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Anthropogenic methane plume detection from point sources in the Paris megacity area and characterization of their $\delta^{13}\text{C}$ signature

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Abstract

Mitigating anthropogenic methane emissions is one of the available tools for reaching the near term objectives of the Paris Agreement. Characterizing the isotopic signature of the methane plumes emitted by these sources is needed to improve the quantification of methane sources at the regional scale. Urbanized and industrialized regions such as the Paris megacity are key places to better characterize anthropogenic methane sources. In this study, we present the results of the first mobile surveys in the Paris region, assessing methane point sources from 10 landfills (which in the regional inventory are the main emission sector of methane in the region), 5 gas storage sites (supplying Paris) and 1 waste water treatment (WWT) facility (Europe's largest, second worldwide). Local atmospheric methane concentration (or mixing ratio) enhancements in the source plumes were quantified and their $\delta^{13}\text{C}$ in CH_4 (further noted $\delta^{13}\text{CH}_4$) signature characterized. Among the 10 landfills sampled, at 6 of them we detected atmospheric methane local enhancements ranging from 0.8 to 8.5 parts per million (ppm) with $\delta^{13}\text{CH}_4$ signatures between -63.7 ± 0.3 permils (‰) to -58.2 ± 0.3 ‰. Among the 5 gas storage sites surveyed, we could observe that 3 of them were leaking methane with local methane concentration enhancements ranging from 0.8 to 8.1 ppm and $\delta^{13}\text{CH}_4$ signatures spanning from -43.4 ± 0.5 ‰ to -33.8 ± 0.4 ‰. Dutch gas with a $\delta^{13}\text{CH}_4$ signature of -33.8 ± 0.4 ‰ (typical of thermogenic gas) was also likely identified. The WWT site emitted local methane enhancements up to 4.0 ppm. For this site, two $\delta^{13}\text{CH}_4$ signatures were determined as -51.9 ± 0.2 ‰ and -55.3 ± 0.1 ‰, typical of a biogenic origin. About forty methane plumes were also detected in the Paris city, leading to local concentration enhancements whose origin was in two cases interpreted as natural gas leaks thanks to their isotopic composition. However, such enhancements were much less common than in cities of North America. More isotopic surveys are needed to discriminate whether such urban methane enhancements are outcoming from gas line leaks and sewer network emanations. Furthermore, our results lead us to the conclusion that the regional

43 emissions inventory could underestimate methane emissions from the WWT sector. Further
44 campaigns are needed to assess the variability and seasonality of the sources and of their
45 isotopic signature, and to estimate their emissions using methods independent of the
46 inventory.

47 *Keywords: methane sources, isotopes, mobile campaigns, Paris*

48 *Highlights:*

- 49 • *CH₄ plumes were located on anthropogenic sites in the Paris megacity*
- 50 • *A mobile CRDS analyzer was used to detect local methane enhancements in the plume*
- 51 • *CRDS and GC-IRMS measurements were performed to provide source isotopic signatures*
- 52 • *These results provide independent constraints to quantify regional methane sources.*

53

54

55 **1- Introduction**

56 Methane (CH₄) is, after carbon dioxide (CO₂), the second anthropogenic greenhouse
57 gas (GHG) contributing to human-induced global warming. According to Saunio et al.
58 (2017), more than 60% of global CH₄ emissions are attributed to human activities. Mitigating
59 anthropogenic methane emissions is therefore of importance for reaching the near term
60 objectives of the Paris Agreement and fighting climate change. Since the pre-industrial era,
61 the global average atmospheric concentration (or mixing ratio) of methane has more than
62 doubled to reach almost 1850 parts per billion (ppb) in 2017 (Dlugokencky, 2018). Methane
63 has a global warming potential much larger than that of carbon dioxide (~28 times more on a
64 100-year horizon ; Saunio et al, 2016), despite its shorter (~10 years) atmospheric lifetime
65 (Gasser et al., 2017). Therefore, effective measures to decrease CH₄ emissions to the
66 atmosphere are expected to have a rapid impact on mitigating global warming, making CH₄ a
67 target for immediate emission reduction efforts (Montzka et al., 2011 ; Nisbet et al., 2019).

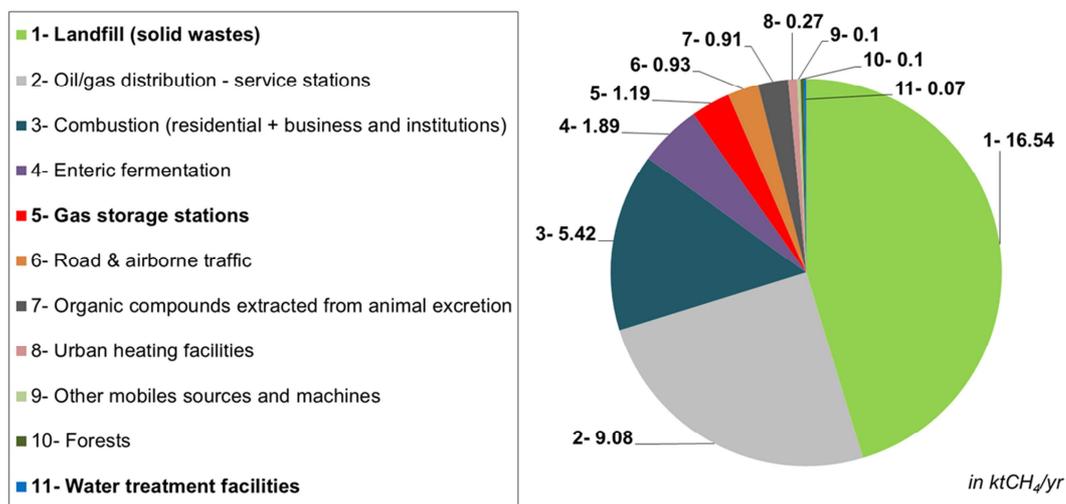
68 After a fast increase of atmospheric methane in the 20th century followed by the
69 stabilisation of the CH₄ global mean concentration between 1999 and 2006, a rapid increase
70 in the atmospheric methane concentration has occurred again since 2007 (Nisbet et al., 2014;
71 Nisbet et al. 2016). However, the causes for the changes in the methane growth rate are
72 poorly understood. A major effort is needed in quantifying individual methane sources
73 (Houweling et al., 2017 ; Dlugokencky et al., 2011), taking into account the high variability of
74 methane emissions at the regional and global scales.

75 Anthropogenic methane emissions come from leaks from the fossil fuel sector such as
76 oil and gas extraction sites, coal mines, gas storage facilities and distribution network,
77 refineries, (Schwietzke et al., 2017), landfills, waste water processing plants and ruminants
78 (Saunio et al., 2017). Emissions data are mostly developed using a “bottom-up” approach,
79 which combines local activity statistics (e.g. volume of gas used, etc.) multiplied by a specific
80 emission factor for each emission sector. The source quantification and partitioning for
81 methane emissions is mainly based on such bottom-up inventories that may underestimate
82 emissions by 50 to 70% at the national level (Miller et al., 2013 ; Karion et al., 2013). Also,
83 these estimates are often reported without uncertainties, as the lack of independent data
84 makes it not possible to assess those correctly. Furthermore, emission factors are most often
85 defined from measurements carried out on a limited number of sources that are taken as
86 representative of an emission sector, or based upon benchmarked measurements or
87 theoretical calculations. The IPCC guidelines provide default (Tier 1) emission factors

88 estimates that are used in most emission inventories, if Tier 2 or Tier 3 (i.e. region-specific or
 89 site-specific emission factors) is not available (IPCC, 2006). However, these Tier 1 estimates
 90 do not reflect the variability of emission factors for the different sources at the regional or
 91 national scales. Therefore, assessing emissions inventories by independent methods is
 92 needed.

93 Atmospheric “top-down” approaches, based on a combination of surface
 94 measurements with atmospheric transport modeling, represent an appropriate tool to
 95 estimate CH₄ emissions (e.g. Houweling et al., 2017). The analysis of carbon stable isotopes
 96 in CH₄ provides a further independent constraint on the budget of atmospheric methane, as
 97 the ¹³C content of methane is source dependent (e.g. Lassey et al., 2011), allowing different
 98 source types to be distinguished : biogenic/microbial methane sources are strongly ¹³C
 99 depleted ($\delta^{13}\text{CH}_4 = -70$ to -50 permils, noted ‰) while pyrogenic CH₄ sources (from
 100 incomplete combustion) and thermogenic sources (oil and gas) are less depleted in ¹³C
 101 ($\delta^{13}\text{CH}_4 = -30$ to -15 ‰ and -50 to -30 ‰, respectively) (e.g. Lopez et al., 2017 ; Zazzeri et
 102 al., 2015 ; Zazzeri et al., 2017). This information can be used in atmospheric modelling to
 103 independently evaluate and improve emissions estimates at the global and regional
 104 scales (e.g. Mikaloff Fletcher, 2004; Bousquet et al., 2006; Monteil et al., 2011 ; Nisbet et al.,
 105 2016 ; Schwietzke et al., 2016). However, the uncertainties on the $\delta^{13}\text{CH}_4$ source signatures
 106 used as inputs in the global modeling framework are large, as each source type can vary
 107 substantially at the regional scale in function of several factors (methane geographical
 108 origine, formation process, season, secondary alteration - e.g. Whiticar, 1999 ; Fisher et al.,
 109 2011 ; Zazzeri et al., 2015 ; Lopez et al., 2017). Therefore, the determination of the specific
 110 $\delta^{13}\text{CH}_4$ signatures of regional sources is needed (and their time variation, ideally) for a
 111 source apportionment of methane emissions at the regional scale.

112



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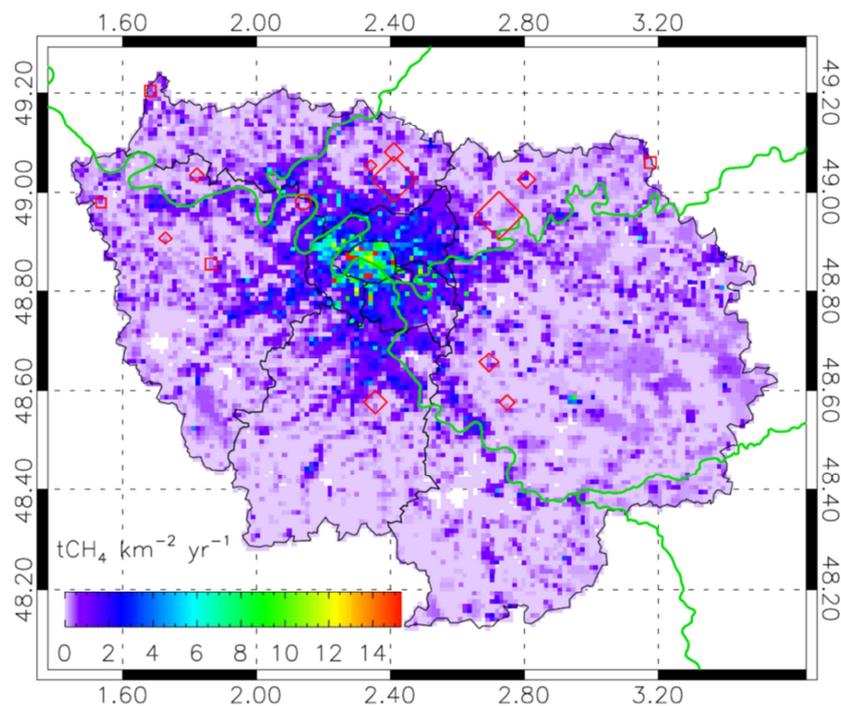
114

115 *Figure 1. Sources of methane in Ile-de-France, in ktCH₄/yr (AIRPARIF, 2013 inventory).*

116

117 As most of methane emissions come from human activities, urbanized and
 118 industrialized regions are key regions to carry out atmospheric surveys. Cities are the major
 119 source of GHG emissions globally and constitute important targets for GHG emissions
 120 mitigation [Duren and Miller, 2012]. Reducing urban emissions of CO₂, the most important
 121 GHG, has been the focus of several cities, but methane emissions have been largely
 122 neglected until recently (e.g. von Fischer et al., 2017; Weller et al., 2018). We do not know

123 precisely which sources and how much these sources contribute to cities methane budget.
124 This makes the use of global modelling for the estimation of regional sources in urbanized
125 areas quite complicated (Townsend-Small et al., 2011b; Townsend-Small et al, 2012), as for
126 example in Los Angeles where large scale transport models underestimate the observed CH₄
127 concentration (Hsu et al., 2010). Urbanized and industrialized regions are equipped with
128 facilities that represent widespread sources of methane, including landfill sites, gas storage
129 and distribution networks, WWT plants, heating systems and vehicles. Stable isotopic
130 signatures provide an important constraint in the evaluation of local methane sources.
131 Previous δ¹³CH₄ sources studies in urbanized areas have been carried out through intensive
132 field campaigns, for example in the London region (Lowry et al., 2001 ; Zazzeri et al., 2017),
133 in Boston (Phillips et al., 2013 ; Boothroyd et al., 2018), in Washington DC (Jackson et al.,
134 2014) and in Los Angeles (Townsend-Small et al., 2012).
135



136
137 *Figure 2. Methane emissions in IDF according to the AIRPARIF 2013 emissions inventory.*
138 *Losanges indicate the positions of landfills, squares the ones of the gas storage sites and the*
139 *circle the one of the Achères waste water treatment facility, that were all surveyed in the*
140 *framework of this study. Another gas storage site located out of IDF further in the North*
141 *was also surveyed (see Table 2).The symbol size is calibrated to the emissions given by*
142 *AIRPARIF inventory.*
143

144 To our best knowledge, this study is the first one on characterizing the individual
145 methane sources and their δ¹³CH₄ signature in the Paris megacity region, and on assessing
146 possible leaks from the Paris gas network underground lines as it was done in other urban
147 areas (e.g. Phillips et al., 2013 ; Jackson et al., 2014). With 12 million inhabitants, Paris is the
148 third biggest megacity in Europe and a large source of GHG (e.g. Xueref-Remy et al., 2018).
149 It is located in the Ile-de-France region (IDF) which represents 2% of the national territory.
150 According to the regional air quality agency (AIRPARIF, <http://www.airparif.asso.fr/>),
151 methane emissions in IDF (Fig.1) are 36.5 ktCH₄/yr and contribute for 2% of GHG emissions
152 from IDF. Fig. 2 shows the methane annual emissions per square kilometer from the

153 AIRPARIF 2013 inventory. According to this inventory, 45% of these emissions result from
154 solid waste landfills, 25% from oil/gas distribution in vehicles refuelling stations, 15% from
155 combustion processes in buildings and 5% from ruminants. Then follows the gas storage
156 sector estimated to emit 3% of the regional methane emissions. Note that there is no coal
157 mine in the Paris region. Several other minor sectors follow, including water treatment
158 facilities estimated to emit 70 kg CH₄/yr i.e. 0.2% of CH₄ emissions in IDF (a surprising low
159 estimate). Unlike diffuse sources (e.g. enteric fermentation, buildings, traffic) which are
160 widely distributed, landfills, WWT sites and gas extraction and compression facilities are
161 intense localized sources. By using atmospheric measurements, methane plumes from those
162 sources can be detected and isotopically characterized (e.g. Zazzeri et al., 2015 ; Lopez et
163 al., 2017). Note that fuel service stations are also point sources, but they are so numerous in
164 IDF that this makes it difficult to survey them exhaustively. Furthermore, according to
165 previous studies (Phillips et al., 2013 ; Jackson et al., 2014 ; Eijo-Rio et al., 2015 ; McKain et
166 al., 2015 ; Boothroyd et al., 2018), urbanized areas may also be affected by leaks on gas
167 storages sites and gas distribution urban networks, as well as sewer networks within the city
168 itself whose emissions are not reported in the inventories.

