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1 Distribution of arsenic and risk assessment of activities on a golf course
2 fertilised with arsenic-containing *Ascophyllum nodosum* seaweed

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8

9 **Abstract**

10 The use of seaweed fertilisers in sports green maintenance has become a common practice
11 across the globe due to its image as an “eco-friendly” alternative to chemical fertilisers. The aim of
12 this study was to characterise the risk of human exposure to arsenic (As), via dermal absorption, from
13 golfing activities on a private golf course in the UK, where As contaminated seaweed fertiliser (~100
14 mg/kgd.wt.) is applied. This was fulfilled by, 1) determining As concentrations in shallow soils with
15 GIS geo-statistical analysis, 2) measuring As concentrations from an on-site borehole groundwater
16 well, and (3) developing a risk assessment calculation for golfing activities based on field and
17 questionnaire data. Total As concentrations in shallow soils were less than the UK threshold for
18 domestic soils, however, frequent and sustained dermal contact between site-users and surface soil
19 attributed to a maximum carcinogenic risk value of 2.75×10^{-4} , which is in the upper limit of the
20 acceptable risk range. Arsenic concentrations in underlying groundwater exceeded the WHO's
21 permissible drinking water standard, demonstrating the risk of groundwater contamination following
22 the application of seaweed fertiliser to golf course soils. This is the first risk study on dermal As
23 absorption via application of a seaweed fertiliser.

24 **Keywords**

25 Arsenic, seaweed fertiliser, golf course, soil, groundwater, risk characterisation.

27 **1.0 Introduction**

28 Arsenic (As) is present throughout the earth's ecosystems in low concentrations. It is
29 prevalent, however, in aquatic environments as a result of weathering of sub-aquatic rocks (Cai et al.
30 2002; Andrewes et al. 2004; Rose et al. 2007). It is primarily present as organometallic species, such
31 as arsenobetaine and arsenosugars (Ascar et al. 2008), which are naturally bioaccumulated by marine
32 products (i.e. seaweed) (Castlehouse et al. 2003; Hansen et al. 2003; Andrewes et al. 2004; Caumette
33 et al. 2007; Rose et al. 2007). Inorganic forms of As, such as arsenate, have also been found in
34 seaweed species (Castlehouse et al. 2003; Almela et al. 2006). Inorganic forms of As are considered
35 to be more toxic than organic forms because they are rapidly absorbed and retained by tissues in the
36 body (Agency for Toxic Substances and Disease Registry 2011). Up to 100 mg/kg dry weight (d.wt.)
37 of As has been observed in brown algae species (Castlehouse et al. 2003; Hansen et al. 2003).
38 Traditionally, seaweed has been used by rural communities as a fertiliser and soil conditioner for
39 many centuries (Castlehouse et al. 2003; Andrewes et al. 2004). In the past few decades, the demand
40 for seaweed fertilisers in horticulture, garden maintenance, sports greens and as animal feed has
41 increased across the globe due to its image as an "eco-friendly" resource (Castlehouse et al. 2003).

42 Arsenic is a known carcinogen (U.S. Environmental Protection Agency 1988) and has many
43 associated health effects. Acute exposure to As can cause vomiting, abdominal pain and associated
44 diarrhoea. Chronic exposure ranges from dermatological manifestations, such as skin lesions and
45 hyperkeratosis on the soles of feet and palms of hands, to cancer of the skin, lungs, kidneys and
46 bladder (Abernathy et al. 1999; Smith et al. 2002; Halder et al. 2013). Arsenic toxicity is heavily
47 dependent upon both its valence state and speciation (Cai et al. 2002; Macedo et al. 2009). Inorganic
48 As is generally more toxic than organic As, because it is rapidly absorbed and retained by tissues in
49 the body (Agency for Toxic Substances and Disease Registry 2011). Arsenosugars are organic and
50 not currently considered to be acutely toxic to humans (Castlehouse et al. 2003; Hansen et al. 2003).
51 However, it is now known that arsenosugars metabolise in the human body in a similar manner to that

52 of inorganic As forms. The organometallic forms reduce in the body (Castlehouse et al. 2003) to
53 dimethylarsinic acid, DMA(V), then to the trivalent DMA(III), which are excreted slowly (Hansen et
54 al. 2003). DMA(III) is more toxic than its pentavalent form, DMA (V); therefore, arsenosugars may
55 pose a risk if dermal absorption occurs(Castlehouse et al. 2003; Andrewes et al. 2004). There is a
56 high degree of ambiguity surrounding organometallic compounds and their associated risk of As
57 exposure. The Joint FAO/WHO Expert Committee on Food Additives recommended that further
58 investigation into the health risks posed by organometallic compounds in marine products was
59 necessary (Joint FAO/WHO Expert Committee on Food additives 2011).

