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Methods, fluxes and sources of gas-phase alkyl nitrates in the coastal air

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34 **Abstract** – The daily and seasonal atmospheric concentrations, deposition fluxes and
35 emission sources of a couple of C3-C9 gaseous alkyl nitrates (ANs) were studied over
36 the Belgian coast (De Haan) at the Southern North Sea. An adapted/further developed
37 sampler design for the low- and high-volume air-sampling, optimized sample
38 extraction and clean-up, as well as identification and quantification of ANs in air
39 samples by means of gas chromatography mass spectrometry, are reported. The air
40 levels of the study Σ ANs ranged from 0.03 to 85 pptv, consisting primarily of the
41 nitro-butane and nitro-pentane isomers. Air-mass backward trajectories were
42 calculated by the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT)
43 model, to determine the influence of main air masses on AN air levels. The shorter
44 chain ANs have been the most abundant in the Atlantic/Channel/United Kingdom air
45 masses, while the longer chain ANs in continental air. The overall mean N-fluxes of
46 the ANs were slightly higher for summer than for winter-spring, although their
47 contributions to the total nitrogen flux were low. In winter/spring the study ANs were
48 correlated to air HNO₂ levels, while in summer the shorter chain ANs were related to
49 precipitation. Source apportionment by means of principal component analysis
50 indicated that the most of the gas phase ANs could be attributed to traffic/combustion,
51 secondary photochemical formation and biomass burning, although marine sources
52 may also have been present and a contributing factor.

53

54 **Keywords** Organic nitrates, N-nutrients, High volume air sampler, Electron
55 ionization ion-trap GC-MS, Breakthrough volume, Source identification

56

57 **Introduction**

58 Photochemical processes and oxidant chemistry in the atmosphere are
59 influenced by nitrogen oxides, ozone, hydrocarbons (HCs), and organosulphur
60 compounds (Crutzen 1979; Logan et al. 1981; Liu et al. 1983; Altshuller 1986; Toon
61 et al. 1987). Amongst these gases, alkyl nitrates (ANs or RONO₂) are of particular
62 interest, especially, within the ozone/nitrogen oxide system, because their formation
63 and degradation play an important role in tropospheric ozone production (Atkinson et
64 al. 1982; Singh 1987; Luke and Dickerson 1988; Roberts and Fajer 1989; Roberts
65 1990). The formation of alkyl nitrates via oxidation of parent hydrocarbons has been a
66 well-known atmospheric mechanism since the 1970s (Darnall et al. 1976). As ozone
67 and organic nitrates are formed through the same reaction, monitoring the air
68 concentrations of organic nitrates can provide information on the role of various
69 peroxy radicals in photochemical ozone formation (Flocke et al. 1991). Besides
70 photochemical AN formation, oceanic sources of ANs have been identified for the
71 past decades (Walega et al. 1992; Atlas et al. 1993; Chuck et al. 2002; Ballschmiter
72 2002). Moreover, biomass burning has been observed as a major point source of C₁-
73 C₄ alkyl nitrates, although these emissions are expected to insignificantly impact
74 global reactive nitrogen levels (Simpson et al. 2002). The primary alkyl nitrate sinks
75 are reported to be photolysis and reaction with hydroxyl radicals (Roberts 1990;
76 Clemitshaw et al. 1997; Talukdar et al. 1997; Aschmann et al. 2011; Russo et al.
77 2013), although the influence of photochemical AN loss decreases with increasing
78 atomic number (Clemitshaw et al. 1997, Talukdar et al. 1997).

79 Several studies have been devoted to investigate the temporal (daily, seasonal)
80 variations and geographical distributions of alkyl nitrates (e.g., Atlas 1988; Simpson
81 et al. 2006). Airborne measurements have shown alkyl and multifunctional nitrates
82 (Σ ANs) to be a significant fraction (~10 %) of NO_y in a number of different chemical
83 regimes (Perring et al. 2010). They have drawn three important conclusions: (1)
84 correlations of Σ ANs with odd-oxygen (O_x) indicate a stronger role for Σ ANs in the
85 photochemistry of Mexico City than is expected on the base of current photochemical
86 mechanisms, (2) Σ AN formation suppresses peak O₃ production rates by as high as 40
87 % near Mexico City and (3) Σ ANs play a significant role in the transport of NO_y from
88 Mexico City to the Gulf Region. Alkyl nitrates have also been proven to form in air
89 pollution originating from oil spill accidents (Neuman et al. 2012).

90 The atmospheric nitrogen-input, especially at coastal regions, triggers
91 increasing interest in the scientific community. Specifically, atmospheric nitrogen
92 fluxes, in terms of inorganic and organic nitrogen deposition, are important to be
93 assessed by experimental and model approaches, in order to get an insight into their
94 contribution to eutrophication processes at coastal regions.

95 The low air concentrations of ANs and the complexity of the atmospheric
96 system in terms of organic gas phase and aerosol components with a wide range of
97 polarity make sampling, direct detection and quantification of ANs in the ambient air
98 a challenging task. Sampling of gas phase ANs in air has been performed in several
99 ways, using Tenax adsorption columns (Luxenhofer et al. 1994; Fischer et al. 2000,
100 2002), a combination of Tenax cartridges and polyurethane (PU) foam (Luxenhofer et
101 al. 1994), silicagel and PU foam (Luxenhofer et al. 1996), silicagel and Tenax
102 (Schneider et al. 1998; Schneider and Ballschmiter 1999), or even charcoal (Atlas and
103 Schauffler 1991; De Kock and Anderson 1994). Simpson et al. (2006) pre-
104 concentrated trace gases from air samples by passing ~1.5 L of canister air through a
105 stainless steel tube filled with 1/8-inch diameter glass beads and immersed in liquid
106 nitrogen. A mass flow controller with a maximum allowed flow of 500 mL min⁻¹
107 controlled the trapping process. The trace gases were re-volatilized using a hot water
108 bath and then reproducibly split into five streams for detection as follows below.

109 Generally, organic nitrates have been measured by high-resolution (HR) gas
110 chromatography (GC) with electron capture detection (ECD) (De Kock and Anderson
111 1994; Moschonas and Glavas 2000; Glavas 2001; Glavas and Moschonas 2001;
112 Fischer et al. 2002; Simpson et al. 2006; Russo et al. 2010; Zhang et al. 2013) and a
113 combination of GC-ECD and GC-MS (Luxenhofer et al. 1994; Luxenhofer et al.
114 1996; Schneider et al. 1998; Schneider and Ballschmiter 1999; Fisher et al. 2000).

115 Both traditional injections of a concentrated extract (De Kock and Anderson
116 1994; Luxenhofer et al. 1994, 1996; Schneider et al. 1998; Schneider and
117 Ballschmiter 1999), as well as thermal desorption from adsorption traps and cryo-
118 trapping have been applied in the analysis of ANs (Fischer et al. 2000; Moschanos
119 and Glavas 2000; Fischer et al. 2002). Nevertheless, pre-separation of ANs is still a
120 critical step of the chemical analysis. For this purpose, diverse procedures have been
121 described, such as adsorption chromatography on silicagel (Luxenhofer et al. 1996;
122 Schneider and Ballschmiter 1999), or normal-phase high-performance liquid
123 chromatography with an organonitrate stationary phase (Fischer et al. 2000).

124 Within the framework of a study aiming at the characterization of nitrogen-
125 containing organic compounds in the marine environment, it appeared to be necessary
126 to develop a sensitive and robust analytical procedure for the determination of ANs,
127 particularly, with the application of GC-MS, it being available in the laboratory of the
128 present research team. In this paper, an adapted and a further developed design of an
129 air sampler for the low and high volume collection of gaseous and aerosol phase
130 atmospheric ANs is reported together with optimized extraction, clean-up, and GC-
131 MS identification and quantification. The preparation of suitable standards of various
132 AN compounds for method calibration is discussed. The daily and seasonal air levels
133 and deposition fluxes of gas phase ANs together with the identification of possible
134 emission sources of these compounds are also reported.

135

136 **Experimental**

137 Sampling and weather data collection

138 A common high volume (HiVol) sampler has been redesigned for the
139 combined collection of aerosol and gas phase components of the ambient air using
140 either a low or high capacity gas adsorption trap (see Supplementary Information).
141 Daily (24-hour) atmospheric air samples were taken four days a week (by starting at
142 14:00 GMT) at a small coastal research/meteorological station of the Flanders Marine
143 Institute (VLIZ), located in De Haan, Belgium (51°17'12.77" N, 3°03'39.53" E, 6 m
144 a.m.s.l.), during two weeks in August 2005 and five months (February-April and
145 June-July) in 2006. Wind direction (WD), wind speed (WS), precipitation, relative
146 humidity (RH), air pressure (P_{air}) and air temperature (T_{air}) were monitored and
147 logged by a computer every minute on each day of the sampling campaigns.

148 For collecting atmospheric PM, a glass fibre filter (Whatmann GF 25) was fitted into
149 the HiVol sampler. Gas phase sampling with low capacity adsorption traps was
150 achieved using 2 g of 60-80 mesh Tenax-TA[®] (Buchem BV, Apeldoorn, the
151 Netherlands) in each of the four tubes of the sampler. The ANs were pre-extracted
152 from the adsorbent with acetone in a Soxhlet-column under reflux for 8 h. A total
153 volume of less than 20 m³ was sampled at a flow rate of 3 m³ h⁻¹ over the four traps.
154 Alternatively, the high capacity adsorption trap was filled with 100 g of 35-70 mesh,
155 silicagel (Sigma Aldrich NV/SA, Bornem, Belgium) for capturing the gas phase
156 components. The silicagel was washed before sampling with a 4:1 (v/v) mixture of
157 pentane-dichloromethane and activated in an electric oven at 160 °C for 24 hours. For

158 each sample, an air volume of typically 250 m³ was pumped through at a flow rate of
159 10 m³ h⁻¹. The chemicals applied in this work were of analytical grade or better, if not
160 stated otherwise. Ultrapure MilliQ water and organic solvents were applied for
161 cleaning, dissolution and dilution (see Supplementary Information).