169

170 In this study, we report the $\delta^{13}\text{C}_{\text{CH}_4}$ emissions signature from non-agricultural intense
171 localized sources (landfill, gas storage and WWT sites, cf Fig.2) in the Paris megacity region
172 calculated by combining CRDS (Cavity Ring Down Spectroscopy) and GC-IRMS (Gas
173 chromatography and Isotope Ratio Mass Spectrometry) measurements. We also assessed
174 whether gas distribution lines and sewer networks were also sources of methane in the Paris
175 city. The measurements were collected between December 2012 and December 2015
176 through several intensive campaigns using mobile in-situ CRDS CH₄ and $\delta^{13}\text{C}_{\text{CH}_4}$ analyzers
177 and an air bag sampling set-up onboard a vehicle for accurate measurements of $\delta^{13}\text{C}_{\text{CH}_4}$ in
178 the laboratory with GC-IRMS, using a similar design as the one described in Zazzeri et al.
179 (2015). The material and methods are detailed in Section 2. Results are presented in Section
180 3. We discuss and compare our results with those of previous studies and the AIRPARIF
181 2013 inventory in section 4. We conclude on the benefits and limitations of such mobile
182 campaigns and CRDS and GC-IRMS technics for better inferring regional CH₄ budgets.

183

184 **2- Material and methods**

185 **2.1 Methodology**

186 The isotopic ¹³C composition of 16 individual intense localized methane sources (5
187 gas storage sites, 10 landfills and 1 large WWT site) and prospective line sources from the
188 gas network underground lines and sewer networks of the Paris megacity region was
189 analyzed through a series of 6 mobile car campaigns (17-20 December 2012 ; 12-15 May
190 2014 ; 10-11 August 2015 ; 8-9 September 2015 ; 19-23 November 2015 ; and 7-10
191 December 2015) through a Keeling plot approach (Keeling, 1958). Each site was studied
192 individually. CH₄ concentration measurements were carried out accross the atmospheric CH₄
193 plume emitted by each site according to wind direction and speed measurements performed
194 simultaneously, allowing us to quantify the local enhancement of methane concentration
195 above background downwind of each source. Since these enhancements are quite large, the
196 methane concentration is given in parts per million (ppm), which is the unit commonly used in
197 similar studies and delivered by the CRDS analyzer (e.g. Zazzeri et al, 2015). If the CH₄

198 enhancement was strong enough (≥ 0.5 parts per million (ppm)), we performed isotopic
199 measurements along the concentration gradient. Note that this study did not aim at
200 characterizing precisely the amplitude of the source plume, which depends largely on
201 meteorological conditions and conditions of sampling. The objective of the present study was
202 rather to detect the source plume emitted by each site and to characterize its $\delta^{13}\text{CH}_4$
203 signature.

204 The isotopic measurements must have a sufficient precision to be used for source
205 apportionment. The difference between the different $\delta^{13}\text{CH}_4$ sources signature is about 10-15
206 ‰. The spatio-temporal variability for each source type is a few ‰ (2-7 ‰ ; e.g. Arata et al,
207 2016). Given these numbers, the ideal precision we aimed at was smaller than ± 0.8 ‰ on
208 the source defined by a Keeling Plot approach (Keeling, 1958) : this requires a high precision
209 on the $\delta^{13}\text{CH}_4$ measurements, achievable using the GC-IRMS facility of RHUL, given a CH_4
210 concentration enhancement along the emission plume higher than 0.5 ppm above
211 background (Zazzeri et al., 2015). The GC precision on the concentration measurements is \pm
212 0.5 ppb and the IRMS precision on the isotopic data is ± 0.05 ‰ for each measurement ;
213 using these data, a precision as low as ± 0.1 ‰ on the $\delta^{13}\text{CH}_4$ source signature could be
214 obtained for certain sites by the Keeling plot approach (see sections 2.4.2 and 3.1). The
215 CRDS analyzer (model G2132-i by PICARRO) could not reach such a precision but could be
216 used for the source $\delta^{13}\text{CH}_4$ signature determination if the increase in the CH_4 concentration
217 due to the studied source is higher than 1.5 ppm (PICARRO, personal communication).
218 According to PICARRO, the precision of the datasets used in this study is 5 ppb + 0.05% of
219 reading on the 5 min average concentration measurements ; ± 0.8 ‰ on 5 min average
220 isotopic measurements ; and a resulting precision of ± 2.0 ‰ to ± 3.7 ‰ on the source
221 signature.

222 On the majority of landfill sites and gas storage sites, and on the WWT site, and
223 whenever the local methane concentration enhancements were above 0.5 ppm, air samples
224 were collected into bags (integration time of about 30 seconds) then analyzed by GC-IRMS
225 at RHUL. Such samples were collected during 4 days in December 2015 campaign, thanks
226 to the INGOS TNA program (<https://www.ingos-infrastructure.eu/access/>). CRDS data were
227 collected during all the campaigns presented in this study in the framework of the
228 CARBOCOUNT-CITY project. Regarding the assessment of possible leaks from Paris
229 underground gas lines and sewer networks and from the WWT site, mobile CH_4
230 measurements were conducted in the Paris city streets to detect possible CH_4 plumes and to
231 attempt to characterize their $\delta^{13}\text{CH}_4$ isotopic signature, but only using CRDS measurements.

232 Furthermore, over the recent years, some studies reported that CRDS $\delta^{13}\text{CH}_4$
233 measurements are affected by the presence in the sampled air of ethane together with
234 methane (Rella et al., 2015 ; Assan et al., 2017). Ethane is co-emitted with methane from
235 fossil fuel sources. Unfortunately, we did not have ethane measurements to apply the
236 correction for ethane on methane CRDS measurements proposed by Assan et al. (2017).
237 Therefore, the isotopic composition of the air samples collected on 6 of our selected sites,
238 analyzed by GC-IRMS, was compared to the isotopic CRDS data for cross-validation of both
239 methods and to assess independently the uncertainty of the CRDS data.

240 **2.2 Site identification and selection**

241 In this study, we focus on the main regional landfills, on the four gas storage sites plus
242 a fifth one located outside IDF but that contributes to feed the Paris natural gas network,
243 Paris city underground gas lines and sewer networks, and a peri-urban WWT site that is the
244 biggest one in Europe. According to the AIRPARIF 2013 emissions inventory, localized
245 intense sources are the main emitter of methane in IDF (Fig.1). These sources are mostly
246 landfills for solid wastes, and represent the most important methane emissions sector in IDF
247 (Fig.1). In landfill sites, part of the wastes that cannot be recycled nor valorized energetically
248 or biologically (e.g. compost) is first treated to reduce its potential toxicity and then buried in
249 soil. Landfills are estimated by the AIRPARIF 2013 inventory to emit 16.54 ktCH₄/yr from 10
250 sites. 44 % of those are emitted by landfills located in the Seine-et-Marne department (77)
251 alone (AIRPARIF emissions inventory, 2013), the eastern part of IDF.

252 Another type of point sources are gas storage sites. There are 4 of them in IDF and a
253 5th one in the Hauts-de-France (HDF) region just north of IDF, which all supply the Paris
254 megacity gas network (<https://www.storengy.com/countries/france/en/our-sites.html>). These
255 sites are reported to leak and emit 1.17 ktCH₄/yr by the inventory which corresponds to more
256 than 98% of the fossil fuels extraction and compression sectors (Fig.1).

257 A third type of point methane sources of interest is WWT facilities. The IDF region
258 comprises the biggest WWT plant in Europe, which is located in Achères (Table 4). In the
259 AIRPARIF 2013 inventory, the WWT facility sector comprises one emission point that
260 corresponds to the Achères facility with estimated emissions of 0.066 ktCH₄/yr i.e. 0.2 % of
261 the regional methane emissions. The access to these sites are usually restricted and
262 requires specific authorization. However, the methane plume coming from the site can be
263 detectable while driving downwind of it.

264 The diffuse source types given in Fig.1 contain road and airborne traffic, but gas leaks
265 from gas distribution pipes, sewer networks and residential buildings are not considered in
266 the AIRPARIF 2013 emissions inventory. These are very poorly known potential sources,
267 and have been shown to represent large non-reported sources in other cities like in Boston
268 (Phillips et al., 2013) and in New-York City (Jackson et al., 2014). In this study, a systematic
269 street survey in Paris was carried out in order to check for possible methane leaks from the
270 gas distribution lines and sewer networks.

271 2.2.1 Landfill sites

272 In landfills, the decomposition of the organic waste by fermentation occurs in a
273 ground-dug locker after it has been compressed. It produces a mix of gases named
274 « biogas », mostly made of methane (50 to 70%) in the case of French facilities (e.g.
275 <https://www.notre-planete.info/ecologie/dechets/methanisation-biogaz.php>). French emission
276 regulation policies state that landfill managers should install inside the locker efficient biogas
277 capture systems, once the locker is fully filled and recovered by a re-vegetalisation process.
278 The captured biogas is then used to produce energy (e.g. burned to produce electricity, or
279 some cases for heat co-generation). However, these systems use only part of the trapped
280 biogas. The rest is being flared using processes that are not strictly regulated by the law.
281 Furthermore, despite the vegetal cover set on the filled lockers, biogas might leak into the
282 atmosphere, contributing to diffuse methane emissions from the landfill site
283 (https://www.oieau.org/eaudoc/system/files/documents/45/226168/226168_doc.pdf).

284 The main landfill sites of IDF included in the AIRPARIF 2013 emissions inventory
285 match the 10 sites for storage of non-dangerous wastes existing in IDF identified in the Atlas
286 delivered by the Regional Observatory of Wastes (ORDIF, 2013), except one, which

287 according to Airparif, is located outside of IDF. This site very likely corresponds to the 10th
 288 site of the ORDIF (2013) Atlas, called Isles-les-Meldeuses.

289 Table 1 gives the list of the 10 sites that we selected for our mobile survey, their
 290 location, and emission estimates from the Airparif 2013 emissions inventory. 9 sites out of 10
 291 are the largest landfills currently active in IDF (Brueil-en-Vexin and Guitrancourt are counted
 292 as one in the table as both sites are very closed one from each other and the second one
 293 now replaces the first one). The 10th selected site is Epinay-Champlatreux, a landfill for non-
 294 dangerous wastes that was closed on 31 December 2008 and that is counted as an active
 295 methane source in the Airparif 2013 inventory
 296 (http://www.dechetcom.com/comptes/jcamille/env_idf3.pdf).

Site code	Name (region, department code)	ktCH ₄ /yr (AIRPARIF)	Latitude (°N)	Longitude (°E)
L1	Claye-Souilly (IDF, 77)	5.58	48.954 48.955	2.724 2.732
L2	Le Plessis-Gassot (IDF, 95)	5.00	49.026 49.047	2.410 2.410
L3	Vert-le-Grand (IDF, 91)	1.33	48.577 48.587	2.356 2.381
L4	Soignolles-en-Brie (IDF, 78)	0.93	48.657 48.641	2.695 2.739
L5	Epinay-Champlatreux (IDF, 95) closed on 31/12/2008.	0.83	49.080 49.051	2.411 2.421
L6	Monthyon (IDF, 77)	0.77	49.025 49.022	2.807 2.798
L7	Fouju-Moisenay - Blandy (IDF, 77)	0.58	48.576 48.576	2.749 2.751
L8	Brueil-en-Vexin (IDF, 78) from 1974 to 24/2/2014, now replaced by Guitrancourt	0.50 0.22	49.034 49.017 48.989 49.011	1.823 1.805 1.796 1.796
L9	Isles-les-Meldeuses (IDF, 77)	0.41	48.908 49.002	1.729 3.031
L10	Moisselles* (IDF, 95) Real location : Attainville	0.32	49.053 49.050	2.342 2.352

297 *Table 1. List and coordinates of the main landfill sites in IDF for the storage of non-*
 298 *dangerous wastes, obtained by combining the AIRPARIF 2013 emissions inventory and*
 299 *ORDIF (2013) information, and their annual CH₄ emissions estimates from AIRPARIF 2013*
 300 *inventory. The actual geographical coordinates are given on the second line of each site.*

301 2.2.2 Gas storage sites

302 There are 4 big gas storage sites in Ile-de-France (according to the EPA
 303 classification, these would fit into the “city gates” and “underground gas storages” terms of
 304 the transmission source sector – see <https://www.epa.gov/natural-gas-star-program/overview-oil-and-natural-gas-industry>). These sites are filled in summertime and
 305

306 used in wintertime to supply gas to the IDF and Normandie (West of IDF) regions. A 5th gas
 307 storage site located in the Hauts-de-France (HDF) region (North of IDF) partly supplies gas
 308 to Ile-de-France as well. These sites are operated by STORENGY, a sub-contractor of Gaz
 309 De France ([http://www.storengy.com/fr/qui-sommes-nous/nos-implantations-](http://www.storengy.com/fr/qui-sommes-nous/nos-implantations-industrielles.html)
 310 [industrielles.html](http://www.storengy.com/fr/qui-sommes-nous/nos-implantations-industrielles.html)). They are made of a number of sinks filled with compressed gas. Table 2
 311 gives for each site the location, capacity of gas storage, number of sinks operated, emission
 312 estimates from the Airparif 2013 emissions inventory, ordered by the site capacity, from the
 313 largest to the smallest.
 314

Site code	Name (region, department code)	Capacity (Mm ³) & sinks number ¹	ktCH ₄ /yr (AIRPARIF)	Latitude (°N)	Longitude (°E)
S1	Gournay-sur-Aronde (HDF, 60)	3500	-	-	-
		59		49.528	2.701
S2	Germigny-sous-Coulombs (IDF, 77)	2200	0.32	49.059	3.176
		22		49.056	3.173
S3	Saint-Illiers-la-ville (IDF, 78)	1200	0.23	48.979	1.537
		31		48.985	1.551
S4	Beynes (IDF, 78)	1185	0.32	48.854	1.865
		36		48.844	1.874
S5	Saint-Clair-sur-Epte (IDF, 95)	1000	0.30	49.204	1.684
		14		49.204	1.707

315 *Table 2. List and coordinates of the gas storage sites ordered by their capacity as given by*
 316 *STORENGY. The first lat/long line of each site indicates the position given by the AIRPARIF*
 317 *2013 emissions inventory. The actual geographical coordinates are given on the second line*
 318 *of the corresponding cell. The Gournay-sur-Aronde site is located in the Hauts-de-France*
 319 *region (HDF) and not in the IDF region, therefore it is not listed in the AIRPARIF database.*

320 2.2.3 Gas distribution lines (and sewer networks)

321 The gas distribution in Ile-de-France is at the charge of GRDF (Gaz Réseau
 322 Distribution France, <https://www.grdf.fr/>). Detailed map of gas pipelines is not available. The
 323 most detailed available map we could find is available from the following link:
 324 <http://www.cre.fr/reseaux/infrastructures-gazieres/description-generale#section5>. The main
 325 pipelines of Ile-de-France appear to be sited along highways. Secondary pipelines are likely
 326 distributed along streets in urbanized areas, but a higher resolution map was not available.
 327 According to previous studies, gas leaks can occur anywhere in a city (Phillips et al., 2013 ;
 328 Jackson et al., 2014). We thus sampled streets in one to several districts in the Paris inner
 329 city area for each campaign day. We also sampled on the road that encompasses Paris city
 330 and also the city of Montrouge close to Paris in the south/southeast (Table 3). Note that there
 331 is a possibility that the sewer networks would also emit methane, but then the methane
 332 isotopic signature would be much more depleted than the one outcoming from gas leaks.
 333 This property can be used to discriminate gas line and sewer network sources.