60 Seaweed horticultural products are currently not subjected to any legislative restrictions within the
61 United Kingdom (UK), Europe or the US (I. Rowland, personal communication, 9th September 2010).
62 Additionally, little information on soils amended with seaweed exists in literature. However, results
63 mainly show that arsenosugars have a tendency to reduce to more toxic forms of As in a soil
64 environment in the few seaweed fertiliser studies that exist (Castlehouse et al. 2003; Andrewes et al.
65 2004; Feng et al. 2005). Therefore, their application in the environment may pose a risk. A
66 combination of increasing use of seaweed fertilisers in agriculture and horticulture, and the significant
67 lack of guidance and legislation could potentially expose many people to unknown toxic effects of
68 this marine product. The presence of As in golf course soils from seaweed fertiliser application has
69 not yet been studied. However, over the past few decades, As contamination of golf course soils due
70 to the use of As-based pesticides has become a topic of interest (Cai et al. 2002; Feng et al. 2005;
71 Pichler et al. 2008). In general, most studies of As based pesticide application to golf course soils
72 have observed As contamination of underlying groundwater (Cai et al. 2002; Feng et al. 2005). The
73 manufactured herbicide monosodium methyl arsenate (MSMA) for example, uses organic As species
74 as its active ingredient and has been observed to leave a residue in amended soils (Rahman et al.
75 2012). Although organic As is not toxic to humans, it can change speciation in soil environments to a
76 more toxic inorganic form following a series of chemical processes (Feng et al. 2005; U.S.
77 Environmental Protection Agency 2005, Zeng et al., 2011). Castlehouse et al. (2003) has reported that
78 arsenosugars present in seaweed fertilisers produce monomethylarsonic acid (MMA) and

79 dimethylarsinic acid (DMA) as degradation products in soil. However, detailed information on the
80 relative toxicity of MMA and DMA to humans is not available. For example, a total DMA value 700-
81 2600 mg/kg body weight has been reported as LD₅₀ (Le, 2001). Experimental results on relative
82 toxicity of DMA (III) and DMA (V) to rat cells have also been reported (Cohen et al., 2002, Arnold et
83 al., 2006, Hirano et al., 2004) in the order, MMA (III), DMA (III) > iAs(III) > iAs(V) > DMA(V),
84 MMA (V) , based on LC₅₀ values, where DMA (V) toxicity is lower than that of DMA (III) by a
85 factor of 10⁻³ to 10⁻⁴. This has also been supported by similar research data (Cohen et al., 2002).

86 The aim of this research was to calculate the risk of human exposure to As due to golfing
87 activities on a private golf course in the UK, where As-contaminated seaweed fertiliser (~100mg/kg d.
88 wt As) is applied regularly onto the greens and fairways. For this purpose, total As in the top soil was
89 considered for risk assessment. Since organic forms of As transform to inorganic forms of As over a
90 period of time, total As concentration as a basis of exposure risk would cover the worst case risk
91 scenario. This was fulfilled by 1) determining As concentrations in shallow soils with GIS
92 geostatistical analysis, 2) measuring As concentrations from an on-site borehole groundwater well,
93 which is used occasionally for irrigation and 3) developing a risk assessment calculation for golfing
94 activities on the golf course based on field and questionnaire data. To the best of the author's
95 knowledge, this is the first risk study regarding dermal absorption of As following application of a
96 liquid seaweed fertiliser.

97

98 **2.0 Materials and methods**

99 *2.1 Study site*

100 The private golf club is situated in the UK. The golf course covers a total area of 335 000 m²
101 and is bordered by public woodlands and a densely populated residential area. The golf course is
102 approximately 30 years old and was built on a section of a large estate that was used for grazing.
103 Much of the course has been top-dressed with sand that was dredged, dried and imported from a
104 nearby lake. The site is underlain by an aquifer, which yields high to moderate flows. An on-site

105 borehole well (total depth 95m) is used to irrigate the grounds at times of low precipitation. A
106 previous survey conducted across the UK showed that surface soil at the study site had an elevated As
107 content (~40 mg/kg), which exceeds the 20 mg/kg threshold for As in domestic soils in the UK
108 (Environment Agency 2009). It was deduced that the source of As at this site was a result of applying
109 a liquid seaweed fertiliser to the soil for the past five years.

110 *Ascophyllum nodosum*, commonly known as knotted wrack, is a brown macro-algae sourced
111 from the coasts of the North Atlantic Ocean. The liquid seaweed fertiliser, from the knotted wrack,
112 has been produced by methods that retain the natural form of the plant. ICP analysis confirmed that
113 the seaweed fertiliser had a total As (tAs) concentration ranging between 43 and 92 mg/kgd.wt., 6 to
114 10 mg/kg wet weight (w.wt.). The fertiliser has been applied three times a month over a five year
115 period to both fairways and greens, referred to as fertilised areas (FA), which make-up 30% of the
116 total site area. Over the five year period, on-site golfing activity has continued during the spraying of
117 this fertiliser onto the golf course surface.

118 The fertilised areas consist solely of grass turf, therefore, vegetation interception is minimal
119 (Cai et al. 2002). Non-manicured grass turf and densely vegetated areas, which are dispersed across
120 the golf course, are referred to as non-fertilised areas (NFA) in this study. In order to prevent water
121 logged conditions, the fertilised areas are mechanically aerated on a weekly basis. On-site golfing
122 activity is primarily dependent upon the local climate and time of year. However, golfing activity
123 increases during the summer months when the weather is generally drier and the days are longer.
124 Additionally, application of the seaweed fertiliser is also at its maximum during the summer months.
125 On average, 200 individuals visit the golf course on a daily basis, and a typical golfing session lasts
126 4.5 hours over 18-holes. Most of the golfers are retired locals and visit the course on a daily basis. A
127 conceptual model depicting the source of As contamination on-site, respective receptors, and potential
128 pathways of exposure is shown in Fig. 1.

