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1 **Contrasts in chemical composition and oxidative potential**  
2 **in PM<sub>10</sub> near flares in oil extraction and refining areas in**  
3 **Ecuador**

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34 **Abstract**

35 For decades, oil extraction in rural sites in the North Amazon Region (NAR) in Ecuador, have  
36 generated mixtures of potentially toxic compounds, such as polycyclic aromatic hydrocarbons  
37 (PAHs) and metal(loid)s. The main national refinery and the thermal power plant located in  
38 Esmeraldas, on the North Pacific Coast (NPC), are also considered as important sources of  
39 air contamination. Particulate matter (PM<sub>10</sub>) emitted at both sites could induce the formation of  
40 reactive oxygen species (ROS) in the lungs upon inhalation and could be associated with  
41 respiratory diseases. In this study, PM<sub>10</sub> mass composition was monitored over a two-year  
42 period in both regions: NAR (close to oil platforms and open flares) and NPC (in a public school  
43 close to the refinery). PM<sub>10</sub> composition was assessed in terms of metal(loid)s, organic and  
44 elementary carbon (OC, EC), monosaccharides (levoglucosan, mannosan, galactosan),  
45 glucose, polyols (sorbitol, mannitol, arabitol), water soluble ions and polycyclic aromatic  
46 compounds (PAHs, oxy-PAHs and nitro-PAHs). Additionally, three complementary  
47 biochemical and acellular tests were performed to evaluate the oxidative potential (OP).  
48 Results show that the PM<sub>10</sub> mass and elemental concentrations were higher in NPC than in  
49 NAR. Barium and Mo concentrations, commonly used in oil operations, were up to 1000-fold  
50 higher than values recorded in other regions of Ecuador. OC/EC ratios and polyols  
51 concentrations were higher in NAR than in NPC, indicating a larger biogenic contribution to the  
52 PM mass in this region. In NAR, the main sources associated with ROS burden were biogenic  
53 emissions and oil production, as indicated by positive correlations between OP, sugars, Ba,  
54 some PAHs and oxy-PAHs. On the other hand, in NPC, associations between NH<sub>4</sub><sup>+</sup>, Ba, As  
55 and Ni imply that oil refining and industrial activities are the main contributors to the OP of  
56 PM<sub>10</sub>.

57

58 **Keywords:** PM<sub>10</sub>; Ecuador; oil extraction; oil refining; chemical composition; PAHs; Trace  
59 metal elements; oxidative potential; air quality.

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**71 1. Introduction**

72 Atmospheric pollution has become a growing public health concern and accounts for almost  
73 10% of human mortality worldwide, according to the Environmental Performance Index (EPI,  
74 2016). Indeed, more than 3.5 billion people live in countries with unsafe levels of air pollution  
75 (Yang and Wang, 2017). Changes in air quality and climate from local to global scales are  
76 influenced by airborne emissions from major urban and industrial areas (Baklanov et al., 2016).  
77 Aerosols are composed of particulate matter (PM) and gaseous constituents. Particles are  
78 classified according to their aerodynamic diameter as coarse particles ( $\geq 2.5\text{--}10\ \mu\text{m}$ ), fine  
79 particles ( $\geq 0.1\text{--}2.5\ \mu\text{m}$ ) and ultrafine particles or nanoparticles ( $< 0.1\ \mu\text{m}$ ) (Bourdrel et al.,  
80 2017). The smaller they are, the deeper they can enter into the respiratory system leading to  
81 many health effects, including cancer (Hoek et al., 2013; Raaschou-Nielsen et al., 2013).  
82 Depending on the source of emission, PM is composed of many different compounds such as  
83 soot, metals and metalloids, salts, PAHs, secondary organic aerosols and even bacterial and  
84 fungal products (Santibáñez-Andrade et al., 2017). Agriculture, residential heating and  
85 cooking, vehicular traffic, fossil fuel combustion, oil refining, mining, steel industries, marine  
86 transport, desert dust and biomass burning are the main anthropogenic sources of outdoor  
87 pollution (Gurjar et al., 2016; Hadidi et al., 2016; Liang et al., 2016; Monks et al., 2009).

88 International air quality standards focus on the quantification of six compounds: ozone, PM,  
89 SO<sub>x</sub>, NO<sub>x</sub> and Pb. In addition, humans are exposed to other harmful substances such as Cd,  
90 As, Ni, Hg, benzo(a)pyrene or benzene (Baldasano et al., 2003; Boyd, 2006; Guerreiro et al.,  
91 2014). In front of this major issue, European Union air quality directives are among the most  
92 complete and restrictive in the world.

93 In Latin America, emissions from industrial sectors have experienced rapid growth. However,  
94 a lack of air monitoring and/or use of obsolete equipment and questionable methodology, have  
95 made the collection of reliable data about air quality difficult (Ossés de Eicker et al., 2010).

96 Among the well-known sources, crude oil industry generates atmospheric emissions from  
97 different sources: gas flaring (Fawole et al., 2016), oil pit evaporation (Avdalović et al., 2016;  
98 Kirkhus et al., 2015) and high temperature combustion processes during refining (Yassaa and  
99 Cecinato, 2005).

100 Nowadays, Ecuador is the 5<sup>th</sup> largest oil producer in South America and the 27<sup>th</sup> worldwide  
101 (Ecuador Oil Production, 2018). Extraction activities have occurred in NAR, while the most  
102 important refinery is located in Esmeraldas, along NPC. The Texaco Oil Company operated  
103 for 30 years (1960s–1992) in NAR, and technologies used for oil production have generated  
104 millions of gallons of untreated toxic waste which were partially released into the environment  
105 (Buccina et al., 2013; San Sebastián and Hurtig, 2005). For example, natural gas collected

106 during oil exploration can be transported and re-used or recycled; however, in developing  
107 countries, excess gas is flared or vented *in situ*, being a prominent source of black carbon  
108 (BC), the second highest contributor to global warming after CO<sub>2</sub> (Fawole et al., 2016). In the  
109 Ecuadorian Amazon, between 1 and 3 million cubic metres of wasted gas was burned daily  
110 without temperature or emissions controls (San Sebastián and Hurtig, 2004).

111 The development of the oil industry, combined with land reform, has significantly contributed  
112 to the reduction of tropical forests in Ecuador (Welford and Yarbrough, 2015). For instance,  
113 approximately 34% of Amazonian forest has been deforested (Mosandl et al., 2008; Rudel et  
114 al., 2002). Even so, the remaining forest acts as an important source of biogenic and  
115 anthropogenic aerosol emissions. These sources include high but intermittent biomass burning  
116 episodes and a consistent production of primary bioaerosols (i.e., pollen, spores, leaves and  
117 soil resuspension) and secondary bioaerosols (low volatile compounds formed in the  
118 atmosphere)(Fröhlich-Nowoisky et al., 2016; Martin et al., 2010). In the Amazon, biomass  
119 burning includes natural forest fires which are most intense during El Niño events, which are  
120 characterised by severe drought and high temperatures (Boy et al., 2008), as well as human-  
121 initiated burning for land clearing or land-use change (Artaxo et al., 2013).

