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1 **Combining measurements and modelling to quantify**
2 **the contribution of atmospheric fallout, local industry**
3 **and road traffic to PAH stocks in contrasting**
4 **catchments**

5
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8
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14
15 **Abstract**

16 Various sources supply PAHs that accumulate in soils. The methodology we developed
17 provided an evaluation of the contribution of local sources (road traffic, local industries) versus
18 remote sources (long range atmospheric transport, fallout and gaseous exchanges) to PAH
19 stocks in two contrasting subcatchments (46-614 km²) of the Seine River basin (France). Soil
20 samples (n=336) were analysed to investigate the spatial pattern of soil contamination across the
21 catchments and an original combination with radionuclide measurements provided new insights
22 into the evolution of the contamination with depth. Relationships between PAH concentrations
23 and the distance to the potential sources were modelled. Despite both subcatchments are mainly
24 rural, roadside areas appeared to concentrate 20% of the contamination inside the catchment
25 while a local industry was found to be responsible for up to 30% of the stocks. Those results

26 have important implications for understanding and controlling PAH contamination in rural areas
27 of early-industrialized regions.

28

29 **Keywords:** PAHs; soil; source contribution; spatial variation; model

30

31 **Capsule:** Source contributions to PAH soil contamination were investigated with distance-
32 based models.

33

34 1. Introduction

35 Polycyclic Aromatic Hydrocarbons (PAHs) are widespread organic contaminants that are
36 well known for their mutagenic or carcinogenic properties, and therefore represent a risk to the
37 ecosystems and the human health (Grimmer et al., 1991; Nielsen et al., 1996; Tsai et al., 1995).
38 They are mainly emitted during the incomplete combustion of fossil fuels or biomass (Wild and
39 Jones, 1995) and they can be disseminated across large regions from their initial source through
40 long-range atmospheric transport (LRT) (Sehili and Lammel, 2007). They are ubiquitous in the
41 environment, but their concentrations were reported to be much higher in soils located in the
42 vicinity of urban or industrialized areas as well as in atmospheric fallout collected in those areas
43 (Wilcke, 2000). As in most early industrialized countries, the PAH issue is particularly
44 problematic in the Seine River basin, in France, where excessive concentrations in Polycyclic
45 Aromatic Hydrocarbons (PAHs) are reported in sediment (AESN, 2010), thereby compromising
46 the achievement of the good chemical status required by the European Union (Water
47 Framework Directive 2000/60/EC). In their study modelling PAH long-range transportation at
48 the worldwide scale, Sehili and Lammel (2007) concluded that 64 to 97 % of some PAHs
49 remained stored in the soils. Similarly, Wild and Jones (1995) estimated that in UK more than
50 90% of PAHs accumulated in soils. This highlights the role of this compartment as a buffer of
51 PAH contamination in the environment. As atmospheric PAH emissions have decreased during
52 the last decades in Western Europe (Fernández et al., 2000; Pacyna et al., 2003), the soils
53 represent secondary sources, and are likely to play an important role in the current and future

54 environmental persistence of those contaminants. Villanneau et al. (2013) reported the presence
55 of higher PAH concentrations driven by historical mining and industrial activities in soils of
56 Northeastern France. In the Seine River basin, certain studies identified Paris City as the main
57 source delivering PAHs into the atmosphere (Garban et al., 2002), whereas other investigations
58 showed that PAH concentrations in soils were mainly associated with the presence of urban or
59 industrial areas in their vicinity (Motelay-Massei et al., 2004). Consequently, to move the
60 debate forward and given the importance of legacy contamination in northwestern Europe, the
61 respective contribution of regional atmospheric fallout and local sources supplying PAHs to the
62 soils must be further investigated.

63 Interactions between soils and PAHs have been extensively studied for many years and
64 appear to be very complex (Xing and Pignatello, 1997). Because of their high lipophilicity,
65 PAHs tend to bind strongly to the particles (Yang et al., 2013). Numerous studies have also
66 highlighted the role played by organic matter (OM) in the sorption of those substances and
67 showed that soils enriched in OM generally contain higher PAH concentrations (Bogan and
68 Sullivan, 2003). Once deposited onto the soil surface, some contaminants gradually migrate to
69 deeper soil horizons. This transfer mainly depends on the solubility of the compounds, their
70 affinity for soil components and the magnitude of water infiltration into the soil (Enell et al.,
71 2004; Yang et al., 2013). PAHs are both poorly soluble in water and highly lipophilic, and
72 leaching is therefore limited to the upper soil layers. This leads to an accumulation of PAHs in
73 the uppermost layers of the substrate as observed in undisturbed forest soils by Krauss et al.
74 (2000). Some laboratory experiments showed that a very small fraction of PAHs is recovered
75 when injecting a large amount of water through a soil core (Enell et al., 2004). In this context,
76 PAH leaching is often considered to be negligible. However, high PAH concentrations have
77 also been observed in deep horizons of heavily contaminated soils (Liao et al., 2012). In
78 conclusion, the entire distribution of PAH contamination in soil horizons must be considered to
79 correctly quantify their inventory in the substrate.

80 Overall, to the best of our knowledge, there is little information in the literature combining
81 PAH contamination in soils, its evolution with depth and the relationship with the distance to
82 the sources at the entire catchment scale. In this study, the PAH distribution is investigated in

83 soils of two agricultural catchments to verify the relevance of factors that need to be taken into
84 account when estimating contaminant stocks. a) The concentrations of PAHs in 336 soil
85 samples collected in 2 catchments are reported. b) The variation of PAH content with depth in
86 soils is investigated. c) The relationships between soil contamination and the distance to
87 potential local sources (charcoal factory or road traffic) are investigated. d) Finally, the relative
88 contribution of local and regional sources within the two catchments are detailed and the
89 corresponding PAH stocks are calculated. Overall, this study is representative of the
90 contaminant concentrations and stocks that may be found in most rural and agricultural
91 catchments of early industrialized countries. The results of this study provide original and novel
92 information on PAH stock distribution at the catchment scale. They may be useful to design and
93 implement large scale remediation programmes required to achieve the legislative
94 environmental targets.

95

96 **2. Materials & Methods**

97 **2.1 Study sites**

98 In order to compare the importance and the relative contribution of several PAH sources in
99 the environment, soils from two catchments located in upstream parts of the Seine River basin
100 (Fig. 1) were sampled and analysed. Site 1 is the Avenelles catchment located 70 km eastward
101 from Paris City and draining a 46-km² area. Site 2 is the Saulx catchment, located 210 km
102 eastward from Paris City and constituted of 3 subcatchments covering a total area of 614 km².
103 According to CORINE Land Cover (2006), both catchments are dominated by cropland and
104 grassland (covering 82% of the total surface in Site 1 and 57 % in Site 2), the rest of the surface
105 being occupied by woodland (Site 1: 17 %; Site 2: 42 %) and sparse human settlements
106 (including roads; 1%). Climate is semi-oceanic in Site 1 and semi-continental in Site 2. Monthly
107 mean temperature varies between 0.6 °C (January) and 18.0 °C (August) in the Avenelles
108 catchment and between -2.0 °C (February) and 18.2 °C (August) in the Saulx catchment.
109 Prevailing winds blow mainly from the southwest and the west, or from the northeast. Altitudes
110 are higher and slopes are steeper in Site 2 (mean altitude: 362 m and mean slope: 3.7 %) than in

111 Site 1 (mean altitude: 148 m and mean slope: 2.5 %). A charcoal factory is located close to the
112 northwestern boundary of Site 2.