Site code	Location
G1	BP (ring road)
G2	Paris districts
G3	Montrouge (SSE of Paris)

334 *Table 3. List of the gas line sites (and sewer network sites)*

335 2.2.4 Water treatment site

336 WWT involves the degradation of organic matter of the effluents in anaerobic
 337 conditions that releases biogenic methane emissions. The different steps are explained in
 338 details for instance in Ars (2017). The SIAAP (Syndicat Interdépartemental pour
 339 l'Assainissement de l'Agglomération Parisienne) is the main operator of WWT facilities in
 340 IDF. There are 5 WWT plants (Seine Crésillons, Seine Aval, Seine Amont, Seine centre and
 341 Marne Aval) in IDF, the biggest WWT facility being Seine Centre, located at Achères
 342 (<http://www.veoliaeau.com/medias/dossiers/acheres.htm>). It is also the biggest in Europe
 343 (and the second worldwide). The Achères WWT facility is located on two sub-sites which
 344 coordinates are given in Table 4. Methane emissions from this facility have not been
 345 isotopically characterized before this study and therefore it was a target of our mobile
 346 campaigns. In this study, we were able to characterize the $\delta^{13}\text{CH}_4$ signature of the second
 347 sub-site (48.986°N, 2.124°E).
 348

Site code	Name	ktCH ₄ /yr (AIRPARIF)	Latitude (°N)	Longitude (°E)
W1	Achères	0.066	48.973	2.167
			48.973	2.166
			& 48.986	& 2.124

349 *Table 4. Coordinate of the selected WWT site and its annual methane emissions estimate*
 350 *from the AIRPARIF (2013) inventory. The first lat/long line indicates the position of the site*
 351 *given by the AIRPARIF inventory. The actual geographical coordinates of the site are indeed*
 352 *double and are given on the second and third lines of the lat/long cells.*

353 2.3 Instrumentation

354 During the mobile campaigns, we used the Picarro Investigator™ Unit (proprietary
 355 product of Picarro) which is made of hardware components and a cloud based software for
 356 providing an integrated solution to 1/ treat and control the datasets ; 2/ detect and locate
 357 methane enhancements above background ; and 3/ distinguish between biogenic and
 358 thermogenic methane sources of these enhancements (Arata et al, 2016). The hardware
 359 components consist of a car equipped with a Picarro G2132-i CRDS (Cavity Ring Down
 360 Spectroscopy) analyzer (<https://naturalgas.picarro.com/overview>). This analyzer was
 361 customized by PICARRO specifically for the Investigator Unit to support mobile
 362 measurements. The analyzer was powered directly from the car through a 12-220 V power
 363 transformer. The air inlet was attached on a 1-m height mast mounted on the roof of the
 364 vehicle. It was made of a ¼ inch outer diameter (O.D.) and 2-m length Nylon tube equipped
 365 with a 2 µm Swagelok particle filter and connected to the entrance of the analyzer inside the
 366 car. The car was also equipped with a Climatronics sonic anemometer for wind measurement
 367 and a Hemisphere GPS receiver fixed on the mast, which allowed a precise determination of
 368 the car location. The analyzer was calibrated before the campaigns with a tank supplied by
 369 Matheson whose methane concentration was 19.6 +/- 0.015 ppm and $\delta^{13}\text{C}$ content was -32.6
 370 +/- 0.05 ‰. During the campaigns, this tank was used to detect any instrumental drift, but the
 371 Picarro analyzer showed a stable behavior. This instrument was designed to monitor in two
 372 modes separately. In the first mode, only CH₄ concentrations were monitored while the car
 373 was moving. The analyzer flow rate was increased to 3.5 L/min and its frequency to 4 Hz to
 374 get a fast instrumental response, which gives a transport time in the tubing of 2 s. The
 375 datasets were corrected for this delay. The car drove at 50 km/h or less, which gives a
 376 maximum uncertainty of 28 m on the source location regarding the vehicle speed. Once a
 377 methane enhancement above background was detected, we drove again into it and much
 378 slower to make sure it was occurring at the same location. The occurrence of the methane

379 enhancement was also confirmed by the isotopic measurements. To perform isotopic
380 measurements, the car was stopped and the CRDS analyzer was turned into its second
381 mode : the analyzer was coupled to a « Megacore » set-up based on a Dekabon tubing of 10
382 m, that was collecting air while we were driving in the plume. In this second mode, once we
383 were sure that we detected a persistent enhancement above background concentrations, the
384 car was stopped, and the air of the « Megacore » was analyzed for its isotopic content at a
385 flowrate of 25 mL/min. The flowing time of the air in the analyzer was used to reconstruct the
386 location of each data point.

387 The data were collected through a bluetooth connection into a central onboard
388 computer, which was also used to monitor the CH₄ concentrations during the survey. The
389 CRDS data were instantaneously sent by 3G or 4G connection to a cloud server. On this
390 latter, a complex software called Pcubed (proprietary product of Picarro) was applied on the
391 datasets to detect isolated peaks that could be attributed to an instrumental artefact (e.g. cell
392 pressure or temperature instabilities) from longer methane enhancements above background
393 that could be attributed to a methane source. Usually, the vibrations of the car do not
394 generate peaks but could damage the mirrors and laser of the cavity ; however, no such
395 damage was observed during our campaigns.

396 After a methane enhancement was detected by CRDS, the car was driven back into it
397 to collect air samples into bags at different locations of the enhancement and outside of it for
398 background assessment. The concentration and $\delta^{13}\text{C}$ content of atmospheric methane in the
399 sample bags were analyzed at the RHUL laboratory straight after the sampling campaign,
400 using the material and methods described in Zazzeri et al. (2015). The car was stopped
401 during each bag sampling. The bags, made of Tedlar (5 L) were filled with outside air during
402 30 s each using a battery operated pump (KNF Neuberger), pumping air through a ¼ inch
403 O.D. Nylon tube attached to the mast in the car. Before the filling, the full set-up was flushed
404 with ambient air for 4 minutes in order to reach equilibrium between gas and solid phases.
405 Five to twelve bags were filled for each identified plume. In total, heighty samples were
406 collected. The isotopic measurements and Keeling plot analysis allowed calculation of a
407 distinct isotopic signature for the main methane sources in the Paris region. The observed
408 source isotopic signatures can be used also for the characterization of methane emissions in
409 more densely populated areas and for regional modelling (see section 1).

410 The location of both CRDS analyser and air sampling inlets on the mast prevented
411 the measurements to be contaminated by the car exhaust. When not driving during bag
412 sampling, we paid attention to choose favorable conditions in order to prevent that the car
413 exhaust plume was advected or thermally uplifted to the air line inlets location.

414

415 **2.4 Data analysis**

416 2.4.1 $\delta^{13}\text{CH}_4$

417 By definition, the isotopic composition of methane is expressed in terms of a ratio in
418 per mil (‰), using the δ notation (Pataki et al., 2003) :

$$419 \quad \delta = (R_A/R_{std} - 1) \times 1000$$

420 where R_A denotes the isotopic ratio $^{13}\text{C}/^{12}\text{C}$ in CO_2 derived by combustion of the methane
 421 sample. R_{std} is the corresponding ratio in the V-PDB (Vienna Pee Dee Belemnite) standard.
 422 Isotopic signatures can vary over time and season : this is the case for landfill sites, due to
 423 changes in landfill management that result in the modification of the fraction of CH_4 oxidised
 424 in the topsoil, and thus, of the $\delta^{13}\text{CH}_4$ signature. This is also the case for natural gas which
 425 isotopic signature depends on the geological origin of the gas (e.g. Lopez et al, 2017).

426 2.4.2 Keeling plot approach

427 We used the Keeling plot method to infer the the $\delta^{13}\text{CH}_4$ signature for each emission
 428 source (Keeling, 1958). This approach consists in plotting the atmospheric $\delta^{13}\text{C}$ in CH_4
 429 values against the inverse of simultaneous atmospheric CH_4 concentration data. The
 430 intercept value of the linear relationship between the two variables constitute the isotopic
 431 signature of the source which generated the methane signal over background (Pataki et al.,
 432 2003). The relative uncertainty of the source signatures were computed by the BCES
 433 (Bivariate Correlated Errors and intrinsic Scatter) estimator (Akritas and Bershad, 1996),
 434 which accounts for correlated errors between two variables and computes the error on the
 435 slope and intercept of the best interpolation line (for additional information on the method,
 436 see Zazzeri et al., 2015).

437

438 3- Results

439 3.1 $\delta^{13}\text{CH}_4$ signatures

440 The CH_4 maximum local concentration enhancement above background detected in
 441 the emission plume of each site and its isotopic signature are summarised in Table 5. This
 442 enhancement is defined as the maximum minus the minimum concentrations that we
 443 measured by driving downwind of the site. In the following, all uncertainties are given as
 444 twice the standard deviation ($2\text{-}\sigma$) of the mean source signature calculated by the Keeling
 445 Plot method.

Site code	Name (region, department code)	Dates of survey	Windspeed in km/h (direction)	ΔCH_4 (ppm)	$\delta^{13}\text{C}$ (‰) CRDS ($2\text{-}\sigma$)	$\delta^{13}\text{C}$ (‰) GC-IRMS ($2\text{-}\sigma$)
Landfill sites						
L1	Claye-Souilly (IDF, 77)	11 Aug 2015 9 Dec 2015	<5 (N) 5 (SW)	0 1.4	- -	- -59.8±0.1
L2	Le Plessis-Gassot (IDF, 95)	19 nov 2015 10 Dec 2015	10 (NW) 10 (S)	3.5 3.8	-53.0±2.0 -59.4±2.0	- -58.2±0.3
L3	Vert-le-Grand (IDF, 91)	18 Nov 2015 8 Dec 2015	15 (SW) 10 (S)	3.5 3.5	-56.0±2.0 & -61.5±2.0 -61.9±2.0	- -61.3±0.2
L4	Soignolles-en-Brie (IDF, 78)	9 Sept 2015 8 Dec 2015	15 (E) 10 (S)	2.8 0.6	- -	- -63.2±0.1
L5	Epinay-Champlâtreux (IDF, 95) closed 31-12-08.	19 Nov 2015	5 (NW)	0	-	-
L6	Monthyon (IDF, 77)	19 Nov 2015	5 (NW)	0	-	-

L7	Fouju-Moisenay - Blandy (IDF, 77)	13 May 2014	10 (SW)	3.5	-59.0±2.0	-
		9 Sep 2015	15 (E)	3.7	-57.9±2.0	-
		18 Nov 2015	10 (NW)	3.2 & 5.2	-65.0±2.0	-
		8 Dec 2015	10 (S)	3.5 & 8.5	-65.3±2.0 & -59.4±2.0	-59.6±2.6
L8	Brueil-en-Vexin (IDF, 78) from 1974 to 24-02- 2014	8 Sep 2015	10 (NE)	0	-	-
		19 Nov 2015	10 (NW)	0	-	-
L9	Isles-les- Meldeuses (IDF, 77)	8 Sep 2015	10 (NE)	3.5	-60.6±2.0	-
		9 Dec 2015	5 (SW)	7.2	-65.9±2.0	-63.7±0.3
L10	Moisselles* (IDF, 95) Real place : Attainville	19 nov 2015	5 (NW)	0	-	-
Gas storage sites						
S1	Gournay-sur- Aronde (HDF, 60)	11 Aug 2015	< 5 (N)	8.1	-31.8±2.0	-
		10 Dec 2015	10 (S)	5.7	-31.7±2.0	-33.8±0.4
S2	Germigny-sous- Coulombs (IDF, 77)	8 Sep 2015	10 (NE)	3.5	-40.4±2.0	-
		9 Dec 2015	5 (SW)	0.6	-	-41.6±2.4
S3	Saint-Illiers-la- ville (IDF, 78)	8 Sep 2015	10 (NE)	0	-	-
		19 Nov 2015	10 (NW)	0	-	-
S4	Beynes (IDF, 78)	8 Sep 2015	10 (NE)	4.8	-	-
		7 Dec 2015	< 5 (SE)	3.5	-45.8±2.0	-43.4±0.5
S5	Saint-Clair-sur- Epte (IDF, 95)	8 Sept 2015	10 (NE)	0	-	-
		19 Nov 2015	10 (NW)	0	-	-
Gas distribution lines						
G1	BP (ring road)	12 May 2014	10 (SW)	0.5-0.8	-	-
G2	Paris city districts	17-20 Dec 2013	10 (SW)	0 -1.4	-	-
		12-15 May 2014	10 (SW)	0 - 2.0	-39.1±2.0	-
		11 Aug 2015	< 5 (N)	0 - 0.6	& -41.8±2.0	-
		20-23 Nov 2015	10 (W)	0 - 0.5	-	-
G3	Montrouge	11 Aug 2015	5 (NE)	0.7	-	-
Waste water treatment site						
W1	Achères* (IDF, 78)	17 Dec. 2012	2 (E)	4.0	-53.2±3.7	-
		11 Aug. 2015	< 5 (N)	3.5	-51.0±2.0	-
		10 Dec. 2015	10 (S)	0.4& 0.5	-	-51.9±0.2 &-55.3±0.1