122 Oil production activities, biomass burning and natural biogenic emissions release common  
123 contaminants such as PAHs, VOCs, metals and water soluble ions into the atmosphere making  
124 source apportionment difficult. However, biomass burning tracers like levoglucosan and its  
125 isomers (mannosan and galactosan) are exclusively generated from pyrolysis of cellulose and  
126 hemicellulose, the main constituents of plant cell walls (Zhu et al., 2015). The combustion of  
127 other materials, such as fossil fuels, does not produce levoglucosan (Cheng et al., 2013).  
128 Polyols such as arabitol and mannitol are considered good markers of biogenic emissions and  
129 are specifically linked to airborne microorganisms (fungal spores, bacteria) (Fu et al., 2016).

130 In this context, inhabitants living in regions of the Amazon affected by oil extraction activities  
131 or refining may be exposed to a substantial mixture of metal(loid)s and PAHs. However, air  
132 quality in Ecuador remains poorly studied (Raysoni et al., 2017) and, to our knowledge,  
133 literature about PM<sub>10</sub> properties and their health impact after inhalation is scarce. In fact, an  
134 epidemiological study conducted on a village surrounded by 30 oil wells and 4 powerful gas  
135 burners in the Ecuadorian Amazon evidenced that the apparent excess of cancer morbidity  
136 and mortality could be linked to the population's exposure to toxic contaminants coming from  
137 oil production (San Sebastián et al., 2001). In addition, the origin of the health effects  
138 experienced from atmospheric PM is categorised by their ability to induce cellular oxidative  
139 stress through generation of ROS in the lung (Idelchik et al., 2017; Secret et al., 2016). ROS  
140 include superoxide radical (O<sub>2</sub>•), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), hydroxyl radical (•OH), alkoxy  
141 radical (RO•) and singlet oxygen (O<sub>2</sub>) (Hedayat et al., 2015). Quinones and transition metals

142 have been identified as redox active species able to generate ROS (Charrier and Anastasio,  
143 2012; Crobeddu et al., 2017). This is why the inherent capacity of PM to oxidise a biological  
144 media is proposed as a unifying exposure metric to assess health risks from air pollution (Kelly  
145 et al., 2012; Sauvain et al., 2013). Several methods coexist for measuring the OP of PM and  
146 are based on the depletion of lung anti-oxidants or surrogates when in contact with PM (Borm  
147 et al., 2006; Calas et al., 2018, 2017; Huang et al., 2016).

148 This study, conducted in the centre of oil extraction and refining activities in the Ecuadorian  
149 NAR and NPC regions aims to survey the air quality and its evolution over two sampling years.  
150 A detailed PM<sub>10</sub> speciation was achieved and its potential link with oil activities (extraction and  
151 refining) was investigated by targeting specific tracers of industrial oil processes. Moreover,  
152 we determined the ability of PM to induce ROS formation in the lungs, a key parameter for  
153 health impact.

154

## 155 **2. Materials and methods**

156

### 157 **2.1 Description of the study area**

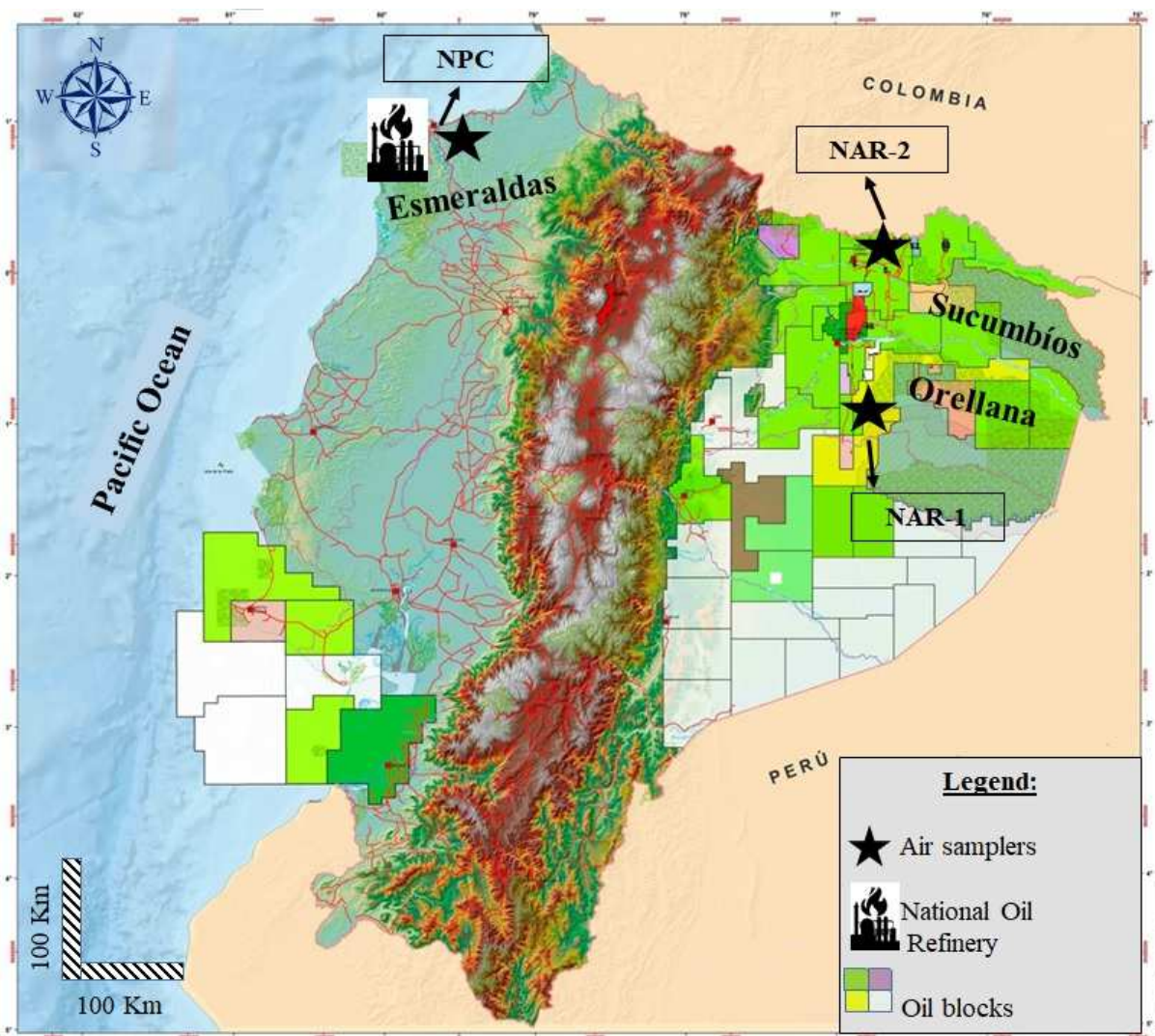
158 Three provinces of Ecuador were selected for this study: Orellana and Sucumbíos located in  
159 NAR and Esmeraldas located in NPC, both areas are impacted by oil extraction and oil refining,  
160 respectively (Fig. 1). Within each province, one site (house or school) was chosen based on  
161 its proximity to oil facilities: Auca Sur (NAR 1: S 0° 42' 16.49", W 76° 53' 15.96") and Shuara  
162 9 (NAR 2: N 0° 3' 33.26", W 76° 33' 37.01"), both 300 m away from gas-burning open flares,  
163 and La Florida (NPC: N 0° 55' 54.21", W 79° 40' 40.91") 1000 m away from the National Oil  
164 Refinery.