113

114 **2.2 Sampling**

115 Transects across the catchments

116 Soil samples (n=106) were collected along two transects across both catchments (Fig. 2)
117 between March 2011 and February 2012. To this end, 10 subsamples of surface material (top 8
118 cm) were systematically collected and well-mixed to provide a homogeneous sample. Coarse
119 organic fragments were removed from the surface layer. Soils were sampled at a minimum
120 distance of 50 m from the closest road to avoid direct PAH deposition and to be representative
121 of the entire plot. Once collected, samples were placed in glass recipients in an ice box (4°C)
122 and carried back to the laboratory to be frozen and freeze-dried.

123

124 Detailed soil profiles under 4 different land covers

125 To investigate the evolution of PAH concentration with depth in the upper layer of the soils, 4
126 soil cores were collected at 3 undisturbed sites (i.e., garden in a built-up area [O9], woodland
127 [O2] and grassland [O15]) as well as under cropland [O8]. Those samples were cut into 1 cm-
128 depth increments and chemical analyses were conducted on each subsample (n=30).

129

130 Detailed transects in a forest plot and a cropland field along roads

131 Two plots of land (CP and WP in Figure 2) were sampled in Site 1 according to a regular grid in
132 order to investigate the local impact of roads on the nearby soils. The two sampled plots were
133 selected in the Choqueuse forest (dense hardwood forest) and in a cropland area (bare soil at the
134 time of sampling). Cropland site was almost flat and situated 1 m above the roadside ditch
135 bottom level. Woodland site was flat as well but situated at the same level as the ditch bottom.
136 The latter was separated from the rest of the plot by a 1 m-high embankment. During sampling,
137 5 transects separated by a distance of 2 m and oriented perpendicularly to the road were
138 followed. The first sampling points of each transect were located in the middle of the roadside

139 ditch, and they were used as reference points to measure the distance to the road. The following
140 samples (n=200) were subsequently taken at 0.5, 1, 2, 3, 5, 10, 20, 30 and 40 m along the
141 transects.

142

143 **2.3 Distance to the local sources**

144 To document the role of road traffic on soil contamination by PAHs, we investigated the
145 relationship between the PAH concentration in soils and the distance to the closest road in both
146 catchments. Distances were calculated using the Route 500® database provided by the French
147 National Geographic Institute. All the roads of the study area are characterized by a similar
148 traffic density typical of this kind of rural zone. In Site 2, a similar approach was performed to
149 investigate the contribution of both the road traffic and the charcoal factory to the catchment
150 contamination. A regression analysis between PAH concentrations in soils and the distance to
151 those sources was conducted. The modelling curves described in Equation (1) were chosen
152 between several models (inverse first order, exponential decay, etc.) as they appeared to better
153 fit with the contamination at both plot and catchment scales:

$$154 \quad y(x) = \frac{aL + bx}{L + x} \quad (1)$$

155 Where y is either the standard or the OC normalized PAH concentration in soils (respectively
156 ng.g^{-1} or ng.g^{-1} OC), and x is the distance (m) to the closest source (road network or charcoal
157 industry). a and b (ng.g^{-1} or ng.g^{-1} OC) are respectively the PAH concentration in the vicinity of
158 the source and the local background signal of the contamination. L (m) is the characteristic
159 distance of the contamination i.e. the distance at which the PAH concentration reaches the mean
160 value between the source and the background signal. Outliers displaying much higher PAH
161 concentrations or different contamination signature were removed from analysis to avoid
162 potential biases due to the contribution of additional unsampled sources or to the local
163 heterogeneity. Curves were fitted using the least squares method. At the plot scale, a lower
164 weight was attributed to the data collected at a shorter distance from the road as they appeared
165 to be more scattered.

166

167 **2.4 Chemical analyses**

168 After extraction and purification, PAHs were analysed by gas chromatography (Agilent GC
169 system 7890A) coupled with a mass spectrometer (Agilent 5975C inert XL MSD). MS signal
170 acquisition was performed in Selected Ion Monitoring (SIM) mode. Thirteen US EPA PAHs
171 could be determined: Acenaphthylene (ACY), Acenaphthene (ACE), Fluorene (FLU),
172 Phenanthrene (PHE), Anthracene (ANT), Fluoranthene (FTH), Pyrene (PYR),
173 Benzo(a)anthracene (BaA), Chrysene (CHR), Benzo(b)fluoranthene + Benzo(k)fluoranthene
174 (BbF+BkF), Benzo(a)pyrene (BaP), and Benzo(g,h,i)perylene (BghiP). More detailed
175 descriptions of extraction and analysis methods can be found in Gateuille et al. (2014).
176 Organic carbon was measured using a CHN Elemental Analyzer to determine the carbon weight
177 percent in soil samples after carbonate removal.

178 Maps of the PAH contamination were drawn using a Geographic Information System
179 software (ArcGis ®). Interpolations were carried out using the inverse distance weighting
180 method.

181

182 **2.5 Radionuclide analyses**

183 Soil samples were packed into 4-ml pre-tared polyethylene specimen cups and sealed
184 airtight. The ^{137}Cs and excess ^{210}Pb activities in this material were determined by gamma
185 spectrometry using the very low-background HPGe detectors available at LSCE (Evrard et al.,
186 2010). Those radionuclides have rather long half-lives, i.e. 30 years for ^{137}Cs and 22 years for
187 ^{210}Pb . The first radionuclide is artificial and was produced by the thermonuclear bomb testing
188 during the 1960s and in 1986 by the Chernobyl accident (Forsberg et al., 2000; Bossew and
189 Kirchner, 2004). The second is supplied to soils by decay of both geogenic ^{238}U and
190 atmospheric ^{222}Rn . The latter source regularly supplies an additional activity (excess ^{210}Pb) to
191 the soil during rainfall. Both radionuclides are concentrated at the soil surface and
192 concentrations rapidly decrease with depth in undisturbed soils (Wallbrink and Murray, 1993).
193

194 **3 Results and discussion**

195 **3.1 Migration of PAHs in depth**

196 Depth profiles of PAH concentrations in soils under different land covers are given in Figure

197 **3.** Three types of behaviour were found.

198 - First, in undisturbed soils (i.e. woodland), concentrations in all measured parameters
199 decreased with depth except for PAH in the two first centimetres. This trend may be explained
200 either by higher PAH losses (**biodegradation or volatilization**) in the uppermost layer of the soil
201 or by lower atmospheric inputs during the last decades. On the one hand, volatilization and
202 degradation are likely to reach higher rates at the air-soil interface and may lead to a decrease in
203 PAH content in the uppermost layer. On the other hand, lower PAH input may lead to lower
204 PAH concentrations in the surface layer because of the slow migration of PAH towards deeper
205 horizons. This slow migration of PAHs in depth is confirmed by a similar behaviour of ^{137}Cs
206 and of $^{210}\text{Pb}_{\text{xs}}$. Based on the $^{210}\text{Pb}_{\text{xs}}$ profile, the maximum PAH emission period may be
207 estimated to ca. 1950. Those results remain consistent with previous findings on PAH emissions
208 in Western Europe (Fernández et al., 2000). PAH concentrations were much higher under
209 woodland than under land covers, but a similar enrichment factor of ca. 6 was found in fallout
210 radionuclide measured in samples collected in close areas under other land uses (PAH: 231
211 ng.g^{-1} ; $^{210}\text{Pb}_{\text{xs}}$: 11 Bq.kg^{-1} ; ^{137}Cs : 4 Bq.kg^{-1}). Traditionally, the forest canopy leads to a higher
212 interception of atmospheric contaminants, and they are found in higher concentrations in areas
213 with elevated organic matter contents (Gaspar and Navas, 2013; Wilcke, 2000). Overall, PAH
214 concentration dropped to less than 20% of its maximum value at a depth of 7 cm showing that
215 PAH stocks were mainly concentrated in the surface layer.