129

130 *2.2 Soil and groundwater sampling and analysis*

131 A total of 248 surface (0-10 cm) soil samples were collected with an auger from the FA (i.e.
132 fairways, tee-off zones and putting greens), and NFA (i.e. densely vegetated areas and the rough)
133 (Fig. 2) using a stratified sampling technique. Nine soil cores (0-24 cm) were collected along three
134 individual transects (A, B and C) located on a gradient that ran across both FA and NFA, in order to
135 determine As concentrations at shallow depths. Each core was divided into four segments at depths
136 of; 0-6 cm, 6-12 cm, 12-18 cm and 18-24 cm. Each transect was orientated from higher to lower
137 elevation, with the first sampling point located up-gradient of the other two. The sampling points
138 along the transects were located 10 m apart. This method was repeated along the three transects to
139 identify whether leaching is occurring across the golf course. All sampling locations were geo-
140 referenced with a GPS unit. Duplicates were collected from every 5th sampling location for data
141 quality purposes. Soil samples were analysed for tAs by ICP-OES after microwave digestion in 10 ml
142 of HNO₃ for 15 minutes, followed by filtering through a 0.45 µm filter. Calibration with reference
143 samples and blanks, and replicate analysis for quality control were carried-out to ensure reliability of
144 analytical data. Fifty soil samples were randomly selected for particle size analysis by a Malvern
145 Particle Sizer, and categorised by percentage weight according to Wentworth (1922).

146 Three groundwater samples were collected from an on-site borehole fitted with a submersible
147 pump. The pump was run prior to sampling to ensure that the water sample was taken directly from
148 the aquifer, and that the oxygen concentration reached a stable value (Buschmann et al. 2007). Each
149 groundwater sample was collected in an acid-washed 500ml glass bottle, which was rinsed with the
150 groundwater thoroughly before sampling (Buschmann et al. 2007). Samples were acidified to a pH of
151 less than 2 with 1% concentrated HNO₃ (Signes et al. 2008) before analysis by ICP-OES.

152 *2.3 Spatial analysis using GIS*

153 Sampling locations were plotted within the study site, and a geochemical map depicting As
154 distribution in surface soils was generated using a GIS software (ArcMap 10). Inverse distance
155 weighting (IDW) was used to examine the distribution of As in the golf course surface soil, as it is a
156 quick and effective method of initially identifying the spatial pattern of a variable across a

157 geographical interface (Lee et al. 2006; Zhou et al. 2007; Qiao et al. 2011; Appleton and Adlam 2012;
158 Chabukdhara and Nema 2013). Using ArcMap10, the geochemical map obtained was overlain with a
159 polygon depicting the outline of the golf course and 1m interval elevation contours. IDW provided
160 the general expected distribution of As on the golf course (Fig. 2).

161 *2.4 Risk characterisation*

162 Table 2 describes the methodology used to characterise the potential on-site carcinogenic risk
163 through the pathway of dermal absorption of As-contaminated soil. Field and laboratory analysis
164 provided a range of values for the tAs concentration in golf course soils (C). Out of 80 questionnaires
165 distributed to the golfers at the club, information regarding golfer's habits on the golf course was
166 obtained from 42 closed questionnaire responses. The responses provided a range of values for the
167 following input parameters (1) exposed body parts (SA), (2) daily contact frequency with grass and
168 soil (EV), (3) yearly exposure frequency (EF), and (4) lifetime exposure duration (ED). Monte Carlo
169 simulation was used to account for the natural uncertainty and variability within a risk assessment.
170 The method derived a set of possible outputs for the site specific exposure parameters, described
171 above, that were observed to have a range of values (Table 2). It was observed that a frequency plot
172 of the exposure time was distributed normally with finite values of minimum and maximum expected
173 exposure times (t_{\min} and t_{\max}). Following this observation, the normal distribution was approximated
174 by a uniform distribution using the method outlined by Sen Gupta and Dutta (1990). Therefore, the
175 relevant equations can be expressed as follows:

176 Exposure time t_i is given by,

$$177 f(t_i) = [1 / \{\sigma_i \sqrt{2\pi}\}] \exp [-(t_i - T_i) / (2 \sigma_i^2)]$$

178 where the exposure time of the i th individual player is t_i and the mean of the distribution and the
179 standard deviation are given by T_i and σ_i , respectively.

180 By approximating the exposure time by a uniform distribution, the lower and upper exposure
181 limits are set to the observed minimum and maximum values for the dermal contact with the soil.
182 This approximation will give a more realistic exposure time history of any player i , within the set
183 limits of t_{\min} and t_{\max} . The approximation by a uniform distribution and the capping of the maximum

184 and the minimum exposure times for any player ensure that unrealistic high and low values of
185 exposure are eliminated from the set of random variates generated by the Monte Carlo simulation.
186 The observed normal distribution and the uniform distribution used for the simulation have identical
187 mean and variance values, such that:

$$188 \quad T_i = (t_{\max} + t_{\min}) / 2$$

$$189 \quad \sigma = (t_{\max} - t_{\min}) / 2\sqrt{3}$$

$$190 \quad t_{\max} = T_i + \sigma\sqrt{3}$$

$$191 \quad t_{\min} = T_i - \sigma\sqrt{3}$$

$$192 \quad t_i = t_{\max} + (t_{\max} - t_{\min}) \cdot \xi$$

193 where, t_i is the random dermal exposure time for the i th player and ξ is a random number such
194 that $0 < \xi < 1$.

195 Monte Carlo simulation was performed using the EasyFitXL add-in for Microsoft Office Excel
196 2007 and applied using the steps below:

197 i. Five hundred random number (RND#) iterations for each exposure input parameter were
198 generated using Microsoft Excel.

199 ii. A set of random variates (RND V) for the random variable t_i were calculated based on the
200 following equation;

$$201 \quad \text{RND V} = t_{\max} + (t_{\max} - t_{\min}) \cdot \xi$$

202 iii. The range of probable exposure input parameter values were then inputted into equation (ii)
203 to provide the possible range of ADI for individual site users of the golf course.