165 Several criteria such as records of oil spills, dumping of formation waters and hotspot maps of  
166 air quality were evaluated prior to site selection. This information was collected from the  
167 Intelligence Subsystem of Environmental Statistics of Productive Activities in Ecuador  
168 (SIESAP, 2015), from surveys conducted in the frame of the MONOIL Research Program  
169 "Monitoring of Oil activities in Ecuador: a cross-disciplinary approach between Environment,  
170 Health and People" or provided by the National Oil Company (EP PetroEcuador, 2013).

171 Regarding meteorological conditions, the predominant wind direction was north-northeast and  
172 south-southwest in Orellana and Sucumbíos, respectively (INAMHI, 2015). In Esmeraldas, the  
173 wind direction was south-southeast and south-southwest, following the Teaone and  
174 Esmeraldas rivers towards the Pacific Ocean in the morning; in the afternoon, the wind comes  
175 from the ocean and the refinery (EP PetroEcuador, 2013).

176 The wet season in NPC usually lasts from mid-December until May and the dry season from  
177 June until mid-November (GADPE, 2017). In contrast, in the Amazon region, precipitation is  
178 continuous throughout the year, but more pronounced between June and September (INAMHI,

179 2015). Total annual precipitation in both areas can reach more than 3000 mm (between 200  
 180 and 500 mm per month). Annual mean temperature is around 25 °C, ranging from 13 up to 38  
 181 °C (Pourrut, 1995).



182  
 183 **Fig 1.** Sampling sites in Orellana (Auca, NAR-1) and Sucumbios (Shuara, NAR-2) provinces  
 184 in the North Amazon Region and in Esmeraldas (La Florida) on the North Pacific Coast.  
 185 According to the Ministry of Non-renewable Resources of Ecuador (SHE, 2015), the white  
 186 blocks have not been assigned to oil exploitation, the others are currently being exploited by  
 187 different companies (indicated by colors).  
 188

## 189 2.2 Sampling strategy

190 PM<sub>10</sub> and its gas phase (outdoor samples) were collected on quartz fibre filters and  
 191 polyurethane foams (PUFs; 75 x 25 mm, Tisch Environmental) every two weeks in NPC (12 h  
 192 per day) and monthly in NAR 1 and 2 (24 h) from January 2015 until December 2016.

193 Prior to sampling, filters were calcinated at 450 °C for 6h and PUFs were pre-cleaned with  
 194 dichloromethane by pressurised solvent extraction (ASE; Thermo Scientific Dionex ASE 350)  
 195 (three extraction cycles, 90 °C, 100 bars, 5 min heat time, 6 min static time and 2 min purge).

196 Filters and PUFs were wrapped in aluminium foil and, after sampling, they were individually  
197 sealed in low-density polyethylene bags.

198 In total, six one-stage low-volume air samplers (MicroVol-1100) operated at a flow rate of 3 L  
199  $\text{min}^{-1}$  were settled by pairs on the roof of houses (NAR 1 and 2) or outside an open window  
200 grate in a primary school (NPC). Air samplers were powered with solar panels connected to a  
201 rechargeable battery pack in NAR 1 and 2 because no electricity was available; and plugged  
202 into the electric service in NPC.

203 During collection and before analysis,  $\text{PM}_{10}$  samples were protected from the light with  
204 aluminum foil, frozen at  $-5\text{ }^{\circ}\text{C}$ , transported to France in a cooler with dry ice blocks and stored  
205 at  $-20\text{ }^{\circ}\text{C}$  until analysis. Filters were weighed before and after sampling using an electronic  
206 microbalance (Mettler Toledo,  $\pm 10\text{ }\mu\text{g}$ ), previously equilibrated over 24 h in a conditioning  
207 chamber until reaching ambient temperature and relative humidity in the clean lab (near  $20\text{ }^{\circ}\text{C}$   
208 and not less than 40%, respectively).

209

## 210 **2.3 Aerosols chemical composition**

211

### 212 **2.3.1 Major and trace element concentrations**

213  $\text{PM}_{10}$  samples ( $0\text{--}10\text{ }\mu\text{m}$ ) impacted on quartz fibre filters (punches of  $5\text{ cm}^2$ ) were digested on  
214 a hot plate using 9 ml of aqua regia, 1 ml of  $\text{H}_2\text{O}_2$  and 2 ml of HF (trace metal grade analysis,  
215 Sigma-Aldrich<sup>®</sup>). Mineralization solutions were evaporated at  $60\text{ }^{\circ}\text{C}$ , the dry residue was then  
216 resuspended adding 0.5 ml of  $\text{HNO}_3$  and diluted with ultra-pure water before ICP-MS (Agilent  
217 7500 and ICP-MS iCAP Q Thermo Scientific) analyses in order to determine elementary  
218 concentrations (adapted from Schreck et al., 2016).

219 Certified reference material SRM 1648a “Urban Particulate Matter” (from NIST) was used to  
220 validate the mineralization method. Recoveries of 80–105% were calculated for all trace  
221 metals. Field blank filters and blank acid samples were included on each batch of analyses to  
222 eliminate the quartz matrix effect (Table SI-1, Supplementary Information).

223

### 224 **2.3.2 Soluble ions**

225 Water soluble cations ammonium ( $\text{NH}_4^+$ ), potassium ( $\text{K}^+$ ), sodium ( $\text{Na}^+$ ), magnesium ( $\text{Mg}^{2+}$ ),  
226 calcium ( $\text{Ca}^{2+}$ ) and anions nitrate ( $\text{NO}_3^-$ ), sulfate ( $\text{SO}_4^{2-}$ ), chloride ( $\text{Cl}^-$ ), oxalate ( $\text{COO})_2^{2-}$  and  
227 methanesulfonate ( $\text{MeSO}_3^-$ ) were analyzed by ion chromatography (Dionex ICS-300) on a  $4\text{ cm}^2$   
228 filter punch after extraction in 15 ml of Milli-Q Water. This technique is based on the  
229 separation of different ionic species in aqueous solution on an ion exchange resin, using KOH  
230 and MSA (methanesulfonic acid) as eluents, followed by the quantification of each one by  
231 conductivity detection.