216 - Second, the cropland sample appeared to be representative for homogeneously
217 disturbed soils where parameters showed very small variations with depth. PAH concentrations
218 decreased until 60% of the maximum value and remained stable below a depth of 4cm. This
219 homogeneity may be explained by the regular ploughing of soils. The higher values found in
220 surface may originate from PAH supply during farming operations. In cropland, PAH
221 contamination likely reaches the maximum ploughing depth (Doick et al., 2005).

222 - Third, soils under built-up areas and grassland were characterized by an increase in
223 PAH content in the two or three first centimetres of the soil. Then, concentration remained
224 stable down to 3 or 4 centimetres before decreasing again. However, the PAH concentration
225 remained high in depth of those samples (78% and 58% of the maximal values for built-up area
226 and grassland, respectively) suggesting that PAH contamination may have reached deeper soil
227 layers. In these samples, OC content decreased with depth as under woodland. However, ^{137}Cs
228 and $^{210}\text{Pb}_{\text{xs}}$ activities displayed different patterns. This suggested that soils may have been
229 disturbed after 1986 (i.e., last significant ^{137}Cs input in the region, Evrard et al., 2012).
230 Contamination depth could therefore not be estimated in these two plots as it was found to
231 depend on local soil disturbances.

232

233 **3.2 Distribution at the catchment scale**

234 Maps of PAH contamination in the soils (normalized to OC) and values of BaA/(BaA+CHR)
235 ratio were drawn for both catchments. Values of other PAH ratios are not presented as they
236 displayed less clear variations within the catchments. The literature suggests that samples with
237 BaA/(BaA+CHR) values higher than 0.35 were likely contaminated by pyrolytic sources
238 whereas low ratio values indicate the contribution of a petrogenic source (Guo et al., 2003;
239 Soclo et al., 2000; Yunker et al., 2002).

240 In Site 1 (Fig. 4) located the closest from Paris, total PAH concentrations in soils varied
241 between 64 and 5618 ng.g^{-1} (mean of 666 ng.g^{-1}). When normalized to the OC content of soils,
242 those concentrations ranged from 5000 to 295 400 ng.g^{-1} OC (mean of 33 600 ng.g^{-1} OC). A
243 poor correlation was observed between the PAH concentrations and the OC contents in soils
244 ($r^2=0.12$; $p < 0.05$). The BaA/(BaA+CHR) ratio varied from 0.38 to 0.56 (mean of 0.44). There
245 was no clear spatial trend in the distribution of those parameters although the highest values of
246 both contamination and ratio were measured in samples collected in the middle part of the
247 catchment. This distinctive feature may be due to its vicinity with Doue village that may
248 provide a very local source of PAHs **because of household heating by fuel oil or wood burning**.
249 At this location, both the PAH concentration (5618 ng.g^{-1}) and the BaA/(BaA+CHR) ratio

250 (0.56) were significantly higher than the corresponding values measured in the other samples
251 inside the catchment.

252 When excluding the samples collected in built-up areas and their surroundings (O12, O9 and
253 OS3), the mean PAH concentration reached $205 \pm 146 \text{ ng.g}^{-1}$ with 95% of the values remaining
254 below 500 ng.g^{-1} . In the following calculations, this value was therefore chosen as a benchmark
255 to distinguish between soils strongly influenced by local sources and those with PAH
256 concentrations close to the regional background signal. A similar value (600 ng.g^{-1}) was
257 previously reported to distinguish between slightly and strongly contaminated soils (Jones et al.,
258 1989; Malisweska-Kordybach, 1996).

259 In Site 2 located further away from Paris (Fig. 5), total PAH concentrations in soils varied
260 between 95 and $13\,657 \text{ ng.g}^{-1}$ (mean of 2137 ng.g^{-1}). Concentrations normalized to the OC
261 content of soils ranged from $5\,700$ to $195\,400 \text{ ng.g}^{-1} \text{ OC}$ (mean of $36\,300 \text{ ng.g}^{-1} \text{ OC}$). Again, a
262 poor correlation was observed between the PAH concentrations and the OC contents in soils
263 ($r^2=0.30$; $p<0.001$). The BaA/(BaA+CHR) ratio varied between 0.39 and 0.54 with a mean of
264 0.45. Pyrolytic sources were therefore likely the main contributor of PAH contamination in both
265 sites. As in Site 1, one sample was significantly more contaminated than the others ($13\,657$
266 ng.g^{-1}). This point may be considered as contaminated by another local source as both PAH
267 concentration and BaA/(BaA+CHR) appeared to have the highest values among all the samples.
268 In this catchment, a clear spatial trend was observed as both PAH concentrations and
269 BaA/(BaA+CHR) ratio values appeared to decrease with increasing distance from the charcoal
270 factory. Site 2 may therefore be representative for catchments under the strong influence of a
271 local industry emitting PAHs.

272 A good relationship (Eq. (2) $r^2=0.66$; $p<0.001$) was found between the normalized
273 concentrations of PAHs in soils and the distance to the road network in Site 1 (Fig. 6). In Site 2,
274 the soil contamination was mainly driven by the distance to the charcoal factory (Eq. (3)
275 $r^2=0.84$; $p<0.01$) as a weaker relationship was found with the distance to the road network
276 (data not shown). Using the benchmark previously determined (500 ng.g^{-1}), it appeared that the
277 pollution plume of this factory had a larger spatial extent than the road contamination and it
278 supplied significant PAH contamination up to 8 km in cropland and 12 km in woodland. The

279 minimum background signals given by the models were lower ((1) 14 ng.g⁻¹ OC; (2) 25 ng.g⁻¹
280 OC) than the minimal values measured in the samples ((1) 5 050 ng.g⁻¹ OC; (2) 5 650 ng.g⁻¹
281 OC). This suggests that the ubiquity of local sources may prevent PAH concentrations to reach
282 the expected background levels in soils. Indeed, the most remote areas that we sampled in Site 1
283 were located at a distance of 1110 m from the road network. In Site 2, no experimental data
284 were available in the most remote areas.

285

286 **3.3 Distribution along roads**

287 Total PAH concentrations in the cropland and woodland fields investigated in detail are
288 shown in Figure 7. The soil samples collected the closest to the roads were the most
289 contaminated as total concentrations reached respectively about 43 000 ng.g⁻¹ under woodland
290 and 45 000 ng.g⁻¹ under cropland at those locations. This highlights the important contribution
291 of road traffic as a local but ubiquitous PAH source at the catchment scale. Then, concentrations
292 gradually decreased when distance from the ditch increased. In both plots, total concentration
293 reached the local background level (about 350 ng.g⁻¹) at less than 40 m from the road except for
294 the middle transect under cropland where contamination remained significantly higher (about
295 800 ng.g⁻¹) at a longer distance from the road. Furthermore, spatial variations in PAH
296 contamination were characterized by different trends in both plots. PAH concentration under
297 cropland regularly decreased from the ditch to the most remote points with some local
298 exceptions that will be detailed below.

299 High values (> 2000 ng.g⁻¹) were observed as far as 10 meters from the roads along all
300 transects except for the middle transect where soil sampled 30 meters away from the road was
301 still heavily contaminated. Under woodland, the pollution range was more limited. High PAH
302 concentrations were restricted to the soils sampled nearby the road (< 5m). Samples taken at 2
303 and 3 meters from the road were more contaminated than the ones collected on the
304 embankment. This may be explained by the spatial redistribution of PAHs due to leaching. Part
305 of PAHs deposited close to the road may have been washed out, explaining the increase in PAH
306 contamination measured at the bank foot.