204 Input parameter values based on published data were used for the remainder of the model input values
205 (Table 2).

206 **3.0 Results and discussion**

207 *3.1 Distribution of As contamination on the golf course*

208 The tAs concentration of surface soil samples in the study site varied between 0.2 and 10.38
209 mg/kg, with a mean of 2.39 ± 2.14 mg/kg ($n=248$). This mean value is significantly lower than that

210 observed by the former soil survey and does not exceed the 32 mg/kg threshold for As in UK
211 domestic soils (Environment Agency 2009). Nevertheless, a seaweed fertiliser with As
212 concentrations ranging between 43 and 92 mg/kg is applied to the soil three times a month. Arsenic is
213 considered to be moderately mobile in sandy soils (Cai et al. 2002), implying that the contaminant is
214 either migrating laterally or percolating into underlying groundwater at this study site. Taking the
215 sample location into account, a significant difference ($P= 3.62E-7$) between mean As concentration in
216 FA ($n=193$) and NFA ($n=55$) was observed on-site, 3.63 and 2.04 mg/kg, respectively (Table 1). Soil
217 fractionation showed that the bulk of the FA soils comprised a sand particle size between 0.125 and 2
218 mm, while the NFA consisted of a mixture of clay and silt sized particles between 0.00006 and 0.125
219 mm (Fig. 3). Although all soil samples contained some fraction of clays, silts and sands, samples
220 collected from the FA were coarser in texture with a 70.7% sand size fraction. Also, most of these
221 sands were in the form of medium sand (32.2%). The NFA had a finer soil texture, where 75.3% of
222 grains were characterised as clays and silts (28.4% as clays) according to the Wentworth grain size
223 classification system (Wentworth 1922). Statistical analysis showed a correlation between As
224 concentration and sample location, where fine to coarse sands were negatively correlated with As, and
225 clays to very fine sands were positively correlated with As. This implies that As prefers sorption to
226 the finer-sized clay and silt particles, such as those found in NFA, compared to the coarser-sized sand
227 particles found in FA. Transect analysis confirms this observation. There is a clear sequential
228 increase in tAs concentration along transects A and B, which run down-gradient from a FA to NFA,
229 and a clear decrease in tAs concentration along transect C that runs down-gradient from a NFA to FA.
230 This suggests that the As present in FA, as a result of seaweed fertiliser application, is mobile and
231 subject to lateral transport as surface runoff. Generally, the IDW output supports these observations
232 (Fig. 2). IDW also indicated a west to east orientation of increasing As concentration in surface soils.
233 The results suggest lateral movement of As from the porous sandy fertilised greens and fairways to
234 the compacted clayey textured soil of the NFA. The NFA primarily consists of clayey textured soils
235 and organic matter. Arsenic is strongly adsorbed by fine grained clay particles (Cai et al. 2002;
236 Camm et al. 2004; Feng et al. 2005), which restrict its mobility, resulting in greater tAs
237 concentrations within clayey textured soils, such as those found in the NFA.

238 Castlehouse et al. (2003) reported the fate of arsenosugars present in the sandy soil fertilised with
239 seaweed in a coastal region. The analysis of the pore water in the fertilised soil showed DMA(V),
240 AS(V) and As(III). Hence, the authors proposed the pathway: arsenosugars → DMA(V) → As(V) →
241 As(III). Zeng et al. (2011) have reported the detailed pathway of degradation of arsenosugars to
242 inorganic arsenic in sediments and groundwater, which supports the degradation hypothesis of
243 Castlehouse et al. (2003).

244 However, Castlehouse et al. (2003) did not focus on relative adsorption or desorption of these arsenic
245 species, to or from soil. Shimizu et al (2011a) have reported that MMA sorption rate is higher than
246 DMA in soil. Al and Fe oxyhydroxides are the main adsorbents for MMA and DMA in the soil and
247 the sorption capacity is proportional to the Al and Fe concentration. The authors found varying
248 desorption rate from the soil, ranging from 77% in one day to 66% in 6 months. They also observed
249 that the retention period of MMA and DMA as sorption complexes with Fe-oxyhydroxides of soil
250 could be as high as one year during which these species react within the soil matrix to inorganic
251 forms. The main reason for the variation in time scale for transformation of the organic species to
252 inorganic species was the variation of Al and Fe concentration in the soil (Shimizu et al., 2011b). This
253 observation explains why the application of arsenic bearing seaweed fertilisers can increase the soil
254 arsenic level by 10 fold as reported by Castlehouse et al. (2003).

255 In order to examine the vertical transport of As on-site, three cores extending to the subsoil
256 layer were collected along three individual transects. Due to the nature of the land use, deeper cores
257 could not be sampled from the golf course. The results indicate increasing As concentration with
258 depth (Table 1). Within these areas, the golf club aerates the surface of the soil to avoid water-
259 logging of the FA, which promote a favourable environment for the leaching of mobile As. The
260 difference between the surface sample (0-6 cm) and the deepest sample (0-24 cm) was greatest when
261 the core was collected from a FA, with differences ranging between 0.63 and 1.72 mg/kg in FA and
262 0.04 to 0.96 mg/kg in NFA. The concentration of As in the deepest sample taken at P9 for example,
263 was approximately twice that of the surface sample (Table 1). This observation agrees with that of
264 Cai *et al.*, who found that As is mobile in golf course soils (Cai et al. 2002) and, As may be

265 percolating downwards. This observation is supported by groundwater analysis of the on-site
266 borehole, where two of the three samples collected were observed as having As concentration
267 exceeding the WHO permissible standard for As in water used for domestic purposes (10 µg/L)
268 (Smith et al. 2000), and a maximum As concentrations of 12.5 µg/L (Fig.1). It is not certain whether
269 the elevated As content is attributed to the natural geology or the application of seaweed fertiliser.
270 However, the groundwater underlying the golf course has between 3 and 12 times more As than that
271 previously observed in surrounding groundwater; thus, it is likely that the presence of As is a result of
272 seaweed fertiliser application and subsequent leaching at the study site, as previously observed in
273 similar studies following MSMA application (Di Carlo and Fuentes 2000; Cai et al. 2002; Feng et al.
274 2005; Chen et al. 2006). The results suggest, therefore, that As can be transported vertically in a golf
275 course profile following application of a seaweed fertiliser. Over the past few decades, elevated
276 concentrations of As have been observed in groundwater underlying golf course greens amended with
277 As-bearing fertilisers, pesticides and herbicides (FPHs), and this has become a significant topic of
278 scientific and environmental health interest (Cai et al. 2002; Feng et al. 2005; Chen et al. 2006;
279 Pichler et al. 2008). As previously discussed, the fertilised areas consist primarily of sand, which
280 have a high silica content (Cai et al. 2002; Bary et al. 2005; Chen et al. 2006). Arsenic is not easily
281 bound to silica, therefore, this type of environment can result in high leaching rates (Feng et al. 2005).
282 Feng *et al.* observed that golf course soils with high sand content and low clay content were
283 favourable for As mobility and subsequent leaching following application of an As-bearing FPH,
284 whereas soils with a higher clay content prevented the leaching of As, reducing the concentration of
285 As in underlying groundwater (Feng et al. 2005). Although the As-containing agricultural products
286 under investigation in these studies are prohibited in the UK, observation of their behaviour in the
287 environment may be applied to that of seaweed fertilisers, as they are primarily present in
288 organoarsenical form (Feng et al. 2005). Also, those arsenical FPHs discussed above are only applied
289 two to three times a year (Feng et al. 2005), whereas the seaweed fertiliser in this study is applied
290 three times per month (a 12-fold increase). Therefore, this practice may cause a greater legacy of
291 contamination.

292 *3.2 Risk assessment of activities on the golf course*

293 Although concentrations of As in the surface soils at the golf course did not exceed UK limits
294 for domestic soils (i.e. As \geq 32 mg/kg) (DEFRA and EA 2004), analysis has shown that there is a
295 positive relationship between As content and fine particle size, which are the fractions that readily
296 adhere to the skin (Ljung et al. 2006) and thus, can cross the dermis absorption barrier (Lim et al.
297 2008). Within a golf course context, golfers can come in to dermal contact with the soil and golf turf
298 through two primary scenarios; frequent non-gloved hand to turf and ball contact on FA and NFA and
299 leg to grass/soil contact when the golfer is looking for a ball in the rough whilst wearing shorts. The
300 latter would be more typical of novice golfers and in the summer months. Although the authors
301 acknowledge inhalation of fine dust particles as pathway for As exposure, the lesser studied potential
302 risk via dermal absorption of As in a golf course scenario was examined, where seaweed fertiliser was
303 applied. The purpose of this exercise was to establish a method that could be used in other
304 environments where seaweed fertiliser is applied, such as rugby and soccer pitches. On these types of
305 sports greens, the frequency and duration of contact and the degree of exposure is significantly greater
306 for the player than that of golfers. The carcinogenic risk of As exposure, through the pathway of
307 dermal absorption with contaminated soil, is based on the assumption that As is in a form that may
308 cause cancer (i.e. in an inorganic form) (Gerba 2000; Qiao et al. 2011). Although the form of As
309 present within the soil at the study site is unknown, a worst case scenario will be assumed as it has
310 been shown that the application of organoarsenicals on a golf course environment can initiate
311 reduction processes that produce several species of As, including inorganic forms (Cai et al. 2002;
312 Feng et al. 2005). Therefore, inorganic As may be present in surface soils on-site. A deterministic
313 risk method was used to calculate the best and worst case carcinogenic risk value for golfing
314 activities, based on the range of risk input parameter values (Table 2). This value was then compared
315 to a published reference value for As to determine whether the risk is acceptable or not (U.S.
316 Environmental Protection Agency 2004; Rose et al. 2007; Mondal and Polya 2008; Qiao et al. 2011).
317 There is some discrepancy regarding the acceptable risk value for As exposure. The USEPA suggests
318 that any risk value greater than 10^{-6} is unacceptable (U.S. Environmental Protection Agency 2004).

319 However, other studies use an acceptable risk range of 10^{-6} to 10^{-4} for similar environmental health
320 studies (Phaneuf et al. 1999; Zakharova et al. 2002; Lim et al. 2008; Mondal and Polya 2008; Liang et
321 al. 2011; Qiao et al. 2011; Hu et al. 2012), which indicate that within a population of one million, it is
322 acceptable for one out of every 10,000 people die from cancer induced from exposure to As (Lim et
323 al. 2008). The lack of an evidence based acceptable risk threshold is indicative of the lack of
324 knowledge surrounding As exposure across a wide range of environmental contexts. The high degree
325 of ambiguity has created a scenario where it is difficult to ascertain whether a particular exposure
326 scenario is hazardous or not. With respect to liquid seaweed fertilisers, the scenario has occurred
327 through uncertainty regarding the toxicity of organic As forms, the lack of epidemiological data on
328 the potential health effects of organic As, and the lack of cohesive legislation regarding the use of As
329 containing natural fertilisers.