446 *Table 5. Synthesis of our results. The precision on CRDS CH₄ concentration reported by*
447 *PICARRO is ± 5 ppb + 0.05% of the measurement and ± 2.0 ‰ (2-σ) on the Keeling plot*
448 *(KP) source signature but for one case noted * for which source uncertainty is -3.7 ‰. The*
449 *precision calculated from the GC-IRMS KP source signature depends on each site, as*
450 *indicated in the corresponding column. The local CH₄ concentration enhancement noted*
451 *ΔCH₄ is calculated as the difference between the maximum and the minimum CH₄*
452 *concentration measured downwind of each site. For cases where both CRDS and GC*
453 *signatures could be measured, the CH₄ enhancement is calculated from GC data.*

454 3.2 Landfill sites

455 Ten landfill sites were surveyed among which Claye-Souilly and Le Plessis-Gassot
456 being by far two main landfills in IDF with emissions five to ten times larger than other

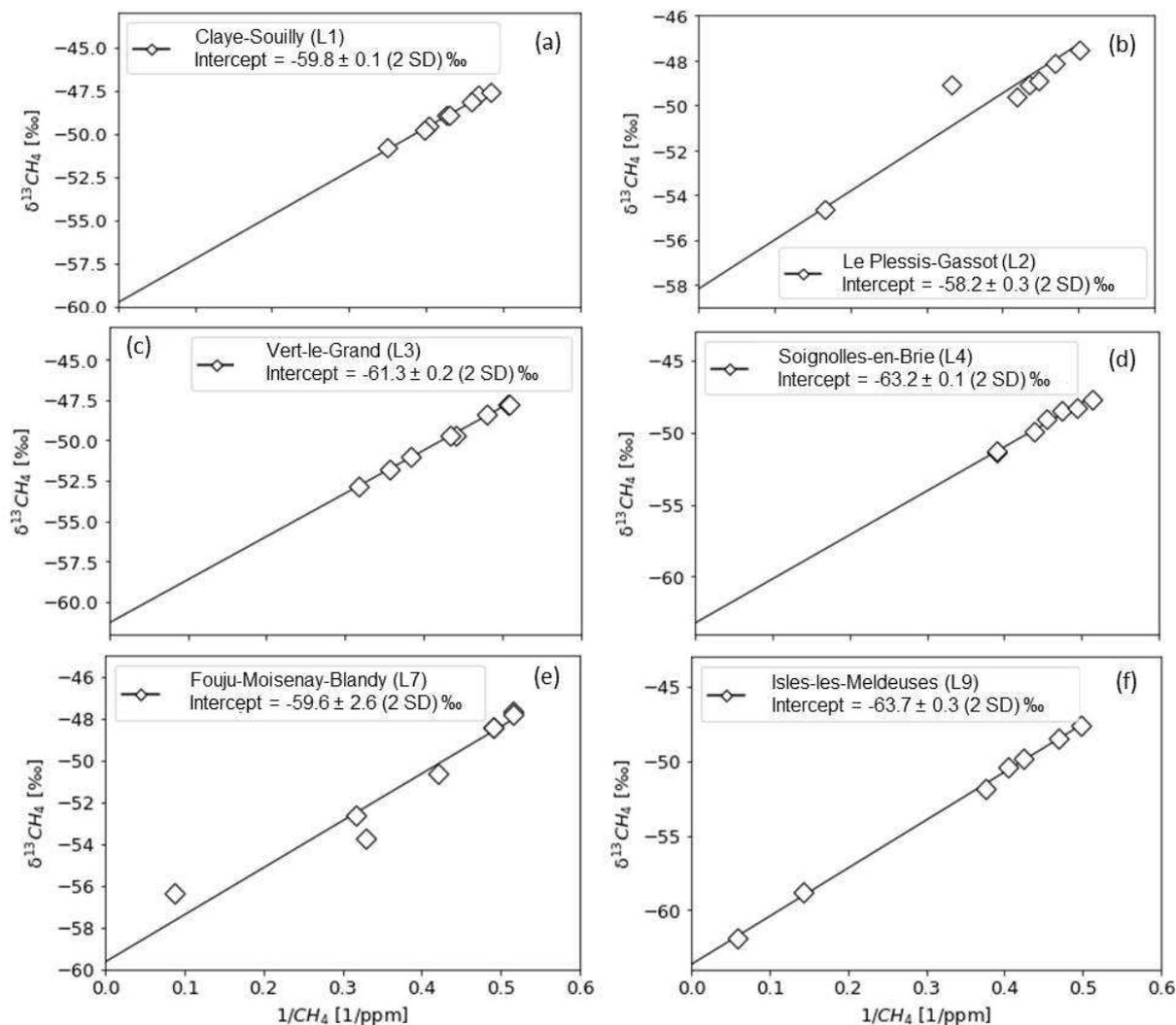
457 landfills. Among those, only 6 of them were shown to emit plumes of methane that ranged
458 from 0.8 ppm to 8.5 ppm above background concentrations recorded off site. No methane
459 plume could be detected on 4 landfills : Epinay-Champlâtreux (site L5) and Brueil-en-Vexin
460 (site L8), that were closed in 2008 and 2014 respectively, and Monthyon (site L6) and
461 Moisselles (site L10, which is indeed located in Attainville). For Brueil-en-Vexin, Monthyon
462 and Moisselles, the exposure of the instrumentation regarding these sites was not satisfying
463 (instrumentation upwind of the site, or no road closer to the site than 1.5 km away, limiting
464 the possibility to cross the site plume if any). For Epinay-Champlâtreux, the wind exposure
465 was satisfying as our instrumentation was close to the site and downwind of it. We can
466 conclude that 1/ the Brueil-en-Vexin, Monthyon and Moisselles sites should be surveyed
467 again with more favorable plume exposure conditions; and 2/ the Epinay-Champlâtreux site
468 does not seem to emit methane, which can be explained by its closure several years ago in
469 2008.

470 The $\delta^{13}\text{C}$ signatures of the methane plumes for the 6 landfills from which we were
471 able to detect a methane plume could be characterized both by CRDS and GC-IRMS. The
472 signatures obtained by GC-IRMS range from $-63.7 \pm 0.3 \text{ ‰}$ to $-58.2 \pm 0.3 \text{ ‰}$. The ones
473 measured by CRDS span a range from $-65.9 \pm 2.0 \text{ ‰}$ to $-53.0 \pm 2.0 \text{ ‰}$. Both techniques give
474 average signatures that are consistent within the error bars. These are typical from biogenic
475 methane emissions and in agreement with the literature (e.g. Lassey et al., 2011; Zazzeri et
476 al., 2015). The mean signature calculated from CRDS data relies on 12 surveys on 4 sites,
477 against 6 surveys on 6 sites for the one obtained from GC-IRMS data. 4 surveys were
478 common to both methods on 4 different sites. On these 4 common sites the mean signature
479 ($\pm 2\text{-}\sigma$ variability) obtained from GC-IRMS measurements equals to $-60.7 \pm 4.7 \text{ ‰}$, which is
480 very close to the mean signature calculated from CRDS data of -61.7 ‰ ($\pm 6.1 \text{ ‰}$). The $2\text{-}\sigma$
481 variability of the measurements obtained by GC-IRMS is lower than by CRDS. This could
482 come from differences in the two instrumental set-ups (flow rate of 25 mL/mn by CRDS vs 5
483 L/mn for the sampling bag set-up ; lengths of tubing of 10 m for CRDS, 2 m for bag sampler),
484 a higher precision on the GC-IRMS measurements and a sampling time uncertainty
485 estimated to be 5 seconds between the clocks of the two sampling systems.

486 4 of the 6 emitting sites were surveyed twice to five times with the Picarro analyzer,
487 on different years and months and revealed a variability of the signature in the range of 5.2 to
488 7.0 ‰ per site ($2\text{-}\sigma$). Indeed, several parameters control the isotopic signature of a landfill
489 such as temperature, waste composition and how strong is the methane oxidation level due
490 to methanotrophic bacteria in the top-soil cover (Zazzeri et al., 2015; Liptay et al., 1998).
491 Changes in these parameters could explain the observed seasonal to annual variability of the
492 $\delta^{13}\text{C}$ signature of each landfill site. Note that the variability on one single landfill site can be
493 higher than the spatial variability inferred by CRDS between these 4 sites (6.2 ‰ , $2\text{-}\sigma$).

494 Claye-Souilly being the largest landfill emitter in the Airparif inventory (Table 1) was
495 sampled twice. On the first survey (11 August 2015), no CH_4 plume could be detected,
496 although the car passed at the edge of the site downwind of it. Windspeed was low (< 5
497 $\text{km}\cdot\text{h}^{-1}$), helping for the stay of the plume on the site, but the temperature at the moment of
498 that survey in summer afternoon was relatively high ($>25^\circ\text{C}$), favouring the vertical dispersion
499 of the plume by turbulence processes over the site. Back there in Dec. 2015, we could detect
500 by CRDS a local methane concentration enhancement of 1.4 ppm above background (Fig. 4
501 site L1) and measured a signature of $-59.8 \pm 0.1 \text{ ‰}$ by GC-IRMS (Fig.3a), typical of biogenic

502 sources. The cold winter and low windspeed conditions ($< 5 \text{ km.h}^{-1}$) favored the
 503 accumulation of the plume at low altitudes over the site. The amplitude of the methane
 504 enhancement that we were able to detect on this site is relatively low compared to other sites
 505 and at such low windspeed.

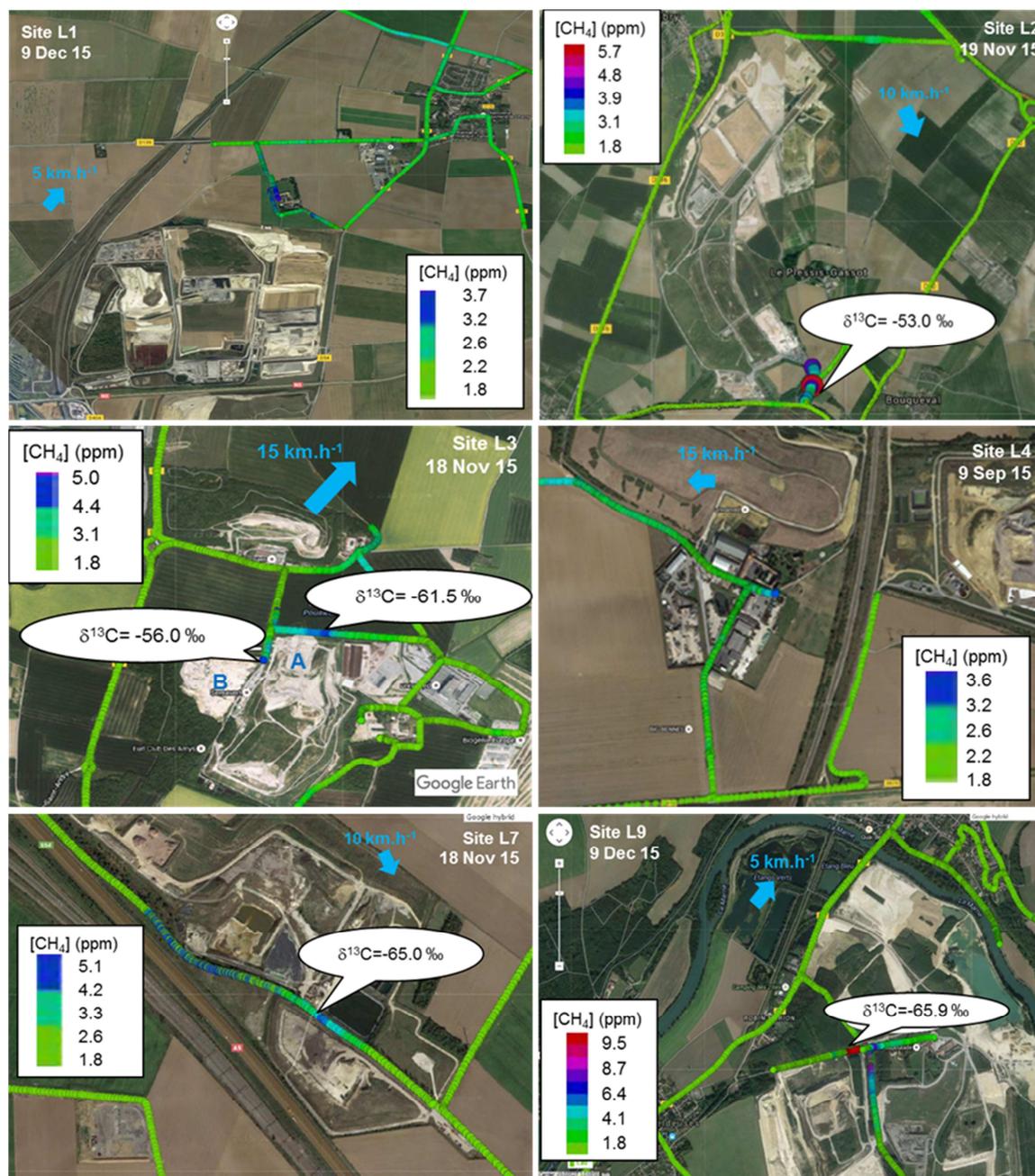


506

507 *Figure 3. $\delta^{13}\text{CH}_4$ signatures obtained by the Keeling plot method from GC-IRMS*
 508 *measurements on landfill sites on which methane plumes could be detected. Error bars are*
 509 *not shown as these are smaller than point marks.*

510 The second largest site named Le Plessis-Gassot was sampled twice and showed
 511 local methane concentration enhancements above background of the order of 3.5 ppm. Fig.4
 512 (site L2) shows the CRDS measurements done on this site on 19 Nov. 2015, with a $\delta^{13}\text{CH}_4$
 513 signature of $-53.0 \pm 2.0 \text{ ‰}$. Both CRDS and GC-IRMS data were collected in Dec. 2015 and
 514 gave consistent isotopic signatures. The p-value calculated on the CH_4 concentration
 515 measurements made simultaneously by GC and CRDS is 0.23 ($n=14$), showing no
 516 statistically significant difference between both datasets. Fig. 3b shows the Keeling plot of
 517 the GC-IRMS signature. The plume sampled in Nov. 2015 was studied by CRDS only and
 518 the isotopic signature was $-53.0 \pm 2\text{‰}$, which is notably above the Dec. 2015 values. This
 519 can be explained by the fact that the plume was not sampled at the same exact location and
 520 the wind was not exactly blowing from the same direction, highlighting the possibility of

521 different isotopic signatures on large landfills that could come from the type of waste and/or
522 level of fermentation.