307 To further investigate the impact of road traffic on PAH pollution, spatial variations in the
308 BaA/(BaA+CHR) ratio values were plotted in Figure 8. Under woodland, a similar pattern was
309 observed for all the transects within the plot. The averaged ratio was almost constant and equal
310 to 0.51 within a distance of 3 m from the road. Then, it decreased until reaching the local
311 background value of 0.42. Under cropland, a similar trend was observed in 3 of the 5 transects
312 although the changes were less pronounced. The ratio measured in the ditch was about 0.48
313 whereas it reached 0.43 in samples collected at a longer distance from the road. Significant
314 variations were only observed in the third transect where the BaA/(BaA+CHR) ratio reached
315 0.80. This suggests the contribution of an additional source responsible for the higher PAH
316 concentrations along this transect. As no change in the ratio was observed along other transects,
317 the locally higher values measured in PAH concentrations within a distance of 10 meters from
318 the ditches may be explained by runoff and contaminant redistribution. Under woodland, the
319 same pattern of variations in both PAH concentration and BaA/(CHR+BaA) ratios confirmed
320 that the high values observed at the embankment foot (at 2 and 3 m) were due to local
321 contaminant redistribution.

322 Regression curves were calculated based on measurement of PAH concentrations in soils of
323 both plots (Figure 9). Some data were removed from further analysis as they appeared to be
324 affected by either contaminant redistribution (i.e., samples from the embankment foot in
325 woodland plot) or by sources other than direct emissions of road vehicles (i.e., middle transect
326 under cropland).

327 A good correlation was observed between PAH concentration in soils and the distance to the
328 road under both woodland (Eq. (4) $r^2=0.98$; $p < 0.001$) and cropland (Eq. (5) $r^2=0.93$; $p <$
329 0.001). The fitted curves highlighted the important role played by the vegetation cover. It
330 appeared that the PAH concentration decreased more rapidly with the distance in the woodland
331 plot. However, the local background signal appeared to be lower (71 ng.g^{-1}) in cropland than in
332 woodland (94 ng.g^{-1}). This difference may be due to the plot location, as they were situated in
333 different parts of Site 1 and along different roads so that limited variations in local background
334 signal may exist between plots at the catchment scale. Moreover, background signals appeared
335 to be higher at the plot scale than at the catchment scale even though they remained in the same

336 order of magnitude. Different processes may therefore be responsible for contaminant diffusion
337 at both scales.

338 The spatial extent of road traffic influence on contamination was determined using the 500
339 ng.g^{-1} value selected as a benchmark to characterize soils under the strong influence of local
340 sources (section 3.2). This extent reached between 20 and 30 m in the two plots. When
341 upscaling the results at the catchment scale, we therefore considered that soils located within
342 less than 30 m from the road were under the strong influence of road traffic.

343

344 **3.4 Source contributions to PAH stocks in soils**

345 The proportions of PAH stocks supplied to the soils by regional atmospheric fallout and
346 local road traffic emissions were calculated (Table 1). To this end, PAH contamination in soils
347 located at less than 30 m from the road were estimated using Equations (4) or (5) depending on
348 the land use. PAH stocks **in the first 30 meters** along the roads reached about 10.4 g.m^{-1} under
349 woodland and 30 g.m^{-1} under cropland **per unit length of road**.

350 In Site 1, PAH stocks supplied by regional atmospheric fallout were calculated using the
351 mean concentrations measured in woodland and cropland. In woodland, a 8-cm depth layer was
352 considered to be contaminated as undisturbed soil profile showed that PAH mainly remained in
353 the surface layer. In cropland fields, contamination was assumed to affect the entire ploughing
354 layer and a soil density of 1.35 g.cm^{-3} was estimated. Consequently, stocks in soils were
355 calculated to vary between 19 mg.m^{-2} in woodland and 76 mg.m^{-2} in cropland.

356 In Site 2, the atmospheric fallout was supposed to be mainly controlled by the distance to the
357 charcoal factory. To quantify associated PAH supply, PAH concentrations were calculated
358 using Equation (3) and OC contents were estimated from values measured on samples collected
359 in plots located under similar land use. As defined previously, soils were considered to be
360 strongly affected by the charcoal factory within a distance of 8 km under cropland and 12 under
361 woodland. Stock in the 1-km radius circle around the charcoal factory was not taken into
362 account as it appeared to strongly depend on the modelling parameters and no experimental data
363 were available in this catchment part. The calculated stocks ranged between 13 mg.m^{-2} in the

364 most remote woodland and 735 mg.m^{-2} in cropland close to the charcoal factory. PAH stocks
365 reached 87 kg.km^{-2} in Site 1 and 74 kg.km^{-2} in Site 2. The presence of local industries may have
366 a large impact on the contamination of rural catchments as a single charcoal factory appeared to
367 be responsible for one third of the total contamination in Site 2. Overall, it appears that even
368 though the close areas along the roads covered only ca. 4% of the total catchment surface, they
369 concentrated 20% of the total PAH contamination. These results showed that the road traffic
370 emissions should not be neglected when calculating the fluxes at the catchment scale, and that
371 they remain of significant importance compared to regional atmospheric fallout. Specific PAH
372 inputs from farming activities could not be distinguished from atmospheric contamination.
373 However, as the two studied catchments were mostly agricultural, they may be responsible for a
374 part of the contamination far from local sources. In this context, implementation of mitigation
375 measures should be concentrated on roadside areas located along cropland.

376

377 **4. Conclusions**

378 This study conducted in two rural catchments located at varying distance from the main
379 regional source of contamination provided original results on PAH contamination in soils. First,
380 soil contamination level and depth was shown to strongly depend on land use. At the catchment
381 scale, PAH concentrations in soils displayed large variations and were shown to be partly
382 controlled by the distance to local sources (road network or a charcoal factory). In terms of
383 stocks, our calculations demonstrated that even though roads covered only 4 % of the total
384 catchment surface, 20% of the soil contaminants were found within a distance of 30 meters from
385 the roads. In future, the management of roadside areas should be given the priority as road
386 traffic appeared to be an important and ubiquitous source of PAHs.

387

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393 during sampling or chemical analyses. This is LSCE contribution No.

394

395 **Figure captions**

396 **Fig. 1:** Location of the Seine River basin and the 2 sampling sites.

397

398 **Fig. 2:** Site 1, Site 2, and location of soil samples. Samples were collected between March 2011
399 and February 2012. **WP and CP are two plots located along roads where samples were**
400 **specifically collected to investigate PAH contamination associated with the road traffic.**

401

402 **Fig. 3:** Changes in concentrations of PAHs, OC, ^{137}Cs , and $^{210}\text{Pb}_{\text{xs}}$ in 4 soil cores collected under
403 different land uses (n=30).

404

405 **Fig. 4:** PAH concentrations (min/max: 5 000/295 400 ng.g⁻¹ OC) and BaA/(BaA+CHR) ratio
406 measured in soils of Site 1 (n=72).

407

408 **Fig. 5:** PAH concentrations (min/max: 5 700/195 400 ng.g⁻¹ OC) and BaA/(BaA+CHR) ratio
409 measured in soils of Site 2 (n=34).

410

411 **Fig. 6:** Relationship between normalized PAH concentrations in soils and distance to the closest
412 road in Site 1 (n=68), and to the charcoal factory in Site 2 (n=32). Number of replicates varied
413 between 2 and 8. **Note that there is no data in the Site 2 at a distance lower than 1000 m from**
414 **the charcoal factory.**

415

416 **Fig. 7:** Concentrations of PAHs in the cropland field (a; n=100) and the woodland plot (b;
417 n=100) (black dots: location of sampling points).