330 In this study, the calculated risk of As exposure via dermal absorption was in the range of
331 2.20×10^{-9} to 2.75×10^{-4} . With respect to the USEPA threshold, the maximum risk value observed at
332 this site exceeds the threshold by two orders of magnitude, indicating that the risk of As exposure to
333 golfers at this study site is unacceptable. With regards to the risk range used in similar studies, the
334 results of the risk characterisation indicate that the maximum soil As concentrations and exposure
335 scenarios did not generate a carcinogenic lifetime risk that is higher than the acceptable risk level. It
336 did, however, produce a risk value that is at the limit of the accepted range. Therefore, future
337 increases in As soil content and event frequency may result in unacceptable exposure values. As
338 previously mentioned, this particular brand of liquid seaweed fertiliser is used on sports grounds and
339 home gardens. Within the scenarios, exposure time, frequency of contact with soil and the fraction of
340 body parts exposed may be significantly greater than that on a golf course. For example, within the
341 sport of rugby, the exposed body parts and the frequency of contact between the soil and the skin (i.e.
342 during scrums and tackles) would be significantly greater. Also, within these contexts, the soils on
343 these types of sporting greens primarily have finer textures consisting of clays and silts. Therefore,
344 they differ greatly from golf course soil. The As applied to the soil, via seaweed fertiliser application,
345 will absorb on to clay particles and may accumulate in the topsoil. This could, therefore, create a

346 scenario where the risk of dermal absorption of As is greater than that observed at this private golf
347 course.

348

349 **4.0 Conclusions and Recommendations**

350 The growing concern and publicity regarding As risk to human health, coupled with the
351 scarcity of published information on As-containing seaweed fertilisers, is the driving force behind this
352 study. The study found that application of seaweed fertiliser to golf course soils does not result in As
353 concentrations that exceed the UK threshold for As in domestic soils. Although UK limits are not
354 exceeded, it is still important to acknowledge the contact time and frequency of use between site users
355 and the soil in order to ascertain whether a risk is present. The results showed that the USEPA
356 acceptable risk level for dermal contact with As through a soil pathway was exceeded for this
357 particular study, despite low concentrations of As present in surface soils. In scenarios of more
358 frequent physical contact with soil, such as during rugby and soccer activities, the risk of exposure
359 may also be greater.

360 The results of this study revealed that As is present at concentrations of potential concern in
361 groundwater underlying the golf course. Although the groundwater is not used for domestic purposes,
362 the results of analysis indicate that there is a risk of groundwater contamination following seaweed
363 fertiliser application in a golf course setting. The greatest As concentration in the groundwater
364 samples was 12.5 µg/L, which exceeds the WHO guideline for As in drinking water. This indicates
365 that As contaminated seaweed fertiliser application to sandy golf soils can result in groundwater
366 contamination. The use of As-containing seaweed fertiliser, therefore, may contribute to the arsenic
367 burden of the environment and as such increase the probability of human exposure to As (Chen et al.
368 2006).

369 This is, to our knowledge, the first study concerned with identifying the presence of As on
370 golf course soils following seaweed fertiliser application. This study suggests that seaweed fertilisers
371 should be used with caution, especially in areas that are underlain by a groundwater source, and in

372 environments where dermal contact with the soil is common (i.e. rugby pitches). This is a pilot study;
373 therefore, further research is required across the various environments where seaweed fertilisers may
374 be used. The study also recommends that a speciation study be conducted within these various
375 environments, and an in depth column study be conducted to assess the fate and transport of As within
376 the various profiles where seaweed fertiliser is applied.

377

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380

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547

Table 1: Total As concentrations (tAs, mg/kg) according to grass cover type and core soil concentrations along each transect and at various depths

Surface Soil Samples									
	n (no of samples)	Mean (mg/kg)	Std error (mg/kg)	Min (mg/kg)	Max (mg/kg)				
FA (all)	193	2.04	0.14	0.2	10.38				
Fairways	139	2.38	0.18	0.2	10.38				
Putting greens	54	1.36	0.17	0.2	5.69				
NFA (all)	55	3.63	0.34	0.2	8.97				
The rough	23	3.37	0.57	0.2	8.97				
Dense vegetation	32	3.81	0.41	0.2	7.77				
Whole golf course	248	2.39	0.14	0.2	10.38				
Core Soil Samples									
Depth, cm	A (FA to NFA) mg/kg			B (FA to NFA) mg/kg			C (NFA to FA) mg/kg		
0-6	3.94	6.79	8.97	2.11	2.67	4.14	5.13	4.75	1.93
6-12	3.34	4.88	8.96	2.37	2.71	4.36	5.01	4.96	2.14
12-18	4.00	5.95	8.97	2.98	3.01	4.78	5.56	5.18	4.36
18-24	4.57	6.94	9.01	3.25	3.96	5.10	5.82	5.49	3.65

548

Table 2. Risk Characterisation Methodology

References for equation: (1) USEPA (2004) and Qiao *et al.* (2011), (2) USEPA (2004). ¹SA was calculated by adding the body-part specific SA calculations for adults as described by USEPA (2004). The lower range body parts included; forearms, hands and neck, whilst the upper range also included lower legs.

$$\text{Risk} = \text{ADI} \times \text{SF} \quad (1)$$

$$\text{Where ADI} = \frac{\text{C} \times \text{AF} \times \text{ABS} \times \text{CF} \times \text{SA} \times \text{EV} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \quad (2)$$