162

163 Synthesis of alkyl nitrate standards

164 Apart from the commercially available isopropyl and isobutyl nitrate (99 %
165 purity, Aldrich Chem. Co., Steinheim, Germany), the other studied ANs were
166 synthesized in the UA-laboratory to produce high-purity standards for the calibration
167 of the GC-MS method. The corresponding alkyl halides (i.e., iodides for methyl and
168 2-butyl nitrates and corresponding bromide for other ANs synthesized) were dissolved
169 in $\sim 10^{-3}$ mol L⁻¹ acetonitrile, then mixed with a solution of silver nitrate in
170 acetonitrile, containing a two-fold excess of the equivalent amount needed in the
171 reaction, and stirred for 24 h in the dark at room temperature (RT) (Ferris et al. 1953;
172 Luxenhofer et al. 1994). During reaction, ANs segregated as a distinct layer at the top
173 of the aqueous solution, which phases were separated in an extraction funnel. The
174 extract, containing the ANs, was washed with water, dried on Na₂SO₄. Afterwards the
175 ANs were recovered from the drying agent with dichloromethane. The reaction yields
176 for these syntheses were higher than 95%. The nomenclature used in this paper for
177 ANs is according to Schneider and Ballschmiter (1996) and Fischer et al. (2002), for
178 instance, 1C3 and 2C5 stand for 1-butyl nitrate and 2-pentyl nitrate, respectively (see
179 Table S1 in Supplementary Information).

180

181 Extraction and clean-up procedures

182 For the recovery of the gas phase AN compounds from Tenax TA[®] adsorbents,
183 Soxhlet extraction with 150 mL of acetone and pentane (8 h for each) was applied.
184 The excess solvent was evaporated at RT under a gentle nitrogen flow to obtain a
185 sample volume of 0.5 mL. Further sample clean-up utilized a glass column with an
186 internal diameter (ID) of 10 mm, containing 4 g Florisil (100-200 mesh, Fluka, Buchs,
187 Switzerland), activated before use at 120 °C for 12 h. Pentane was used as an eluent
188 and the fraction between 9 and 27 mL was kept for analysis. Subsequently, the sample
189 volume was reduced to about 0.5 mL under a nitrogen stream at RT and the samples
190 were stored at -20 °C in a deep-freezer prior to injection onto the GC-MS.

191 The organic compounds were eluted from the silicagel samples with a 400 mL
192 aliquot of 4:1 (v/v) mixture of pentane-dichloromethane in a water cooled glass
193 column (25.6 cm length, 4 cm ID) (Schneider and Ballschmiter 1999). The extract
194 was concentrated to 150 μ L at RT under a gentle nitrogen flow. The 2-fluoro-toluene
195 was used as a recovery and an internal standard for the optimization steps and for the
196 GC-MS analysis.

197

198 GC-MS separation, detection and quantitation

199 All measurements were performed on a Varian Model Saturn 2000 GC-MS
200 (Varian Inc., Lake Forest, CA, USA) equipped with ion-trap and electron ionization
201 (EI) units. A VF-1ms capillary column (100% dimethylpolysiloxane, Varian Inc.)
202 with a length of 30 m, an ID of 0.25 mm and a film thickness of 1 μ m was used with a
203 helium flow rate of 1 $\text{cm}^3 \text{min}^{-1}$. Sample aliquots of 1 μ L were injected splitless. The
204 temperatures of the injector, the transfer line and the ion-trap were set at 250, 220 and
205 240 $^{\circ}\text{C}$, respectively. The temperature program for the GC oven was as follows: 40 $^{\circ}\text{C}$
206 for 5.8 min, increase to 51 $^{\circ}\text{C}$ with 3 $^{\circ}\text{C} \text{min}^{-1}$ and hold for 2 min, increase to 75 $^{\circ}\text{C}$
207 with 3.5 $^{\circ}\text{C} \text{min}^{-1}$ and hold for 3.5 min, increase to 96 $^{\circ}\text{C}$ with 5 $^{\circ}\text{C} \text{min}^{-1}$ and hold for
208 2.5 min and increase with 10 $^{\circ}\text{C} \text{min}^{-1}$ to 260 $^{\circ}\text{C}$ and hold for 8.13 min. A total
209 chromatographic cycle of 51 min provided the best separation for all AN isomers
210 detected in the air samples. The mass selective detection, following EI of ANs was
211 based on the formation of the intense NO_2^+ fragment at m/z 46. Analytical
212 performance data of the developed GC-MS method are listed in Table S2. The LODs
213 obtained with this method (0.001-0.005 pptv) are sufficiently low to quantify the
214 study ANs in most of the samples on the condition of an air volume of 250 m^3 is
215 collected.

216

217 Calculation of air-mass trajectories and alkyl nitrate fluxes

218 Single-tracks and ensembles of air-mass backward trajectories (BWTs) were
219 calculated for the start and end time of each day of the sampling by the Hybrid Single-
220 Particle Lagrangian Integrated Trajectory (HYSPLIT) Model (Draxler and Rolph
221 2003; Rolph 2003). The BWTs were applied to determine the influence of main air-
222 masses, i.e., the Atlantic Ocean, the North Sea, and the continent, on the air levels of
223 ANs. Typical ensembles of BWTs representing the main air-masses are depicted on
224 Fig. 1.

225 The literature has not yet reported dry deposition velocities (v_d) for individual
226 alkyl nitrates over sea surfaces. Therefore, to estimate of the AN-fluxes, a generalized
227 literature (model) value on organic nitrate deposition for sea water surfaces (0.027
228 cm/s) was selected (Hertel et al. 1995). It is to be noted that the model and
229 experimental v_d values for over-land dry deposition are around an order of magnitude
230 higher, e.g., for organic nitrates: 0.12 cm/s (Hertel et al. 1995), for MeONO₂: 0.13
231 cm/s (Russo et al. 2010), which corresponds to ~4.5-times higher N-fluxes of ANs
232 over land, implying the same air AN levels and weather conditions. The 24 h N-flux
233 data of individual ANs were assorted according to the origin of main air-masses on
234 the base of the single-track BWTs, i.e., Atlantic/Channel, North Sea, continental, or
235 mixed. From these data, the average N-fluxes, their fluctuations, expressed as the
236 standard deviation (SD), and the total N-contributions were calculated.

237

238 Statistical methods

239 The method of bivariate correlation analysis with the Pearson's correlation
240 coefficient (r) at a two-tailed significance level (p) was used with the IBM® SPSS®
241 Statistics software package (version 20). Since there is no data in the literature on
242 PCA of alkyl nitrates, their daily concentrations together with the data on inorganic
243 gases and ionic species of PM sampled concurrently (Bencs et al. 2009; Horemans et
244 al. 2009) were processed using PCA, in order to assist the recognition of contributing
245 factors/emission sources. For PCA, Varimax rotation and Kaiser normalization were
246 applied as described in the literature (Costello and Osborne 2005). Principal
247 components (PCs) having eigenvalues higher than one in the component data set were
248 retained, i.e., those which could still be classified as plausible emission sources on the
249 basis of the component loadings. In PCs, species having loadings above 0.7 and below
250 0.4 were characterized as high and low, respectively. Species having PC loading of
251 less than 0.4 were considered either not be related to the other species or were
252 explored in an additional PC (Costello and Osborne 2005). Reference data on source
253 apportionment published in a comprehensive review (Viana et al. 2008) were also
254 utilized for comparison.

255

256 **Results and discussion**

257 Sampling methodology

258 The use of adsorption columns is the most common method to collect organic
259 compounds from the gas phase (e.g., Atlas and Schauffler 1991). A critical parameter
260 to be considered is the breakthrough volume of the gas adsorption system. On one
261 hand, the sampled volume should be as high as possible to facilitate the detection of
262 air-components present at ultra-trace levels. On the other hand, overloading of the gas
263 adsorption trap may result in partial losses due to evaporation. It is a common practice
264 to determine the limiting volume by connecting two adsorption columns in series
265 (Atlas and Schauffler 1991; Luxenhofer and Ballschmiter 1994; Schneider and
266 Ballschmiter 1999). However, in this case, the limit of detection (LOD) of the
267 analytical method determines the extent, to which the breakthrough volume of the first
268 adsorption column must be exceeded.

269 As an alternative approach, isothermal adsorption chromatography has been
270 applied in the present study. For this purpose, a conventional glass column was
271 packed with an accurately weighed amount of the adsorbent. The retention volume in
272 isothermal elution on a GC-ECD system was determined at various temperatures.
273 Plotting the logarithms of the corrected retention volumes as a function of the
274 reciprocal temperature gives a linear relationship, which can be extrapolated with
275 good accuracy to derive a realistic value for the breakthrough volume. The
276 breakthrough volumes from 1C3 to 1C7 for 2 g Tenax TA[®] were 0.5 to 300 m³,
277 respectively, and for 1C3 on 100 g silicagel, the value was 310 m³. For this adsorbent,
278 only the breakthrough volume for the most volatile AN was determined, otherwise,
279 the retention time would have become too long for AN-analogues of longer carbon
280 chains at the maximal allowable column temperature. Specifically, whenever the
281 accurate sampling of C3 is aimed at, the sampling volume should be lower than 0.26
282 and 3.1 m³ per g Tenax TA[®] and silicagel, respectively. Besides the substantially
283 higher retention capacity of silicagel, it is more cost effective than Tenax TA[®]. Thus it
284 can be advantageously used even in large adsorption traps without any need of
285 adsorbent recovery after extraction and analysis. Therefore, for ambient air sampling,
286 100 g silicagel was applied in this study.