418

419 **Fig. 8:** BaA/(BaA+CHR) ratio values in the cropland field (a; n=100) and the woodland plot (b;
420 n=100) (black dots: location of sampling points).

421

422 **Fig. 9:** Relationship between the normalized PAH concentrations in soils and the distance to the
423 road in the cropland field [excluding the third transect] (n=80) and in the woodland plot
424 [excluding samples collected at 2 and 3m from the road] (n=80).

425

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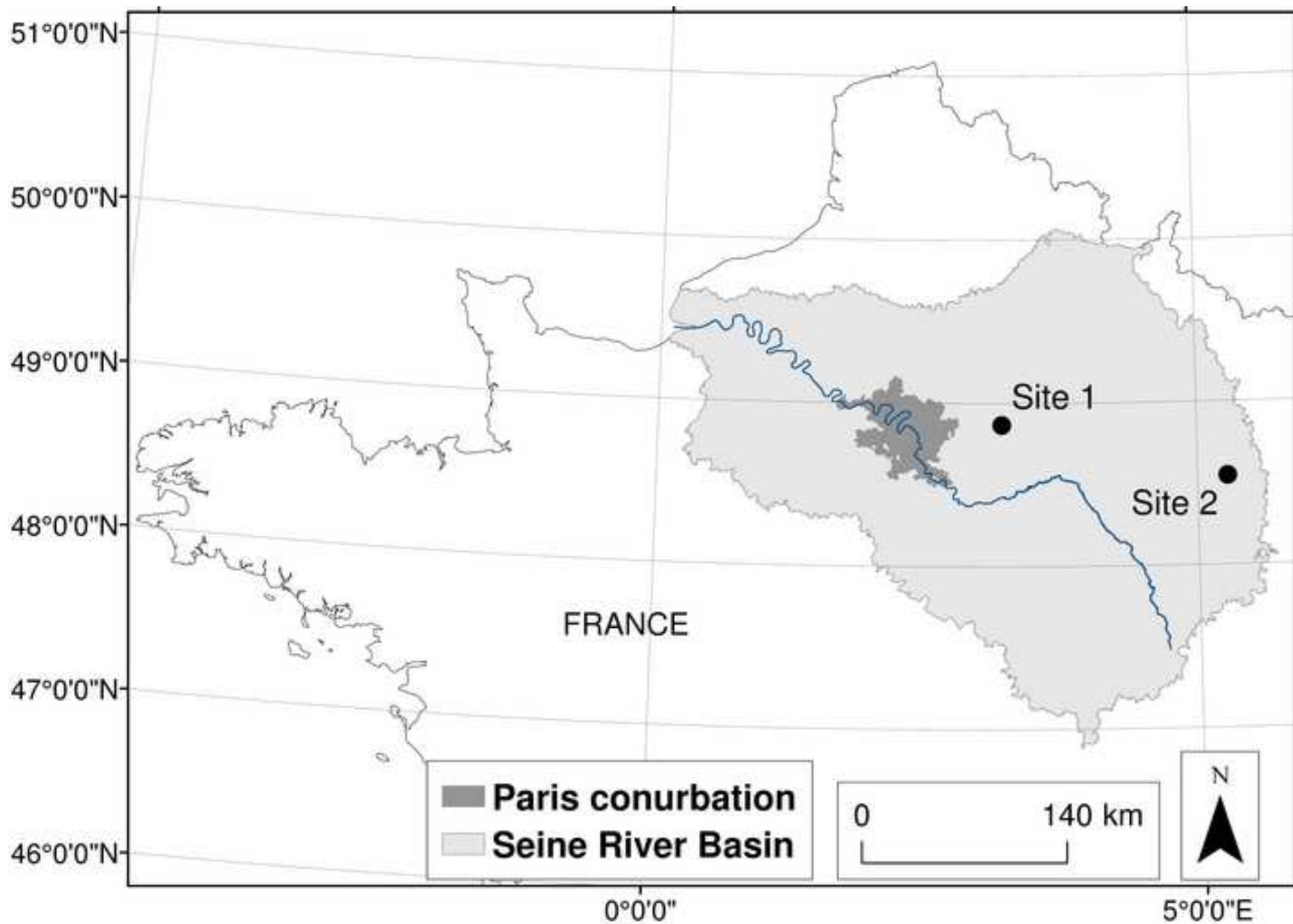
1 **Table 1**

2 Relative contribution of several PAH sources to the stocks accumulated in soils of the two catchments.

		Roadside areas	Factory contaminated areas	Remote areas	Total
Site 1	Surface (km ²)	1.6 (3.5 %)	-	44 (96.5 %)	45.6
	Stocks (kg)	754 (19 %)	-	3201 (81 %)	3955
Site 2	Surface (km ²)	22.4 (3.7 %)	90.1 (14.8 %)	498.2 (81.5 %)	610.7
	Stocks (kg)	9000 (20 %)	14 310 (31 %)	22 190 (49 %)	45 500