Exposure parameter	Description	Value	Source
Risk	The probability of an individual developing cancer over a lifetime		Site specific
ADI (mgkg ⁻¹ -day)	Absorbed Daily Intake		Site specific
SF (mgkg ⁻¹ -day) ⁻¹	Absorbed Cancer Slope Factor	3.66	RAIS (2013)
C (mgkg ⁻¹)	Concentration of As in soil	0.2 – 10.38	Site specific
AF (mgcm ⁻²)	Resident Soil Adherence Factor	0.07-0.1	USEPA (2004) Qiao <i>et al.</i> (2011)
ABS	Absorption Factor for As	0.03	USEPA (2004)
CF (kgmg ⁻¹)	Conversion Factor	10 ⁻⁶	USEPA (2004)
SA ¹ (cm ²)	Available Exposed Surface Area	2733 - 5293	Site specific USEPA (2004)
EV (eventsday ⁻¹)	Event Frequency	18-108	Site specific
EF (daysyr ⁻¹)	Exposure Frequency	0-260	Site specific
ED (yrs)	Exposure Duration	1-29	Site specific
BW (kg)	Body Weight	70	USEPA (2004) Qiao <i>et al.</i> (2011)
AT (daysyr ⁻¹)	Averaging Lifetime for Carcinogens	25 550	ATSDR (2005)

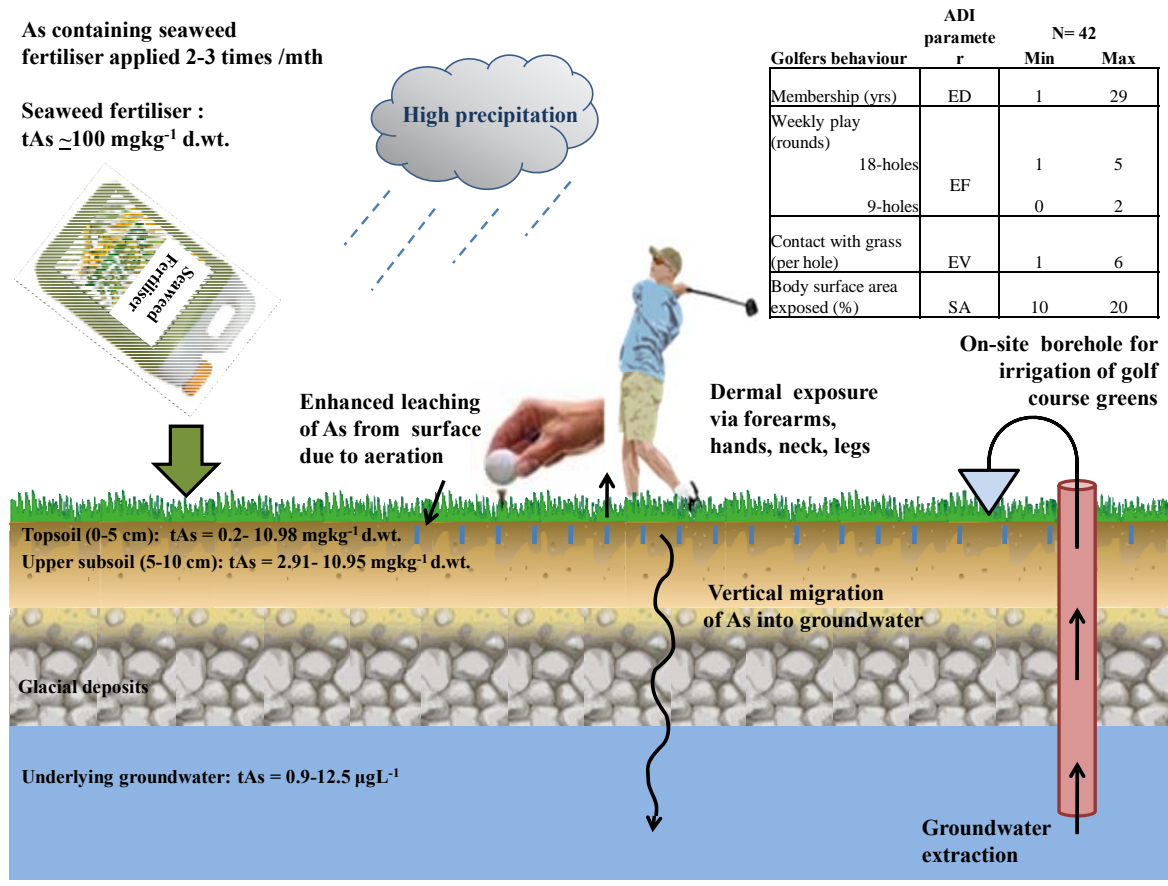


Fig. 1. Refined conceptual model identifying the two pathways of concern with respect to As contamination; dermal absorption via contact with soil and groundwater contamination via leaching. ¹Golfing statistics are based on 42 closed questionnaire responses acquired out of 80 from members of the private golf club under study.