523
524 *Figure 4. CRDS measurements on the 6 landfill sites on which methane plumes were*
525 *detected. The date of the survey is labelled on the figure together with the site code. The*
526 *color indicates the atmospheric CH₄ concentration according to the color scale, which is*
527 *automatically adapted to each survey by the Picarro investigator unit software. The*
528 *δ¹³CH₄ signature was inferred by Picarro from a Keeling plot analysis (uncertainty is ± 2.0 ‰). The*
529 *blue arrow indicates the wind direction together with wind speed. For site L3, the A and B*
530 *letters indicate the possible locations of the two methane sources that were detected on that*
531 *site that day.*

532 Vert-le-grand (3rd emitting landfill in Table 1, site L3) was sampled twice. In each case
533 a methane plume with a local CH₄ concentration enhancement of 3.5 ppm above background

534 was detected and with a signature of -61.5 ± 2.0 ‰ (18 Nov. 2015) and -61.9 ± 2.0 ‰ (8
535 Dec. 2015) by CRDS and -61.3 ± 0.2 ‰ by GC-IRMS (8 Dec. 2015) (Fig.3c). Although the
536 CRDS and GC-IRMS methods give signatures that are very close one from each other, the
537 p-value calculated on the CH₄ concentration measurements made simultaneously by GC and
538 CRDS is 0.019 (n=16), which means there is likely a statistically significant difference
539 between both datasets. In Nov 2015, a second plume could be detected by CRDS close to
540 the first one with a signature of -56.0 ± 2.0 ‰ (Fig.4, site L3). Wind was blowing from the SW
541 on 18 Nov.2015, while it was blowing from the S on 8 Dec. 2015. In regards to this, the
542 signature of -61.5 ± 2.0 ‰ (CRDS value) could be attributed to a source located in the A part
543 of the site (Fig.4) while the -56.0 ± 2.0 ‰ signature (CRDS data) could be coming from a
544 methane source located in the B part of the site (Fig.4). The two distinct signatures
545 measured by CRDS on the same site highlight here as well the possibility of the co-existence
546 of various biogenic signatures on a same site.

547 The Soignolles-en-Brie landfill, estimated to be the fourth landfill emitter (Table 1),
548 was observed to emit a CH₄ plume with a local methane concentration enhancement of 2.8
549 ppm above background in Sept. 2015 (Fig.4, site L4). A technical issue did not allow us to
550 characterize the isotopic signature of this enhancement by CRDS. We went back to the site
551 in Dec. 2015 and measured a local methane concentration enhancement of 0.8 ppm above
552 background and a source signature of -63.2 ± 0.1 ‰ by GC-IRMS, typical of biogenic
553 methane emissions (Fig.3d). Note that additional surveys were carried out on this site in
554 December 2016 with a CRDS analyzer by S. Assan et al. (<https://tel.archives-ouvertes.fr/tel-01760131/document>),
555 for which a signature of -60.0 ± 1.3 ‰ was reported with local
556 enhancements ranging from 2 to 12 ppm above background atmospheric methane
557 concentration.

558 Fouju-Moisenay-Blandy showed the largest variability (but was the one the most
559 sampled), with CRDS $\delta^{13}\text{C}_{\text{CH}_4}$ signature values ranging from -65.3 ± 2.0 ‰ to -57.9 ± 2.0 ‰
560 and measured over 4 surveys between 13 May 2014 and 8 Dec. 2015. The CRDS
561 measurements for 18 Nov. 2015 are shown on Fig. 4 (site L7), where a signature of $-65.0 \pm$
562 2.0 ‰ was measured. On 8 Dec. 2015, two distinct plumes were detected by CRDS at this
563 site with signatures of -59.4 ± 2.0 ‰ and -65.3 ± 2.0 ‰. The GC-IRMS signature equals $-$
564 59.6 ± 2.6 ‰ (Fig.3e) and matches well the first CRDS plume signature, which corresponds
565 to a local methane concentration enhancement of 8.5 ppm above background, the largest
566 one detected on this site, but also on all of the landfills that we surveyed in this study. The p-
567 value computed on the corresponding CH₄ concentration measurements made
568 simultaneously by GC and CRDS is 0.024 (n=16), revealing likely some statistically
569 significant difference between the two datasets.

570 Isles-les-Meldeuses was sampled twice (Sept. and Dec. 2015) and was shown to
571 produce a local methane concentration enhancement reaching 7.2 ppm above background.
572 The GC-IRMS mean signature measured in Dec.2015 (-63.7 ± 0.3 ‰) is higher than that
573 from CRDS (-65.9 ± 2.0 ‰) shown on Fig.4 (site L9), but both means superimpose within the
574 measurements error bars. Indeed, the p-value of 0.145 obtained on these simultaneous
575 CRDS and GC measurements does not reveal any statistically significant difference between
576 the two datasets. Fig.3f shows the Keeling plot drawn from the GC-IRMS measurements.
577 The CRDS signature measured in Sept. 2015 is notably higher (-60.6 ± 2.0 ‰). The
578 difference could be explained by the wind direction which was not the same, so that we did

579 not sample exactly the same plume, highlighting here again the possible variability of the
580 signature of one same site.

581

582 3.3 Gas storage sites

583 The five gas storages sites were surveyed twice, firstly in Summer 2015 and secondly
584 in Winter 2015. On two of them (Saint-Illiers-la-Ville, S3, and Saint-Clair-sur-Epte, S5) we did
585 not detect any local enhancement of the methane concentration. At Saint-Clair-sur-Epte
586 during both surveys the car passed at least 450 m away downwind of the site and could not
587 get closer to it. This could explain why we did not detect any methane plume there, but there
588 is a possibility too that the site does not emit any methane plume at all. At Saint-Illiers-la-
589 Ville, the car passed at different places within the site and was well exposed downwind of it.
590 Therefore, it seems very likely that this site does not leak methane to the atmosphere.

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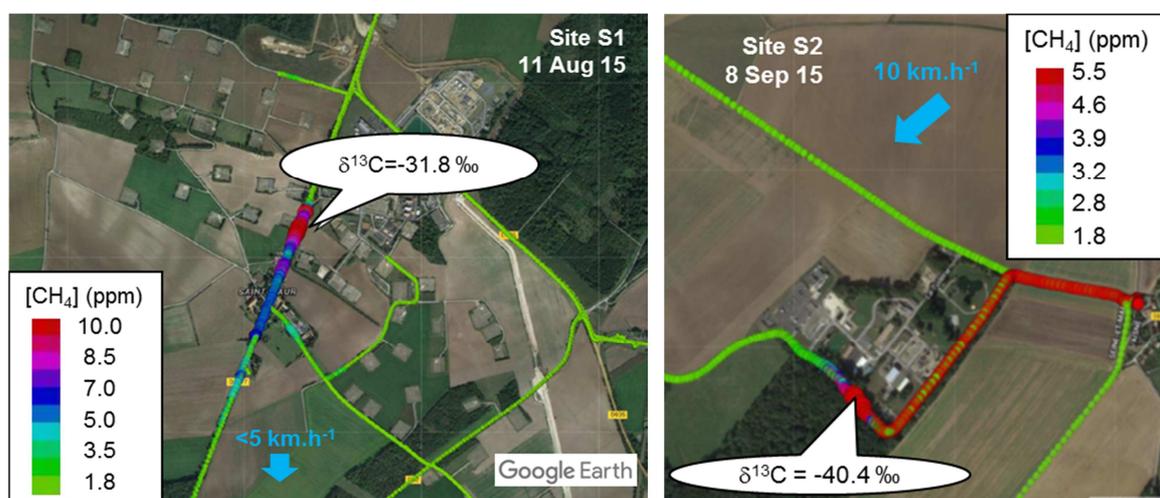
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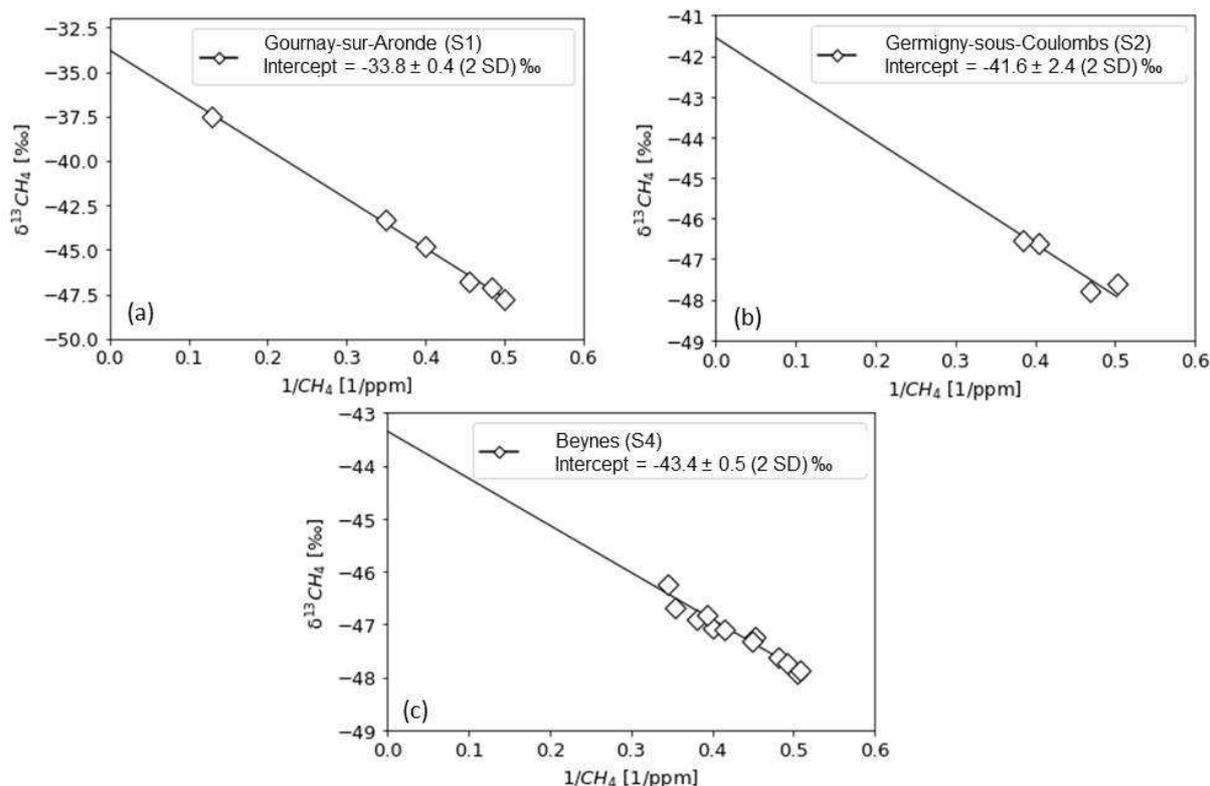


599 *Figure 5. Left : Methane concentration measured by CRDS on 11 Aug. 2015 at Gournay-sur-
600 Aronde (site S5) showing a local methane enhancement of 8.1 ppm above background
601 concentration with a $\delta^{13}\text{CH}_4$ signature of -31.8 ± 2.0 ‰. Right : Same but at Germigny-sous-
602 Coulombs on 8 September 2015 at Germigny-sous-Colombs (site S2) showing a local
603 methane enhancement of 3.5 ppm above background with a $\delta^{13}\text{CH}_4$ signature of -40.4 ± 2.0
604 ‰ (CRDS, 8 September 2015). The blue arrow and label indicate wind direction and speed.
605 The color scale is automatically adapted to each survey by the Picarro investigator unit
606 software.*

607 The three other sites (Gournay-sur-Aronde, S1, Germigny-sous-Coulomb, S2, and
608 Beynes, S4) emitted methane plumes with local CH₄ concentration enhancements ranging
609 from 0.6 ppm to 8.1 ppm over background concentrations. The $\delta^{13}\text{CH}_4$ signature of the
610 methane plumes detected on the three leaking gas storages sites are highly variable. The
611 signature obtained from the CRDS data ranges from -45.8 ± 2.0 ‰ to -31.7 ± 2.0 ‰. Using
612 GC-IRMS data, it ranges from -43.4 ± 0.5 ‰ to -33.8 ± 0.4 ‰ depending on the site and on
613 the period but all stay within the expected range for natural gas of -50 ‰ to -30 ‰ as given
614 by the literature (e.g. Dlugokencky et al., 2011 ; Zazzeri et al., 2015 ; Sherwood et al., 2016).

615 Among the gas storage sites, the highest concentration was measured by CRDS on
616 the Gournay-sur-Aronde on 10 August 2015, leading to an enhancement of 8.1 ppm above

617 background with a signature of $-31.8 \pm 2.0 \text{ ‰}$ (Fig. 5, site S1). According to the Airparif 2013
 618 emissions inventory, Gournay-sur-Aronde is the most emitting gas storage site of IDF (Table
 619 2). This site was sampled once again on 10 Dec. 2015 with local methane concentration
 620 enhancements higher than 1.5 ppm above background, allowing us to measure the $\delta^{13}\text{CH}_4$
 621 signature of the methane plume by CRDS during both surveys. The CRDS signature is
 622 consistent for both measurements ($-31.7 \pm 2.0 \text{ ‰}$ and $-31.8 \pm 2.0 \text{ ‰}$). Bag samples were
 623 also taken and analyzed by GC-IRMS on 10 December 2015, which gave a $\delta^{13}\text{CH}_4$ signature
 624 of $-33.8 \pm 0.4 \text{ ‰}$, at the lowest edge of the CRDS error bar (Fig. 6a). The p-value computed
 625 on the CH_4 concentration simultaneous measurements made by GC and CRDS is 0.046
 626 ($n=10$), revealing likely some statistically significant difference between the two datasets.