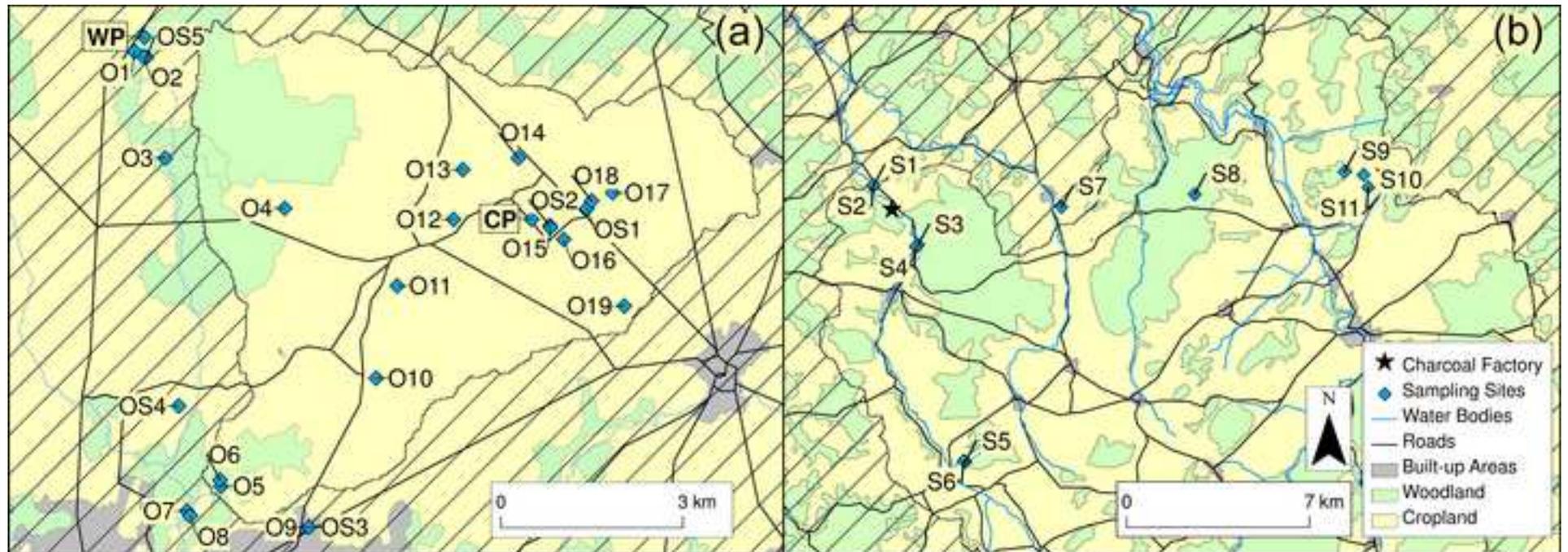
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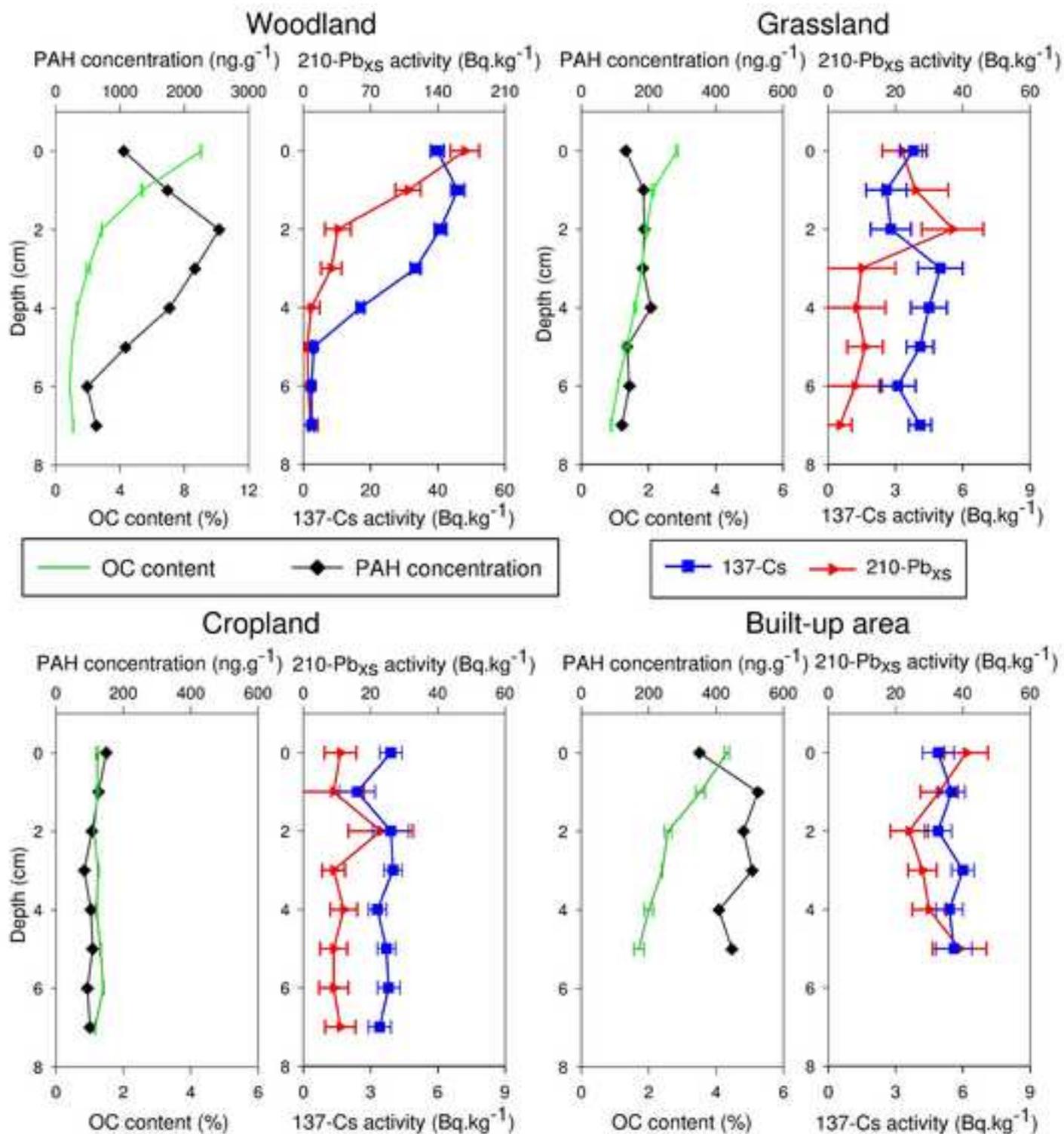
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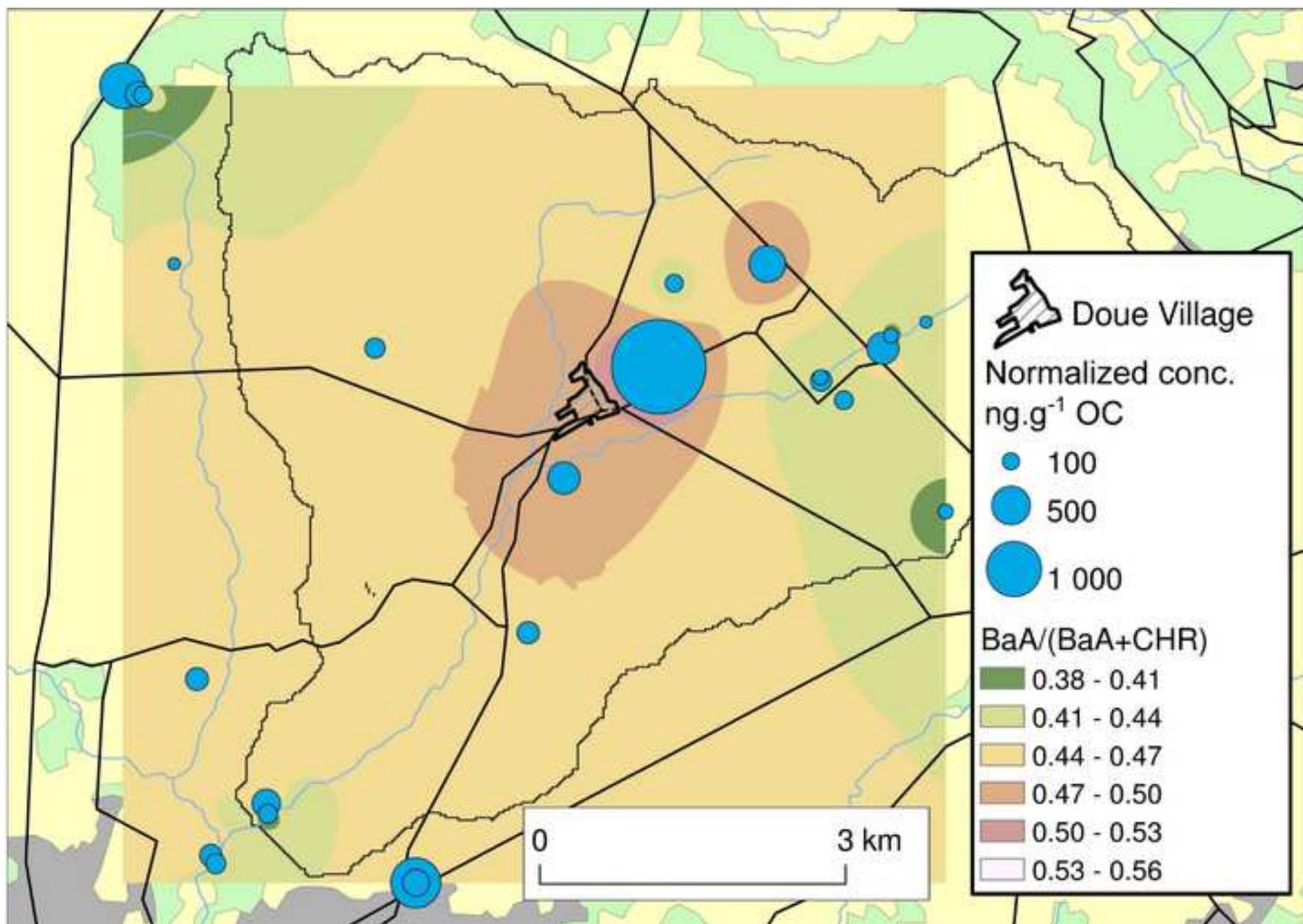


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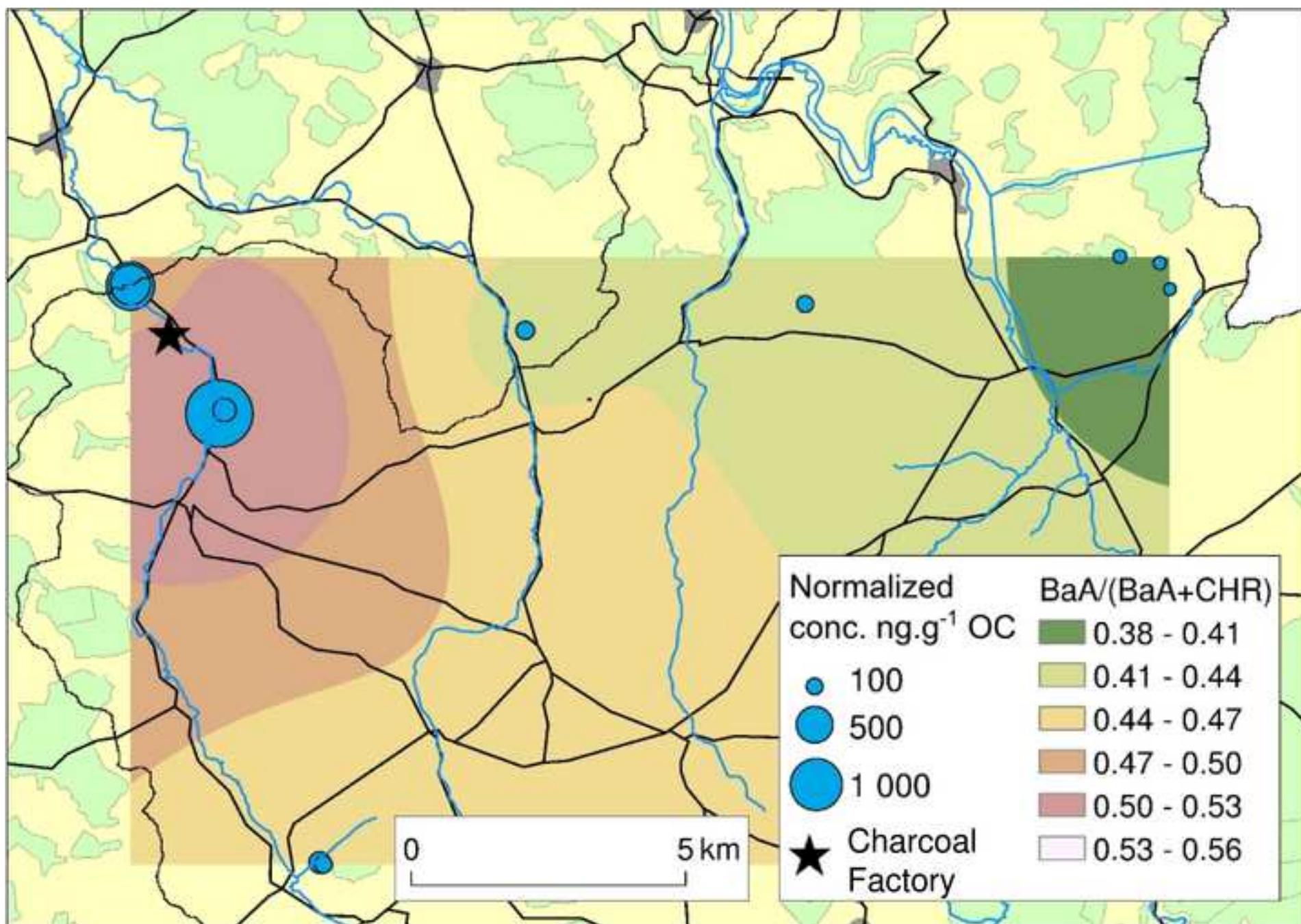
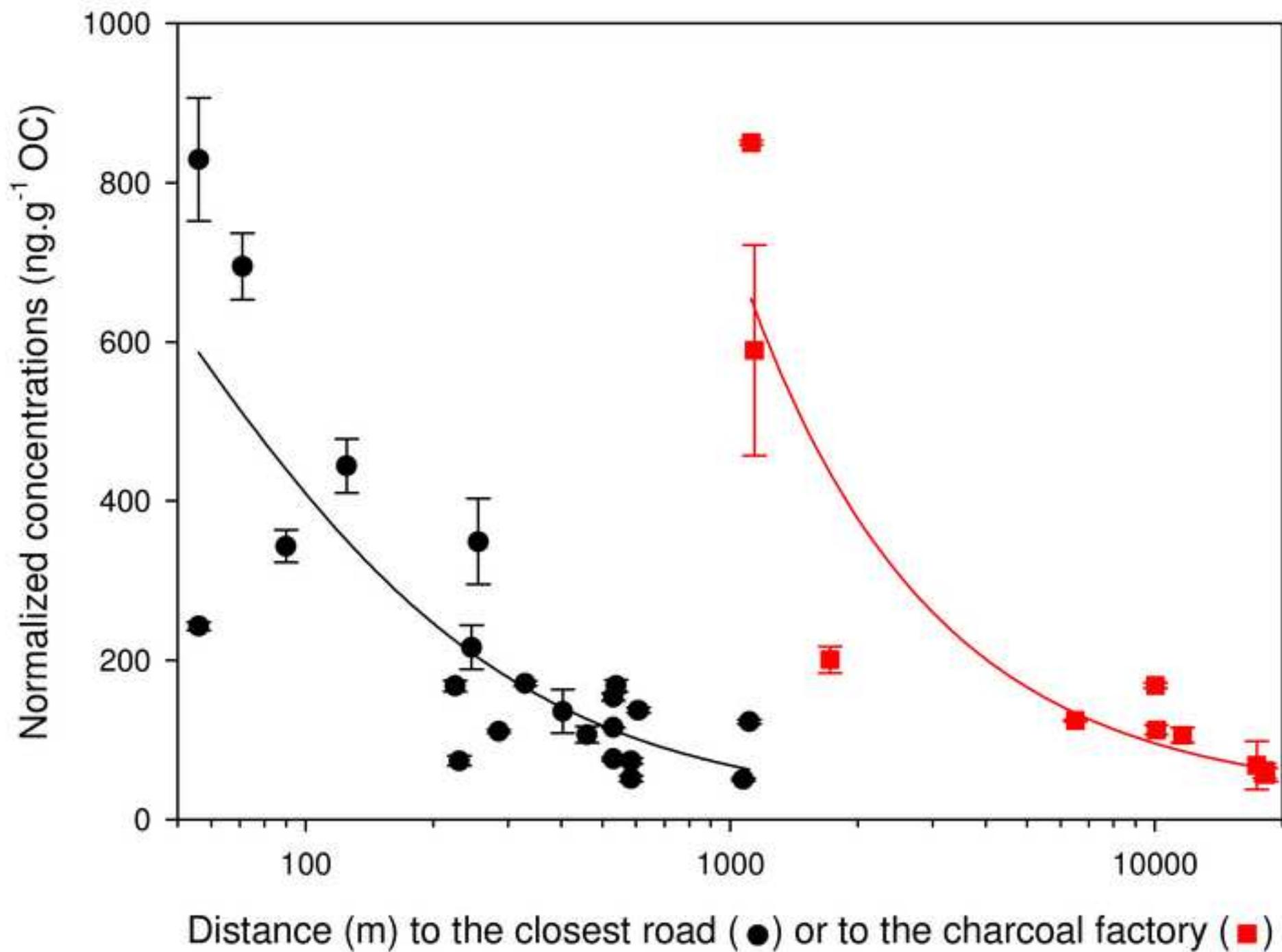