232



### 233 **2.3.3 Organic and elementary carbon (OC, EC)**

234 Carbonaceous material was quantified by a thermal-optical analyzer (Sunset Laboratory,  
235 EUSAAR2 method<sup>®</sup>) separating the OC from the EC in the same sample. To separate the  
236 two fractions, a punch of 1 cm<sup>2</sup> was heated at different temperature ramps (up to 850 °C) in  
237 more or less oxidizing atmospheres. Total carbon (TC) was calculated as the sum of OC and  
238 EC.

### 239 240 **2.3.4 Organic compounds**

241 Monosaccharide anhydrides (levoglucosan, mannosan, galactosan), polyols (arabitol,  
242 mannitol, sorbitol), and sugars (glucose) were analyzed in a 4 cm<sup>2</sup> filter punch, using NaOH  
243 as eluent and liquid chromatography-pulsed amperometric detection (LC-PAD, Dionex DX  
244 500<sup>®</sup>) as described elsewhere (Samaké et al., 2019b, 2019a).

245 It is important to note that low-volume air samplers (connected to solar panels and batteries)  
246 and the one-month sampling protocol must have led to the degradation of the aforementioned  
247 compounds towards secondary species and thus, could have led to underestimation.

248  
249 Quantification limits for each analysis are presented in Table SI-1 (Supplementary  
250 Information).

### 251 252 **2.3.5 Polycyclic aromatic compounds (PACs)**

253 Parent PAHs, oxygenated-PAHs (oxy-PAHs) and nitrated-PAHs (nitro-PAHs) were determined  
254 in both particulate (quartz filters) and gas (PUFs) phases. All monitored PACs and their  
255 respective surrogate standards are listed in Table SI-2 (Supplementary Information).

256 The PAH, oxy-PAH and nitro-PAH analytical procedures were adapted from previous works  
257 (Albinet et al., 2006; Perraudin et al., 2005). Briefly, quartz fiber filters and PUFs were spiked  
258 with the surrogate standards (9, 7 and 3 perdeuterated congeners of PAHs, nitro-PAHs and  
259 oxy-PAHs, respectively) prior to extraction. Two types of quality controls were performed for  
260 each series of extraction: a laboratory blank and a control filter/PUF (spiked at low level with  
261 analytes and related surrogates) underwent the entire analytical procedure in order to check  
262 background contamination and analytical performance (accuracy).

263  
264 Both filters and PUFs were individually extracted by ASE Thermo Scientific ASE 350, Dionex,  
265 France) with dichloromethane (3 extraction cycles, 90 °C, 100 bars, 5 min heat time, 6 min  
266 static time and 2 min purge). Extracts were purified through alumina (aluminium oxide 150  
267 basic, 0.063–0.200 mm, Merck) micro-columns with 3 x 5 mL of dichloromethane in order to  
268 remove all macromolecules and polar interfering compounds. Extracts were divided into two  
269 weighed aliquots: one for the nitro- and oxy-PAHs (aliquot 1) and the other for PAH

270 determination (aliquot 2), and then reduced to about 500  $\mu\text{L}$  using a RapidVap<sup>®</sup> vacuum  
271 evaporator (Labconco, Kansas City, MO, USA) (50 °C, 900 mbars, 40% speed). Regarding  
272 extracts for nitro- and oxy-PAHs (aliquot 1), they were then concentrated to 100  $\mu\text{L}$   
273 dichloromethane under a gentle flow of ultrapure nitrogen (TS2B Toulemonde, Mery-sur-Oise).  
274 After the addition of a few  $\mu\text{L}$  of isooctane, extracts for PAHs (aliquote 2) in filter samples were  
275 evaporated (near to dryness at 45 °C) under a gentle flow of ultrapure nitrogen, and  
276 reconstituted in 100  $\mu\text{L}$  isooctane; whereas extracts of PUF samples were further purified on  
277 silica micro-columns to separate the alkane fraction from the aromatic one in order to keep a  
278 clean GC/MS injection port. Alkanes were desorbed using *n*-pentane, then PAHs were eluted  
279 with a 65/35 *n*-pentane/dichloromethane mixture. Finally, the pyrene-d10 and  
280 benzo[b]fluoranthene-d12 internal solution was gravimetrically added to all the final extracts  
281 for recovery control of surrogate standards.

282 The 21 parent PAHs were determined by gas chromatography/mass spectrometry using  
283 electron ionisation (GC/EI-MS) (7890A GC and 5975C MSD, Agilent Technologies). PAHs  
284 were separated at 1.3 mL/min (Helium 6.0, Linde Gas s.a., Bassens, France) on a HP5MS-UI  
285 column (30 m x 0.25 mm x 0.25  $\mu\text{m}$ , Agilent Technologies) with the following oven temperature  
286 program: 50 °C (2 min) - 10 °C/min - 250 °C (5 min) - 2 °C/min - 280 °C (2 min) - 10 °C/min -  
287 310 °C (3 min). The injection volume was 1  $\mu\text{L}$  (pulsed splitless mode: 25 psi for 1.5 min) and  
288 the injector temperature was 280 °C. MS parameters were set as follows: source and  
289 quadrupole temperatures: 300 and 180 °C, respectively; electron energy: 70 eV; ions  
290 monitored in SIM mode: molecular ions of each native and perdeuterated PACs (dwell time:  
291 30 ms).

292 The 20 nitro-PAHs and the 10 oxy-PAHs were determined by GC-MS using negative ion  
293 chemical ionisation (GC/NICI-MS) (7890A GC and 5975C MSD, Agilent Technologies) with  
294 selected ion monitoring (SIM) mode. Nitro- and oxy-PAHs were separated at 1.5 mL/min  
295 (helium 6.0, Linde Gas, s.a.) in an OPTIMA-5MS column (30 m x 0.25 mm x 0.25  $\mu\text{m}$ ,  
296 Macherey-Nagel) with the following oven temperature program: 40 °C (1.6 min) - 45 °C/min -  
297 150 °C (5 min) - 5 °C/min - 300 °C (5 min). Injection was performed with a programmable  
298 temperature vaporising (PTV) inlet using the following parameters: temperature from 40 °C  
299 (1min) to 280 °C (5 min) at a rate of 10 °C.min<sup>-1</sup>; purge time: 2 min at 100 mL.min<sup>-1</sup>. The MS  
300 parameters were set as follows: transfer line and source temperatures: 250 and 150 °C,  
301 respectively; electron energy: 200 eV; emission current: 150  $\mu\text{A}$ ; reagent gas: methane (4.5)  
302 at a flow rate of 60%; ions monitored in SIM mode: molecular ions of each native and  
303 perdeuterated PACs (dwell time: 100 to 250 ms depending on the compound).

304 PACs were quantified by their perdeuterated surrogate standards using their molecular ions  
305 (SIM mode). Whole-method accuracy was determined on spiked samples (at about 10–20

306 ng/filter or 30–60 ng/PUF) and remained generally between 77–110% for PAHs and 65–135%  
307 for nitro-PAHs and oxy-PAHs (except for two of them). Limits of quantification (LOQ) were  
308 determined from a 10 signal-to-noise ratio (SNR) observed in low-spiked samples and  
309 extrapolated for an air sample volume of 100 m<sup>3</sup> that typically ranged from 0.1 to 10 pg.m<sup>-3</sup>,  
310 although higher for a few compounds present in field PUF blanks.

311

## 312 **2.4 Oxidative potential (OP) of PM<sub>10</sub>**

313 The OP was assessed through three complementary acellular assays: DTT (dithiothreitol), AA  
314 (ascorbic acid) and DCFH (dichlorofluorescein). Extraction of PM from the substrate (filters) for  
315 OP assays are usually performed in water, methanol or dichloromethane (Eiguren-Fernandez  
316 et al., 2010; Yang et al., 2014). However, to mimic physiological processes when PM enters in  
317 contact with lungs, it is suitable to use a medium close to the human respiratory lining fluid—  
318 an important interface between inspired air and respiratory tract cells (Schock et al., 2004;  
319 Visentin et al., 2016). For this purpose, a Gamble solution supplemented with surfactants such  
320 as dipalmitoylphosphatidylcholine (DPPC) was used according to Boisa et al. (2014).

321 Samples (punches of around 0.5 cm<sup>2</sup>) were extracted according to Calas et al. (2017) in the  
322 Gamble + DPPC solution as described in Section 1 and Table SI-3 (both in Supplementary  
323 Information) to reach a constant volume of PM extracted from the solution (25 µg ml<sup>-1</sup> based  
324 on filter surface and PM mass) and vortexed for 75 min at 37 °C. To take into account potential  
325 turbidity or intrinsic absorbance of particles, before starting the assay, depletion intrinsic  
326 absorbance was determined for every sample (from each well) by spectrophotometry (using  
327 TECAN spectrophotometer Infinite<sup>®</sup> M 200 pro), and then subtracted from measurements.  
328 Blank filters were also extracted in the same solution.

329

### 330 **2.4.1 Dithiothreitol (DTT) assay (OP<sup>DTT</sup>)**

331 DTT consumption by formation of DTT-disulfide in the presence of ROS (Yang et al., 2014)  
332 was measured in a 96 well CELLSTAR<sup>®</sup> multiwall plates from Greiner Bio-One<sup>®</sup>. For each  
333 sample, 40 µL of PM extraction (in triplicate) with 205 µL of phosphate buffer (pH=7.4) were  
334 incubated at 37 °C in 12.5 nmol of DTT (DTT solution in phosphate buffer). Reaction was  
335 stopped at 0, 15 and 30 minutes adding 50 nmol of 5,5'-dithiobis (2-nitrobenzoic acid) (DTNB  
336 in phosphate buffer). A solution of 40 µL of 1,4 naphthoquinone (1,4-NQ 24.7 µM) was used a  
337 positive control. DTT loss after DTNB titration was read at 412 nm. The OP was obtained from  
338 the slope of the linear regression of the consumed DTT (corrected from blank measurements  
339 and from intrinsic absorbance of particles) normalized by the PM<sub>10</sub> air volume (nmol DTT min<sup>-1</sup>  
340 m<sup>-3</sup>).

341

#### 342 **2.4.2 Ascorbic acid (AA) assay (OP<sup>AA</sup>)**

343 Depletion of AA by ROS production when in contact with PM was monitored at 265 nm. Eighty  
 344  $\mu\text{L}$  of PM extraction and 120  $\mu\text{L}$  of water were injected manually in each well of the Greiner  
 345 UV-Star<sup>®</sup> (UV transparent) 96 well plate. Absorbance was read at 265 nm every 4 min for 32  
 346 min after injection of 24 nmol of AA (100  $\mu\text{L}$  of AA solution in Milli-Q water). The 1,4  
 347 naphthoquinone (NQ) was used as a positive control (Calas et al., 2018)  
 348 The AA loss rate ( $\text{nmol}\cdot\text{min}^{-1}$ ) was determined from the slope of the linear regression of the  
 349 calculated nmol of consumed AA vs time (corrected for blank and matrix). Units of OP<sup>AA</sup> were  
 350 calculated in the same manner as for OP<sup>DTT</sup>.

351

#### 352 **2.4.3 Dichlorofluoresceine (DCFH) assay (OP<sup>DCFH</sup>)**

353 The oxidation of DCFH with horseradish peroxidase (HRP) by ROS and the formation of its  
 354 fluorescent product 2',7'-dichlorofluorescein (DCF) was measured every minute for 15 min by  
 355 fluorescence (470 nm excitation/530 nm emission) (Foucaud et al., 2007).

356 In brief, 40  $\mu\text{L}$  of sample extraction in Gamble + DPPC solution with 220  $\mu\text{L}$  of HRP/DCFH (5  
 357  $\text{U ml}^{-1}$  and 40  $\mu\text{M}$  respectively, in phosphate buffer) were injected in each well of the ROTH<sup>®</sup>  
 358 96 black multiwall plates. A solution of  $\text{H}_2\text{O}_2$  at different concentrations (20, 40, 60, 100, 200  
 359 and 300 nM), 50 nM of  $\text{H}_2\text{O}_2$  (used as a positive control) and two blanks of Milli-Q water were  
 360 included on each batch in order to calibrate the formation rate of superoxide anions, expressed  
 361 as  $\text{nmol} [\text{H}_2\text{O}_2] \text{ eq. m}^{-3}$ . Detection limits (DL) for each analysis are summarized in Table SI-4  
 362 (Supplementary information).

363

### 364 **2.5 Mass reconstruction**

365 Reconstructed mass of PM is usually expressed as the sum of its representative chemical  
 366 components: organic matter (OM), EC, inorganic ions, soil minerals, salts (sea salts near  
 367 oceans), trace elements and the remaining mass (Chow et al., 2015). General equations used  
 368 in this study were adapted from methodology developed by Chow et al. (2015), Guinot et al.  
 369 (2007) and Amato et al. (2016) in agreement with the environmental parameters of the sites:

$$370 \quad \text{PM}_{10} \mu\text{g}\cdot\text{m}^{-3} = \text{OM} + \text{EC} + (\sum \text{ions}) + \text{Soil elements} + \text{Trace metals} \quad (1)$$

371 where:

$$372 \quad \text{OM} = f \times \text{OC}, \text{ with } f = 1.7$$

$$373 \quad \text{OC} = \text{organic carbon}$$

$$374 \quad \sum \text{ions} = \text{anions} + \text{cations} + \text{sea salts (only for NPC)}$$

$$375 \quad \text{Soil elements} = 1.15 \times (3.79 \text{ Al} + 2.14 \text{ Si} + 1.67 \text{ Ti}) + \text{Fe}$$

376

377 The conversion factor ( $f$ ) to transform OC in OM depends on the production of primary organic  
 378 aerosol (by combustion sources), the extent of OM oxidation and the formation of secondary  
 379 organic aerosol (SOA) from anthropogenic or biogenic sources (Chow et al., 2015; Philip et  
 380 al., 2014). Values for  $f$  can vary from 1.2 in fresh aerosol from urban areas to 2.6 in aged  
 381 aerosol (Chow et al., 2015; Dai et al., 2018). The  $f$  values (up to 1.6) are commonly applied to  
 382 oxygenated and/or functionalized organic species that can be expected in emissions from oil  
 383 activities. Thus, for this study we assumed  $f = 1.7$ .

384  
 385 Because the NPC sampling station was located 5 km from the seashore, sea salts (ss) were  
 386 also added to Equation 1 (included within “ $\Sigma$ ions”), as proposed by Amato et al. (2016):

387

$$388 \quad \Sigma \text{sea salt (ss)} = \text{ssNa} + \text{ssCa} + \text{ssK} + \text{ssMg} + \text{ssSO}_4^{2-} \quad (2)$$

389 where:

390  $\text{ssNa} = \text{Na} - \text{nssNa} (=0.348\text{Al})$ ;  $\text{ssCa} = 0.038 \text{ssNa}$ ;  $\text{ssK} = 0.037 \text{ssNa}$ ;  $\text{ssMg} = 0.119$

391  $\text{ssNa}$  and  $\text{ssSO}_4^{2-} = 0.253 \text{ssNa}$

392 *\*nss (non-sea salt).*

393

## 394 2.6 Statistical analyses

395 The software R<sup>®</sup> version 3.1.1 was used for all statistical analyses. The non-parametric  
 396 Spearman correlation ( $r_s$ ) with a level of significance set at 5% (p-value 0.05), based on rank  
 397 and not dependent on data distribution, was chosen for the regression analyses to measure  
 398 the strength and relationship between OP and the chemical composition of PM<sub>10</sub> for each  
 399 sampling site.

400 Correlation degree was interpreted as follows:

- 401 • Less than 0.40: weak
- 402 • 0.41–0.60: moderate
- 403 • 0.61–0.79: strong
- 404 • 0.79–1: very strong.

405

## 406 3. Results

407

### 408 3.1 PM<sub>10</sub> mass in oil production and refining areas

409

410 PM<sub>10</sub> contents over two years of sampling in NAR (1 and 2) and in NPC are presented in Table  
 411 1 as annual mean concentrations  $\pm$  standard deviation (SD). In 2015 and 2016, PM<sub>10</sub> mass  
 412 concentration in the oil production area was slightly higher in NAR-2 than in NAR-1, reaching  
 413 values of  $27.2 \pm 8.3$  (2015) and  $25.3 \pm 9.6 \mu\text{g m}^{-3}$ . In NPC (oil refining area), concentrations

414 were two to four times higher than in NAR, exceeding the European and Ecuadorian legislation  
 415 limits of 40 and 50  $\mu\text{g m}^{-3}$ , respectively (Table SI-5). In 2015,  $\text{PM}_{10}$  mean concentration was  
 416 lower than in 2016 because the refinery was not operating at full capacity.

417 Regarding monthly and seasonal variations (Fig. SI-1, Supplementary Information),  $\text{PM}_{10}$   
 418 mean concentration in the wet season was 1.6 times lower than in the dry season, but only in  
 419 NAR-2. In the case of NAR-1,  $\text{PM}_{10}$  remained similar in both seasons whereas the  
 420 concentration was slightly higher in NPC in the dry season (Fig. SI-1). However, these apparent  
 421 seasonality patterns have to be interpreted carefully as there were several samples missing  
 422 and other technical issues occurred at the three sampling stations (Table 1).

423

### 424 3.2 Elemental and ionic species concentration

425

426 Mean concentrations of major elements in NAR (Al, Ca, Fe, Na, Si) ranged between 300 and  
 427 up to 10 000  $\text{ngm}^{-3}$ , two to four times lower than in NPC (Table 1). Trace elements have been  
 428 classified into four categories according to their concentrations. The first one is represented by  
 429 Ti and Mo, with annual mean concentrations varying from 36 to 60 and from 56 to 227  $\text{ng m}^{-3}$   
 430 in NAR and NPC, respectively. Barium, Zn and Cr were part of the second group, with annual  
 431 mean concentrations ranging from 3 to 33  $\text{ng m}^{-3}$  in NAR and from 22 to 95  $\text{ng m}^{-3}$  in NPC.

432

433 **Table 1.** Annual chemical composition of  $\text{PM}_{10}$  in the three sampling sites of Ecuador: NAR-1  
 434 (Auca in Orellana) and NAR-2 (Shuara in Sucumbios), both in NAR and NPC (La Florida in  
 435 Esmeraldas).

436

Sampling site	NAR-1		NAR-2		NPC	
	N=11	N=9	N=12	N=10	N=9	N=23
N° of Samples*						
Year	2015	2016	2015	2016	2015	2016 <sup>a</sup>
$\text{PM}_{10}$	23.7±8.6	23.3±8.2	27.2±8.3	25.3±9.6	51.6±23.4	107.2±40.4
Na	7785±1601	1451±3068	10260±1887	247±145	41150±5263	10549±17954
Al	2144±400	1089±686	2525±605	868±567	10347±1139	2620±3231
Ca	3575±664	859±1341	4266±526	219±175	17144±1249	3972±6639
Si	1455±266	1423±266	1816±736	1783±749	8354±2824	8393±2423
Fe	436±133	310±235	472±236	387±247	1308±131	577±174
Ti	41.92±9.25	35.67±24.01	60.91±34.50	46.15±27.85	196.44±194.03	51.83±14.37
Mo	49.00±11.10	38.80±8.21	59.37±8.07	43.13±7.51	226.67±24.79	225.97±60.40
Ba	16.92±3.76	22.09±8.13	14.75±5.37	29.36±6.80	61.04±42.47	94.60±42.05
Zn	14.72±5.58	17.32±7.77	32.53±24.40	24.22±5.65	56.50±39.50	75.95±36.95
Cr	16.91±6.90	4.19±4.48	24.06±2.18	2.48±1.06	61.39±5.73	21.75±20.71
Mn	9.75±2.29	6.09±4.01	9.98±3.24	6.89±3.95	30.25±15.98	11.56±5.45
V	4.13±1.75	5.60±5.37	4.53±1.65	6.75±3.93	22.10±6.87	31.83±10.09
Ni	3.51±1.26	3.76±2.53	4.37±1.29	4.39±2.09	16.59±3.93	19.98±3.84
Sn	3.21±0.71	1.23±1.97	4.49±0.81	0.37±0.18	16.76±2.63	5.97±8.16
Cu	2.19±0.85	1.05±0.72	3.39±2.52	1.41±0.82	10.65±8.89	3.81±1.86
Pb	1.26±0.38	0.52±0.11	2.62±1.86	0.61±0.37	8.11±4.09	2.16±0.82
As	0.60±0.33	0.24±0.17	0.63±0.34	0.37±0.16	2.60±1.41	1.81±1.03
Sb	0.54±0.15	0.29±0.23	0.58±0.14	0.31±0.22	2.76±1.17	1.74±1.12
U	0.45±0.08	0.21±0.18	0.57±0.07	0.14±0.06	2.10±0.24	1.00±0.81
Co	0.26±0.06	0.17±0.11	0.52±0.35	0.18±0.10	0.90±0.25	0.40±0.21
Cd	0.11±0.02	0.09±0.06	0.17±0.09	0.11±0.07	0.44±0.13	0.41±0.26
$\text{SO}_4^{2-}$	1109±524	997±705	731±555	804±557	2556±737	3119±909.