287

288 Daily and seasonal variations in the air levels of alkyl nitrates

289 In summer, 11 ANs have been identified and quantified, but only 8 of them
290 were detected in winter-spring (Table 1). The mean air concentrations and the relative
291 abundance of individual AN analogues/isomers have shown seasonal differences. The
292 air levels of individual ANs in the late summer, winter/spring, and midsummer
293 seasons ranged from 0.001-0.005 pptv (below LOD) to 78 pptv (Table 1), with
294 median concentrations of 0.07, 0.08, and 0.11 pptv, respectively. These median air
295 concentrations rather represent a marine/coastal background. These concentrations are
296 generally lower than those reported in the literature for marine air (De Kock and
297 Anderson 1994), though the sampling for the latter was performed at least a decade
298 earlier. The study Σ AN fraction consists primarily of the 1C4, 2C4, 3C5 and 2C5
299 compounds.

300 The daily trends of the Σ AN concentrations and the corresponding (average)
301 weather data are depicted on Fig. 3. As it can be seen, the Σ AN level exhibits high
302 day-to-day variation, as a result of the influence of various air masses and
303 meteorological conditions. The high extent of rainfall, high RH, and/or high wind
304 speed caused a decrease in the air concentrations of Σ ANs. The higher air temperature
305 also resulted in drop in the Σ AN air levels. This could be expected on the base of the
306 literature, since under higher incoming solar radiation, the atmosphere works more
307 effectively as a sink of ANs, due to more photolysis and an increased rate of AN
308 decomposition (Talukdar et al. 1997).

309 Seasonality of ANs at the coastal site can be observed too, in terms of their usually
310 higher levels during winter-spring than summer (Fig. 3). The occasionally occurring
311 high peaks of Σ ANs in summer have also been observed, which is most probably due
312 to the prevailing continental air masses, transporting high pollution load to the coastal
313 site. Another factor is assumed to be the higher local traffic density during summer at
314 and around the seaside resort as compared to winter/spring.

315

316 Estimation of alkyl nitrate fluxes

317 *Late summer season in 2005*

318 The highest average daily deposition was observed for 3C5 and for
319 Atlantic/Channel/UK air-masses ($0.47 \text{ ng N m}^{-2} \text{ day}^{-1}$), followed by lower values for
320 the mixed North Sea/continental air-masses ($0.23 \text{ ng N m}^{-2} \text{ day}^{-1}$), but around the
321 LOD ($0.12 \text{ ng N m}^{-2} \text{ day}^{-1}$) for North Sea air-masses. The contribution of 2C4 was
322 also significant for Atlantic/Channel/UK air-masses (i.e., $0.45 \text{ ng N m}^{-2} \text{ day}^{-1}$),

323 whereas lower contributions were found for 1C3, 1C4, 2C5, 1C5, 3C6, 2C6, 1C6, and
324 1C8 ANs with similar fluxes (0.02-0.09 ng N m⁻² day⁻¹). For the North Sea influenced
325 air masses, the contributions from 2C4 and 2C5 were found to be very significant,
326 with average deposition values of 0.14 and 0.12 ng N m⁻² day⁻¹, respectively.
327 Moreover, 1C4, 1C5, 3C6, 2C6, and 1C6 also contributed to the flux, with 0.03-0.07
328 ng N m⁻² day⁻¹. Under mixed continental-North Sea influence, the contribution was
329 significant for 1C4, 3C5, 2C5, and 1C9 compounds, with deposition rates of 0.1, 0.23,
330 0.15, and 0.08 ng N m⁻² day, respectively. The 1C5, 3C6, 2C6, 1C6, 1C7, and
331 1C8 contributed lower to the N-flux, each with around 0.025-0.06 ng N m⁻² day⁻¹.

332 The average fluxes of ANs for the Atlantic/Channel/UK, North Sea and the
333 mixed continental-North Sea air masses were found to be 1.5, 0.72, and 0.96 ng N m⁻²
334 day⁻¹, corresponding to an overall AN flux of 1.1 ng N m⁻² day⁻¹ for this short late
335 summer period. In late summer, the contribution of shorter chain ANs prevails from
336 Oceanic air-masses, while for continental and North Sea air-masses, the longer chain
337 ANs also contribute to the N-flux of the study ANs (Fig. 4).

338

339 *Late winter/spring season in 2006*

340 In the late winter/spring period, a high average daily flux of 3C5 has also been found
341 for all the three main air-masses, ranging from 1.1 to 2.5 ng N m⁻² day⁻¹. For the
342 Atlantic/Channel/UK air-masses, the average contribution of 3C5 was 1.2 ng N m⁻²
343 day⁻¹, i.e. ~60 % of the total flux of the study ANs (Fig. 4). Lower contributions were
344 found for 2C5 (0.26 ng N m⁻² day⁻¹), 2C6 with 0.12 ng N m⁻² day⁻¹, whereas the fluxes
345 of 1C4, 1C5, 1C6, 1C8, and 1C9 were much lower, i.e., 0.05, 0.08, 0.08, 0.03, and
346 0.03 ng N m⁻² day⁻¹, respectively.

347 For continental air-masses, fairly intensive average fluxes of 2C4, 3C5, 2C5,
348 2C6, 1C6, and 1C7, i.e., 2.3, 1.1, 0.4, 0.8, 1.4, and 1.1 ng N m⁻² day⁻¹, respectively,
349 have been observed. The 1C8 and 1C9 only contributed with negligibly low fluxes of
350 0.07 and 0.03 ng N m⁻² day⁻¹, respectively. For air-masses, arriving from the North
351 Sea, the flux of 3C5 was extremely high, i.e., with an average value of 2.5 ng N m⁻²
352 day⁻¹, corresponding to ~70 % of the total average N-flux of the detected ANs. The
353 other ANs, characteristic for this air-mass, were 2C5, 1C5, 2C6, 1C6 and 1C8 with
354 medium N-fluxes, ranging between 0.13-0.24 ng N m⁻² day⁻¹. Negligibly low fluxes of
355 1C3, 1C4, 2C4, 1C7 and 1C9 were found with values of 0.01-0.05 ng N m⁻² day⁻¹.

356 The average fluxes of ANs for the Atlantic/Channel/UK, continental and
357 North Sea air-masses were found to be 2.0, 7.4, and 3.6 ng N m⁻² day⁻¹, corresponding
358 to an overall AN-flux of 3.8 ng N m⁻² day⁻¹ for winter/spring. It can be concluded that
359 the highest contribution of AN-fluxes originate from air-masses approaching from the
360 continent, whereas the contributions of Atlantic and the North Sea air masses are
361 lower by 73% and 51%, respectively. The contribution of shorter chain ANs is
362 dominant from marine air-masses, while for continental air-masses, the longer chain
363 ANs also considerably contribute to the N-fluxes of the study ANs (Fig. 4).

364

365 *Midsummer season in 2006*

366 In midsummer, similarly to the late summer period, the AN-fluxes were the
367 most significant from the Atlantic/Channel/UK air-masses and again from 3C5, but
368 also 1C4 with average values of 0.9 and 2.1 ng N m⁻² day⁻¹. The 2C5 and 1C8
369 compounds also contributed to the N-flux, but to a much lower extent than the former
370 ANs, i.e., with depositions around 0.01-0.12 ng N m⁻² day⁻¹. The fluxes of 2C6, 1C5,
371 1C6, and 1C7 were negligibly low, ranging between 0.01-0.06 ng N m⁻² day⁻¹,
372 respectively.

373 For continental air masses, the daily average fluxes of 1C4, 3C5 and 1C8 were
374 found to be the most significant contributors, i.e., 0.26, 0.77 and 0.54 ng N m⁻² day⁻¹,
375 respectively. The fluxes of 1C5, 2C6, 1C6, and 1C7 were lower, ranging between
376 0.08-0.11 ng N m⁻² day⁻¹. For North Sea air-masses, the flux of 3C5 was the most
377 decisive with an average value of 0.9 ng N m⁻² day⁻¹. The 1C4, 2C5, 1C5, and 2C6
378 contributed to the N-flux to a low and varying extent, i.e., 0.21, 0.15, 0.34, 0.28, while
379 the fluxes of 1C6, 1C7, 1C8 and 1C9 were similar, i.e., each ~0.5, ng N m⁻² day⁻¹.

380 The average fluxes of ANs for the Atlantic/Channel/UK, continental and
381 North Sea air-masses were found to be 3.6, 2.2, and 4.1 ng N m⁻² day⁻¹, corresponding
382 to an overall average AN-flux of 3.2 ng N m⁻² day⁻¹. For midsummer, generally the
383 contribution of lower chain ANs prevails for Atlantic and continental air-masses,
384 while for North Sea air-masses, the longer chain ANs also similarly contribute to the
385 N-flux of the study ΣANs, which is similar observation to that made for late summer
386 (Fig. 4).