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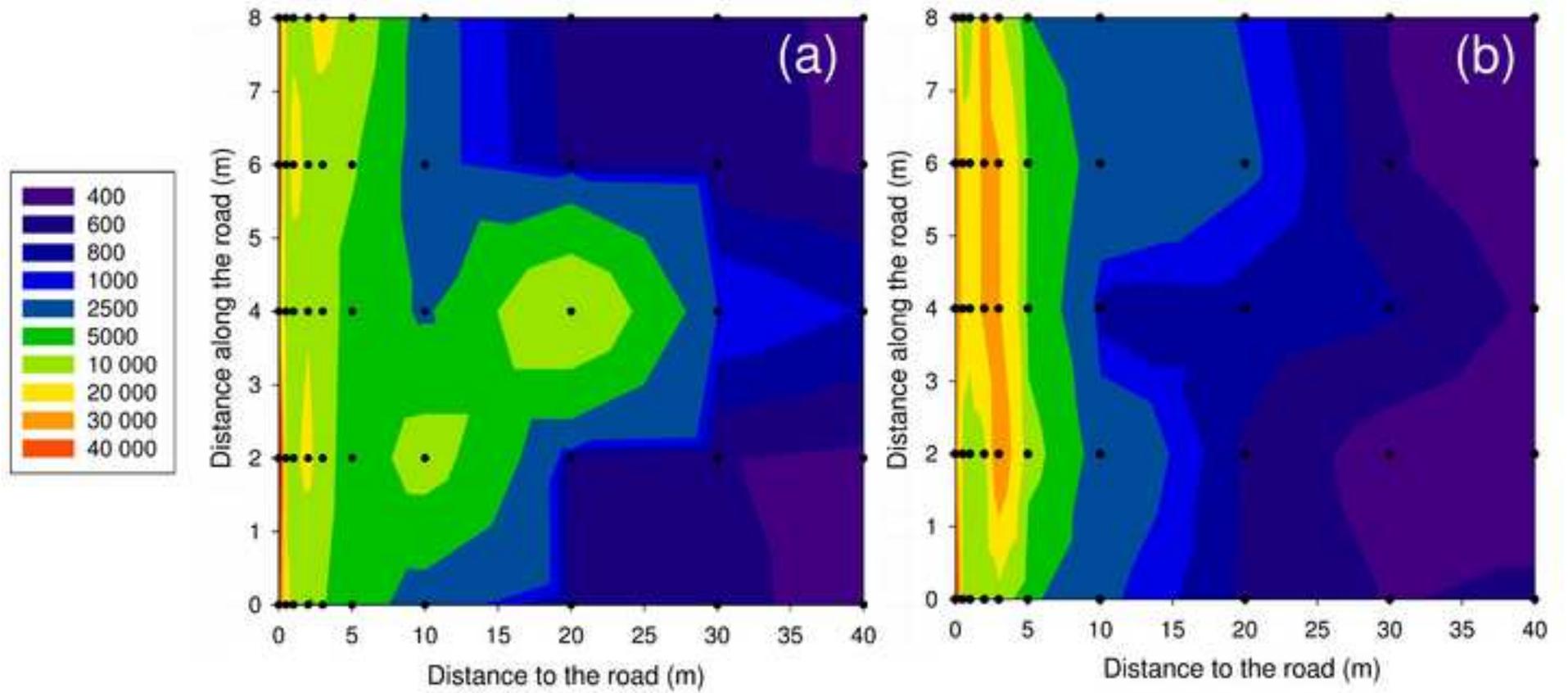


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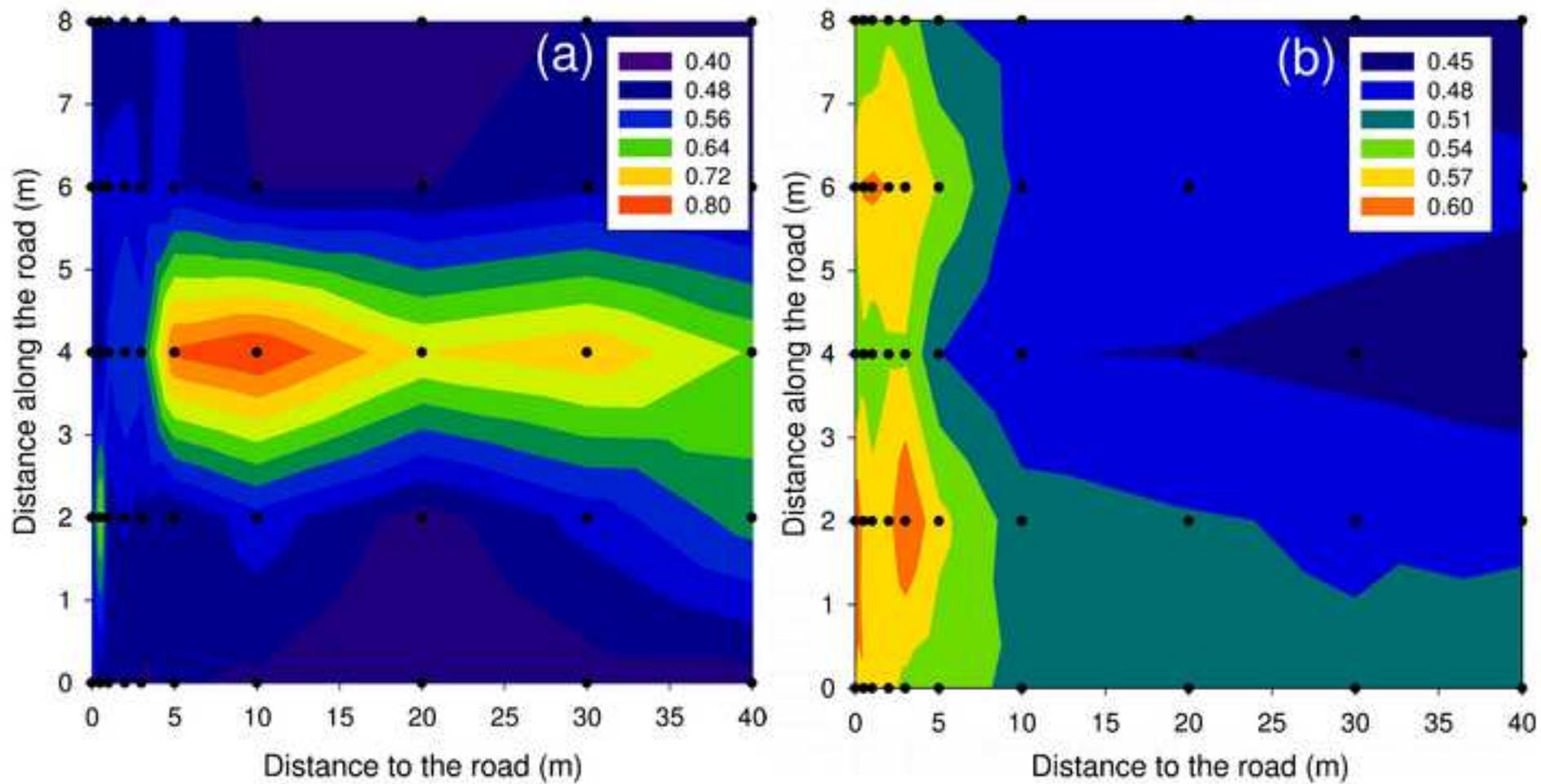


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