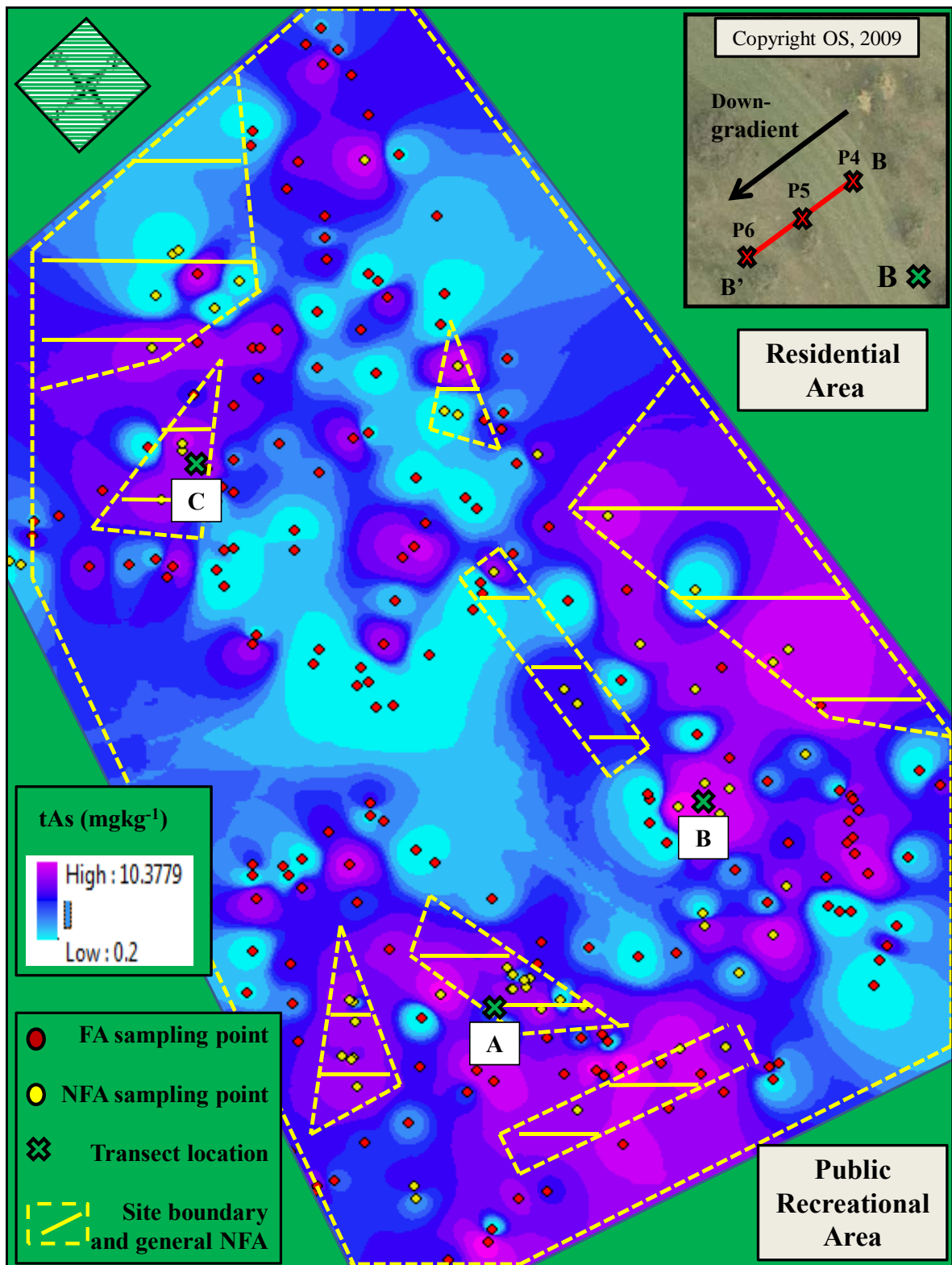


Fig. 2. Geochemical map of tAs concentration in the surface soils by IDW. Sampling locations, type of grass cover and an example of transect orientation are also provided.

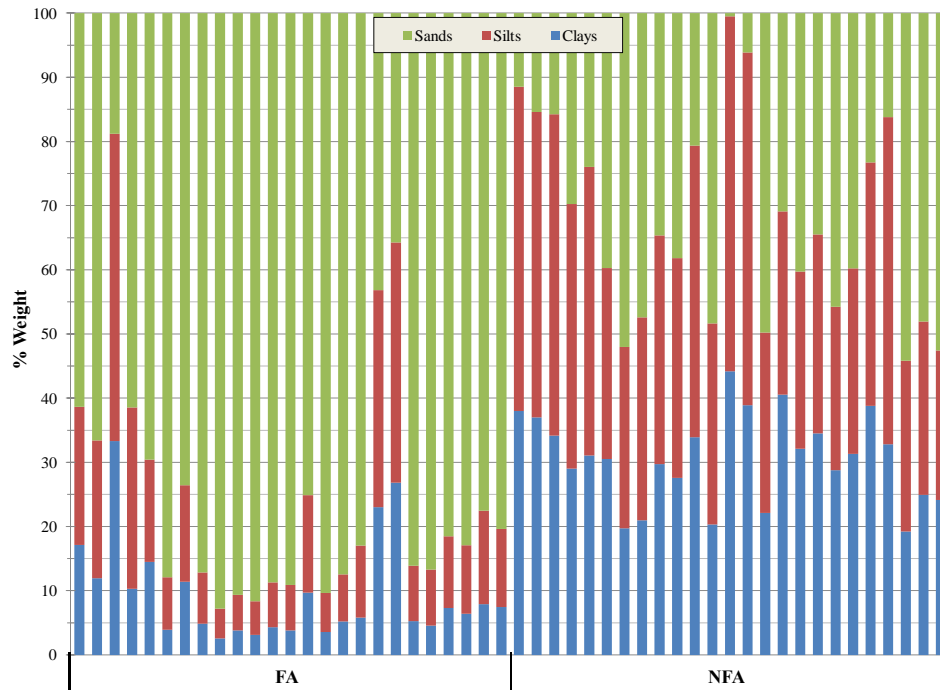


Fig. 3. Soil particle size distribution (%) in 50 samples collected from fertilised areas (FA) and non-fertilised areas (NFA) at the study site.