627
 628 *Figure 6. $\delta^{13}\text{CH}_4$ signatures obtained by the Keeling plot method from GC-IRMS*
 629 *measurements on gas storage sites on which methane plumes could be detected. Error bars*
 630 *are not shown as these are smaller than point marks.*

631 The Germigny-sous-Coulombs site (S2) is the second most emitting gas storage site
 632 in the Airparif inventory (Table 2). We measured plumes with local CH_4 enhancements
 633 ranging from 0.6 to 3.5 ppm above background. CRDS measurements gave a $\delta^{13}\text{CH}_4$
 634 signature of $-40.4 \pm 2.0 \text{ ‰}$ in September 2015 (Fig. 5, site S2), and GC-IRMS measurements
 635 provided in December 2015 a source signature of $-41.6 \pm 2.4 \text{ ‰}$ (Fig. 6b). The main leaks
 636 were mostly detected along the road (likely from underground pipelines) northeast of the site
 637 (Fig. 5, site S2). These values are lower of several ‰ than the signature of the methane
 638 plume detected on the Gournay-sur-Aronde site (see section 4.2).
 639

640 The last gas storage site on which a CH_4 plume could be detected was Beynes (S4),
 641 with local methane concentration enhancements ranging between 1.5 and 4.8 ppm above

642 background (Fig. 7). The $\delta^{13}\text{CH}_4$ signature of the plume was measured on 7 December 2015
 643 both by CRDS ($45.8 \pm 2.0 \text{ ‰}$) and by GC-IRMS ($-43.4 \pm 0.6 \text{ ‰}$) (Fig. 6c). Opposite to the two
 644 other leaking gas storage sites, the GC-IRMS signature is here higher than the CRDS one
 645 and out of the upper edge of the CRDS measurement error bar. The p-value calculated on
 646 these CH_4 concentration measurements made simultaneously by GC and CRDS is 0.003
 647 ($n=24$), revealing likely a statistically significant difference between both datasets.
 648 Unfortunately, a technical problem did not allow us to characterize the plume signature by
 649 CRDS on 8 September 2015 survey. The existence of a possible bias due to ethane co-
 650 emitted with methane in the CRDS $\delta^{13}\text{CH}_4$ signature calculation is evaluated in Section 4.
 651 According to the wind direction, the two surveys show that the methane plume are likely
 652 emitted from the surface facilities of the site (zone A on Fig. 7) rather than from the wheels
 653 (zones B and B' on Fig. 7) that are connected to the 2 deep aquifer storages of natural gas of
 654 this site (https://www.storengy.com/countries/france/images/contenuFR/nos_sites/stockage_en_nappe_aquifere.jpg).
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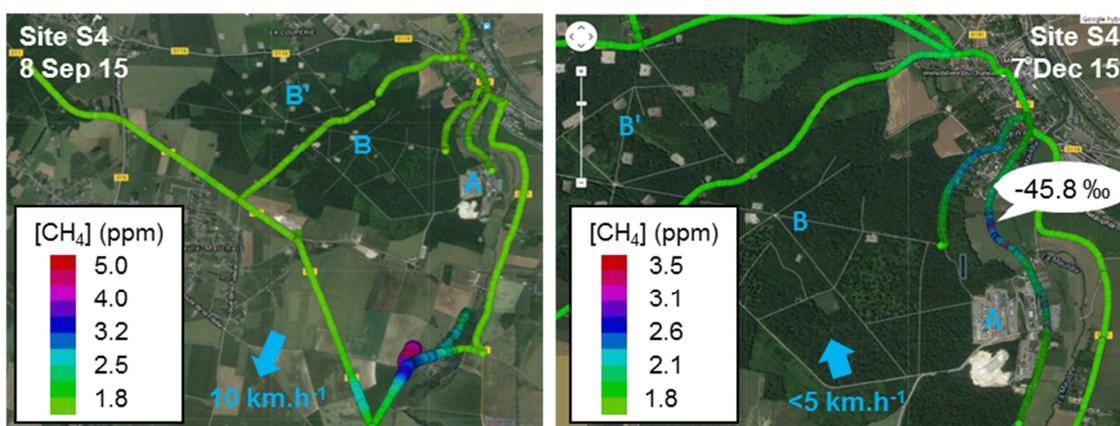
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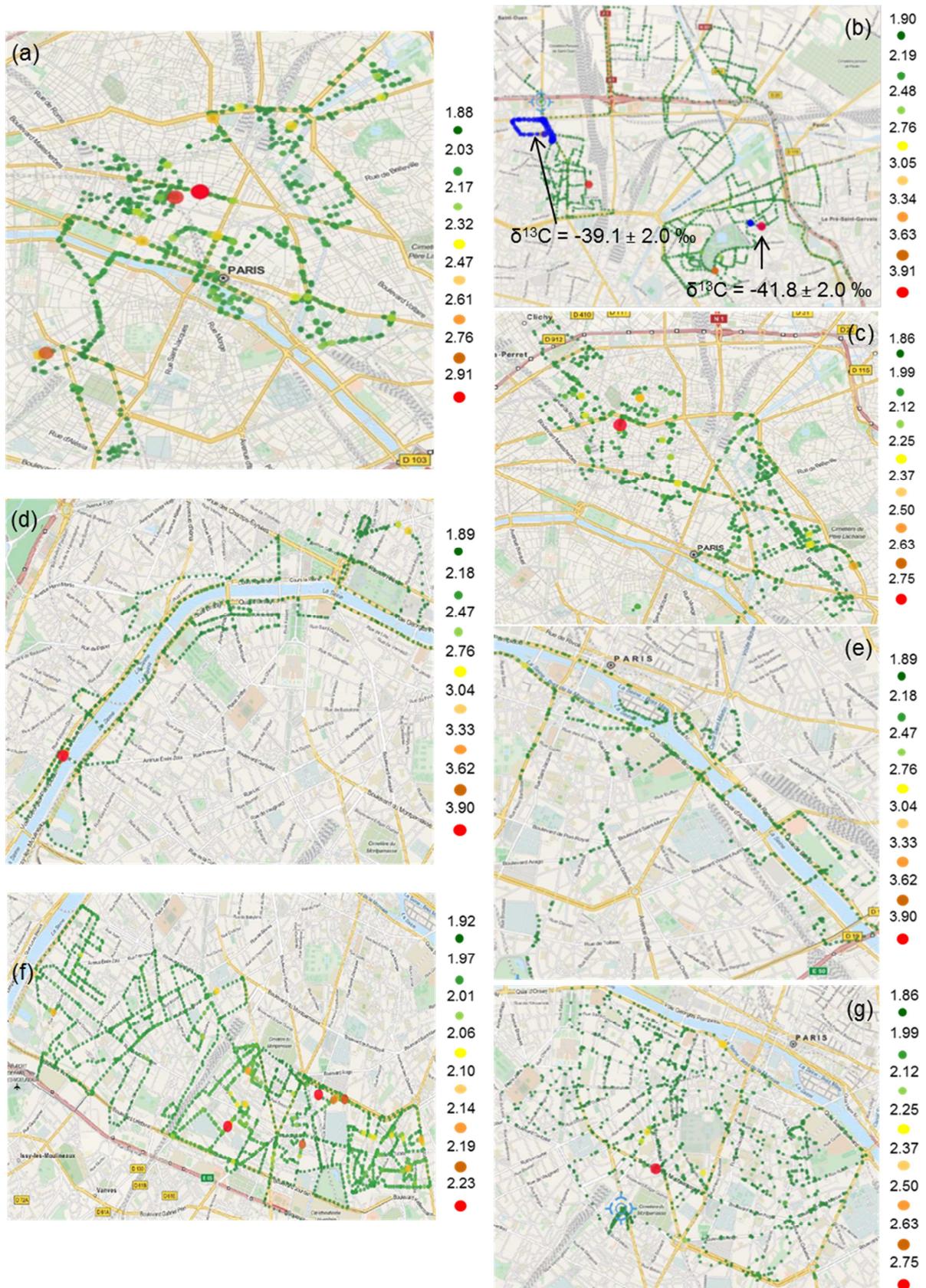


664 *Figure 7. Methane concentration measured by CRDS at Beynes (S4) on 8 Sept. 2015 (left)*
 665 *and 7 Dec. 2015 (right) revealing local CH_4 enhancements. On the second survey the*
 666 *signature of the enhancement was characterized as $-45.8 \pm 2.0 \text{ ‰}$ by CRDS and -43.4 ± 0.5*
 667 *‰ by GC-IRMS. Unfortunately the signature was not characterized on 8 Sept. 2015. The*
 668 *blue arrow and label indicate wind direction and speed. The A letter indicates the location of*
 669 *the surface facilities of the site (compressors, pumps, pipelines...). The B and B' letters*
 670 *indicate the location of wheels connected to two deep aquifer storages of natural gas. The*
 671 *color scale is automatically adapted to each survey by the Picarro investigator unit software.*

672

673 3.4 Gas distribution network of Paris

674 About 1000 kilometers were driven to survey the streets of Paris and surrounding
 675 suburbs (Fig. 8, Table 3). No methane plume was detected on the Paris ring road but one at
 676 Porte d'Orléans (south of Paris) with a local CH_4 enhancement of ~ 0.7 ppm above
 677 background. Furthermore, more than forty local CH_4 enhancements were detected in streets
 678 of Paris. In two places in the Northern districts of Paris (Fig. 8b) the local methane
 679 concentration enhancements were strong enough (3.5 and 3.9 ppm above background to
 680 characterize their isotopic signatures by CRDS ($-39.1 \pm 2.0 \text{ ‰}$ and $-41.8 \pm 2.0 \text{ ‰}$).



681

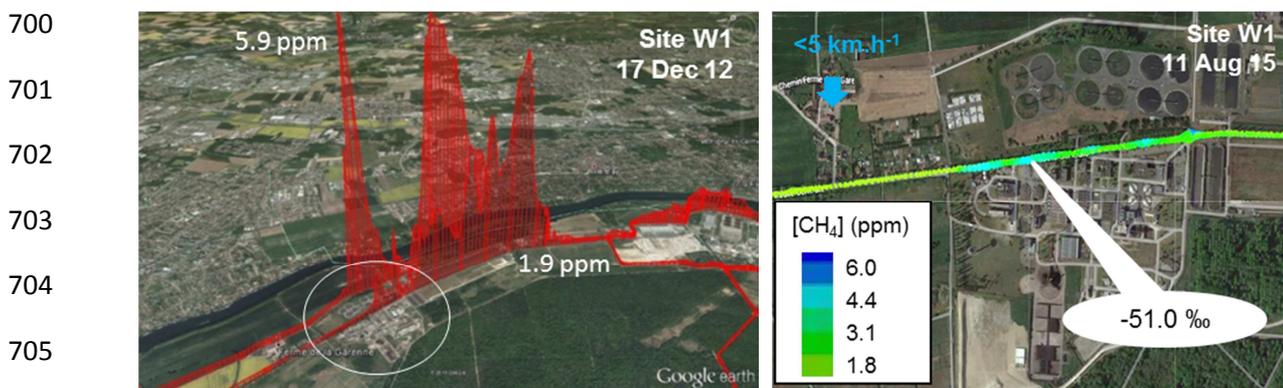
682 *Figure 8. Picarro CRDS atmospheric methane concentration measurements in the districts of*
 683 *the Paris city (site G2) performed between December 2013 and November 2015 (colored*
 684 *points indicate the atmospheric CH₄ concentration according to the color scale in ppm, that is*
 685 *adapted automatically to each survey by the Picarro investigator unit software) – (a) mostly*

686 Paris 1st, 2nd, 3rd, 4th, 6th, 7th, 8th, 9th and 10th districts ; (b) North of the center of Paris (mostly
687 18th, 19th and 20th districts) with CRDS isotopic signatures of the detected leaks – (c) Paris
688 11th to 17th districts survey – (d) and (e) along the Seine river – (f) Paris 13th, 14th and 15th
689 districts. Blue dots represent periods of measurement interruption due to isotopic analysis.

690 These values are close to the value measured on the gas storage of Germigny-sous-
691 Coulombs and are typical of thermogenic methane. Here we can exclude a biogenic origin of
692 methane and therefore emanations from the sewer networks. We can clearly attribute these
693 signatures to natural gas, proving the existence of leaks on the gas pipelines of the Paris
694 network. In about 40 other places, very local methane concentration enhancements were
695 also found but they were too small for CRDS isotopic analysis (< 3.5 ppm) and they would
696 have required bag sampling to distinguish leaks from the natural gas network or emanations
697 from sewage facilities.

698
699

3.5 Waste water treatment site

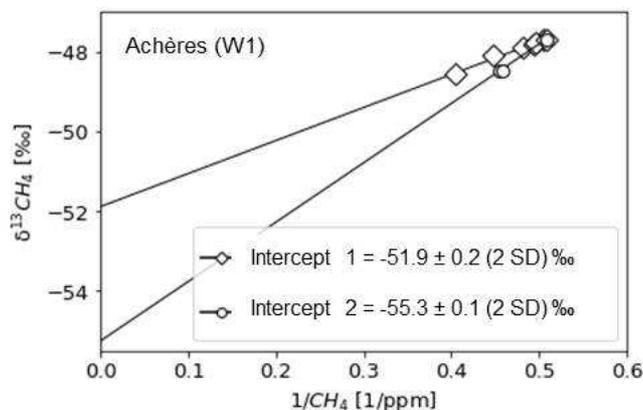


706 Figure 9. Left : Google Earth view of methane plumes detected by CRDS on the Achères
707 WWT facility on 17 Dec. 2012 (site W1) revealing several local methane concentration
708 enhancements above background (background concentration is 1.9 ppb and maximum
709 concentration is 5.9 ppm). The white ellipse indicates the location of the right figure. Right :
710 methane concentration measured on the same site (white ellipse on the left figure) by CRDS
711 on 11 Aug. 2015 showing a methane enhancement of 3.5 ppm above background and
712 $\delta^{13}\text{CH}_4$ signature of $-51.0 \pm 2.0 \text{ ‰}$. The blue arrow indicates wind direction together with
713 windspeed. The color scale is automatically adapted by the Picarro investigator unit software.

714 The Achères WWT facility (site W1) was first surveyed by the Picarro mobile unit on
715 17 December 2012 (Fig. 9). Both weak wind conditions (wind speed $\sim 2 \text{ km.h}^{-1}$) and cold
716 temperatures ($\sim -5^\circ\text{C}$) favored the accumulation of the methane plume on the site. The
717 background concentration is in the range of 1.9 ppm and the maximum concentrations reach
718 5.9 ppm. A local CH_4 methane concentration enhancement of 4.0 ppm above background
719 was detected on this site, as in Ars (2017) with a $\delta^{13}\text{CH}_4$ signature of $-53.2 \pm 3.7 \text{ ‰}$ on that
720 day. The same plume was detected again on 10 August 2015 and 10 December 2015 with
721 enhancements of 3.5 ppm (windspeed $< 5 \text{ km.h}^{-1}$) and 0.4 ppm (windspeed $\sim 10 \text{ km.h}^{-1}$),
722 respectively, and a signature of $-51.0 \pm 2.0 \text{ ‰}$ (CRDS) and $-51.9 \pm 0.2 (2-\sigma) \text{ ‰}$ (GC-IRMS)
723 (Fig. 10), respectively.