387

388 Source apportionment

389 *Correlation analysis*

390 The results for winter-spring and summer show several correlations between
391 ANs, the inorganic species sampled concurrently and the corresponding daily weather
392 data (Table S3). Furthermore, seasonal trends can be observed too. In winter-spring,
393 especially 1C4 is highly correlated with HNO₂, fine-Cl⁻, 3C5, 1C5, 2C6, 1C7 and 1C9
394 air levels, but anti-correlated with T_{air} and RH. Apparently, 3C5 showed similar
395 correlations, also for medium-NH₄⁺, but anti-correlated with coarse-NH₄⁺ and WS.
396 The 2C5 was correlated to medium&fine-NH₄⁺/NO₃⁻/SO₄²⁻/K⁺ and WS, but anti-
397 correlated to T_{air}. The 1C5 was also highly correlated with fine-Cl⁻, 1C4, 3C5, 2C6,
398 1C7 and 1C9. It is notable that 2C6 and 1C6 are correlated, also with HNO₂ and
399 medium-NH₄⁺/NO₃⁻/SO₄²⁻, which shows that these compounds may take part in
400 secondary reactions with aerosols, likely via photochemical ways. The resulting
401 HNO₂ may assist in secondary aerosol formation and/or growth. The 2C6 is also
402 related to rain-NO₃⁻ and P_{air}. The 1C8 was correlated to coarse-NH₄⁺, while 1C9 was
403 anti-correlated to medium-NO₃⁻.

404 In summer, a higher number of between species correlations are experienced
405 compared to the winter-spring season. For instance, 1C4 was strongly correlated with
406 3C5, 2C6, 1C6, 1C7, 1C9, medium-NH₄⁺/SO₄²⁻/K⁺, and fine-Mg²⁺. The 3C5 showed
407 the same correlation with the latter inorganic species, but in terms of ANs, it was only
408 correlated with 2C5 and 1C4. The 2C5 was correlated with medium/fine-NO₃⁻/SO₄²⁻
409 /Na⁺, fine-Cl⁻, and also with 2C6, 1C6, 1C7 and RH, but anti-correlated with 3C5, T_{air}
410 and WS. These results point to a lower extent of 2C5 formation at higher T_{air}
411 (corresponding to higher incoming solar radiation flux), and/or intensified
412 photochemical decomposition of this compound. The 1C5 and 2C6 correlated well
413 with each other and longer chain alkyl nitrates. Shorter chain alkyl nitrates (C3-C5)
414 were generally correlated with medium/fine fractions of NH₄⁺/SO₄²⁻/K⁺, which points
415 towards sources of biomass burning. The longer chain alkyl nitrates were related with
416 each other and coarse K⁺. Interestingly, 1C4 and 3C5 correlated well with
417 precipitation in summer.

418

419 *Principal component analysis*

420 For winter-spring, several PCs have been found (Table S4). PC1 has high
421 loadings of coarse-Cl⁻/Mg²⁺/Ca²⁺, medium loadings for coarse Na⁺, SO₄²⁻, NO₃⁻, and
422 for medium-sized Na⁺ and Cl⁻ too, corresponding to sea spray aerosol component.
423 Similar loadings have been found for sea salt components sampled over Amsterdam

424 (Valius et al. 2005), which is also reported to be common for this type of aerosol
425 (Viana et al. 2008). PC2 has high loadings of medium/fine K^+ , fine NH_4^+/SO_4^{2-} ,
426 medium loadings of 2C5 and fine NO_3^- , and low loading for 1C9. Biomass burning
427 has been reported as a source of short chain alkyl nitrates (Simpson et al. 2002). PC2
428 accounts for emissions from local combustion, most likely vehicular traffic and/or
429 biomass burning. PC3 has high loadings for coarse $K^+/NH_4^+/SO_4^{2-}$, medium loadings
430 of coarse Na^+/NO_3^- , and fine Na^+/Cl^- , which demonstrates coagulated secondary
431 aerosols, combined likely with freshly formed sea salt. When including the weather
432 data in PCA, this component was also closely related to WS and T_{air} , which supports
433 long-range transport. Interestingly, PC4 has high loadings of the longer chain alkyl
434 nitrates, like 1C6, 2C6 and 1C7, and a low loading of 3C5, while PC6 has high
435 loadings of the shorter chain ANs, i.e., 1C4 and 1C5, a low loading of 2C5, and
436 medium loadings of 3C5 and 1C9. It is presumed that PC4 accounts for the
437 photochemical formation of alkyl nitrates, likely, through secondary processes in the
438 troposphere, as reported by Atkinson et al. (1982). This is also supported by low
439 loadings of HNO_2 , HNO_3 and medium- $NH_4^+/NO_3^-/SO_4^{2-}$, received in this PC. On the
440 other hand, PC6 may suggest a marine source of alkyl nitrates, which is presumed to
441 be on the base of a weak correlation to sea salt components. PC5 has high loadings of
442 medium-sized $NH_4^+/NO_3^-/SO_4^{2-}/Mg^{2+}$ and medium loadings for HNO_2 and Ca^{2+} ,
443 which points towards diesel emissions. PC7 has medium loadings for HNO_3 and
444 medium-size Na^+ , corresponding to local combustion. PC8 has medium loadings of
445 HNO_3 and coarse/medium Ca^{2+} , corresponding to local background pollution. PC 9
446 has high loadings for NH_3 and medium loadings for HNO_2 . This factor represents
447 emissions originating from extensive animal farming activities over nearby
448 agricultural areas of West Flanders (Bencs et al. 2008).

449 For the summer season in 2006 (Table S5), PC1 has high loadings of most
450 alkyl nitrates (i.e., 1C5, 2C5, 1C6, 2C6, 1C7, 1C8, and 1C9), and a medium loading
451 for HNO_3 . These longer chain alkyl nitrates seem to have the same source in summer,
452 i.e., secondary processes, most likely through photochemical conversion of the
453 corresponding radicals of parent hydrocarbons (Atkinson et al. 1982). PC2 has high
454 loadings for several species of fine PM ($Na^+/Cl^-/NO_3^-/K^+/Mg^{2+}/Ca^{2+}$) and medium
455 loadings for NH_4^+/SO_4^{2-} , which points toward freshly formed secondary aerosols ,
456 possibly through fresh, finely dispersed sea spray particles as nucleation centers
457 (Horemans et al. 2009). PC3 has high loadings for coarse NH_4^+ , Na^+ , K^+ , Mg^{2+} and

458 Ca^{2+} , which shows soil dust resuspension. PC4 is characterized by high loadings of
459 medium-sized Na^+/Cl^- , which clearly points to sea spray origin, as mentioned above.
460 PC5 is characterized by high loadings of 1C4, 3C5, medium-sized K^+ , medium
461 loadings of medium-sized $\text{NH}_4^+/\text{SO}_4^{2-}$, and low loadings of fine $\text{Mg}^{2+}/\text{SO}_4^{2-}$, which
462 factor most possibly reflects the contribution of biomass burning activities at nearby
463 agricultural fields. PC6 has a high loading of medium-sized NO_3^- , and a medium
464 loading of HNO_2 , medium/fine- $\text{NH}_4^+/\text{SO}_4^{2-}$ and coarse NO_3^- , corresponding to
465 secondary aerosol. PC7 has high loadings of coarse $\text{SO}_4^{2-}/\text{Cl}^-$ and medium loading of
466 NO_3^- , which factor corresponds likely to regional/coastal background. PC9 has high
467 loadings for NH_3 and medium loadings for HNO_2 , which represents emissions from
468 animal farming activities as noted above.

469

470 **Conclusions**

471 The redesigned HiVol sampler allows the simultaneous collection of aerosol
472 and gas phase components of the ambient air using either a low, or high capacity gas
473 adsorption trap. This sampling and the developed analytical methodology exhibits the
474 accurate determination of gas phase ANs (e.g., those with 3-9 carbon atoms) from
475 ambient air samples with minimal pre-separation using the species selectivity and
476 high sensitivity of EI-GC-MS.

477 The N-fluxes of the study ΣANs at the coastal sampling site are slightly more
478 pronounced in summer than in winter-spring, although their contribution to the total
479 (wet+dry) nitrogen flux is still considered to be low (cf. Bencs et al. 2009). Higher
480 ΣAN -fluxes have been observed from the continent and the North Sea in winter/spring
481 compared to those from Atlantic/Channel/UK air-masses, while in summer the fluxes
482 from the latter air-mass were also increased. In summer, most of the shorter chain
483 gaseous ANs are correlated with precipitation, while in winter-spring, the study
484 compounds are related with the HNO_2 content of air. Some ANs were anti-correlated
485 with air temperature, suggesting a photochemical sink.

486 Occasional high peaks of ANs, originating from continental air pollution, have
487 also been experienced in summer over De Haan. These were likely due to higher local
488 traffic density and more frequency of continentally influenced air during summer near
489 this seaside resort as compared to winter/spring. It is important to note, however, that
490 these effects can mask the regular seasonality of ANs, reported in the literature, i.e.,

491 the peak and the lowest AN air levels in the cold and warm season, respectively (e.g.,
492 Swanson et al. 2003).

493 The principal component analysis showed at least 3-4 sources of gaseous alkyl
494 nitrates at the coastal study site (depending on the season), the most important being
495 local combustion (e.g., diesel emissions of vehicular traffic/shipping), secondary
496 photochemical formation from parent hydrocarbons, and biomass burning. On the
497 other hand, one cannot rule out the marine origin of a part of the shorter chain alkyl
498 nitrates (e.g., 1C4, 2C5), they being evidently correlated to certain sea salt aerosol
499 components.