NO <sub>3</sub> <sup>-</sup>	72±38	32±31	198±165	24±17	764±570	774±369
(COO) <sub>2</sub> <sup>2-</sup>	59±38	35±18	42±25	33±22	201±178	432.±240
Cl <sup>-</sup>	13±14	46±68	413±616	15±13	732±473	697±306
MeSO <sub>3</sub> <sup>-</sup>	3±2	4±3	4.±2	4±2	18±14	43±30
Na <sup>+</sup>	311.67±102.04	104.00±104.18	685.50±604.47	41.78±43.24	1486.15±1150.06	1158.99±460.05
K <sup>+</sup>	224.04±83.76	220.24±185.34	257.56±167.53	191.94±122.52	190.26±70.09	200.68±42.10
NH <sub>4</sub> <sup>+</sup>	81.41±68.56	167.64±117.76	165.63±150.05	135.15±120.96	231.59±151.86	380.89±181.14
Ca <sup>2+</sup>	155.52±55.98	60.50±45.14	139.61±173.35	49.19±43.34	472.72±284.36	315.12±138.85
Mg <sup>2+</sup>	23.48±8.37	23.42±18.88	16.58±8.06	13.17±8.35	76.55±44.23	107.22±36.77
EC	1.07±0.44	1.12±0.89	0.94±0.21	0.74±0.20	0.97±0.32	0.99±0.21
OC	4.58±1.57	5.05±3.67	4.89±1.30	4.44±1.34	3.37±0.72	2.79±0.72
OC/EC	4.56±1.15	4.56±1.58	5.48±1.98	5.99±1.06	3.59±0.49	2.91±0.80
Levoglucosan	4.67±2.25	31.48±10.49	8.35±4.87	56.58±33.80	19.33±12.89	50.83±27.09
Galactosan	<DL	2.55±0.85	0.80±0.53	1.60±0.51	0.59±0.54	1.88±1.16
Mannosan	4.04±2.81	45.66±15.22	0.63±0.38	5.83±3.21	3.81±1.38	5.82±3.47
Glucose	54.86±36.19	54.58±60.71	35.53±32.63	56.79±40.80	33.30±18.84	30.25±20.49
Manitol	151.56±63.47	175.12±144.64	59.20±86.24	134.49±46.30	63.62±31.02	46.77±33.76
Arabitol	50.70±23.43	48.27±44.98	43.40±82.46	34.26±13.59	45.71±24.10	29.93±21.03
Sorbitol	5.46±3.19	2.08±1.48	2.15±1.74	3.63±2.16	6.85±3.80	4.29±2.87
<b>Particulate phase</b>						
∑PAHs-PM <sup>b</sup>	123.1±43.9	316.4±330.1	44.6±35.5	190.6±402.3	790.0±566.5	1192±885.3
∑oxy-PAHs-PM	641±898	333±270	64±87	139±221	1529±1213	844±1045
∑nitro-PAHs-PM	2.4±0.9	2.4 ±1.4	1.4±2.0	0.8±1.1	2.9±0.5	5.3±39
<b>Gas phase</b>						
∑PAHs-gas	2632±1529	--	4215±2056	--	27492±8875	34469±4808
∑oxy-PAHs-gas	551±350	--	1068±388	--	4470±1958	6208±966
∑nitro-PAHs-gas	10±6.4	--	46±48	--	96±54	157±72

437 **Units:** mean concentrations of elements and ions (± SD) expressed in ng m<sup>-3</sup>. PM<sub>10</sub> mass, EC and OC are  
 438 expressed in µg m<sup>-3</sup> and PACs (∑PAHs, ∑oxy-PAHs, and ∑nitro-PAHs) in pg m<sup>-3</sup>.

439 \*Number of samples was not the same due to several technical issues (e.g., lost samples, broken air samplers)

440 <sup>a</sup>National Oil refinery operated with only 9 smokestacks in January 2015 and 18 (full capacity) since December  
 441 2015.

442 <sup>b</sup>∑PAHs refers to 15 compounds classified as carcinogenic by the US-EPA (NTP, 2016). Chrysene and  
 443 triphenylene were included in this sum (see Table SI-2, Supplementary Information). Oxy- and nitro-PAHs are  
 444 also listed in Table SI-2.

445 -- No samples collected during this period.

446 Ambient temperature during sampling ranged between 32 and 38 °C.

447

448 The third group, ranging from 1.7 to 29 ng m<sup>-3</sup>, corresponds to Mn, V, Ni, Sn and Cu. Finally,  
 449 Pb, As, Sb, U, Co and Cd comprise the fourth group, with concentrations below 3 and 8 ng m<sup>-3</sup>  
 450 in NAR and NPC, respectively. For trace elements regulated by Ecuadorian (Cd) and  
 451 European (As, Cd, Ni and Pb) legislation, concentrations remained below the thresholds (Table  
 452 SI-5) during the two years of sampling for all sites except for Ni in NPC (25 ngm<sup>-3</sup> in July 2016).  
 453 Cation concentrations in NPC are ranked in the following order: Na<sup>+</sup>>Ca<sup>2+</sup>>NH<sub>4</sub><sup>+</sup>>K<sup>+</sup>> Mg<sup>2+</sup>,  
 454 whereas in NAR-1 and NAR-2 the order is K<sup>+</sup> >Na<sup>+</sup>>NH<sub>4</sub><sup>+</sup>> Ca<sup>2+</sup>>Mg<sup>2+</sup> and  
 455 Na<sup>+</sup>>K<sup>+</sup>>NH<sub>4</sub><sup>+</sup>>Ca<sup>2+</sup>>Mg<sup>2+</sup>, respectively.