724 A second plume (Fig. 10) with a different isotopic signature was detected on 10
725 December 2015 with a local methane concentration enhancement of 0.4 ppm above

726 background (windspeed $\sim 10 \text{ km.h}^{-1}$) and a signature of -55.3 ± 0.1 ($2\text{-}\sigma$) ‰ (GC-IRMS). All
727 these isotopic these values are typical of biogenic sources. We note here that the lower the
728 windspeed is, the higher the methane enhancement is, as the car was able to pass at the
729 edges of the site and could easily catch the methane plumes.



730
731 *Figure 10. $\delta^{13}\text{CH}_4$ signatures obtained by the Keeling plot method from GC-IRMS*
732 *measurements on the Achères WWT site (W1) on 10 December 2015. Two plumes could be*
733 *identified, both with a $\delta^{13}\text{CH}_4$ signature typical of biogenic sources. Error bars are not shown*
734 *as these are smaller than point marks.*

735 736 4- Discussion and conclusions

737 4.1 Overview

738 Fig.11 synthesises the local CH_4 concentration enhancements that we measured and
739 their $\delta^{13}\text{CH}_4$ signatures on the landfills, gas storages, gas lines and WWT facility in the Paris
740 megacity region that we characterized for the first time, by CRDS and/or by GC-IRMS.
741 Overall, methane plumes could be detected on 6 over 10 landfills surveyed, 3 over 5 gas
742 storage sites studied and on the surveyed WWT facility. About forty local CH_4 enhancements
743 were also found in streets of Paris city as well as in Montrouge in the South-West suburbs of
744 Paris, and on the Boulevard Périphérique : using CRDS we could assign a $\delta^{13}\text{CH}_4$ signature
745 typical of natural gas to 2 of them, but we did not have the fundings to characterize the
746 precise signature of all of them by GC-IRMS. Very likely, these 2 enhancements come from
747 leaks on the pipelines of the Paris natural gas distribution network.

748 4.2 Comparison of CRDS and GC-IRMS results

749 The studies of Rella et al. (2015) and Assan et al. (2017) demonstrated the
750 importance of a careful determination of cross sensitivities and a good calibration strategy for
751 precise isotope measurements with a CRDS analyzer. A few recent studies reported that the
752 methane concentration measured by PICARRO CRDS analyzers could be biased by the
753 presence of ethane with methane (e.g. Rella et al., 2015; Assan et al., 2017; Lopez et al.,
754 2017). This bias would generate an error on the determination of the $\delta^{13}\text{CH}_4$ signature of
755 sources. It is difficult to make a comparison of the concentrations measured directly by
756 CRDS and the concentrations of the samples collected at the same time measured in

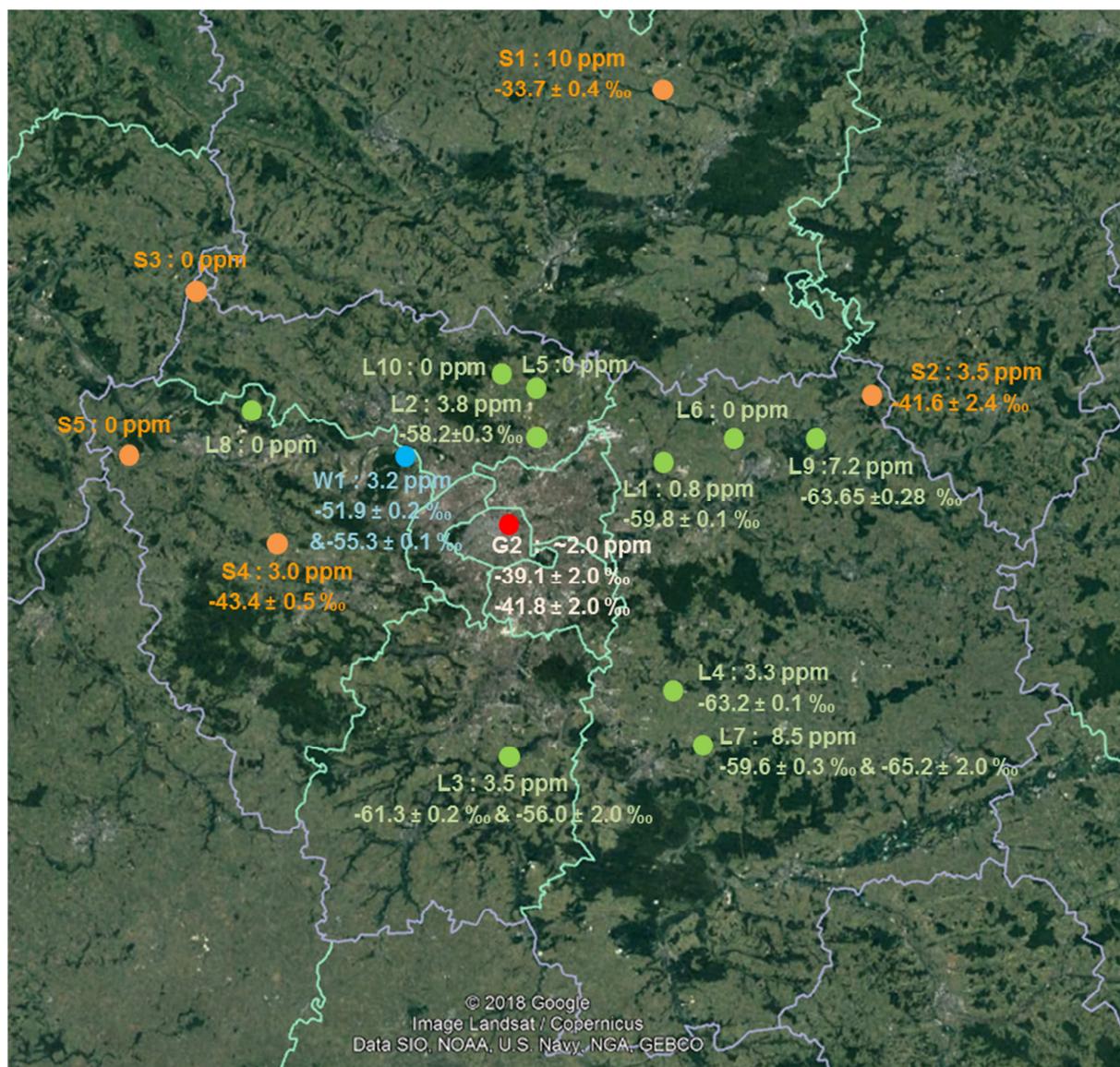
757 laboratory, because the bag sampling took about 30 seconds of sampling, atmospheric
758 concentration enhancements within the plume were often highly variable and we could not
759 measure that time with a precision higher than several seconds. We thus compared the
760 $\delta^{13}\text{CH}_4$ signatures obtained from the CRDS and GC-IRMS measurements, which represent
761 the main focus of this study, but not the values of the CH_4 enhancements obtained by both
762 technics, as the precise quantification of these enhancements is not the aim of our study as
763 mentioned earlier. Fig.12 synthesises the $\delta^{13}\text{CH}_4$ signatures measured by CRDS and GC-
764 IRMS, which we can use to assess any error in the CRDS measurements, taking the GC-
765 IRMS signature as a reference. We compare here only the 6 cases when both CRDS and
766 GC-IRMS samples were taken simultaneously, indicated by black-framed markers on Fig.12.

767 Atmospheric ethane sources are mostly fossil fuels, biomass burning and biogas (e.g.
768 Assan et al., 2017). There is no ethane source known from landfills. An additional survey in
769 2016 in Soignolles-en-Brie revealed no ethane source on that landfill (F. Vogel, personal
770 communication), supporting this hypothesis. For this type of sites, the CRDS minus GC-
771 IRMS $\delta^{13}\text{CH}_4$ signature difference ranges from -0.2 to 2.3 ‰ with a mean value of 1.0 ± 2.2
772 ‰ (2- σ). The mean difference and its standard deviation are higher than the GC-IRMS data
773 mean uncertainty (0.85 ‰) but stay close to the CRDS mean uncertainty (2.0 ‰). While for
774 two landfill sites (Le Plessis-Gassot and Isles-les-Meldeuses) no statistically significant
775 difference was found, for two others (Fouju-Moisey and Vert-le-Grand), the p-values
776 calculated from the methane concentration simultaneous measurements made by CRDS and
777 bag sampling / GC analysis indicate likely a statistically significant difference between both
778 datasets, although both match within the CRDS error bars. This difference could be
779 explained by the much higher precision and accuracy of the GC dataset.

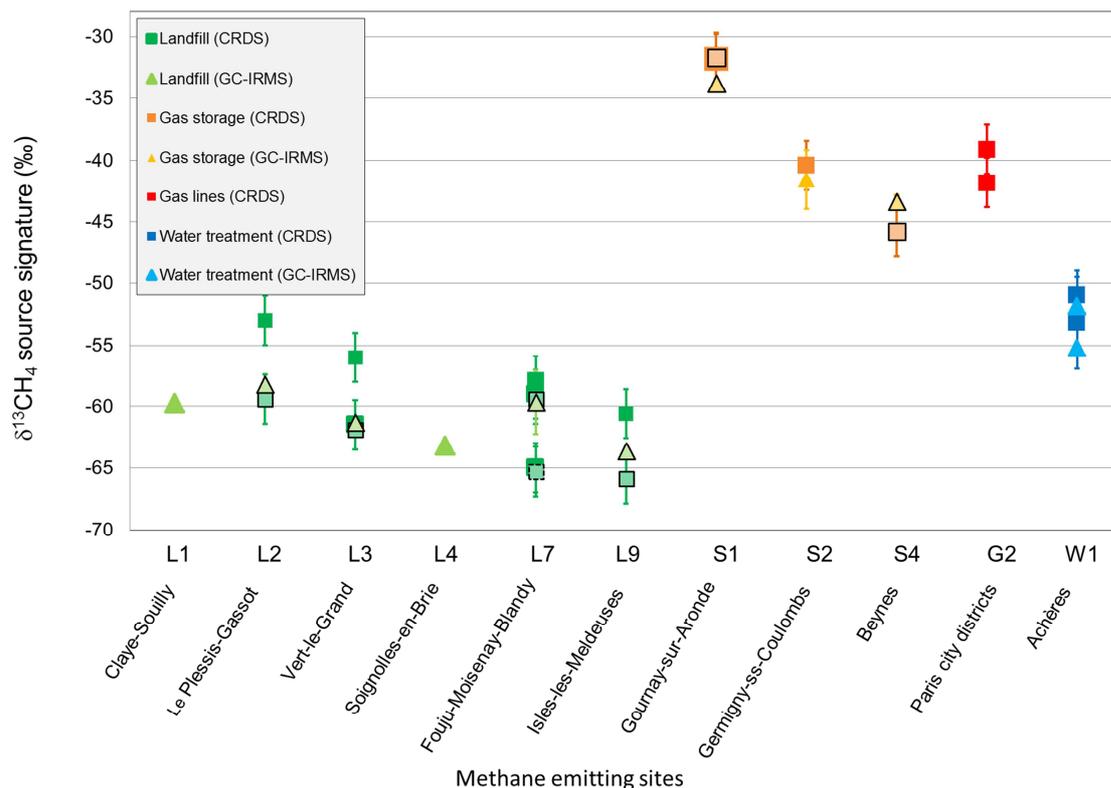
780 Conversely to landfills, methane leaks in gas storage sites are found together with
781 ethane leaks, as natural gas is one of the main natural biogenic sources of ethane (Assan et
782 al., 2017). On these sites, the CRDS – GC-IRMS difference ranges from -2.1 to 2.5 ‰ with a
783 mean difference of -0.7 ± 4.2 (2- σ). The standard deviation of the mean is higher than the
784 CRDS and GC-IRMS data uncertainties (2.0 ‰ and 1.13 ‰, respectively) and this could be
785 explained by ethane – methane cross-sensitivity in the CRDS analyzer (but no ethane data
786 were available to verify this hypothesis). On both gas storage sites where CRDS
787 measurements and bag samples / GC analysis were performed, the p-values indicate likely a
788 statistically significant difference between both datasets, which could be due to the presence
789 of ethane, but also to the higher precision/accuracy of the GC dataset. For the WWT site,
790 there was no simultaneous CRDS and GC – IRMS results. However, WWT facilities are not
791 known to be ethane sources.

792 For the gas storage sites, we thus recommend not to use the $\delta^{13}\text{CH}_4$ signature
793 obtained by CRDS measurements but rather the GC – IRMS ones, as some bias larger than
794 the instrumental uncertainty could explain the CRDS – GC-IRMS differences observed here,
795 which might depend on the amount of ethane content into each methane plume. The landfills
796 and the WWT plant signatures do not overlap with the gas storage sites ones. Overall, the
797 mean signature of both source types can be disentangled by GC- IRMS and even by CRDS.
798 But in two cases (L2 and L3 sites in Nov. 2015), the individual signatures obtained by CRDS
799 for landfills overlap the WWT facility signature measured by GC-IRMS and CRDS. We
800 therefore recommend to better use GC –IRMS also for landfills and WWT facilities, which
801 provides more precise measurements than the CRDS ones. It would be also interesting to go

802 back regularly to L2 and L3 sites to conduct a deeper study on the temporal variability
 803 observed on these sites, as discussed further below.



