), not because high concentrations of beryllium are expected there. It is possible
419 that a site located to monitor a confirmed source of beryllium emissions would yield higher
420 concentrations than those observed from the existing network sites. Additionally, only two Urban
421 traffic sites are included in the network site configuration. As road transport is known to contribute
422 to a significant proportion of beryllium emissions (NAEI, 2016), and the roadside study in
423 Birmingham, UK (Harrison et al., 2003) found daily concentrations from $0.01 - 0.15 \text{ ng m}^{-3}$ (EPAQS,
424 2008), further monitoring at roadside locations would be advantageous to gain a better
425 understanding of levels of beryllium emissions from transport.

426 The beryllium levels measured in the network samples were compared to levels of the other metals
427 reported in the same samples to meet the requirements of the Heavy Metals Network, to ascertain if
428 there were any correlations that could suggest shared point sources. The highest correlations found
429 were with lead, manganese and vanadium (using the whole dataset) and iron (at the two Scunthorpe
430 sites, monitoring the Tata iron and steelworks). Beryllium, manganese and lead are all emitted by the
431 combustion of coal from industrial and domestic sources (NAEI, 2016). A significant proportion of
432 beryllium and vanadium emissions are attributed to road transport combustion of DERV (diesel oil for
433 road vehicles) from cars, LGVs and HGVs (NAEI, 2016). Beryllium emissions from iron and steelmaking
434 processes comprise only 0.1 % of total UK emissions (NAEI, 2016), but locally this still produces
435 significant beryllium concentrations.

436 The median beryllium concentration observed in this study was compared to estimated beryllium
437 emissions (NAEI, 2016), to gain an insight into the nature of emissions sources. The ratio of
438 concentrations: emissions yielded a value indicative of industrial point sources contributing the
439 largest proportion of emissions. However the NAEI suggests the largest emission of beryllium are
440 from diffuse traffic sources. Similarly to previous observations for vanadium (Brown, 2010) this
441 indicates that emissions of beryllium may be overestimated by the NAEI, probably by at least an
442 order of magnitude. These observations should only be considered indicative, as the only available
443 concentrations from which to calculate a ratio were from the present study.

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

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

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

462

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468

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