500

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509

510

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670

671 **Figure Captions**

672

673 **Fig. 1** Typical ensembles of air-mass backward trajectories calculated by the
674 HYSPLIT Model, representing (a) Atlantic/Channel/UK, (b) North Sea, and (c)
675 continental air-masses

676

677 **Fig. 2** Mass chromatograms at m/z 46 for a reference mixture of alkyl nitrates (IS –
678 internal standard) and mass spectra for 2C4 and 1C9

679

680 **Fig. 3** Daily and seasonal variation of the Σ AN concentration and meteorological
681 parameters (abbreviations for air-masses: C – continental, AC – Atlantic/Channel/UK,
682 and NS – North Sea)

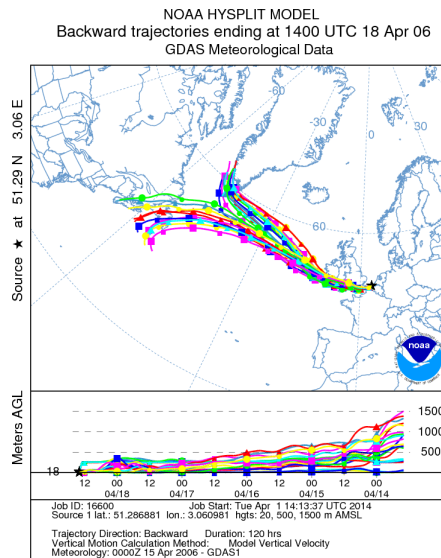
683

684 **Fig. 4** Percent contributions of individual alkyl nitrates to the N-flux of Σ ANs from
685 the main air-masses during various seasons

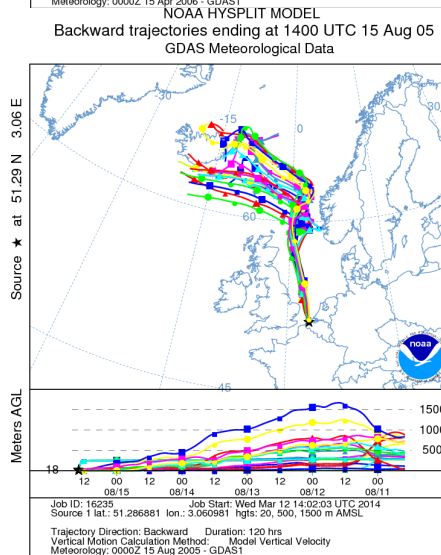
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687 **Fig. 1.**

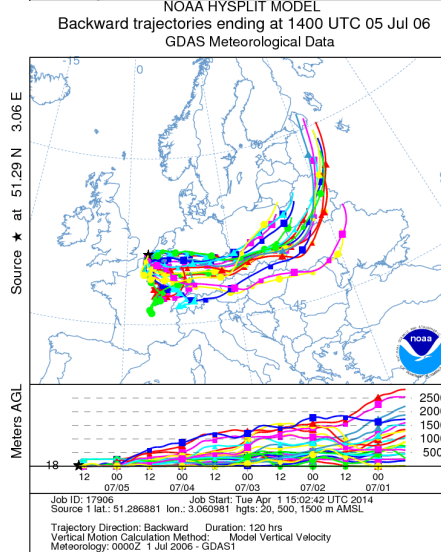
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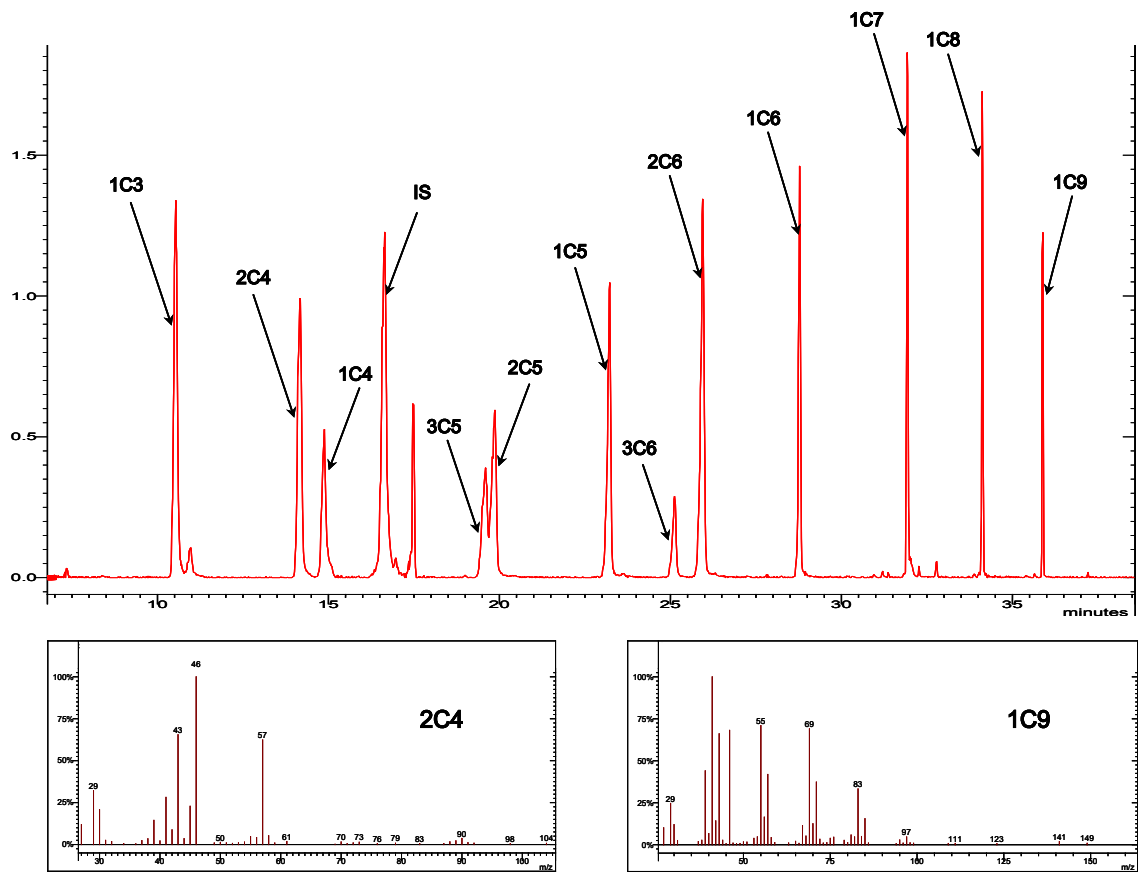


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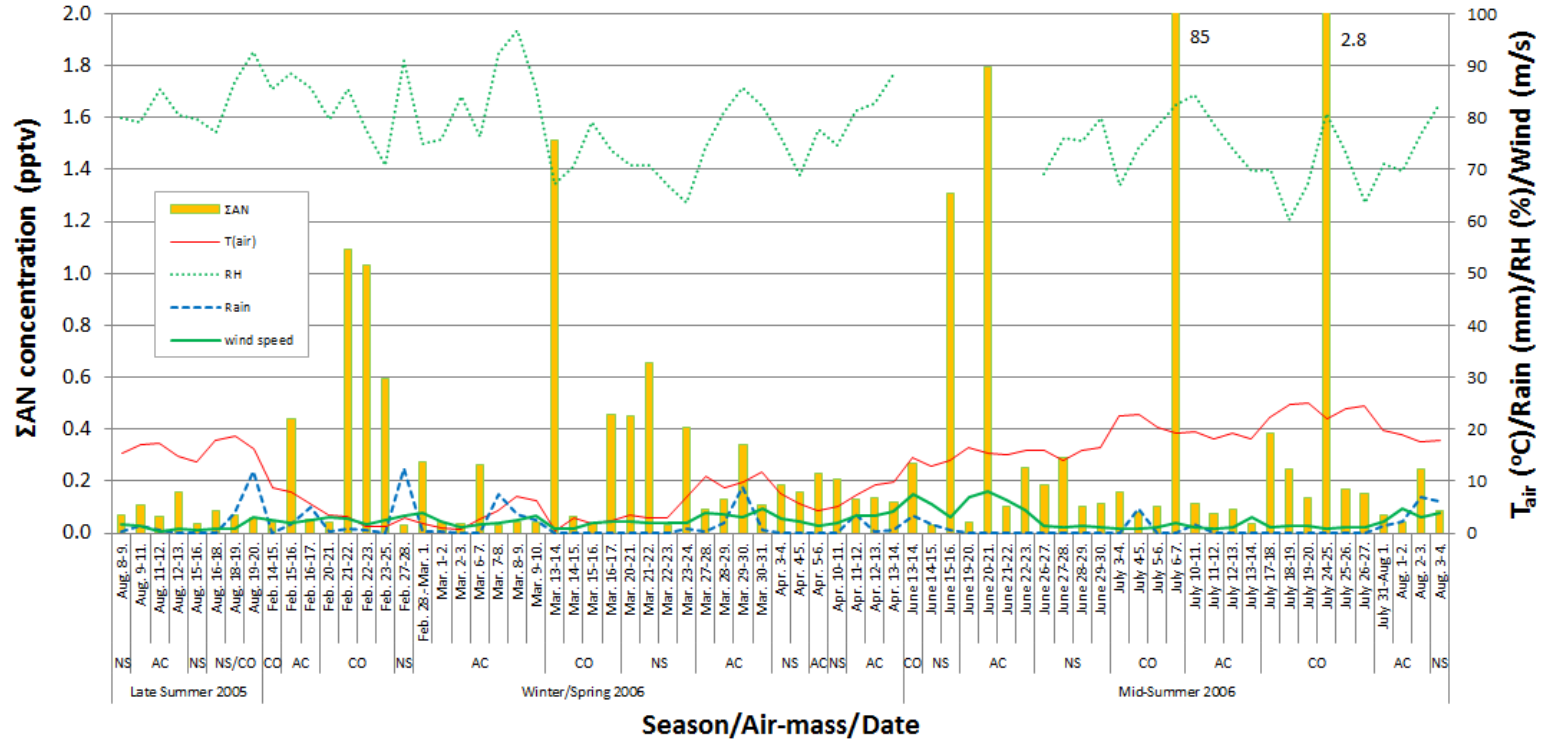
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Fig. 2.



1 Fig. 3.

2



3

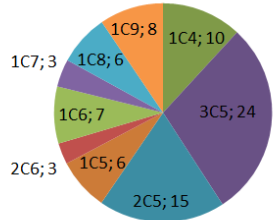
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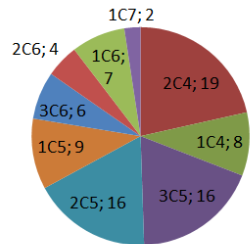
6 **Fig. 4.**

7

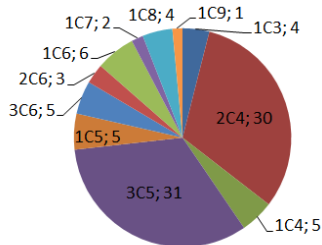
Late summer 2005



North Sea/Continental

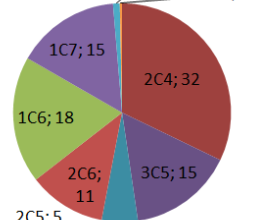


North Sea

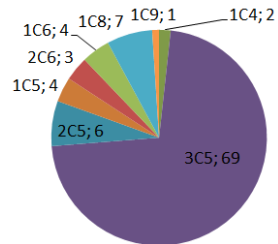


Atlantic/Channel/UK

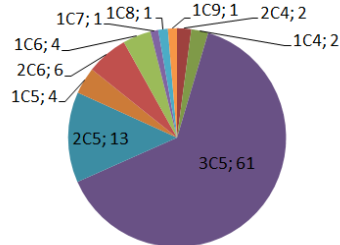
Winter/spring 2006



Continental

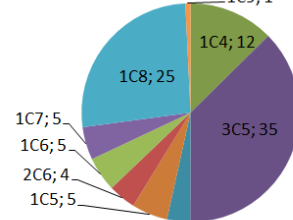


North Sea

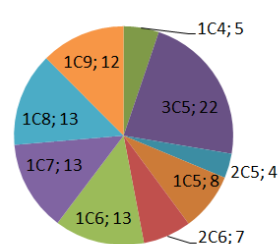


Atlantic/Channel/UK

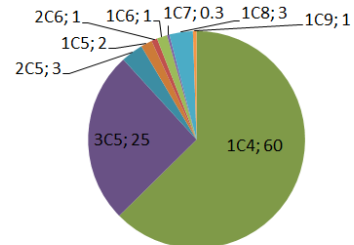
Mid-summer 2006



Continental



North Sea



Atlantic/Channel/UK

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Table 1 Atmospheric alkyl nitrate concentrations and detection frequencies in various seasons over De Haan, Belgium

Parameter	Season	Alkyl nitrate concentration (pptv)												ΣAN	
		1C3	2C4	1C4	3C5	2C5	1C5	3C6	2C6	1C6	1C7	1C8	1C9		
Median	Late summer 2005	0.005	0.01	0.006	0.014	0.009	0.005	0.004	0.003	0.005	0.002	0.003	0.002	0.07	
	Winter/spring 2006	n.d.	n.d.	0.003	0.048	0.007	0.002	n.d.	0.003	0.003	0.001	0.002	0.002	0.08	
	Midsummer 2006	n.d.	n.d.	0.005	0.065	0.008	0.004	n.d.	0.003	0.002	0.001	0.006	0.001	0.11	
Range	min	Late summer 2005	n.d.	0.002	0.003	n.d.	n.d.	0.002	n.d.	n.d.	0.002	n.d.	n.d.	n.d.	~0.04
	Winter/spring 2006	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	~0.03	
	Midsummer 2006	n.d.	n.d.	n.d.	0.0023	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	~0.03	
max	Late summer 2005	0.008	0.044	0.011	0.073	0.014	0.008	0.007	0.004	0.01	0.004	0.009	0.008	0.2	
Winter/spring 2006	n.d.	1.5	0.013	0.54	0.22	0.035	n.d.	0.25	0.38	0.38	0.13	0.008	3.5		
Midsummer 2006	n.d.	0.007	6.4	78.8	0.042	0.10	n.d.	0.12	0.22	0.25	0.25	0.24	86.4		
Quartiles	1st	Late summer 2005	0.004	0.006	0.004	0.008	0.003	0.004	0.003	0.002	0.004	0.001	0.002	0.001	0.04
		Winter/spring 2006	n.d.	n.d.	0.002	0.01	0.004	0.002	n.d.	0.002	0.0013	0.001	0.001	0.001	0.03
		Midsummer 2006	n.d.	0.002	0.003	0.037	0.005	0.002	n.d.	0.002	0.0012	0.001	0.002	0.001	0.06
	3rd	Late summer 2005	0.005	0.026	0.006	0.027	0.012	0.006	0.006	0.004	0.006	0.003	0.005	0.004	0.11
		Winter/spring 2006	n.d.	0.0054	0.005	0.16	0.024	0.004	n.d.	0.019	0.014	0.001	0.002	0.003	0.25
		Midsummer 2006	n.d.	0.0053	0.006	0.092	0.009	0.01	n.d.	0.006	0.01	0.002	0.04	0.002	0.19
Detection frequency (%)	Late summer 2005	13	50	100	50	38	100	38	75	100	88	50	38	n.a.	
	Winter/spring 2006	0	2	8	18	11	6	0	16	14	6	3	4	n.a.	
	Midsummer 2006	0	0	38	83	7	41	0	41	41	28	55	10	n.a.	

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Note: ΣAN –sum of the study alkyl nitrates; n.d. – not detected (i.e, below the LOD of the applied method); n.a. – not applicable.

SUPPLEMENTARY INFORMATION

“Methods, fluxes and sources of gas-phase alkyl nitrates in the coastal air”

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Description of the modified HiVol sampler

A common HiVol sampler has been redesigned for combined collection of aerosol and gas phase components of the ambient air using either a low or high capacity gas adsorption trap. Particular attention has been paid to redesign the shape of the housing to reduce the effects of the changes in the wind direction on sampling, and to improve protection of samples during sample change. Furthermore, a rugged pump system and rotameter control of the sampling rate have been incorporated to ensure reliable and maintenance-free operation over long periods without the need to calibrate the flow rate, as a function of the under-pressure over a calibrated orifice.

The particles are collected on a filter with a diameter of 11 cm in a stainless steel filter holder with separate pressing and tightening rings to avoid filter damage during mounting (Fig. S1). A Viton O-ring is used for sealing. The filter is mounted on the top of a cylindrical manifold with a length of 30 cm and an internal diameter (ID) of 9 cm. The large capacity adsorption trap with an ID of 70 mm and a height of 50 mm can be inserted in the cylinder and is sealed by a Viton O-ring, of which groove is calculated for dynamic sealing. The adsorption trap can take up about 175 cm³ of adsorbent, corresponding to 100 g of silicagel (35-70 mesh). The cylinder is also fitted with four aspiration tubes for the four low capacity adsorption traps. The tube diameters are calculated to maintain isokinetic sampling to avoid turbulences in the system. The low capacity traps consist of glass tubes (ID: 8 mm, length: 95 mm), mounted in stainless steel protection tubes with the aid of two external O-rings. Screw connections of generous dimensions allow the tubes to be mounted leak-free with finger tightening only. Connections and protection tubes are again sealed by O-rings and the pressing rings are separated from the turning fittings. The exits of the four gas traps are connected to a housing of which the internal design allows combination of the flows into one exit under laminar conditions. The flow through the four gas traps together is measured by a rotameter (RAGH02-D2ST-G161A-PP16, Rota Yokogawa, Wehr, Germany) and directed to another housing, where it is combined with the flow through the main aspiration line at the bottom of the manifold cylinder. Also, here the bottom of the cylinder is conically shaped inside to avoid any turbulence. To

compensate for the hydrodynamic resistance of the gas traps, a 2 inch diameter ball valve is fitted between the manifold and the second connection housing. From that housing, the air flows through a large rotameter (Model RAGH06-D2ST-G471A-PPN45, Rota Yokogawa, Wehr, Germany) to the vacuum pump (max. flow rate 40 m³ h⁻¹, DT4.40 Becker GmbH, Wuppertal, Germany) with constant flow characteristics over a wide range of low-pressure conditions.

Except the pump, the sampling system is mounted in an aluminum housing (50x50x100cm) with a pyramidal roof (height: 40 cm). The pyramidal shape avoids the asymmetry of the roof section, common for commercial HiVol samplers (with two vertical and two angular surfaces) and thereby avoids the effect of the wind direction on the sampling characteristics. A completely radial symmetry would be ideal, but it complicates construction, and in addition, field studies require easy (de)mounting of the set-up. The sampler is mounted on lightweight rods extending at an angle of 45° with lead-filled supports to ensure stable positioning without the aid of additional means and under stormy wind conditions. The housing has a door and opening section on two opposite sites, so that the sample can be exchanged either side, under protection against wind and rain, as opposed to commercial HiVol samplers.

Fig. S1 Scheme of sampler: 1 - adsorption trap for high volume air sampling, 2 - valve, 3 – traps for low volume air sampling, 4 and 4' - rotameters, 5 - vacuum pump

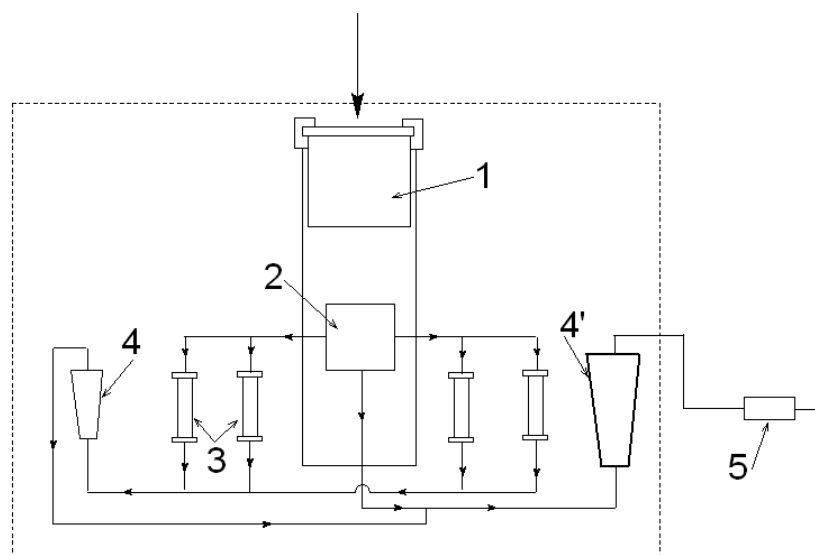


Table S1 The nomenclature of alkyl nitrates and the corresponding halides used for synthesis and yields of the synthesis reactions

Alkyl nitrate		Yield (%)
Methyl*	1C1	98
Ethyl	1C2	96
1-Propyl	1C3	97
1-Butyl	1C4	96
2-Butyl*	2C4	98
1-Pentyl	1C5	96
2-Pentyl	2C5	92
3-Pentyl	3C5	96
1-Hexyl	1C6	95
1-Heptyl	1C7	98
1-Octyl	1C8	99
1-Nonyl	1C9	97

* - synthesized from RI; all the others from RBr

Analytical methodology

The small amounts of adsorbents in Tenax TA[®] sampling makes Soxhlet extraction the most adequate. The extraction efficiency has been checked by spiking 8 g Tenax TA[®] with 10 μL aliquots of a reference mixture containing all the ANs in acetone at a concentration of 50 $\mu\text{g mL}^{-1}$. The recovery values for extraction of the reference compounds using the described method ranged from 85% for 1C3 to 95% for 1C9. In contrast, the large gas trap containing 100 g silicagel needed another extraction method. Specifically, the adsorbent is flushed with 400 mL of pentane and dichloromethane in a glass cooled column. The extraction efficiency was determined in the same way as for the Tenax TA[®] and yielded a recovery of 93 to 97 % for silicagel. Solvent desorption after adsorptive sampling combines the advantages of multiply injections with various detection methods in GC, including in sample pre-separation to reduce the complexity of the analytes (Luxenhofer et al. 1996).

In spite of the selective elution applied for silicagel, or the cleaning procedure applied to Tenax TA[®] after extraction, the materials still contained significant amounts of trace contaminants. However, the species selectivity of the applied GC-MS method was sufficiently high to avoid further pre-cleaning. For quantification, the mass chromatogram at m/z 46 is the best compromise between specificity and intensity. The calibration fits for the intensity (area) ratios as a function of the relative abundance of the ANs to 2-fluorotoluene is linear over 1.5 orders of magnitude, while the precision with 5 replicate injections is within 6 % and the LOD is around 30 pg injected (cf. Table S2). A substantial difference in sensitivity for each alkyl nitrate analogue has been noticed, requiring separate calibration curves to be constructed.

The instrumental LODs and LOQs were assessed by diluting standard solutions and injecting three replicates of 1 μL of each reference mixture into the GC. The concentration giving a signal 3-time higher than the background (noise) value was considered as the minimum amount the instrument can detect. The instrumental LOQ was considered with the most diluted standard solution, which could be plotted in the calibration curve, corresponding to 3.33LOD. For the calculation of the method LOQs, the volume of the air sampled for the analysis was also taken into account.

Samples with a level below LOQ were assigned a value of $(1-p) \times \text{LOQ}$, with “p” being the proportion of measurements with levels below LOQ (Voorspoels et al. 2002).

Table S2 Analytical performance of the GC-MS method for the study alkyl nitrates

	1C3	2C4	1C4	3C5	2C5	1C5	3C6	2C6	1C6	1C7	1C8	1C9
S	1.322	1.092	1.590	0.312	0.522	0.877	0.287	1.328	0.815	0.672	0.550	0.402
r²	0.9996	0.9996	0.9991	0.9992	0.9989	0.9998	0.9988	0.9990	0.9997	0.9996	0.9992	0.9989
Instrumental LOD (pg injected)	18	17	14	42	29	10	17	10	11	6	10	11
Instrumental LOQ (pg injected)	56	53	45	133	92	33	55	31	34	17	30	35
Method LOD (pptv)	0.003	0.002	0.002	0.005	0.003	0.001	0.002	0.001	0.001	0.001	0.001	0.001
Method LOQ (pptv)	0.008	0.007	0.006	0.015	0.01	0.004	0.006	0.003	0.004	0.002	0.003	0.003
Precision (%), n=5 (0.5 µg mL⁻¹)	1.9	1.9	0.9	6.2	4.3	2.3	6.0	3.1	2.7	2.0	3.5	1.9

S – slope of the calibration graph, r – correlation coefficient of calibration, LOD – limit of detection, LOQ – limit of quantification, n – number of replicate determinations.

Table S3 Correlation of alkyl nitrates with inorganic species and meteorological conditions

AN	Season	
	Winter-spring	Midsummer
1C3	-	-
2C4	-	-
1C4	HNO ₂ , fine Cl ⁻ , 3C5, 1C5, 2C6, 1C7, 1C9, T _{air} (a), RH(a)	medium-NH ₄ ⁺ /SO ₄ ²⁻ /K ⁺ , fine-Mg ²⁺ , 3C5, 2C6, 1C6, 1C7, 1C9, rain
3C5	HNO ₂ , medium-NH ₄ ⁺ , coarse-NH ₄ ⁺ (a), medium-Mg ²⁺ (a), 1C5, 2C6, T _{air} (a), RH(a), WS(a)	medium-NH ₄ ⁺ /SO ₄ ²⁻ /K ⁺ , fine-Mg ²⁺ , 2C5(a), rain

2C5	medium&fine-NH ₄ ⁺ /NO ₃ ⁻ /SO ₄ ²⁻ /K ⁺ , T _{air} (a), WS	coarse-K ⁺ /Mg ²⁺ , medium-SO ₄ ²⁻ /NO ₃ ⁻ /Na ⁺ , fine-NO ₃ ⁻ /SO ₄ ²⁻ /Na ⁺ /Cl ⁻ , 1C5, 2C6, 1C6, 1C7, T _{air} (a), P _{air} , WS(a)
1C5	fine-Cl ⁻ , 2C6, 1C7, 1C9	2C6, 1C6, 1C7, 1C8
3C6	-	-
2C6	HNO ₂ , medium-NH ₄ ⁺ /NO ₃ ⁻ /SO ₄ ²⁻ , 1C6, 1C7, rain-NO ₃ ⁻ , P _{air}	coarse-K ⁺ , 1C6, 1C7, 1C8
1C6	HNO ₂ , medium-NH ₄ ⁺ /NO ₃ ⁻ /SO ₄ ²⁻ /Ca ²⁺ /Mg ²⁺ /K ⁺ ,	1C7, 1C8, 1C9
1C7	HNO ₂ , 1C8	coarse-Na ⁺ /K ⁺ /Mg ²⁺ , 1C8, 1C9
1C8	coarse-NH ₄ ⁺ ,	HNO ₃ , 1C9
1C9	medium-NO ₃ ⁻ (a)	fine-NO ₃ ⁻ /K ⁺ ,

Note: (a) – anti-correlation; the fine, medium, and coarse aerosol fractions correspond to aerodynamic diameter ranges of 0.17-0.84, 0.84-4.2, and >4.2 μm, respectively.

Table S4 Results of PCA for 2006 winter-spring

	Rotated Component Matrix ^a									
	L1	L2	L3	L4	L5	L6	L7	L8	L9	L10
HNO ₂	-0.154	-0.032	0.076	0.159	0.342	-0.035	0.083	0.003	0.654	0.277
HNO ₃	0.061	0.163	0.016	0.154	-0.060	-0.089	0.538	-0.053	0.372	-0.302
NH ₃	-0.060	-0.043	-0.093	-0.048	-0.104	-0.066	0.075	0.026	0.794	-0.055
Coarse NO ₃ ⁻	0.122	-0.018	0.305	-0.146	-0.055	-0.136	0.172	0.695	-0.283	-0.157
Coarse NH ₄ ⁺	-0.005	-0.080	0.832	-0.070	-0.026	-0.019	0.265	0.187	-0.251	-0.035
Coarse SO ₄ ²⁻	0.373	-0.022	0.851	-0.094	0.069	0.058	-0.086	0.013	-0.090	-0.093
Coarse Cl ⁻	0.829	-0.147	0.306	-0.117	-0.177	0.151	0.125	-0.053	-0.110	-0.023
Coarse Na ⁺	0.649	-0.036	0.632	-0.074	-0.097	0.151	0.142	-0.061	-0.039	-0.020
Coarse K ⁺	0.145	0.064	0.873	-0.079	-0.089	0.147	-0.093	-0.021	0.077	0.015
Coarse Mg ²⁺	0.853	-0.086	0.179	-0.036	-0.078	-0.007	-0.049	0.341	-0.144	0.028
Coarse Ca ²⁺	0.796	-0.023	0.063	-0.034	0.013	-0.086	-0.074	0.476	-0.088	0.078
Medium NO ₃ ⁻	-0.220	0.236	-0.013	0.170	0.857	-0.069	-0.031	-0.025	-0.005	-0.013
Medium NH ₄ ⁺	-0.312	0.166	-0.016	0.341	0.791	-0.106	0.025	0.028	0.091	0.105
Medium SO ₄ ²⁻	0.002	0.148	-0.017	0.281	0.829	-0.097	-0.023	0.105	-0.024	-0.157
Medium Cl ⁻	0.676	-0.148	-0.082	-0.183	-0.092	0.159	-0.127	-0.227	0.217	-0.168
Medium Na ⁺	0.706	-0.052	0.204	-0.143	0.101	0.010	0.444	-0.067	-0.098	-0.091
Medium K ⁺	0.114	0.892	0.033	-0.033	-0.035	-0.033	0.053	-0.022	0.080	-0.007
Medium Mg ²⁺	0.186	-0.152	-0.017	-0.206	0.812	0.009	0.006	0.073	-0.001	0.036

Medium Ca ²⁺	0.301	-0.029	0.039	-0.080	0.220	-0.134	0.038	0.644	0.077	0.233
Fine NO ₃ ⁻	-0.305	0.699	-0.108	-0.053	0.143	-0.051	-0.384	-0.189	0.038	0.252
Fine NH ₄ ⁺	-0.365	0.738	-0.069	-0.002	0.186	-0.102	-0.329	0.036	-0.025	0.213
Fine SO ₄ ²⁻	-0.140	0.787	-0.044	-0.064	0.183	-0.114	-0.077	0.341	-0.133	0.074
Fine Cl ⁻	0.005	0.160	0.485	-0.056	-0.101	0.100	-0.653	-0.008	0.284	-0.079
Fine Na ⁺	0.076	0.340	0.667	0.028	0.103	-0.056	-0.348	0.097	0.137	0.020
Fine K ⁺	-0.103	0.805	0.320	-0.109	0.023	0.078	0.000	-0.030	0.040	-0.051
Fine Mg ²⁺	-0.061	0.133	-0.005	-0.041	0.034	-0.145	-0.592	-0.055	-0.238	-0.164
Fine Ca ²⁺	-0.063	0.108	-0.078	-0.011	-0.042	-0.037	0.026	-0.049	0.047	0.803
1C4	0.072	-0.097	0.101	-0.011	-0.152	0.914	-0.095	-0.004	-0.022	0.069
3C5	0.076	0.038	-0.094	0.199	0.045	0.651	0.138	-0.139	0.114	-0.158
2C5	-0.015	0.597	-0.057	-0.011	0.051	0.340	0.389	-0.069	-0.179	-0.220
1C5	0.035	-0.116	0.125	-0.021	-0.137	0.927	-0.081	0.012	-0.060	0.064
2C6	-0.078	-0.031	-0.075	0.934	0.093	0.085	0.062	-0.118	0.008	0.027
1C6	-0.124	-0.089	-0.076	0.940	0.149	0.074	0.039	-0.059	0.024	-0.056
1C7	-0.122	-0.097	-0.072	0.957	0.117	-0.017	0.011	-0.052	0.027	0.009
1C8	0.116	-0.135	0.089	0.100	-0.050	-0.138	0.139	-0.554	-0.271	0.200
1C9	0.030	0.374	0.137	-0.006	0.052	0.636	0.286	0.019	-0.218	-0.089
Eigenvalue (total)	6.962	4.681	3.457	3.306	2.383	1.814	1.751	1.577	1.393	1.127
Variance (%)	19.338	13.004	9.604	9.183	6.618	5.039	4.863	4.381	3.870	3.129
Cumulative (%)	19.338	32.341	41.945	51.128	57.747	62.876	67.649	72.030	75.901	79.030
Major source	sea spray	biomass burning	secondary aerosol	photochem. from HCs	diesel emission	marine emission	local combustion	local background	animal farming	unidentified local source

^a – rotation converged in 14 iterations; Note: L1, L2, etc. stands for “loading on Component 1”, “loading on Component 2”, and so on.

Table S5 Results of PCA for 2006 summer

	Rotated Component Matrix ^a								
	L1	L2	L3	L4	L5	L6	L7	L8	L9
HNO ₂	0.009	-0.213	-0.154	-0.133	0.017	0.558	-0.352	0.094	-0.273
HNO ₃	0.399	0.101	-0.117	-0.217	-0.100	-0.026	-0.013	0.688	-0.023
NH ₃	0.165	-0.052	0.008	0.140	0.026	0.000	-0.047	-0.019	0.883
Coarse NO ₃ ⁻	0.195	0.219	0.035	-0.045	-0.021	0.413	0.680	0.334	-0.051
Coarse NH ₄ ⁺	0.034	0.099	0.821	0.060	0.189	0.272	-0.058	-0.178	0.090
Coarse SO ₄ ²⁻	0.097	0.033	0.049	0.078	0.142	0.086	0.933	0.002	0.008
Coarse Cl ⁻	0.107	-0.101	0.168	-0.012	-0.103	-0.213	0.838	-0.257	-0.058
Coarse Na ⁺	0.098	-0.048	0.822	0.116	-0.082	-0.119	0.206	-0.359	0.053
Coarse K ⁺	0.118	-0.073	0.463	-0.007	-0.151	0.071	0.097	-0.571	0.015
Coarse Mg ²⁺	0.008	0.013	0.936	0.170	-0.053	-0.159	0.083	-0.049	0.015
Coarse Ca ²⁺	-0.059	-0.067	0.884	0.170	-0.023	-0.009	0.046	0.198	-0.114
Medium NO ₃ ⁻	0.051	0.259	0.111	0.175	-0.030	0.700	0.391	-0.131	-0.211
Medium NH ₄ ⁺	-0.097	0.180	0.089	-0.109	0.505	0.575	-0.184	0.036	0.275
Medium SO ₄ ²⁻	-0.073	0.290	-0.027	0.057	0.569	0.620	0.207	-0.122	0.151
Medium Cl ⁻	-0.016	-0.075	-0.256	0.925	-0.026	-0.052	0.054	-0.101	-0.030
Medium Na ⁺	-0.015	0.024	0.324	0.844	0.024	0.065	0.124	-0.216	-0.020
Medium K ⁺	0.176	0.057	0.054	0.078	0.733	0.290	-0.143	0.306	0.088
Medium Mg ²⁺	-0.100	-0.055	0.203	0.906	-0.032	-0.096	-0.001	0.024	0.159

Medium Ca ²⁺	-0.091	-0.073	0.337	0.897	-0.026	0.038	-0.076	0.086	0.069
Fine NO ₃ ⁻	-0.041	0.964	-0.088	-0.040	-0.040	0.075	0.033	-0.005	0.014
Fine NH ₄ ⁺	0.000	0.639	0.008	-0.134	0.057	0.539	-0.081	0.262	0.175
Fine SO ₄ ²⁻	-0.016	0.572	-0.093	-0.070	0.170	0.597	0.122	-0.165	0.180
Fine Cl ⁻	-0.030	0.942	-0.001	0.008	-0.021	-0.071	0.118	-0.002	-0.098
Fine Na ⁺	0.002	0.980	0.028	-0.033	-0.031	0.041	0.021	-0.017	-0.047
Fine K ⁺	-0.032	0.719	-0.051	-0.075	-0.097	0.293	-0.121	0.110	0.200
Fine Mg ²⁺	-0.067	0.915	-0.011	-0.012	0.280	-0.061	0.054	-0.011	-0.105
Fine Ca ²⁺	-0.120	0.902	0.098	0.006	-0.039	0.121	-0.011	0.082	-0.035
1C4	-0.046	-0.042	-0.033	-0.048	0.956	-0.012	0.068	-0.081	-0.050
3C5	-0.043	-0.046	-0.037	-0.045	0.969	-0.016	0.054	-0.040	-0.037
2C5	0.876	-0.045	0.027	0.005	-0.008	-0.004	0.172	-0.140	0.133
1C5	0.936	-0.073	-0.001	-0.065	-0.023	-0.028	0.059	0.118	-0.023
2C6	0.994	-0.038	0.005	-0.037	0.004	-0.003	0.014	0.040	0.018
1C6	0.991	-0.033	0.032	-0.023	0.007	0.003	0.047	0.026	0.013
1C7	0.993	-0.024	0.020	-0.019	0.015	0.017	0.023	0.015	0.015
1C8	0.880	-0.096	-0.022	-0.094	-0.056	-0.021	0.028	0.275	0.035
1C9	0.973	0.005	0.040	0.008	0.028	0.029	0.019	-0.098	0.029
Eigenvalue (total)	7.220	6.623	4.998	3.496	2.547	2.307	1.718	1.306	1.044
Variance (%)	20.057	18.396	13.884	9.711	7.075	6.409	4.772	3.627	2.900
Cumulative (%)	20.057	38.453	52.337	62.048	69.122	75.532	80.304	83.931	86.831
Major source	photochem. from HCs	fossil fuel burning	resuspended dust	sea salt	biomass burning	secondary aerosols	regional/coastal background	local traffic	animal farming

^a – rotation converged in 8 iterations; Note: L1, L2, etc. stands for “loading on Component 1”, “loading on Component 2”, and so on.

Reference for Supplementary Information Section

Voorspoels, S., Covaci, A., Maervoet, J., & Schepens, P. (2002). Relationship between age and levels of organochlorine contaminants in human serum of a Belgium population. *Bulletin of Environmental Contamination and Toxicology*, 69(1), 22-29.