804
 805 *Figure 11. Synthesis of our results showing the maximum of methane concentration*
 806 *enhancements measured in the local plumes (in ppm above background) and their $\delta^{13}\text{CH}_4$*
 807 *signature (in ‰) on the sites surveyed in this study. Sites code are the following ; Landfills :*
 808 *L1 = Claye-Souilly, L2 = Le Plessis-Gassot, L3 = Vert-le-Grand, L4=Soignolles-en-Brie, L5 =*
 809 *Epinay-Champlâtreux, L6 = Monthyon, L7 = Fouju-Moisenay-Blandy, L8 = Brueil-enVexin, L9*
 810 *= Isles-les-Meldeuses, L10 = Moisselles – Attainville ; Gas storage sites : S1 = Gournay-sur-*
 811 *Aronde, S2 = Germigny-sous-Coulombs, S3 = Saint-Clair-sur-Epte, S4 = Beynes, S5 =*
 812 *Saint-Illiers-la-Ville ; WWT facility : W1 = Achères ; and Paris streets : G2.*



813

814 *Figure 12. Synthesis of the $\delta^{13}\text{CH}_4$ signatures of the plumes emitted by several landfills, gas*
 815 *storages, gas lines and WWT sites of the Paris megacity region and measured by CRDS and*
 816 *GC-IRMS technics. The CRDS and GC-IRMS results obtained on the same date are*
 817 *indicated by black-framed markers. One specific point indicated with a dashed-line frame*
 818 *corresponds to a second plume detected on L7 site by CRDS on the same day that the*
 819 *joined CRDS – GC-IRMS measurements. The error bars are given according to Table 5.*
 820 *Error bars for sites L1 and L4 are smaller than the mark size.*

821 4.3 Source attribution

822 Regarding landfills, the GC-IRMS mean signature that we measured ($-61.0 \pm 2.2 \text{ ‰}$)
 823 show some variability which is partly due to landfill emissions seasonal variability (Börjesson
 824 et al., 2001) that relies on several parameters : temperature, the waste composition and the
 825 strength of the methane oxidation level due to methanotrophic bacteria in the top-soil cover :
 826 methanotrophic bacteria in the upper soil layers, under aerobic conditions, mineralize
 827 methane to CO_2 , leaving the residual methane that diffuses through the soil cover relatively
 828 ^{13}C enriched, as methanotrophs use preferentially the lighter isotope (Zazzeri et al., 2015 ;
 829 Liptay et al., 1998). Zazzeri et al. (2015) reported a signature of $-58 \pm 3 \text{ ‰}$ (2- σ) for waste
 830 disposal and landfills in SE England. Bergamaschi et al. (1998b) reported for German and
 831 Dutch landfill signatures ranging between $-59.0 \pm 2.2 \text{ ‰}$ and $-45.9 \pm 8.0 \text{ ‰}$ (where the most
 832 enriched signature was attributed to the activity of methanotrophic bacteria). Phillips et al.
 833 (2013) reported signatures of $-57.8 \pm 1.6 \text{ ‰}$ for landfills in the Boston area. Our results are
 834 close to the values reported by Zazzeri et al. (2015), Phillips et al. (2013) and also by
 835 Bergamaschi et al. (1998b) in no presence of methanotrophic bacteria. Following this first
 836 study, more surveys are needed to assess the seasonal variability of the sources, and
 837 possible landfill management changes. Note that landfill practice has changed greatly, and

838 topsoil oxidation that drives heavier the isotopic signature of residual emitted methane is no
839 longer a significant source in NW Europe (D. Lowry, personal communication).

840 The largest variability in the $\delta^{13}\text{CH}_4$ signature is observed on the gas storage sites.
841 Our dataset do not allow us to assess the temporal variability of the $\delta^{13}\text{CH}_4$ signature on
842 each gas storage site. By computing a mean signature including the GC-IRMS values for the
843 sites S1, S2 and S4, we obtain a mean signature and its associated 2- σ variability of $-39.6 \pm$
844 10.2‰ (2- σ). The CRDS mean signature and its associated 2- σ variability are $-38.4 \pm 11.2\text{‰}$
845 (2- σ). While our mean value is close to the one of $-39.1 \pm 1.1 \text{‰}$ reported for the natural gas
846 signature in Paris by Widory and Javoy (2003), it is characterized by a large variability
847 between the sites and possibly the temporal variability at each site. This variability can be
848 explained by the geological origin of the natural gas. According to SEDS (2018), natural gas
849 is delivered to France by Norway (40 %), Russia (26 %) followed by the Netherlands (11 %),
850 Algeria (9 %) and a few other countries. Gas from Norway and the North Sea has a reported
851 signature spanning a large range from -43.9‰ (Sherwood et al., 2016) to -24‰ (Zazzeri et
852 al., 2015) and typically around -35‰ (Dlugokencky et al., 2011). Natural gas from Russia is
853 more ^{13}C depleted with a signature that can reach -50‰ (Dlugokencky et al., 2011), and
854 reported as -46.4‰ by Sherwood et al. (2016). Natural gas from the Netherlands has a more
855 ^{13}C enriched signature ranging from -32.8‰ (Sherwood et al., 2016) to $-29.5 \pm 0.1 \text{‰}$
856 (Zazzeri et al., 2015). Eventually, natural gas from Nigeria is reported with a $\delta^{13}\text{CH}_4$ signature
857 of -43.1‰ (Sherwood et al., 2016).

858 The gas storages sites that we surveyed are distributed among 3 zones defined by
859 the gas exploitation company Storengy (<https://www.cre.fr/Gaz-naturel/Reseaux-de-gaz-naturel/Presentation-des-reseaux-de-gaz-naturel>). The natural gas sampled in the Gournay-
860 sur-Aronde site has the heaviest $\delta^{13}\text{CH}_4$ signature ($-33.7 \pm 0.44\text{‰}$) of the 3 emitting gas
861 storages sites surveyed in this study. Its $\delta^{13}\text{CH}_4$ signature is indeed typical of thermogenic
862 gas coming from the Netherlands and the North Sea. According to STORENGY
863 (<https://www.storengy.com/countries/france/fr/nos-sites/gournay-sur-aronde.html>), this site is
864 the only one in France is supplied by the Netherlands. Therefore, according to our results,
865 this information pushes for attributing from this study a signature of $-33.7 \pm 0.4 \text{‰}$ to Dutch
866 gas ; but this possible attribution should be confronted with further investigation on the Dutch
867 gas signature. Gournay-sur-Aronde is part of the north zone called « Sédiane B » by
868 Storengy and is effectively on the path of the main gas line of the North of France that
869 receives gas from the Netherlands. Natural gas in Germigny-sous-Coulombs and in Beynes
870 is more ^{13}C depleted ($-41.6 \pm 2.4 \text{‰}$ and $-43.4 \pm 0.5 \text{‰}$, respectively). Germigny-sous-
871 Coulombs is part of the so-called STORENGY « Serène Nord » north-east zone, which is
872 connected to gas lines from Russia ; therefore this source of methane could be attributed to
873 Russian gas. Beynes is part of the north-west « Sédiane » north-west zone of STORENGY
874 which is connected both to the gaslines from Russia and to the methane terminal of
875 Montoir-sur-Bretagne, where natural gas from Nigeria and other African countries is shipped
876 to France; the signature of this site can likely be attributed to Russian gas or less likely to
877 Nigerian gas. However, although we provide the most probable picture of the natural gas
878 distribution network, STORENGY does not clearly indicate the gas origin for the Beynes and
879 Germigny-sous-Coulombs sites. As these sites are interconnected to all the gaslines network
880 of the north of France, their isotopic signature could either be attributed to gas from Norway,
881 North Sea, Russia or African sources, which signature is not unique and could match with
882 our measurements. Furthermore, the isotopic signature of sources can change with season
883

884 (e.g. Zazzeri et al., 2015), as well as the source itself. Therefore, further surveys are needed
885 to assess the seasonal variability of the gas storage sites signature.

886 For the street survey measurements, we only collected CRDS measurements which
887 are not much reliable. The mean signature that we measured from 2 local methane
888 enhancements among the forty ones that we detected is -40.5 ± 2.0 ‰. This signature is
889 clearly not biogenic and eliminates an attribution to methane emanations from sewage
890 facilities. It is typical from natural gas (thermogenic source) and in agreement with the value
891 of -39.1 ± 1.1 ‰ reported by Widory and Javoie (2003) for the gas supply in Paris as well as
892 with the $^{13}\text{CH}_4$ signature that we found for the gas storage site of Germigny-sous-Coulombs.
893 Among the 1000 km that were surveyed in the Paris city, we found very local methane
894 enhancements on about ~forty locations only, unlike in other cities of the United States of
895 America where numerous and occasionally large methane leaks on the natural gas
896 distribution network were found, such as in Boston (Phillips et al., 2013 ; Boothroyd et al.,
897 2018), in Washington DC (Jackson et al., 2014) and in Los Angeles (Townsend-Small et al.,
898 2012). Additional surveys are needed using the bag sampling technic/ GC-IRMS to attribute
899 sources (gas pipelines leaks, sewage emanations) to the ~forty of local methane
900 enhancements that were detected in the Paris streets.

901 The two plumes detected at the WWT site of Achères give an average signature of -
902 53.6 ± 3.4 ‰ by GC-IRMS. By comparison, Phillips et al. (2013) measured a mean signature
903 of -53.1 ‰ for Boston main WWT plant that is consistent with our results. Toyoda et al.
904 (2011) reported $\delta^{13}\text{CH}_4$ enriched signatures of -50.7 ‰ for WWT facilities in Japan.
905 Townsend-Small et al. (2012) reported even heavier signatures of -46.3 ‰ and -47.0 ‰ for
906 WWT facilities in Los Angeles and Orange counties. The causes of enrichment in ^{13}C of
907 these plants compared to Achères and to the Boston's WWT facility is not clear. As
908 mentioned by Townsend-Hall et al. (2012), this could be linked to denitrification processes
909 and requires dedicated studies. However, our study reports for the first time the $\delta^{13}\text{CH}_4$
910 signature of the Achères emission plumes. More surveys should be performed to assess any
911 variability in the $\delta^{13}\text{CH}_4$ signature of this source.

912 **4.4 Comparison to the regional inventory**

913 In this section, we compare the location of the sites and more qualitatively the
914 strength of the methane emissions observed in our study with those of the AIRPARIF 2013
915 methane emissions inventory.

916 The AIRPARIF 2013 IDF methane emissions inventory includes all the sites that we
917 surveyed appart the gas storage site of Gournay-sur-Aronde, which is located outside the
918 IDF region. The location of the sites (cf Tables 1 to 4) could be slightly revised in order to
919 reach a better accuracy when estimating emissions using fine-scale regional top-down
920 modeling approaches. Indeed, differences of more than 10 km between the position given in
921 the inventory and the actual position were detected, while the inventory is delivered at the 1
922 km scale. The latitude of the Isles-les-Meldeuses landfill is not given in the AIRPARIF
923 inventory, although its longitude matches with the one of landfill L9. As we could not find any
924 large landfill at the position given by AIRPARIF, we suggest that possibly the inventory does
925 not report correctly the Isles-les-Meldeuses latitude which is located about 130 km eastern
926 than suggested for landfill L9 in the inventory. Finally in the inventory, the name of Moisselles
927 should be replaced by Attainville.

928 Regarding landfills, methane plumes with local CH₄ enhancements of several ppm
929 above background were detected on 6 of the 10 main landfill sites given by the inventory. The
930 Claye-Souilly site showed a local methane concentration enhancement that was smaller than
931 the one measured at the other landfill sites, while it is supposed to be the biggest methane
932 emitter within the landfill sector. On that site, we might have not been close enough to the
933 source and might have missed the strongest plume, due to the roads configuration, and/or
934 meteorological conditions not favorable. This site would benefit from additional surveys in
935 order to verify our results. At comparable windspeed and plume downwind exposure
936 conditions, the Fouju-Moisenay and Isles-les-Meldeuses sites show local methane
937 concentration enhancements as high as the landfills of Le Plessis-Gassot and Vert-le-Grand,
938 while, according to the AIRPARIF 2013 inventory, these two first sites emit 2 to 10 times less
939 methane than the two latter sites. But of course, we can not correlate directly the amplitude of
940 atmospheric concentration enhancements with the intensity of source emissions. This would
941 require dedicated atmospheric tools: it would be very interesting to investigate each emitting
942 site further by calculating their emissions rate, for example by coupling a tracer release
943 technique and local-scale transport modelling (Ars et al., 2017). Among the 10 sites that we
944 studied, no local methane enhancement could be detected. For 3 of these 4 sites (Brueil-en-
945 Vexin, Monthyon and Moisselles), as the sampling conditions were not satisfying, additional
946 surveys with favorable conditions are needed on these sites (see section 3.2). The 4th site
947 (Epinay-Champlâtreux) was closed in 2008 and this can explain why we did not detect any
948 methane plume downwind of this old landfill. Finally, the Guitrancourt site that now replaces
949 the Brueil-en-Véxin site should be surveyed in a future study.

950 Regarding the gas storage sites of IDF, our study demonstrated the occurrence of
951 methane leaks giving rise to local methane concentration enhancements of several ppm
952 above background in Germigny-sous-Coulombs and Beynes, which are both estimated to
953 emit 0.32 ktCH₄/yr by the inventory. We did not detect any leak at the Saint-Illiers-la-Ville and
954 Saint-Clair-sur-Epte sites. For Saint-Illiers-la-Ville the sampling conditions were favorable to
955 detect any methane plume. For Saint-Clair-sur-Epte, the car was maybe passing too far away
956 from the site (see section 3.3) which could explain that we did not detect any methane
957 enhancement on this site ; but this could be the case that this site does not emit methane at
958 all. For these two sites, the emission rates given by AIRPARIF 2013 are 0.23 and 0.30
959 ktCH₄/yr, respectively. One explanation could be that these sites are equipped with high
960 performance compression technology that cuts out the emissions of greenhouse gases to the
961 atmosphere, conversely to Germigny-sous-Coulombs and Beynes
962 (<https://www.storengy.com/countries/france/en/our-sites.html>) - note that the Germigny-sous-
963 Coulombs site should benefit of such improved technology in the near future. But at the
964 Saint-Clair-sur-Epte site, as the car did not pass closer than 450 m downwind of the site,
965 more surveys closer to the site downwind of it are needed there to validate this
966 hypothesis. Therefore, we conclude that 1/ the AIRPARIF emissions inventory should be
967 revised for the Saint-Illiers-la-Ville for zero emissions, 2/ additional surveys are needed on
968 Saint-Clair-sur-Epte closer to the site ; and 3/ the Germigny-sous-Coulombs and Beynes sites
969 should be surveyed to monitor emission mitigation resulting from future technological
970 improvements.

971 Regarding the Paris streets, about forty methane concentration enhancements above
972 background were detected and two of them could be attributed to natural gas network leaks
973 from δ¹³CH₄ measurements. These urban methane enhancements are much less numerous

974 and intense than in some cities in North-America (Phillips et al., 2013 ; Boothroyd et al.,
975 2018 ; Jackson et al., 2014 ; Townsend-Small et al., 2012). It is possible that the technology
976 used to ensure the tightness of the gas lines seals in Paris is much more performant than the
977 one in the USA. However, additional surveys are needed to attribute all of the methane
978 enhancements detected in the Paris streets to either natural gas pipeline leaks or sewage
979 emanations. Such leaks should then be quantified by independent top-down methods and
980 taken into account in the AIRPARIF inventory.

981 Regarding the Achères WWT site, we detected large local methane enhancements of
982 several ppm above background. According to the inventory, this site emits only 0.066
983 ktCH₄/yr. This is much lower compared to gas storage or landfills sites that are also observed
984 to emit methane enhancements of similar extent to the WWT site for similar wind exposure
985 and sampling distance conditions. There could be an underestimation of methane emissions
986 from this facility and from the WWT sector in the AIRPARIF 2013 emissions inventory, but
987 this should be assessed by independent emission quantification methods such as the ones
988 proposed in Ars et al. (2017). We thus conclude that dedicated campaigns should be
989 performed on the sites surveyed in our study in order to compute estimates of their methane
990 emissions and to answer whether the AIRPARIF inventory can be validated or should be
991 revised.

992

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1001

1002 **References**

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Declaration of interests

- The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
- The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: