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DOI:

[10.1016/j.envint.2016.09.010](https://doi.org/10.1016/j.envint.2016.09.010)

Document Version

Peer reviewed version

[Link to publication record in King's Research Portal](#)

Citation for published version (APA):

Balducci, C., Green, D. C., Romagnoli, P., Perilli, M., Johansson, C., Panteliadis, P., & Cecinato, A. (2016). Cocaine and cannabinoids in the atmosphere of Northern Europe cities, comparison with Southern Europe and wastewater analysis. *Environment International*. <https://doi.org/10.1016/j.envint.2016.09.010>

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Cocaine and cannabinoids in the atmosphere of Northern Europe cities, comparison with Southern Europe and wastewater analysis

Catia Balducci^{1*}, David C. Green², Paola Romagnoli¹, Mattia Perilli¹, Christer Johansson^{3,5}, Pavlos Panteliadis⁴, Angelo Cecinato¹.

Abstract

This study reports the first investigation of atmospheric illicit drug concentrations in Northern Europe using measurements of cocaine and cannabinoids in Amsterdam, London and Stockholm. Further, these measurements were compared to those made in Rome to explore the geographical and inter-city variability. Co-located measurements of atmospheric particulate mass and PAHs were used to help describe and interpret the illicit drug measurements with respect to atmospheric dispersion. Cocaine concentrations ranged from 0.03 to 0.14 ng/m³ in Amsterdam, from 0.02 to 0.33 ng/m³ in London and were below quantification limit (3 pg/m³) in Stockholm. Cannabinol was the only cannabinoid molecule detected in the three cities. During this campaign, London reported the highest concentrations of cocaine and meaningful differences were detected between the urban background and city centre London sites. Mean cocaine concentrations measured in Amsterdam during March 2011 were also compared with those measured simultaneously in eight Italian cities. The cocaine concentration in Amsterdam was comparable to that measured at an urban background in Milan and at a densely populated site in Florence. Although correlating atmospheric concentrations directly with drug prevalence is not possible using current data, links between concentrations of cocaine and estimates of abuse prevalence assessed by the more routinely used wastewater analysis were also examined. A statistically significant correlation was found between the two sets of data ($R^2 = 0.66$; $p = 0.00131$). Results confirmed that meteorology, population rate and habits of consumption influence the atmospheric concentrations of drugs. If these confounding factors were better controlled for, the techniques described here could become an easy and cost effective tool to index the impact of cocaine abuse in the area; especially where local hot spots need to be identified.

Highlights

The presence of illicit drugs in the air of Amsterdam, London and Stockholm was investigated. The highest concentration of cocaine was found in London.

Cannabinoid concentrations were lower in Northern than in Southern Europe.

Air concentrations of cocaine and abuse estimates by wastewater analysis were compared.

Population density and abuse fluctuations influence the air load/abuse estimate correlation.

Cocaine and cannabinoids in the atmosphere of Northern Europe cities, comparison with Southern Europe and wastewater analysis

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Keywords: Illicit drugs; cocaine; atmosphere, PM₁₀; wastewater analysis.

Abstract

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concentrations directly with drug prevalence is not possible using current data, links between concentrations of cocaine and estimates of abuse prevalence assessed by the more routinely used wastewater analysis were also examined. A statistically significant correlation was found between the two sets of data ($R^2 = 0.66$; $p = 0.00131$). Results confirmed that meteorology, population rate and habits of consumption influence the atmospheric concentrations of drugs. If these confounding factors were better controlled for, the techniques described here could become an easy and cost effective tool to index the impact of cocaine abuse in the area; especially where local hot spots need to be identified.

1. Introduction

In recent years, environmental research has gained an increasing interest in new classes of compounds, comprising illicit psychotropic substances (PS). Although the potency of the biological effects of illicit drugs is recognized, very little is known about their potential harmful impact on the environment (Daughton, 2011). Most investigations have focused on developing tools to evaluate the abuse prevalence by measuring levels of drug residuals in wastewater (Zuccato et al., 2005; Thomas et al., 2012; Mastroianni et al., 2013; Ort et al., 2014; Castiglione et al. 2014). Traces of illicit substances have also been found worldwide in surface and drinking waters (Seabra Pereira et al., 2016; van der Aa et al., 2013; Huerta-Fontela et al., 2008) and in sediments and sludges (Álvarez-Ruiz et al., 2015). In this context the ambient atmospheric concentrations have been less well studied despite evidence of cocaine presence in the atmospheric particulate being reported since 1998 (Hannigan et al., 1998). Acute health risk associated with exposure to typical ambient concentrations of illicit drugs has been regarded as negligible (Viana et al., 2010). Nonetheless, the occurrence of illicit drugs in the air merits concern, taking into account that the atmosphere is a key pathway of dispersion both at local and global scale, and the risks posed by chronic exposure to these substances are completely unknown (Mastroianni et al., 2015). This issue is even more important when considering that dedicated investigations have reported that indoor air (houses, offices, primary schools and shops) can be more contaminated by illicit drugs than ambient air (Cecinato et al. 2014, 2016; Bianchi et al., 2014) even where drugs are not consumed. To date little information exists at this regard (McKenzie et al. 2013), but this phenomenon is expected to be accentuated at locations close to drug abuse or manufacture. In fact, cases of positive response to bioassays have been reported both in children and adults even in the absence of direct drug consumption (Kidwell et al. 1997; De Giorgio et al. 2004; Garcia-Bournissen et al 2009; Pichini et al. 2014). In ambient air the highest concentrations of these substances have been reported from spot measurements carried out in Latin America. Cocaine concentrations as high as 17 ng/m^3 were

69 found in Mexico City, and 3.3 ng/m^3 in Santiago De Chile (Cecinato et al. 2016). Cocaine was not
70 found in Algeria, both in Algiers and surrounding areas (Ladji et al. 2009; Moussaoui et al. 2013),
71 while traces of cannabinoids were detected. In Europe, some measurements have been made in
72 Oporto, Portugal, and Pančevo, Serbia, but most have been made in Italy and Spain (Cecinato et al.,
73 2009, 2010, 2012; Postigo et al., 2009; Viana et al., 2010, 2011; Mastroianni et al., 2015). In Italy, a
74 number of localities have been investigated for cocaine and three important cannabinoids, i.e. Δ^9 -
75 tetrahydrocannabinol (THC), cannabinol (CBL) and cannabidiol (CBD) (Balducci et al., 2009). In
76 Spain, only three cities have been investigated, but a wider range of substances were studied,
77 including native species, by-products and metabolites (e.g., amphetamines, heroin, cocaethylene,
78 ecstasy, benzoylecgonine, 6-acetylmorphine). This study reports the first atmospheric
79 measurements of cocaine and cannabinoids carried out in London, Stockholm and Amsterdam.
80 Wide differences in meteorological and social contexts, as well as in the drug abuse prevalence,
81 characterize the northern European cities studied; differences also exist between them and the
82 southern European cities so far investigated. From this perspective, the first aim of this study is to
83 provide new information on the variability of the ambient concentration of illicit drugs which reflect
84 the differences between these cities. The second aim is to investigate the possible associations
85 between the atmospheric concentrations and the abuse rate in the area detected there.
86 The concentration of illicit drugs in the atmosphere is controlled by meteorological dispersion, and
87 little is known about drug suspension and transport from sources to the measurement locations.
88 Using ambient concentration measurements of illicit drugs for consumption estimates is therefore
89 unreliable using the current, limited datasets and significant challenges exist to control for
90 variability in atmospheric dispersion. Nonetheless, studies conducted so far provide evidence that
91 this approach can capture differences among geographical localities, locations or zones within a
92 given area, as well as time variations from a few days to consecutive years (Cecinato et.al., 2014).
93 Therefore, measuring illicit drug concentrations in the air could potentially be applied as a new tool
94 to identify local hot spots, which can be associated with consumption, trafficking and manufacture
95 of substances. Recent studies suggest cocaine may be feasible for this purpose. In fact, cocaine is
96 overall associated to the particulate phase (Cecinato and Balducci 2007) and its determination in the
97 PM accounts for total amount in the air. Although no specific studies have been carried out to assess
98 the stability of illicit drugs in the atmosphere, the relative stability of cocaine seems to be inferred
99 by its seasonal behavior, which looks analogous to that of the PM (Perrino et al. 2001; Hu et al.,
100 2011; Kelly et al., 2016), and the winter/summer concentration ratios for cocaine and $\text{PM}_{2.5}$ were
101 broadly similar. For instance, in Rome, taking in account 11 sites, ratios as high as 2.1 ± 1.2 and 2.5
102 ± 0.9 , respectively, were observed for cocaine and $\text{PM}_{2.5}$. On the contrary cannabinoids (the other

103 extensively investigated class) have been shown to be markedly less stable showing a reduction of
104 concentration (Cecinato et al., 2012, 2014).

105 The determination of cocaine and cannabinoids in the atmosphere of Northern Europe cities
106 allowed us to further investigate links between ambient concentration and the drug addiction
107 phenomenon. Accepting that the current knowledge is not advanced enough to quantify usage rates
108 using ambient samples, these measurements may allow an indexing system of illicit drug prevalence
109 to be developed using the existing sampling infrastructure available in all cities. To investigate this,
110 atmospheric illicit drug concentrations were compared between London, Amsterdam and Rome in
111 March 2013 as well as concentrations measured in Amsterdam and eight Italian cities in 2011. This
112 allowed the influence of meteorology and population habits on the illicit drug concentrations to be
113 examined.

114 The psychotropic compounds nicotine (NIC) and caffeine (CAF) (reported in the text as licit drugs)
115 and polycyclic aromatic hydrocarbons (PAH) were monitored in addition, to provide insights into
116 the characteristics of the sites and eventual peculiarities in the behaviour of illicit drugs (cocaine
117 and cannabinoids). The improvement of the existing illicit drug concentration database, obtained
118 through this study, allowed an examination of the concentrations of atmospheric cocaine over
119 Northern and Southern Europe cities in the light of the drug prevalence in the respective countries.
120 Measurements were also compared to estimates of collective consumption obtained through
121 analysis of drug residuals in wastewater. The effectiveness of this methodology in assessing drug
122 abuse prevalence is ascertained, and the comparison between the outcomes of the two types of study
123 provides important information to verify if the illicit drugs impact over a certain area can be
124 indexed through measurements in the air.

125

126 **2. Experimental**

127 *2.1. Sites and periods of sampling*

128 In Amsterdam, two series of measurements were performed from 9 to 16 March 2011 and from 7 to
129 27 March 2013. Three monitoring locations were investigated in the first campaign: A-BG1, urban
130 background, A-SM1, and A-SM2, all belonging to the Amsterdam Public Health Service (GGD),
131 Dept. of Air Quality Monitoring Network. A-BG1 was located along the perimeter of an important
132 city park, while A-SM1 and A-SM2 were street monitoring sites in the proximities of busy roads;
133 anyway, the three sites lied in residential areas.

134 In 2011, PM_{2.5} and PM₁₀ samples were collected daily at A-BG1, PM_{2.5} at A-SM1 and PM₁₀ at A-
135 SM2; samples were pooled to form composite weekly samples. In 2013, the above mentioned sites
136 were investigated, but the whole period of monitoring was covered only at A-SM2. Two further

137 samples were collected at *A-BG2* on 23-24 March. The *A-BG2* monitoring site was in a very quiet
 138 residential zone free from strong influence of traffic or other pollution sources. Samples were
 139 aggregated into weekday and weekend pools before laboratory analysis to increase the analyte
 140 amount while still allowing behavioural aspects to be examined.
 141 In London, two campaigns were conducted, 7-27 March 2013 and 10-22 July 2014, aimed at
 142 determining the concentration levels of PS in the city, and the differences related to year and season
 143 (spring vs. summer). Daily PM₁₀ samples were collected at two stations belonging to London Air
 144 Quality Network, i.e. *L-BG*, urban background in a quiet residential area and *L-KS* (kerbside) close
 145 to a road frequently congested and hosting education buildings, tourist attractions, shops and
 146 housing in the surrounding area. In both campaigns the samples were aggregated on weekday and
 147 weekend basis before analysis.
 148 In Stockholm, samples were taken at an urban background station in the city centre. The site is
 149 located on top of a building (ca. 20 m above the street) and can be regarded as representative of a
 150 large area of central Stockholm (Gidhagen et al., 2003; Johansson et al., 2009). The measurements
 151 were carried out between September and November, 2014. Daily PM₁₀ and PM_{2.5} samples were
 152 collected and pooled into three groups, corresponding to 18 Sep - 1 Oct, 2-15 Oct and 30 Oct - 12
 153 Nov.
 154 The March 2011 campaign in Amsterdam was simultaneous to that carried out in the framework of
 155 the *Ariadrug* Project in Italy (Cecinato et al., 2012). The cities of Milan, Turin, Verona, Bologna,
 156 Florence, Rome, Naples and Palermo were investigated as representative of large and medium
 157 urban areas with different economic aptitudes, social contexts, and spread all over the Italian
 158 Peninsula. The March 2013 campaigns in Amsterdam and London were contemporary with that
 159 carried out in Rome (7-27 March) within a research activity dealing with pollution of interiors
 160 (Cecinato et al., 2014; Romagnoli et al., 2014). Four stations of ARPA Lazio Regional Network for
 161 Air Pollution Control were monitored in Rome, namely Cipro (CI) and Belloni (BE), residential,
 162 Francia (FR), street monitoring, and Villa Ada (VA), urban background inside the second largest
 163 green park in Rome.
 164 Table 1 reports the sampling dates, size fraction sampled, and type of sites investigated in
 165 Amsterdam, London, Stockholm and Rome, together with data on population and population
 166 density of the cities.
 167
 168 *Table 1.*
 169
 170 *2.2 Sampling and chemical analysis procedures*

171 Airborne particulate was collected daily onto PTFE or pure quartz fibre filters using medium
172 volume samplers (38.3 L/min in Amsterdam and Rome, 16.7 L/min in London and Stockholm)
173 equipped with size selective inlets. After collection, samples were sealed in clean holders, wrapped
174 with aluminium foils and stored at low temperature prior to be analysed. Depending on the site,
175 groups of 2 up to 14 individual particulate samples were assembled and processed as pools.
176 The method used for the analytical determination of licit and illicit drugs is an extension of the
177 reference method EN 15549:2008, 'Air quality – Standard method for the measurement of
178 concentration of benzo[a]pyrene in ambient air'. This aspect is very important when considering
179 that cocaine could be easily determined in the frame of the routine activities imposed by the Air
180 Quality Legislation for the monitoring of benzo(a)pyrene. An extensive description of the method
181 applied is presented elsewhere (Cecinato et al., 2009, 2010). Briefly, the composite samples were
182 spiked with deuterated standards and extracted through sonication using a dichloromethane:acetone
183 mixture (4:1 in volume), reduced close to dryness under ultra-pure nitrogen and transferred onto a
184 neutral alumina chromatographic column. Three fractions were collected by eluting with isooctane,
185 isooctane-dichloromethane (3:2) and dichloromethane:acetone (1:1), in sequence. PAHs were in the
186 second fraction while cocaine, nicotine, caffeine, THC, CBL and CBD were in the third (Cecinato
187 et al., 2010).

188 After solvent evaporation and back dissolution into chloroform, the eluates containing PS were
189 processed through GC-MSD (*Trace GC Ultra* coupled with *Trace DSQ*, both from Thermo Fisher,
190 Rodano, Italy). Glass capillary chromatography was operated in temperature gradient (from 60°C to
191 280 °C) using a programmed-temperature vaporizer for injection (split-less time 1.25 min). A DBX
192 type column (length = 25 m, i.d. = 0.20 mm, film thickness = 0.25 µm, purchased from
193 Superchrom, Milan, Italy) to obtain the necessary separation of compounds was used. Mass
194 spectrometric detection was operated in selected ion monitoring mode (SIM), using three ion
195 current signals for each analyte and (minimum) two ion traces for the respective internal reference
196 substance (Cecinato et al., 2012). The limits of detection (LODs) of cocaine and cannabinoids were
197 of the order of 0.0003 µg/ml. The entire analytical features of the method was investigated by using
198 the standard addition method (SAM) (Gonzales and Herrador 2007) on real samples. For this
199 purpose, portions of a homogeneous substrate of atmospheric particulate were fortified with
200 different amount of analytes (three levels of concentrations plus blank, three replicates each level).
201 The overall accuracy was calculated through the differences observed between the pure drug
202 concentrations determined experimentally in the drug fortified samples and those added to them.
203 The accuracy was quantified as $2.3 \pm 6.1\%$ for cocaine. The precision was calculated by comparing
204 the analyte concentrations detected in the samples and expressed as percent standard deviation; this

205 ranged between 4.7% and 6.9% for cocaine but was higher for cannabinoids. For this class, matrix
206 effects and blanks contamination were observed by using SAM and a corresponding increase of
207 uncertainty was observed (accuracy: 13-18%, precision 15-25%). Taking into account the
208 performances of the analytical method and the necessary blank subtraction for cannabinoids the
209 experimental limit of quantifications (LOQs) were defined. Samples analysed in this study were
210 representative of different volumes of air collected. Considering the weekend samples of London,
211 where $\sim 55 \text{ m}^3$ of air were analysed (the lowest in this study) and the purified extracts were
212 dissolved in 100 μL of solvent for analysis, the limits of quantifications of cocaine and
213 cannabinoids were 0.003 ng/m^3 and 0.01 ng/m^3 , respectively.
214 12 PAH compounds ranging from benz[a]anthracene (molecular mass = 228.2) up to
215 dibenz[a,h]anthracene (molecular mass = 278.3) were characterized. Considering PAHs, caffeine
216 and nicotine, the LOQs never exceeded 0.01 ng/m^3 and the overall accuracy was always better than
217 20%. Concentrations of PM_{10} in Amsterdam, London and Rome were extracted from publicly
218 available online databases (GGD Amsterdam 2016; London Air Quality Network, 2016;
219 ARPALAZIO, 2016). The values of common meteorological variables (mean and maximum daily
220 temperature, relative humidity, mean and maximum wind speed, precipitation occurrence) were also
221 downloaded from free accessible web sites (Weather Underground, 2016) and are reported in Table
222 S1.

224 2.3 Cocaine and cannabis abuse prevalence in the investigated countries

225 According to the latest survey data provided by the European Monitoring Centre for Drugs and
226 Drug Addiction (EMCDDA), in the United Kingdom and in Netherlands, drug abuse is widespread.
227 In 2013 in the United Kingdom, the drugs abuse lifetime prevalences of cannabis and cocaine
228 among adults (number of individuals that have experienced the abuse in the age range 15-64 y)
229 were 29.9% and 9.5% respectively. In Netherland the last lifetime data, referring to 2009, report
230 estimates equal to 25.7% and 5.2%, respectively, for the same substances. By contrast in Sweden
231 the illicit drugs abuse looks less common and the lifetime prevalence recorded for cannabis is
232 14.4%, whereas the last year 15-34y prevalence is in the range 1.1-2%. (EMCDDA, 2015).

233

234 3. Results and discussion

235 3.1. Concentrations of PAHs, licit and illicit drugs in PM_{10} and $\text{PM}_{2.5}$

236 PM_{10} was collected in London, while in Amsterdam and Stockholm the PM size fraction changed
237 with the sampling periods and sites. Previous studies show that cocaine and cannabinoids are found
238 in $\text{PM}_{2.5}$ with percentages never lower than 75% (Cecinato et al., 2010). To ensure a valid

comparison between countries it was first verified that PM₁₀ and PM_{2.5} samples collected simultaneously and at the same site contained similar amounts of PAH and drug substances. Figure 1 illustrates the results for the PM_{2.5} and PM₁₀ collected in Amsterdam at A-BG1, the percentages of individual PAH congeners in PM_{2.5} compared to PM₁₀ were 89% ± 8%, and the percentages of drugs reached 102% ± 3%. A comparison was not made for cannabinoids due to the absence of these compounds in the samples. Cannabinol distribution was checked in Stockholm and its preponderance in PM_{2.5} was confirmed.

246

Figure 1.

248

3.2. Psychotropic substances concentrations

3.2.1. Amsterdam

Due to the lack of preliminary information concerning the atmospheric concentrations of illicit drugs in Northern Europe, daily filters collected during March 2011 in Amsterdam were pooled to weekly samples in order to achieve LOQs for the analytical procedure. Table 2A shows the average values of the target compounds measured over the period. The A-BG1 urban background site was the least polluted for all classes. Considering regulated pollutants, small differences in the PM₁₀ levels were recorded among the sites (average 36±4 µg/m³), by contrast, total PAHs showed larger variations. Total PAHs reached 1.13± 0.06 ng/m³ at A-BG1, whereas they were 80% higher in A-SM1 (2.03 ng/m³) and 50% higher in A-SM2 (1.68 ng/m³). As for the psychotropic substances, caffeine ranged from 0.9 ng/m³ at A-BG1 to 1.2 ng/m³ at A-SM2. More marked differences among sites were observed for nicotine and cocaine. In particular, 0.03 ng/m³ of cocaine and 6.7 ± 0.2 ng/m³ of nicotine were valued at A-BG1 when at A-SM2 these compounds were over 4 times more (0.14 and 30.7 ng/m³ respectively). Intermediate concentrations were measured at A-SM1. Cannabinoid concentrations were all below the quantification limit (< 0.01 ng/m³ for each THC, CBL and CBD).

265

Table 2.

267

The concentrations measured in the 2013 campaign are reported in Table 2B. March was the coldest month of the 2013 in Amsterdam (see Table S1), with an average daily temperature of 0°C. This period was also characterized by the presence of rain and snow that could contribute to the decrease of atmospheric PM and nicotine recorded in 2013 compared with 2011. Meanwhile the PAH concentration increased, possibly due to the increased use of domestic heating (Alam et al., 2015).

273 Atmospheric cocaine variations were not consistent across the sites; a slight increase was observed
274 at A-BG1 and A-SM1 and a drop at A-SM2. The maximum value of cocaine concentration detected
275 in 2013 (0.12 ng/m^3) was recorded at A-SM2 (as it was in 2011) together with the peaks of nicotine
276 (20.6 ng/m^3) and caffeine (9.1 ng/m^3) on 7-8 March. It is worth noting that A-SM2 site was close to
277 a bus stop, and these peaks were probably related to variations in very local sources. Unlike 2011,
278 cannabinal was quantifiable in almost all sites, except at A-BG2; this latter, confirming its feature
279 of urban background, was the less affected by both PS and PAHs.

280

281 3.2.2. London

282 Table 3A/B reports the mean PS, PAH and PM₁₀ concentrations recorded at L-BG and L-KS during
283 winter and summer seasons. Taking into account both seasons, the concentrations of PM, PAHs and
284 nicotine were higher at L-KS. In particular, in March 2013 the maximum differences between sites
285 were observed for nicotine. In this period at L-KS nicotine reached $27.5 \pm 25.5 \text{ ng/m}^3$, almost twice
286 the level detected at L-BG ($14.3 \pm 12.1 \text{ ng/m}^3$), even though the variability was large. Less
287 important increases were observed for PAHs and PM₁₀. In July 2014 the biggest differences were
288 found for PAHs ($1.03 \pm 0.24 \text{ ng/m}^3$ at L-KS compared to 0.67 ± 0.41 at L-BG), while nicotine and
289 PM at L-KS exceeded 35- 40% of that measured at L-BG. The same behaviour was observed for
290 caffeine that showed the highest mean concentrations at L-KS. This finding confirms that L-KS
291 was, unsurprisingly, more influenced by traffic than L-BG, while the concentration of caffeine and
292 nicotine could depend on peoples' activity in the area, due to its touristic and commercial
293 attractions. By contrast, the maximum amounts of atmospheric cocaine were recorded at L-BG,
294 with average values over the whole campaigns 3-4 times higher than those of L-KS.
295 The adverse weather conditions that affected the Northern Europe in March 2013 hit also London,
296 with low average temperatures, rain and snow events which were expected to decrease the
297 contaminants in the air. In this context, in London the highest value of cocaine concentration was
298 detected again on 7-8 March (0.33 ng/m^3 at L-BG), and average cocaine concentration over the
299 period reached $0.23 \pm 0.11 \text{ ng/m}^3$ at L-BG and $0.05 \pm 0.03 \text{ ng/m}^3$ at L-KS. In July, cocaine ranged
300 between $0.18 \pm 0.05 \text{ ng/m}^3$ at L-BG and $0.06 \pm 0.01 \text{ ng/m}^3$ at L-KS. Rainy weather accompanied the
301 July 2014 campaign, nonetheless almost all targeted compounds were, on average, more in March
302 than in July. For cocaine, this finding confirms the results of the *Ariadrugs* project where
303 measurements of illicit drugs were carried out weekly over one year. At all the eight cities
304 investigated the lowest concentrations occurred in the summer period (June to August). This trend
305 is not directly connected to any emission reduction, but relates to the increase of dispersion and of
306 boundary layer height during the summer months. The only significant exception to this behaviour

307 is represented by cannabinal, the sole cannabinoid detected in London. This compound occurred at
308 low but quantifiable concentrations in both seasons and sites (see Table 3). Comparing the sites,
309 cannabinal at L-BG was of the same order of magnitude of that measured at L-KS. Comparing the
310 seasons, the cannabinal behaviour in London was peculiar, because the highest concentration were
311 recorded in July. According to the *Ariadrugs* Project results, in Italy cannabinoids dropped during
312 the summer due to degradation effects induced by solar radiation (Carbone et al., 2010; Cecinato et
313 al., 2012, 2016). The summer increase of atmospheric cannabinal measured in London probably
314 depended on the increase or proximity of drug use.

315

316 Table 3.

317

318

319 3.2.3 Stockholm

320 In Stockholm, due to the low concentrations expected for all chemicals, airborne particulates (PM_{2.5}
321 and PM₁₀) were gathered into three composite samples, corresponding to 18 Sep - 1 Oct, 2-15 Oct
322 and 30 Oct - 12 Nov, 2014. The results are summarized in Table 4. Cocaine occurred only at
323 detectable but not quantifiable levels. Cannabinal did not exceed 0.02 ng/m³; meanwhile, the other
324 contaminants occurred at lesser extents than in other cities.

325

326 Table 4.

327

328

329 3.3. Weekends vs. weekdays atmospheric concentrations

330 Various attempts have been made to evaluate differences between weekdays and weekend
331 concentrations of PSs in the atmosphere and to verify if they depended on the weekly trends in drug
332 abuse rate, which are expected to be higher at the weekend. No clear difference was observed,
333 probably due to the impact of atmospheric dispersion, however, the input of special events was
334 detectable. For instance, an increase in cocaine concentration was observed in Rome during the
335 celebration of the White Night Holidays in 2007, and a similar increase in cannabinoid
336 concentrations was found in Barcelona during a massive street protest (Cecinato et al., 2009; Viana
337 et al., 2010; Mastroianni et al., 2015).

338

339

340 Figure 2.

341

342 Figure 2 reports the weekend and weekday average concentrations of the investigated compounds
343 (together with the associated variability over the period), measured in London during the sampling
344 campaign carried out in March and July at L-BG (A and B) and L-KS (C and D).

345 With regard to cocaine, two distinct behaviours were observed. In March, the average concentration
346 of cocaine on weekdays exceeded those measured on weekends both at L-BG and L-KS (though the
347 differences were not statistically significant); the reverse behaviour was observed in July. To
348 illustrate the influence of meteorology and local emission rate on the illegal drug ambient
349 concentrations, the weekend vs. weekdays concentration ratio of cocaine was compared with those
350 of PM and other pollutants (see Table 5).

351

352 Table 5.

353

354 During March 2013, all substances, except PAHs and caffeine at L-BG, decreased on weekends; the
355 percent decrease of cocaine and PM were very similar at both sites, suggesting that atmospheric
356 dispersion was an important driver of this trend. Thus, the increase of cocaine concentration during
357 the weekdays cannot be associated to the increase of consumption. The reverse was observed in
358 July at L-BG site. There, the cocaine and cannabinal concentrations were higher on weekends,
359 despite the concurrent decrease of PM and other pollutants. In this case, the peculiar behaviour of
360 cocaine could depend on the emission rate in the area, probably associated to consumption, rather
361 than to an increase of population attending at the area. No marked differences were measured at L-
362 KS in July between weekend and weekdays and between cocaine and other pollutants patterns.
363 In Amsterdam this approach was applicable only with regard to the March 2013 campaign. The
364 particularly adverse meteorological conditions and the consequent strong influence of atmospheric
365 mixing on the pollutant concentrations, combined with the shortness of data series available,
366 hindered any clear observation of possible PS weekly trends. In fact, a widespread reduction in
367 pollutant concentrations was recorded during weekends. The most important decrease was
368 measured for caffeine at A-SM2 (weekend vs weekdays ratio equal to 0.1). This was possibly due to
369 the different habits and number of people at the bus stop close to monitoring site.

370

371 3.4. *Comparison of the contemporary monitoring campaigns*

372

373 A monitoring campaign was carried out in Rome from 7 to 27 March 2013, to compare the PS
374 behaviour in the Northern and Southern Europe cities. Also in Rome the measurement period was

rainy and cold, which hindered the accumulation of atmospheric pollutants. Figure 3 illustrates the cocaine concentrations, site by site, in each city; the boxplots reported in the Supplementary Material (Figure S1) illustrate the distributions and principal statistical parameters of all concentrations detected in the cities (the A-BG2 sample in Amsterdam was not considered).

Figure 3.

Meteorology seems to regulate the general trend of the illicit drug concentrations, although this can be overwhelmed by strong local sources. Analogous conclusions were drawn by Mastroianni et al. (2015) studying 12 sites simultaneously monitored in Barcelona. Comparing the average concentrations measured over the period in London, Amsterdam and Rome, London was the most contaminated city with regards to cocaine, in agreement with the highest levels of abuse associated to the UK (EMCDDA, 2015).

The average cocaine concentration calculated over the whole period at both London sites was equal to $0.15 \pm 0.11 \text{ ng/m}^3$. Slightly higher levels of consumptions are estimated for the Netherlands compared to Italy, however in Amsterdam the mean concentration of cocaine was lower than in Rome, $0.06 \pm 0.03 \text{ ng/m}^3$ vs. $0.09 \pm 0.03 \text{ ng/m}^3$. This finding probably depended on the higher population in Rome and the small scale house density at the sites investigated (two or three times higher than the average all over the city for Belloni, Cipro and Francia). This hypothesis is confirmed by the fact that, although the Spanish prevalence of consumption is comparable to that of UK, the average amount of cocaine detected by Mastroianni in the densely populated Barcelona was equal to 0.27 ng/m^3 . Barcelona population and population density reach 1,600,000 units and $15,700 \text{ inhabitants/km}^2$, respectively. Another opportunity to compare contemporary data of illicit atmospheric drugs in Northern and Southern Europe was offered by data collected in Amsterdam and eight Italian cities in March 2011. Table 6 reports the cocaine and cannabinoids levels detected in Italy and the features of the sites. Mean cocaine concentration in Amsterdam during 2011 reached $0.07 \pm 0.03 \text{ ng/m}^3$ and was similar to amounts detected at the urban background site of Milan (Pascal station, located in a public garden) and at the traffic site of Florence, lying in a densely populated city district. Concerning cannabinoids, in Italy only cannabinal was detected in Turin and Palermo, whereas in the other cities most of the investigated cannabinoids occurred at levels above LOQ. Rome showed the highest level of the cannabis active principle THC. Contemporarily cannabinoids were not detected in Amsterdam and, as reported in the text, their concentrations in Northern Europe were in general lower than in Italy even though the consumption

408 is more widespread there. Our hypothesis is that cannabinoids were consumed more indoors in
409 Northern Europe, or that air ventilation of buildings favoured in Italy resulted in greater emissions.

410

411 Table 6.

412

413

414 *3.5. Comparison of atmospheric cocaine concentrations with wastewater analysis*

415 Estimates of consumption rates are principally acquired using statistics of crimes or phenomenon
416 related to drugs abuse and population surveys. Relevant uncertainty exists on data produced on this
417 basis due to the difficulties in the acquisition of correct information, as a consequence results
418 produced by different areas are scarcely comparable. However, these tools are very expensive, time
419 consuming and unsuitable for the rapid identification of drug prevalence variations. Illicit
420 substances and their metabolites are excreted by consumers in known percentages, and the
421 characterization of residues in wastewater is currently accepted as a new suitable tool to assess the
422 drug consumption, appearing as a direct and relatively cost effective “measurement” of drug abuse
423 (EMCDDA 2016a).

424 Though the per capita drug consumption is not deliverable from concentrations in air, the cocaine
425 method used here is a simple extension of procedures adopted for measuring particulate bound
426 PAHs at the regional Air Quality Monitoring networks, and a possible cost-effective tool to index
427 the impact of phenomenon on the territory. In fact cocaine is stable in the atmosphere, and its
428 atmospheric concentration looks less affected than cannabinoids by consumption habits. In this
429 perspective, the comparison with results of measurement performed in wastewater (the sole
430 quantitative method to obtain per capita drug consumption estimates) is crucial to verify whether
431 this is achievable. The present study, together with previous investigations, allowed us to combine
432 the data sets of atmospheric concentrations for the first time at a European level, to correlate
433 atmospheric concentrations of cocaine with the abuse estimates obtained by wastewater analysis for
434 the same year (See Figure 4). When available (2012 and 2013), data were taken from the EMCDDA
435 database (EMCDDA 2016b), otherwise they were collected from literature (Thomas et al., 2011;
436 Zuccato and Castiglioni, 2012; DPA, 2012). Cocaine abuse estimates for Stockholm in 2014 were
437 not available, therefore the wastewater data refer to 2013 (Ort et al., 2014).

438

439 Figure 4.

440

441 Taking in account all Italian cities, London, Stockholm and Amsterdam in 2013, a good level of
442 correlation was found between the atmospheric concentration of cocaine and the amount of the
443 residues in wastewater ($R^2 = 0.66$; $p = 0.00131$). The R^2 value was improved (0.88 ; $p = 1.9828 \times 10^{-5}$)
444 by omitting Turin, where the atmospheric monthly concentration was generated by analysing five
445 daily samples, which reduced the sample representativeness. Poor correlation ($R^2 = 0.22$) is obtained
446 by inserting data from Barcelona and Amsterdam 2011. The large differences in the results of
447 wastewater analysis recorded for Amsterdam in 2011 and 2013 do not correspond to the range of
448 variation observed for cocaine in the atmosphere. On the other hand the large amount of cocaine in
449 the air of Barcelona does not fit with daily consumption estimate produced by wastewater analysis
450 for the same year, perhaps due to the high population density in the city.
451 These findings highlight further limitations of atmospheric measurements to assess the drugs
452 prevalence in the community (in addition to meteorology), that a at much minor extent also belong
453 to the wastewater analysis tool. These are principally due to the large fluctuations in abuse over
454 time, which requires consistent time coverage of the data collected to be mediated, and to the need
455 of an additional tool able to account for local population. (van Nuijs et al., 2011).
456 The population data is required to normalize the absolute values of illicit substances affecting the
457 atmosphere and wastewater. In this regard, the number of residents is a useful but incomplete
458 parameter because population can widely exceed the resident population due to the daily influx of
459 commuters and visitors, especially in the big cities. Therefore, attempts to define normalization
460 factors are important for both approaches (Cecinato et al., 2013; Bruno et al., 2014).

461

462 **Conclusions**

463 This study reports the first European data series of ambient psychotropic substances with the
464 respective geographical and temporal variations, and compares them with the outcomes of
465 wastewater analysis method for assessing population drug consumption. Ambient measurements in
466 Amsterdam, Stockholm and London confirmed the presence of both licit (nicotine, caffeine) and
467 illicit drugs (cocaine, cannabinoids) in the atmosphere and the corresponding concentrations rates
468 were compared with measurements performed in Italian cities. The concentration of PSs were found
469 to vary with both city location and season, which provided the opportunity to investigate
470 geographical and temporal variations in some detail. Among cannabinoids, only cannabinal was
471 detected in the Northern Europe cities. In Amsterdam and London, the cannabis prevalence is
472 reported as higher than in Italy, whilst concentration in air was not. This is likely the result of
473 consumer behavior. Further studies are necessary to clarify this issue but the rate of indoor drug
474 consumption, or the average amount per dose could play a key role. The highest concentrations of

475 cocaine were recorded in London, where the background site investigated was unexpectedly more
476 affected by cocaine than the city centre location. In Stockholm cocaine was not detected in
477 quantifiable amounts ($>3 \text{ pg/m}^3$). The average concentration detected in March 2011 in Amsterdam
478 was similar to that contemporarily detected in a densely populated area in Florence and in a
479 background site in Milan. A measurement campaign carried out in London, Amsterdam and Rome
480 in March 2013 showed that meteorology was the principal driver of atmospheric cocaine
481 concentrations, but that the inputs of local sources were very relevant. A clear observation of
482 weekly consumption modulation through ambient concentration of illicit drugs was masked by the
483 effect of variations in atmospheric dispersion. This phenomenon could not be controlled for in these
484 short studies, however an attempt was made through comparing the drug concentrations with those
485 of other pollutants. This allowed us to detect a clear weekend-weekday cocaine modulation in July,
486 at one site in London. Further studies are necessary to better understand how meteorology and
487 consumption behavior relate to ambient concentrations of PSs. Nevertheless measuring atmospheric
488 drug concentrations provides a feasible method to capture the differences in drugs consumption
489 between areas and over time. The suitability of this approach to become a tool to index the impact
490 of drug abuse (e.g. cocaine) was investigated by comparing the results of this study to those of the
491 wastewater analysis, routinely used to estimate the consumption prevalence. A good correlation
492 was found when the temporal variability of the consumption and the population were accounted for.
493 Atmospheric measurements of PSs could therefore offer a useful complementary approach to
494 wastewater analysis of PSs, especially where local hot spots need to be identified.

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629

630 **Table headings**

631

632 Table 1. Population rate and density of the cities investigated. PM fraction sampled, sampling dates
633 and typology of the monitoring sites in each city.

634 Symbols adopted for sites: BG = urban background; KS= kerbside; SM= street monitoring.

635

636 Table 2. Average concentrations of nicotine (NIC), caffeine (CAF), cocaine (COC), polycyclic
637 aromatic hydrocarbons (PAH), PM₁₀ and cannabinal (CBL) in the atmosphere of Amsterdam. A) 9-
638 16 March 2011; B) 7-27 March 2013. na: not available.

639 (*) Sampling limited to 23– 24 March.

640

641 Table 3. Average concentrations of nicotine, caffeine, cocaine, cannabinal, polycyclic aromatic
642 hydrocarbons and PM₁₀ in the atmosphere of London A) 7-27 March 2013; B) 10-22 July 2014.

643 For compound symbols see Table 2

644

645 Table 4. Average concentrations of nicotine, caffeine, cocaine, cannabinal and polycyclic aromatic
646 hydrocarbons in the atmosphere of Stockholm. For compound symbols see Table 2

647

648 Table 5. Ratios of weekend vs. weekdays pollutants concentrations recorded in London in March
649 2013 and July 2014 and in Amsterdam in March 2013.

650

651 Table 6. Concentrations of cocaine (COC), cannabinal (CBL), Δ^9 -tetrahydrocannabinal (THC) and
652 cannabidiol (CBL) detected in 8 Italian cities in March 2011. Population, population density and
653 sites typology. TR= traffic site, BG= urban background.

654

655 Table S1. Mean values of average (T_{ave}) and maximum (T_{max}) daily temperature, relative humidity
656 (RH), barometric pressure (P), precipitation days (%), maximum (w_{max}) and minimum (w_{min}) daily
657 wind speed, and prevailing wind direction (w_{dir}) in London, Amsterdam and Rome. 7-27 March,
658 2013.

659

660 **Figure captions**

661

662 Figure 1. PM_{2.5}/PM₁₀ concentration ratio of polycyclic aromatic hydrocarbons and psychotropic
663 substances. Amsterdam, A-BG1 station, 9-16 March 2011.

664 Symbols: BaA = benz[a]anthracene; BbF = benzo[b]fluoranthene; BjF = benzo[j]fluoranthene; BkF
665 = benzo[k]fluoranthene; BaP = benzo[a]pyrene; IP = indeno[1,2,3-cd]pyrene; DBA = dibenz[a,h]
666 anthracene; BPE = benzo[ghi]perylene; NIC = nicotine; CAF = caffeine; COC = cocaine.

667

668 Figure 2. Weekends and weekdays average concentrations valuated in March and July at L-BG (A
669 and B) and L-KS (C and D) and associated variability of the concentrations over the periods. PM₁₀
670 are given in $\mu\text{g}/\text{m}^3$ units, all other chemicals in ng/m^3 .

671 Symbols: NIC = nicotine; CAF = caffeine; COC = cocaine; CBL = cannabinol.

672

673 Figure 3. Cocaine concentrations detected in London, Amsterdam and Rome. Sampling period 7-27
674 March 2013.

675

676 Figure 4. Average aerial concentration of cocaine in European cities and estimates of the drugs
677 abuse produced by wastewater analysis in the same year.

678

679 Figure S1. Box plots reporting values of cocaine concentrations recorded in London, Amsterdam
680 and Rome in March 2013. Box boundaries represents 25 and 75 percentiles, the average is indicated
681 with the dotted line, median with continuous line. Whiskers represent minimum and maximum.

Cocaine and cannabinoids in the atmosphere of Northern Europe cities, comparison with Southern Europe and wastewater analysis

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Keywords: Illicit drugs; cocaine; atmosphere, PM₁₀; wastewater analysis.

Abstract

This study reports the first investigation of atmospheric illicit drug concentrations in Northern Europe using measurements of cocaine and cannabinoids in Amsterdam, London and Stockholm. Further, these measurements were compared to those made in Rome to explore the geographical and inter-city variability. Co-located measurements of atmospheric particulate mass and PAHs were used to help describe and interpret the illicit drug measurements with respect to atmospheric dispersion. Cocaine concentrations ranged from 0.03 to 0.14 ng/m³ in Amsterdam, from 0.02 to 0.33 ng/m³ in London and were below quantification limit (3 pg/m³) in Stockholm. Cannabinol was the only cannabinoid molecule detected in the three cities. During this campaign, London reported the highest concentrations of cocaine and meaningful differences were detected between the urban background and city centre London sites. Mean cocaine concentrations measured in Amsterdam during March 2011 were also compared with those measured simultaneously in eight Italian cities. The cocaine concentration in Amsterdam was comparable to that measured at an urban background in Milan and at a densely populated site in Florence. Although correlating atmospheric

concentrations directly with drug prevalence is not possible using current data, links between concentrations of cocaine and estimates of abuse prevalence assessed by the more routinely used wastewater analysis were also examined. A statistically significant correlation was found between the two sets of data ($R^2 = 0.66$; $p = 0.00131$). Results confirmed that meteorology, population rate and habits of consumption influence the atmospheric concentrations of drugs. If these confounding factors were better controlled for, the techniques described here could become an easy and cost effective tool to index the impact of cocaine abuse in the area; especially where local hot spots need to be identified.

1. Introduction

In recent years, environmental research has gained an increasing interest in new classes of compounds, comprising illicit psychotropic substances (PS). Although the potency of the biological effects of illicit drugs is recognized, very little is known about their potential harmful impact on the environment (Daughton, 2011). Most investigations have focused on developing tools to evaluate the abuse prevalence by measuring levels of drug residuals in wastewater (Zuccato et al., 2005; Thomas et al., 2012; Mastroianni et al., 2013; Ort et al., 2014; Castiglione et al. 2014). Traces of illicit substances have also been found worldwide in surface and drinking waters (Seabra Pereira et al., 2016; van der Aa et al., 2013; Huerta-Fontela et al., 2008) and in sediments and sludges (Álvarez-Ruiz et al., 2015). In this context the ambient atmospheric concentrations have been less well studied despite evidence of cocaine presence in the atmospheric particulate being reported since 1998 (Hannigan et al., 1998). Acute health risk associated with exposure to typical ambient concentrations of illicit drugs has been regarded as negligible (Viana et al., 2010). Nonetheless, the occurrence of illicit drugs in the air merits concern, taking into account that the atmosphere is a key pathway of dispersion both at local and global scale, and the risks posed by chronic exposure to these substances are completely unknown (Mastroianni et al., 2015). This issue is even more important when considering that dedicated investigations have reported that indoor air (houses, offices, primary schools and shops) can be more contaminated by illicit drugs than ambient air (Cecinato et al. 2014, 2016; Bianchi et al., 2014) even where drugs are not consumed. To date little information exists at this regard (McKenzie et al. 2013), but this phenomenon is expected to be accentuated at locations close to drug abuse or manufacture. In fact, cases of positive response to bioassays have been reported both in children and adults even in the absence of direct drug consumption (Kidwell et al. 1997; De Giorgio et al. 2004; Garcia-Bournissen et al 2009; Pichini et al. 2014). In ambient air the highest concentrations of these substances have been reported from spot measurements carried out in Latin America. Cocaine concentrations as high as 17 ng/m^3 were

69 found in Mexico City, and 3.3 ng/m^3 in Santiago De Chile (Cecinato et al. 2016). Cocaine was not
 70 found in Algeria, both in Algiers and surrounding areas (Ladji et al. 2009; Moussaoui et al. 2013),
 71 while traces of cannabinoids were detected. In Europe, some measurements have been made in
 72 Oporto, Portugal, and Pančevo, Serbia, but most have been made in Italy and Spain (Cecinato et al.,
 73 2009, 2010, 2012; Postigo et al., 2009; Viana et al., 2010, 2011; Mastroianni et al., 2015). In Italy, a
 74 number of localities have been investigated for cocaine and three important cannabinoids, i.e. Δ^9 -
 75 tetrahydrocannabinol (THC), cannabinol (CBL) and cannabidiol (CBD) (Balducci et al., 2009). In
 76 Spain, only three cities have been investigated, but a wider range of substances were studied,
 77 including native species, by-products and metabolites (e.g., amphetamines, heroin, cocaethylene,
 78 ecstasy, benzoylecgonine, 6-acetylmorphine). This study reports the first atmospheric
 79 measurements of cocaine and cannabinoids carried out in London, Stockholm and Amsterdam.
 80 Wide differences in meteorological and social contexts, as well as in the drug abuse prevalence,
 81 characterize the northern European cities studied; differences also exist between them and the
 82 southern European cities so far investigated. From this perspective, the first aim of this study is to
 83 provide new information on the variability of the ambient concentration of illicit drugs which reflect
 84 the differences between these cities. The second aim is to investigate the possible associations
 85 between the atmospheric concentrations and the abuse rate in the area detected there.
 86 The concentration of illicit drugs in the atmosphere is controlled by meteorological dispersion, and
 87 little is known about drug suspension and transport from sources to the measurement locations.
 88 Using ambient concentration measurements of illicit drugs for consumption estimates is therefore
 89 unreliable using the current, limited datasets and significant challenges exist to control for
 90 variability in atmospheric dispersion. Nonetheless, studies conducted so far provide evidence that
 91 this approach can capture differences among geographical localities, locations or zones within a
 92 given area, as well as time variations from a few days to consecutive years (Cecinato et.al., 2014).
 93 Therefore, measuring illicit drug concentrations in the air could potentially be applied as a new tool
 94 to identify local hot spots, which can be associated with consumption, trafficking and manufacture
 95 of substances. Recent studies suggest cocaine may be feasible for this purpose. In fact, cocaine is
 96 overall associated to the particulate phase (Cecinato and Balducci 2007) and its determination in the
 97 PM accounts for total amount in the air. Although no specific studies have been carried out to assess
 98 the stability of illicit drugs in the atmosphere, the relative stability of cocaine seems to be inferred
 99 by its seasonal behavior, which looks analogous to that of the PM (Perrino et al. 2001; Hu et al.,
 100 2011; Kelly et al., 2016), and the winter/summer concentration ratios for cocaine and $\text{PM}_{2.5}$ were
 101 broadly similar. For instance, in Rome, taking in account 11 sites, ratios as high as 2.1 ± 1.2 and 2.5
 102 ± 0.9 , respectively, were observed for cocaine and $\text{PM}_{2.5}$. On the contrary cannabinoids (the other

103 extensively investigated class) have been shown to be markedly less stable showing a reduction of
104 concentration (Cecinato et al., 2012, 2014).

105 The determination of cocaine and cannabinoids in the atmosphere of Northern Europe cities
106 allowed us to further investigate links between ambient concentration and the drug addiction
107 phenomenon. Accepting that the current knowledge is not advanced enough to quantify usage rates
108 using ambient samples, these measurements may allow an indexing system of illicit drug prevalence
109 to be developed using the existing sampling infrastructure available in all cities. To investigate this,
110 atmospheric illicit drug concentrations were compared between London, Amsterdam and Rome in
111 March 2013 as well as concentrations measured in Amsterdam and eight Italian cities in 2011. This
112 allowed the influence of meteorology and population habits on the illicit drug concentrations to be
113 examined.

114 The psychotropic compounds nicotine (NIC) and caffeine (CAF) (reported in the text as licit drugs)
115 and polycyclic aromatic hydrocarbons (PAH) were monitored in addition, to provide insights into
116 the characteristics of the sites and eventual peculiarities in the behaviour of illicit drugs (cocaine
117 and cannabinoids). The improvement of the existing illicit drug concentration database, obtained
118 through this study, allowed an examination of the concentrations of atmospheric cocaine over
119 Northern and Southern Europe cities in the light of the drug prevalence in the respective countries.
120 Measurements were also compared to estimates of collective consumption obtained through
121 analysis of drug residuals in wastewater. The effectiveness of this methodology in assessing drug
122 abuse prevalence is ascertained, and the comparison between the outcomes of the two types of study
123 provides important information to verify if the illicit drugs impact over a certain area can be
124 indexed through measurements in the air.

125

126 **2. Experimental**

127 *2.1. Sites and periods of sampling*

128 In Amsterdam, two series of measurements were performed from 9 to 16 March 2011 and from 7 to
129 27 March 2013. Three monitoring locations were investigated in the first campaign: A-BG1, urban
130 background, A-SM1, and A-SM2, all belonging to the Amsterdam Public Health Service (GGD),
131 Dept. of Air Quality Monitoring Network. A-BG1 was located along the perimeter of an important
132 city park, while A-SM1 and A-SM2 were street monitoring sites in the proximities of busy roads;
133 anyway, the three sites lied in residential areas.

134 In 2011, PM_{2.5} and PM₁₀ samples were collected daily at A-BG1, PM_{2.5} at A-SM1 and PM₁₀ at A-
135 SM2; samples were pooled to form composite weekly samples. In 2013, the above mentioned sites
136 were investigated, but the whole period of monitoring was covered only at A-SM2. Two further

137 samples were collected at *A-BG2* on 23-24 March. The *A-BG2* monitoring site was in a very quiet
 138 residential zone free from strong influence of traffic or other pollution sources. Samples were
 139 aggregated into weekday and weekend pools before laboratory analysis to increase the analyte
 140 amount while still allowing behavioural aspects to be examined.
 141 In London, two campaigns were conducted, 7-27 March 2013 and 10-22 July 2014, aimed at
 142 determining the concentration levels of PS in the city, and the differences related to year and season
 143 (spring vs. summer). Daily PM₁₀ samples were collected at two stations belonging to London Air
 144 Quality Network, i.e. *L-BG*, urban background in a quiet residential area and *L-KS* (kerbside) close
 145 to a road frequently congested and hosting education buildings, tourist attractions, shops and
 146 housing in the surrounding area. In both campaigns the samples were aggregated on weekday and
 147 weekend basis before analysis.
 148 In Stockholm, samples were taken at an urban background station in the city centre. The site is
 149 located on top of a building (ca. 20 m above the street) and can be regarded as representative of a
 150 large area of central Stockholm (Gidhagen et al., 2003; Johansson et al., 2009). The measurements
 151 were carried out between September and November, 2014. Daily PM₁₀ and PM_{2.5} samples were
 152 collected and pooled into three groups, corresponding to 18 Sep - 1 Oct, 2-15 Oct and 30 Oct - 12
 153 Nov.
 154 The March 2011 campaign in Amsterdam was simultaneous to that carried out in the framework of
 155 the *Ariadrug* Project in Italy (Cecinato et al., 2012). The cities of Milan, Turin, Verona, Bologna,
 156 Florence, Rome, Naples and Palermo were investigated as representative of large and medium
 157 urban areas with different economic aptitudes, social contexts, and spread all over the Italian
 158 Peninsula. The March 2013 campaigns in Amsterdam and London were contemporary with that
 159 carried out in Rome (7-27 March) within a research activity dealing with pollution of interiors
 160 (Cecinato et al., 2014; Romagnoli et al., 2014). Four stations of ARPA Lazio Regional Network for
 161 Air Pollution Control were monitored in Rome, namely Cipro (CI) and Belloni (BE), residential,
 162 Francia (FR), street monitoring, and Villa Ada (VA), urban background inside the second largest
 163 green park in Rome.
 164 Table 1 reports the sampling dates, size fraction sampled, and type of sites investigated in
 165 Amsterdam, London, Stockholm and Rome, together with data on population and population
 166 density of the cities.
 167
 168 *Table 1.*
 169
 170 *2.2 Sampling and chemical analysis procedures*

171 Airborne particulate was collected daily onto PTFE or pure quartz fibre filters using medium
172 volume samplers (38.3 L/min in Amsterdam and Rome, 16.7 L/min in London and Stockholm)
173 equipped with size selective inlets. After collection, samples were sealed in clean holders, wrapped
174 with aluminium foils and stored at low temperature prior to be analysed. Depending on the site,
175 groups of 2 up to 14 individual particulate samples were assembled and processed as pools.
176 The method used for the analytical determination of licit and illicit drugs is an extension of the
177 reference method EN 15549:2008, 'Air quality – Standard method for the measurement of
178 concentration of benzo[a]pyrene in ambient air'. This aspect is very important when considering
179 that cocaine could be easily determined in the frame of the routine activities imposed by the Air
180 Quality Legislation for the monitoring of benzo(a)pyrene. An extensive description of the method
181 applied is presented elsewhere (Cecinato et al., 2009, 2010). Briefly, the composite samples were
182 spiked with deuterated standards and extracted through sonication using a dichloromethane:acetone
183 mixture (4:1 in volume), reduced close to dryness under ultra-pure nitrogen and transferred onto a
184 neutral alumina chromatographic column. Three fractions were collected by eluting with isooctane,
185 isooctane-dichloromethane (3:2) and dichloromethane:acetone (1:1), in sequence. PAHs were in the
186 second fraction while cocaine, nicotine, caffeine, THC, CBL and CBD were in the third (Cecinato
187 et al., 2010).

188 After solvent evaporation and back dissolution into chloroform, the eluates containing PS were
189 processed through GC-MSD (*Trace GC Ultra* coupled with *Trace DSQ*, both from Thermo Fisher,
190 Rodano, Italy). Glass capillary chromatography was operated in temperature gradient (from 60°C to
191 280 °C) using a programmed-temperature vaporizer for injection (split-less time 1.25 min). A DBX
192 type column (length = 25 m, i.d. = 0.20 mm, film thickness = 0.25 µm, purchased from
193 Superchrom, Milan, Italy) to obtain the necessary separation of compounds was used. Mass
194 spectrometric detection was operated in selected ion monitoring mode (SIM), using three ion
195 current signals for each analyte and (minimum) two ion traces for the respective internal reference
196 substance (Cecinato et al., 2012). The limits of detection (LODs) of cocaine and cannabinoids were
197 of the order of 0.0003 µg/ml. The entire analytical features of the method was investigated by using
198 the standard addition method (SAM) (Gonzales and Herrador 2007) on real samples. For this
199 purpose, portions of a homogeneous substrate of atmospheric particulate were fortified with
200 different amount of analytes (three levels of concentrations plus blank, three replicates each level).
201 The overall accuracy was calculated through the differences observed between the pure drug
202 concentrations determined experimentally in the drug fortified samples and those added to them.
203 The accuracy was quantified as 2.3±6.1% for cocaine. The precision was calculated by comparing
204 the analyte concentrations detected in the samples and expressed as percent standard deviation; this

205 ranged between 4.7% and 6.9% for cocaine but was higher for cannabinoids. For this class, matrix
 206 effects and blanks contamination were observed by using SAM and a corresponding increase of
 207 uncertainty was observed (accuracy: 13-18%, precision 15-25%). Taking into account the
 208 performances of the analytical method and the necessary blank subtraction for cannabinoids the
 209 experimental limit of quantifications (LOQs) were defined. Samples analysed in this study were
 210 representative of different volumes of air collected. Considering the weekend samples of London,
 211 where $\sim 55 \text{ m}^3$ of air were analysed (the lowest in this study) and the purified extracts were
 212 dissolved in 100 μL of solvent for analysis, the limits of quantifications of cocaine and
 213 cannabinoids were 0.003 ng/m^3 and 0.01 ng/m^3 , respectively.
 214 12 PAH compounds ranging from benz[a]anthracene (molecular mass = 228.2) up to
 215 dibenz[a,h]anthracene (molecular mass = 278.3) were characterized. Considering PAHs, caffeine
 216 and nicotine, the LOQs never exceeded 0.01 ng/m^3 and the overall accuracy was always better than
 217 20%. Concentrations of PM_{10} in Amsterdam, London and Rome were extracted from publicly
 218 available online databases (GGD Amsterdam 2016; London Air Quality Network, 2016;
 219 ARPALAZIO, 2016). The values of common meteorological variables (mean and maximum daily
 220 temperature, relative humidity, mean and maximum wind speed, precipitation occurrence) were also
 221 downloaded from free accessible web sites (Weather Underground, 2016) and are reported in Table
 222 S1.

223 224 *2.3 Cocaine and cannabis abuse prevalence in the investigated countries*

225 According to the latest survey data provided by the European Monitoring Centre for Drugs and
 226 Drug Addiction (EMCDDA), in the United Kingdom and in Netherlands, drug abuse is widespread.
 227 In 2013 in the United Kingdom, the drugs abuse lifetime prevalences of cannabis and cocaine
 228 among adults (number of individuals that have experienced the abuse in the age range 15-64 y)
 229 were 29.9% and 9.5% respectively. In Netherland the last lifetime data, referring to 2009, report
 230 estimates equal to 25.7% and 5.2%, respectively, for the same substances. By contrast in Sweden
 231 the illicit drugs abuse looks less common and the lifetime prevalence recorded for cannabis is
 232 14.4%, whereas the last year 15-34y prevalence is in the range 1.1-2%. (EMCDDA, 2015).

233 234 **3. Results and discussion**

235 *3.1. Concentrations of PAHs, licit and illicit drugs in PM_{10} and $\text{PM}_{2.5}$*

236 PM_{10} was collected in London, while in Amsterdam and Stockholm the PM size fraction changed
 237 with the sampling periods and sites. Previous studies show that cocaine and cannabinoids are found
 238 in $\text{PM}_{2.5}$ with percentages never lower than 75% (Cecinato et al., 2010). To ensure a valid

comparison between countries it was first verified that PM₁₀ and PM_{2.5} samples collected simultaneously and at the same site contained similar amounts of PAH and drug substances. Figure 1 illustrates the results for the PM_{2.5} and PM₁₀ collected in Amsterdam at A-BG1, the percentages of individual PAH congeners in PM_{2.5} compared to PM₁₀ were 89% ± 8%, and the percentages of drugs reached 102% ± 3%. A comparison was not made for cannabinoids due to the absence of these compounds in the samples. Cannabinol distribution was checked in Stockholm and its preponderance in PM_{2.5} was confirmed.

246

Figure 1.

248

3.2. Psychotropic substances concentrations

3.2.1. Amsterdam

Due to the lack of preliminary information concerning the atmospheric concentrations of illicit drugs in Northern Europe, daily filters collected during March 2011 in Amsterdam were pooled to weekly samples in order to achieve LOQs for the analytical procedure. Table 2A shows the average values of the target compounds measured over the period. The A-BG1 urban background site was the least polluted for all classes. Considering regulated pollutants, small differences in the PM₁₀ levels were recorded among the sites (average 36±4 µg/m³), by contrast, total PAHs showed larger variations. Total PAHs reached 1.13± 0.06 ng/m³ at A-BG1, whereas they were 80% higher in A-SM1 (2.03 ng/m³) and 50% higher in A-SM2 (1.68 ng/m³). As for the psychotropic substances, caffeine ranged from 0.9 ng/m³ at A-BG1 to 1.2 ng/m³ at A-SM2. More marked differences among sites were observed for nicotine and cocaine. In particular, 0.03 ng/m³ of cocaine and 6.7 ± 0.2 ng/m³ of nicotine were valued at A-BG1 when at A-SM2 these compounds were over 4 times more (0.14 and 30.7 ng/m³ respectively). Intermediate concentrations were measured at A-SM1. Cannabinoid concentrations were all below the quantification limit (< 0.01 ng/m³ for each THC, CBL and CBD).

265

Table 2.

267

The concentrations measured in the 2013 campaign are reported in Table 2B. March was the coldest month of the 2013 in Amsterdam (see Table S1), with an average daily temperature of 0°C. This period was also characterized by the presence of rain and snow that could contribute to the decrease of atmospheric PM and nicotine recorded in 2013 compared with 2011. Meanwhile the PAH concentration increased, possibly due to the increased use of domestic heating (Alam et al., 2015).

273 Atmospheric cocaine variations were not consistent across the sites; a slight increase was observed
274 at A-BG1 and A-SM1 and a drop at A-SM2. The maximum value of cocaine concentration detected
275 in 2013 (0.12 ng/m^3) was recorded at A-SM2 (as it was in 2011) together with the peaks of nicotine
276 (20.6 ng/m^3) and caffeine (9.1 ng/m^3) on 7-8 March. It is worth noting that A-SM2 site was close to
277 a bus stop, and these peaks were probably related to variations in very local sources. Unlike 2011,
278 cannabinal was quantifiable in almost all sites, except at A-BG2; this latter, confirming its feature
279 of urban background, was the less affected by both PS and PAHs.

280

281 3.2.2. London

282 Table 3A/B reports the mean PS, PAH and PM₁₀ concentrations recorded at L-BG and L-KS during
283 winter and summer seasons. Taking into account both seasons, the concentrations of PM, PAHs and
284 nicotine were higher at L-KS. In particular, in March 2013 the maximum differences between sites
285 were observed for nicotine. In this period at L-KS nicotine reached $27.5 \pm 25.5 \text{ ng/m}^3$, almost twice
286 the level detected at L-BG ($14.3 \pm 12.1 \text{ ng/m}^3$), even though the variability was large. Less
287 important increases were observed for PAHs and PM₁₀. In July 2014 the biggest differences were
288 found for PAHs ($1.03 \pm 0.24 \text{ ng/m}^3$ at L-KS compared to 0.67 ± 0.41 at L-BG), while nicotine and
289 PM at L-KS exceeded 35- 40% of that measured at L-BG. The same behaviour was observed for
290 caffeine that showed the highest mean concentrations at L-KS. This finding confirms that L-KS
291 was, unsurprisingly, more influenced by traffic than L-BG, while the concentration of caffeine and
292 nicotine could depend on peoples' activity in the area, due to its touristic and commercial
293 attractions. By contrast, the maximum amounts of atmospheric cocaine were recorded at L-BG,
294 with average values over the whole campaigns 3-4 times higher than those of L-KS.
295 The adverse weather conditions that affected the Northern Europe in March 2013 hit also London,
296 with low average temperatures, rain and snow events which were expected to decrease the
297 contaminants in the air. In this context, in London the highest value of cocaine concentration was
298 detected again on 7-8 March (0.33 ng/m^3 at L-BG), and average cocaine concentration over the
299 period reached $0.23 \pm 0.11 \text{ ng/m}^3$ at L-BG and $0.05 \pm 0.03 \text{ ng/m}^3$ at L-KS. In July, cocaine ranged
300 between $0.18 \pm 0.05 \text{ ng/m}^3$ at L-BG and $0.06 \pm 0.01 \text{ ng/m}^3$ at L-KS. Rainy weather accompanied the
301 July 2014 campaign, nonetheless almost all targeted compounds were, on average, more in March
302 than in July. For cocaine, this finding confirms the results of the *Ariadrugs* project where
303 measurements of illicit drugs were carried out weekly over one year. At all the eight cities
304 investigated the lowest concentrations occurred in the summer period (June to August). This trend
305 is not directly connected to any emission reduction, but relates to the increase of dispersion and of
306 boundary layer height during the summer months. The only significant exception to this behaviour

307 is represented by cannabinal, the sole cannabinoid detected in London. This compound occurred at
308 low but quantifiable concentrations in both seasons and sites (see Table 3). Comparing the sites,
309 cannabinal at L-BG was of the same order of magnitude of that measured at L-KS. Comparing the
310 seasons, the cannabinal behaviour in London was peculiar, because the highest concentration were
311 recorded in July. According to the *Ariadrugs* Project results, in Italy cannabinoids dropped during
312 the summer due to degradation effects induced by solar radiation (Carbone et al., 2010; Cecinato et
313 al., 2012, 2016). The summer increase of atmospheric cannabinal measured in London probably
314 depended on the increase or proximity of drug use.

315

316 Table 3.

317

318

319 3.2.3 Stockholm

320 In Stockholm, due to the low concentrations expected for all chemicals, airborne particulates (PM_{2.5}
321 and PM₁₀) were gathered into three composite samples, corresponding to 18 Sep - 1 Oct, 2-15 Oct
322 and 30 Oct - 12 Nov, 2014. The results are summarized in Table 4. Cocaine occurred only at
323 detectable but not quantifiable levels. Cannabinal did not exceed 0.02 ng/m³; meanwhile, the other
324 contaminants occurred at lesser extents than in other cities.

325

326 Table 4.

327

328

329 3.3. Weekends vs. weekdays atmospheric concentrations

330 Various attempts have been made to evaluate differences between weekdays and weekend
331 concentrations of PSs in the atmosphere and to verify if they depended on the weekly trends in drug
332 abuse rate, which are expected to be higher at the weekend. No clear difference was observed,
333 probably due to the impact of atmospheric dispersion, however, the input of special events was
334 detectable. For instance, an increase in cocaine concentration was observed in Rome during the
335 celebration of the White Night Holidays in 2007, and a similar increase in cannabinoid
336 concentrations was found in Barcelona during a massive street protest (Cecinato et al., 2009; Viana
337 et al., 2010; Mastroianni et al., 2015).

338

339

340 Figure 2.

341

342 Figure 2 reports the weekend and weekday average concentrations of the investigated compounds
343 (together with the associated variability over the period), measured in London during the sampling
344 campaign carried out in March and July at L-BG (A and B) and L-KS (C and D).

345 With regard to cocaine, two distinct behaviours were observed. In March, the average concentration
346 of cocaine on weekdays exceeded those measured on weekends both at L-BG and L-KS (though the
347 differences were not statistically significant); the reverse behaviour was observed in July. To
348 illustrate the influence of meteorology and local emission rate on the illegal drug ambient
349 concentrations, the weekend vs. weekdays concentration ratio of cocaine was compared with those
350 of PM and other pollutants (see Table 5).

351

352 Table 5.

353

354 During March 2013, all substances, except PAHs and caffeine at L-BG, decreased on weekends; the
355 percent decrease of cocaine and PM were very similar at both sites, suggesting that atmospheric
356 dispersion was an important driver of this trend. Thus, the increase of cocaine concentration during
357 the weekdays cannot be associated to the increase of consumption. The reverse was observed in
358 July at L-BG site. There, the cocaine and cannabinol concentrations were higher on weekends,
359 despite the concurrent decrease of PM and other pollutants. In this case, the peculiar behaviour of
360 cocaine could depend on the emission rate in the area, probably associated to consumption, rather
361 than to an increase of population attending at the area. No marked differences were measured at L-
362 KS in July between weekend and weekdays and between cocaine and other pollutants patterns.
363 In Amsterdam this approach was applicable only with regard to the March 2013 campaign. The
364 particularly adverse meteorological conditions and the consequent strong influence of atmospheric
365 mixing on the pollutant concentrations, combined with the shortness of data series available,
366 hindered any clear observation of possible PS weekly trends. In fact, a widespread reduction in
367 pollutant concentrations was recorded during weekends. The most important decrease was
368 measured for caffeine at A-SM2 (weekend vs weekdays ratio equal to 0.1). This was possibly due to
369 the different habits and number of people at the bus stop close to monitoring site.

370

371 *3.4. Comparison of the contemporary monitoring campaigns*

372

373 A monitoring campaign was carried out in Rome from 7 to 27 March 2013, to compare the PS
374 behaviour in the Northern and Southern Europe cities. Also in Rome the measurement period was

rainy and cold, which hindered the accumulation of atmospheric pollutants. Figure 3 illustrates the cocaine concentrations, site by site, in each city; the boxplots reported in the Supplementary Material (Figure S1) illustrate the distributions and principal statistical parameters of all concentrations detected in the cities (the A-BG2 sample in Amsterdam was not considered).

Figure 3.

Meteorology seems to regulate the general trend of the illicit drug concentrations, although this can be overwhelmed by strong local sources. Analogous conclusions were drawn by Mastroianni et al. (2015) studying 12 sites simultaneously monitored in Barcelona. Comparing the average concentrations measured over the period in London, Amsterdam and Rome, London was the most contaminated city with regards to cocaine, in agreement with the highest levels of abuse associated to the UK (EMCDDA, 2015).

The average cocaine concentration calculated over the whole period at both London sites was equal to $0.15 \pm 0.11 \text{ ng/m}^3$. Slightly higher levels of consumptions are estimated for the Netherlands compared to Italy, however in Amsterdam the mean concentration of cocaine was lower than in Rome, $0.06 \pm 0.03 \text{ ng/m}^3$ vs. $0.09 \pm 0.03 \text{ ng/m}^3$. This finding probably depended on the higher population in Rome and the small scale house density at the sites investigated (two or three times higher than the average all over the city for Belloni, Cipro and Francia). This hypothesis is confirmed by the fact that, although the Spanish prevalence of consumption is comparable to that of UK, the average amount of cocaine detected by Mastroianni in the densely populated Barcelona was equal to 0.27 ng/m^3 . Barcelona population and population density reach 1,600,000 units and $15,700 \text{ inhabitants/km}^2$, respectively. Another opportunity to compare contemporary data of illicit atmospheric drugs in Northern and Southern Europe was offered by data collected in Amsterdam and eight Italian cities in March 2011. Table 6 reports the cocaine and cannabinoids levels detected in Italy and the features of the sites. Mean cocaine concentration in Amsterdam during 2011 reached $0.07 \pm 0.03 \text{ ng/m}^3$ and was similar to amounts detected at the urban background site of Milan (Pascal station, located in a public garden) and at the traffic site of Florence, lying in a densely populated city district. Concerning cannabinoids, in Italy only cannabinal was detected in Turin and Palermo, whereas in the other cities most of the investigated cannabinoids occurred at levels above LOQ. Rome showed the highest level of the cannabis active principle THC. Contemporarily cannabinoids were not detected in Amsterdam and, as reported in the text, their concentrations in Northern Europe were in general lower than in Italy even though the consumption

408 is more widespread there. Our hypothesis is that cannabinoids were consumed more indoors in
409 Northern Europe, or that air ventilation of buildings favoured in Italy resulted in greater emissions.

410

411 Table 6.

412

413

414 *3.5. Comparison of atmospheric cocaine concentrations with wastewater analysis*

415 Estimates of consumption rates are principally acquired using statistics of crimes or phenomenon
416 related to drugs abuse and population surveys. Relevant uncertainty exists on data produced on this
417 basis due to the difficulties in the acquisition of correct information, as a consequence results
418 produced by different areas are scarcely comparable. However, these tools are very expensive, time
419 consuming and unsuitable for the rapid identification of drug prevalence variations. Illicit
420 substances and their metabolites are excreted by consumers in known percentages, and the
421 characterization of residues in wastewater is currently accepted as a new suitable tool to assess the
422 drug consumption, appearing as a direct and relatively cost effective “measurement” of drug abuse
423 (EMCDDA 2016a).

424 Though the per capita drug consumption is not deliverable from concentrations in air, the cocaine
425 method used here is a simple extension of procedures adopted for measuring particulate bound
426 PAHs at the regional Air Quality Monitoring networks, and a possible cost-effective tool to index
427 the impact of phenomenon on the territory. In fact cocaine is stable in the atmosphere, and its
428 atmospheric concentration looks less affected than cannabinoids by consumption habits. In this
429 perspective, the comparison with results of measurement performed in wastewater (the sole
430 quantitative method to obtain per capita drug consumption estimates) is crucial to verify whether
431 this is achievable. The present study, together with previous investigations, allowed us to combine
432 the data sets of atmospheric concentrations for the first time at a European level, to correlate
433 atmospheric concentrations of cocaine with the abuse estimates obtained by wastewater analysis for
434 the same year (See Figure 4). When available (2012 and 2013), data were taken from the EMCDDA
435 database (EMCDDA 2016b), otherwise they were collected from literature (Thomas et al., 2011;
436 Zuccato and Castiglioni, 2012; DPA, 2012). Cocaine abuse estimates for Stockholm in 2014 were
437 not available, therefore the wastewater data refer to 2013 (Ort et al., 2014).

438

439 Figure 4.

440

441 Taking in account all Italian cities, London, Stockholm and Amsterdam in 2013, a good level of
442 correlation was found between the atmospheric concentration of cocaine and the amount of the
443 residues in wastewater ($R^2 = 0.66$; $p = 0.00131$). The R^2 value was improved (0.88 ; $p = 1.9828 \times 10^{-5}$)
444 by omitting Turin, where the atmospheric monthly concentration was generated by analysing five
445 daily samples, which reduced the sample representativeness. Poor correlation ($R^2 = 0.22$) is obtained
446 by inserting data from Barcelona and Amsterdam 2011. The large differences in the results of
447 wastewater analysis recorded for Amsterdam in 2011 and 2013 do not correspond to the range of
448 variation observed for cocaine in the atmosphere. On the other hand the large amount of cocaine in
449 the air of Barcelona does not fit with daily consumption estimate produced by wastewater analysis
450 for the same year, perhaps due to the high population density in the city.
451 These findings highlight further limitations of atmospheric measurements to assess the drugs
452 prevalence in the community (in addition to meteorology), that a at much minor extent also belong
453 to the wastewater analysis tool. These are principally due to the large fluctuations in abuse over
454 time, which requires consistent time coverage of the data collected to be mediated, and to the need
455 of an additional tool able to account for local population. (van Nuijs et al., 2011).
456 The population data is required to normalize the absolute values of illicit substances affecting the
457 atmosphere and wastewater. In this regard, the number of residents is a useful but incomplete
458 parameter because population can widely exceed the resident population due to the daily influx of
459 commuters and visitors, especially in the big cities. Therefore, attempts to define normalization
460 factors are important for both approaches (Cecinato et al., 2013; Bruno et al., 2014).

461

462 **Conclusions**

463 This study reports the first European data series of ambient psychotropic substances with the
464 respective geographical and temporal variations, and compares them with the outcomes of
465 wastewater analysis method for assessing population drug consumption. Ambient measurements in
466 Amsterdam, Stockholm and London confirmed the presence of both licit (nicotine, caffeine) and
467 illicit drugs (cocaine, cannabinoids) in the atmosphere and the corresponding concentrations rates
468 were compared with measurements performed in Italian cities. The concentration of PSs were found
469 to vary with both city location and season, which provided the opportunity to investigate
470 geographical and temporal variations in some detail. Among cannabinoids, only cannabinal was
471 detected in the Northern Europe cities. In Amsterdam and London, the cannabis prevalence is
472 reported as higher than in Italy, whilst concentration in air was not. This is likely the result of
473 consumer behavior. Further studies are necessary to clarify this issue but the rate of indoor drug
474 consumption, or the average amount per dose could play a key role. The highest concentrations of

475 cocaine were recorded in London, where the background site investigated was unexpectedly more
476 affected by cocaine than the city centre location. In Stockholm cocaine was not detected in
477 quantifiable amounts ($>3 \text{ pg/m}^3$). The average concentration detected in March 2011 in Amsterdam
478 was similar to that contemporarily detected in a densely populated area in Florence and in a
479 background site in Milan. A measurement campaign carried out in London, Amsterdam and Rome
480 in March 2013 showed that meteorology was the principal driver of atmospheric cocaine
481 concentrations, but that the inputs of local sources were very relevant. A clear observation of
482 weekly consumption modulation through ambient concentration of illicit drugs was masked by the
483 effect of variations in atmospheric dispersion. This phenomenon could not be controlled for in these
484 short studies, however an attempt was made through comparing the drug concentrations with those
485 of other pollutants. This allowed us to detect a clear weekend-weekday cocaine modulation in July,
486 at one site in London. Further studies are necessary to better understand how meteorology and
487 consumption behavior relate to ambient concentrations of PSs. Nevertheless measuring atmospheric
488 drug concentrations provides a feasible method to capture the differences in drugs consumption
489 between areas and over time. The suitability of this approach to become a tool to index the impact
490 of drug abuse (e.g. cocaine) was investigated by comparing the results of this study to those of the
491 wastewater analysis, routinely used to estimate the consumption prevalence. A good correlation
492 was found when the temporal variability of the consumption and the population were accounted for.
493 Atmospheric measurements of PSs could therefore offer a useful complementary approach to
494 wastewater analysis of PSs, especially where local hot spots need to be identified.

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630 **Table headings**

631

632 Table 1. Population rate and density of the cities investigated. PM fraction sampled, sampling dates
633 and typology of the monitoring sites in each city.

634 Symbols adopted for sites: BG = urban background; KS= kerbside; SM= street monitoring.

635

636 Table 2. Average concentrations of nicotine (NIC), caffeine (CAF), cocaine (COC), polycyclic
637 aromatic hydrocarbons (PAH), PM₁₀ and cannabinol (CBL) in the atmosphere of Amsterdam. A) 9-
638 16 March 2011; B) 7-27 March 2013. na: not available.

639 (*) Sampling limited to 23– 24 March.

640

641 Table 3. Average concentrations of nicotine, caffeine, cocaine, cannabinol, polycyclic aromatic
642 hydrocarbons and PM₁₀ in the atmosphere of London A) 7-27 March 2013; B) 10-22 July 2014.

643 For compound symbols see Table 2

644

645 Table 4. Average concentrations of nicotine, caffeine, cocaine, cannabinol and polycyclic aromatic
646 hydrocarbons in the atmosphere of Stockholm. For compound symbols see Table 2

647

648 Table 5. Ratios of weekend vs. weekdays pollutants concentrations recorded in London in March
649 2013 and July 2014 and in Amsterdam in March 2013.

650

651 Table 6. Concentrations of cocaine (COC), cannabinol (CBL), Δ^9 -tetrahydrocannabinol (THC) and
652 cannabidiol (CBL) detected in 8 Italian cities in March 2011. Population, population density and
653 sites typology. TR= traffic site, BG= urban background.

654

655 Table S1. Mean values of average (T_{ave}) and maximum (T_{max}) daily temperature, relative humidity
656 (RH), barometric pressure (P), precipitation days (%), maximum (w_{max}) and minimum (w_{min}) daily
657 wind speed, and prevailing wind direction (w_{dir}) in London, Amsterdam and Rome. 7-27 March,
658 2013.

659

660 **Figure captions**

661

662 Figure 1. PM_{2.5}/PM₁₀ concentration ratio of polycyclic aromatic hydrocarbons and psychotropic
663 substances. Amsterdam, A-BG1 station, 9-16 March 2011.

664 Symbols: BaA = benz[a]anthracene; BbF = benzo[b]fluoranthene; BjF = benzo[j]fluoranthene; BkF
665 = benzo[k]fluoranthene; BaP = benzo[a]pyrene; IP = indeno[1,2,3-cd]pyrene; DBA = dibenz[a,h]
666 anthracene; BPE = benzo[ghi]perylene; NIC = nicotine; CAF = caffeine; COC = cocaine.

667

668 Figure 2. Weekends and weekdays average concentrations valuated in March and July at L-BG (A
669 and B) and L-KS (C and D) and associated variability of the concentrations over the periods. PM₁₀
670 are given in $\mu\text{g}/\text{m}^3$ units, all other chemicals in ng/m^3 .

671 Symbols: NIC = nicotine; CAF = caffeine; COC = cocaine; CBL = cannabinol.

672

673 Figure 3. Cocaine concentrations detected in London, Amsterdam and Rome. Sampling period 7-27
674 March 2013.

675

676 Figure 4. Average aerial concentration of cocaine in European cities and estimates of the drugs
677 abuse produced by wastewater analysis in the same year.

678

679 Figure S1. Box plots reporting values of cocaine concentrations recorded in London, Amsterdam
680 and Rome in March 2013. Box boundaries represents 25 and 75 percentiles, the average is indicated
681 with the dotted line, median with continuous line. Whiskers represent minimum and maximum.

city	population	population density	Site symbols	site type	PM fraction	sampling period
Amsterdam	820000	4892	A-BG1	BG	10-2.5	9-16/03/2011 7-27/03/2013 23-24/03/2013
			A-SM1	SM	2.5	
			A-SM2	SM	10	
			A-BG2	BG	10	
London	8538689	5432	L-BG	BG	10	7-27/03/2013
			L-KS	KS	10	10-22/07/2014
Stockholm	912000	4872	S-BG	BG	10-2.5	18/09-15/10/2014 30/10-12/11/2014
Rome	2761477	2231	Francia (FR)	SM	10	7-27/03/2013
			Belloni (BE)	BG	10	
			Cipro (CI)	BG	10	
			Villa Ada (VA)	BG	10	

Table 1. Population rate and density of the cities investigated. PM fraction sampled, sampling dates and typology of the monitoring sites in each city.

Symbols adopted for sites: BG = urban background; KS= kerbside; SM= street monitoring.

A. March 2011	A-BG1	A-SM1	A-SM2	A-BG2
n. of samples	2	1	1	na
NIC, ng/m ³	6.7 ± 0.2	8.4	30.7	na
CAF, ng/m ³	0.80 ± 0.01	0.9	1.2	na
CBL, ng/m ³	<0.01	<0.01	<0.01	na
COC, ng/m ³	0.03 ± 0.00	0.06	0.14	na
PAH, ng/m ³	1.13 ± 0.06	2.03	1.68	na
PM ₁₀ , µg/m ³	32	36	40	na
B. March 2013	A-BG1	A-SM1	A-SM2	A-BG2*
n. of samples	4	3	7	1
NIC, ng/m ³	5.4 ± 3.0	3.5 ± 2.0	12.5 ± 5.3	0.4
CAF, ng/m ³	0.18 ± 0.11	0.21 ± 0.17	2.21 ± 3.42	0.06
COC, ng/m ³	0.05 ± 0.02	0.07 ± 0.05	0.06 ± 0.04	< 0.003
CBL, ng/m ³	0.02 ± 0.01	0.01 ± 0.00	0.03 ± 0.03	< 0.003
PAH, ng/m ³	3.11 ± 0.93	3.01 ± 2.26	2.92 ± 1.06	2.56
PM ₁₀ , µg/m ³	27 ± 11	30 ± 6	26 ± 17	na

Table 2. Average concentrations of nicotine (NIC), caffeine (CAF), cocaine (COC), polycyclic aromatic hydrocarbons (PAH), PM₁₀ and cannabinal (CBL) in the atmosphere of Amsterdam. A) 9-16 March 2011; B) 7-27 March 2013. na: not available.

(*) Sampling limited to 23–24 March.

A. March 2013	L-BG	L-KS
n. of samples	7	5
NIC, ng/m ³	14.3 ± 12.1	27,5 ± 25.5
CAF, ng/m ³	0.59± 0.30	0.65 ± 0.31
COC, ng/m ³	0.23 ± 0.11	0.05 ± 0.03
CBL, ng/m ³	0.02 ± 0.02	0.01 ± 0.01
PAH, ng/m ³	1.93 ± 1.04	2.24 ± 0.4
PM ₁₀ , µg/m ³	28 ± 11	35 ± 12
B. July 2014	L-BG	L-KS
n. of samples	5	5
NIC, ng/m ³	20.6 ± 13.3	27.0 ± 7.3
CAF, ng/m ³	0.45± 0.14	0.47 ± 0.17
COC, ng/m ³	0.18 ± 0.05	0.06 ± 0.01
CBL, ng/m ³	0.06 ± 0.02	0.05 ± 0.02
PAH, ng/m ³	0.67 ± 0.41	1.03 ± 0.24
PM ₁₀ , µg/m ³	17 ± 3	24 ± 6

Table 3. Average concentrations of nicotine, caffeine, cocaine, cannabinol, polycyclic aromatic hydrocarbons and PM₁₀ in the atmosphere of London A) 7-27 March 2013; B) 10-22 July 2014. For compound symbols see Table 2

period	18 Sep - 1 Oct	2 - 15 Oct	30 Oct - 12 Nov
n. of samples	2	1	2
NIC, ng/m ³	3.5 ± 0.1	3.4	4.4 ± 0.2
CAF, ng/m ³	0.48 ± 0.03	0.20	0.08 ± 0.01
COC, ng/m ³	< 0.003	< 0.003	< 0.003
CBL, ng/m ³	0.02 ± 0.00	0.02	< 0.01
PAH, ng/m ³	0.28 ± 0.02	0.46	0.47 ± 0.03

Table 4. Average concentrations of nicotine, caffeine, cocaine, cannabinol and polycyclic aromatic hydrocarbons in the atmosphere of Stockholm. For compound symbols see Table 2

weekends vs. weekdays	London				Amsterdam	
	March		July		March	
	L-BG	L-KS	L-BG	L-KS	A-BG1	A-SM2
PM ₁₀	0.9	0.7	0.9	1.2	0.8	0.6
PAHs	1.3	0.9	0.7	1.1	1.4	0.7
NIC	1.0	0.6	0.8	0.8	0.4	0.6
CAF	1.4	0.6	0.8	1.8	0.5	0.1
COC	0.9	0.7	1.4	1.1	0.8	0.4
CBL	nd	nd	1.1	0.9	1.1	1.5

Table 5. Ratios of weekend vs. weekdays pollutant concentrations recorded in London in March 2013 and July 2014 and in Amsterdam in March 2013.

	Population	Population density	Site	Site type	COC	CBL	THC	CBD
Turin	907563	6972	Via della Consolata	TR	0.19	0.02	<0.005	<0.005
Milan	1324110	7363	Via Pascal	BG	0.07 ± 0.03	0.03 ± 0.01	<0.005	0.04 ± 0.06
Verona	263964	1308	Via Dominutti	BG	0.05 ± 0.02	0.02 ± 0.01	0.02 ± 0.02	<0.005
Bologna	380181	2701	Porta San Felice	TR	0.06	0.08	0.03	0.01
Florence	371282	3625	Via Ponte alle Mosse	TR	0.07 ± 0.03	0.09 ± 0.04	0.02 ± 0.02	0.10 ± 0.09
Rome	2761477	2231	Cinecittà	BG	0.14 ± 0.04	0.12 ± 0.07	0.05 ± 0.06	0.12 ± 0.15
Naples	959574	8226	Via Metastasio	TR	0.13 ± 0.05	0.09 ± 0.07	0.04 ± 0.03	0.16 ± 0.08
Palermo	655875	4128	Via dei Cappuccini	BG	0.02 ± 0.01	0.01 ± 0.01	<0.005	<0.005

Table 6. Concentrations of cocaine (COC), cannabinol (CBL), Δ^9 -tetrahydrocannabinol (THC) and cannabidiol (CBL) detected in 8 Italian cities in March 2011. Population, population density and sites typology. TR= traffic site, BG= urban background.

Figure 1. PM_{2.5}/PM₁₀ concentration ratio of polycyclic aromatic hydrocarbons and psychotropic substances. Amsterdam, A-BG1 station, 9-16 March 2011.

Symbols: BaA = benz[a]anthracene; BbF = benzo[b]fluoranthene; BjF = benzo[j]fluoranthene; BkF = benzo[k]fluoranthene; BaP = benzo[a]pyrene; IP = indeno[1,2,3-cd]pyrene; DBA = dibenz[a,h]anthracene; BPE = benzo[ghi]perylene; NIC = nicotine; CAF = caffeine; COC = cocaine.

Figure(s)

Figure 2. Weekends and weekdays average concentrations valuated in March and July at L-BG (A and B) and L-KS (C and D) and associated variability of the concentrations over the periods. PM₁₀ are given in $\mu\text{g}/\text{m}^3$ units, all other chemicals in ng/m^3 . Symbols: NIC = nicotine; CAF = caffeine; COC = cocaine; CBL = cannabinol.

Figure(s)

Figure 3. Cocaine concentrations detected in London, Amsterdam and Rome. Sampling period 7-27