456 Among the water soluble anions, SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> showed the highest mean concentrations in  
 457 NAR and NPC, ranging from 24 to 3119 ng m<sup>-3</sup>. Sulfates, Cl<sup>-</sup> and (COO)<sub>2</sub><sup>2-</sup> concentrations in  
 458 NPC were between 2 and 16 times higher than in the NAR area.

459

**460 3.3 Organic components, sugars and polyols composition of PM<sub>10</sub>**

461

462 In NAR 1 and 2, OC/EC ratios were similar, ranging from 3 to 10, but higher than those  
463 calculated for NPC as can be seen in Fig. SI-2 (Supplementary Information). The highest  
464 contents of OC were 11.4, 7.0 and 4.1  $\mu\text{g m}^{-3}$  for NAR-1, NAR-2 and NPC, respectively. In  
465 NPC, OC/EC varied between 0.6 and 4.2, half the values found in NAR.

466 Marked differences were observed for some polyols and sugars between sites and sampling  
467 years (Table 1).

468 Levoglucosan reached a maximum monthly concentration of 107  $\text{ng m}^{-3}$  in NAR-2 (August  
469 2016) and 111  $\text{ng m}^{-3}$  in NPC (March 2016). Mannosan and galactosan total mean  
470 concentrations ranged from 0.9 to 10  $\text{ng m}^{-3}$ .

471 Monthly concentrations of the sum of polyols (Fig. SI-2, Supplementary Information) varied  
472 from 9 to 609 and from 6 to 171  $\text{ng m}^{-3}$  in the NAR and NPC areas, respectively. Polyols  
473 concentrations over the three sampling sites were classified in decreasing order as follows:  
474 mannitol>arabitol>sorbitol, with the highest concentrations recorded in NAR.

475

**476 3.4 PACs content of PM<sub>10</sub>**

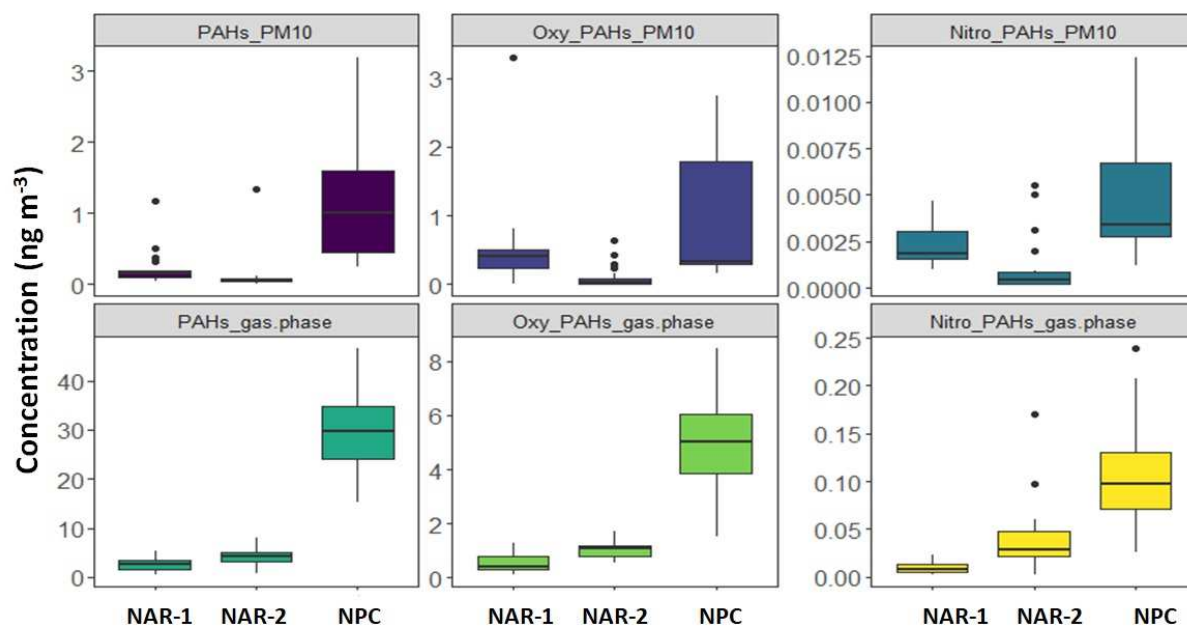
477 The sum of oxy-PAHs, nitro-PAHs and PAHs in PM<sub>10</sub> was four to six times higher in NPC than  
478 in NAR. Nitro-PAH concentrations were not significant (under 5  $\text{pg m}^{-3}$ ) for all the sites.  
479 Concentrations of these compounds were higher in NAR-1 than in NAR-2 (Table 1).

480 Among the PAHs: naphthalene, benzo[b]fluoranthene + benzo[j]fluoranthene +  
481 benzo[k]fluoranthene, indeno[1,2,3-c,d]pyrene and benzo[g,h,i]perylene reached the highest  
482 annual mean concentrations in NPC, varying from 180 to 373  $\text{pg m}^{-3}$  (Table SI-6). There are  
483 no maximum permissible limits for all of these compounds.

484 In all sampling sites, benzo[a]pyrene concentrations in PM<sub>10</sub> remained below the maximum  
485 annual average permissible level of 1  $\text{ng m}^{-3}$  according to the European Union (Table SI-5). As  
486 mentioned in the methodology for levoglucosan results, sampling time (one month in the  
487 Amazon region) may have led to volatilisation or degradation of these compounds towards  
488 secondary species contributing to underestimation. For this reason, we have also analysed the  
489 gas phase (Fig. 2).

490





491  
 492 **Fig. 2.** Mean concentration ( $\text{ng m}^{-3}$ )\* of PACs<sup>§</sup> in the particulate ( $\text{PM}_{10}$ ) and gas phase  
 493 (PAHs<sub>gas</sub>) from the three sampling sites: NAR-1 (Auca in Orellana) and NAR-2 (Shuara in  
 494 Sucumbios), both in NAR of Ecuador and NPC (La Florida in Esmeraldas).  
 495 \*two years of sampling  
 496 <sup>§</sup>List of PACs is available in Table SI-2 of Supplementary Information.  
 497

498 The gas phase contributes 95, 98 and 97% of the total PAHs, to 46, 94, 95% of the total oxy-  
 499 PAHs and 80, 91, 97% of the total content of nitro-PAHs in NAR-1, NAR-2 and NPC,  
 500 respectively. The NPC displayed the highest content in the gas phase with an average of 32  
 501  $\text{ng m}^{-3}$  for PAH and 7  $\text{ng m}^{-3}$  for oxy-PAHs (Table 1).  
 502

502

### 503 3.5 OP assays and ROS generation

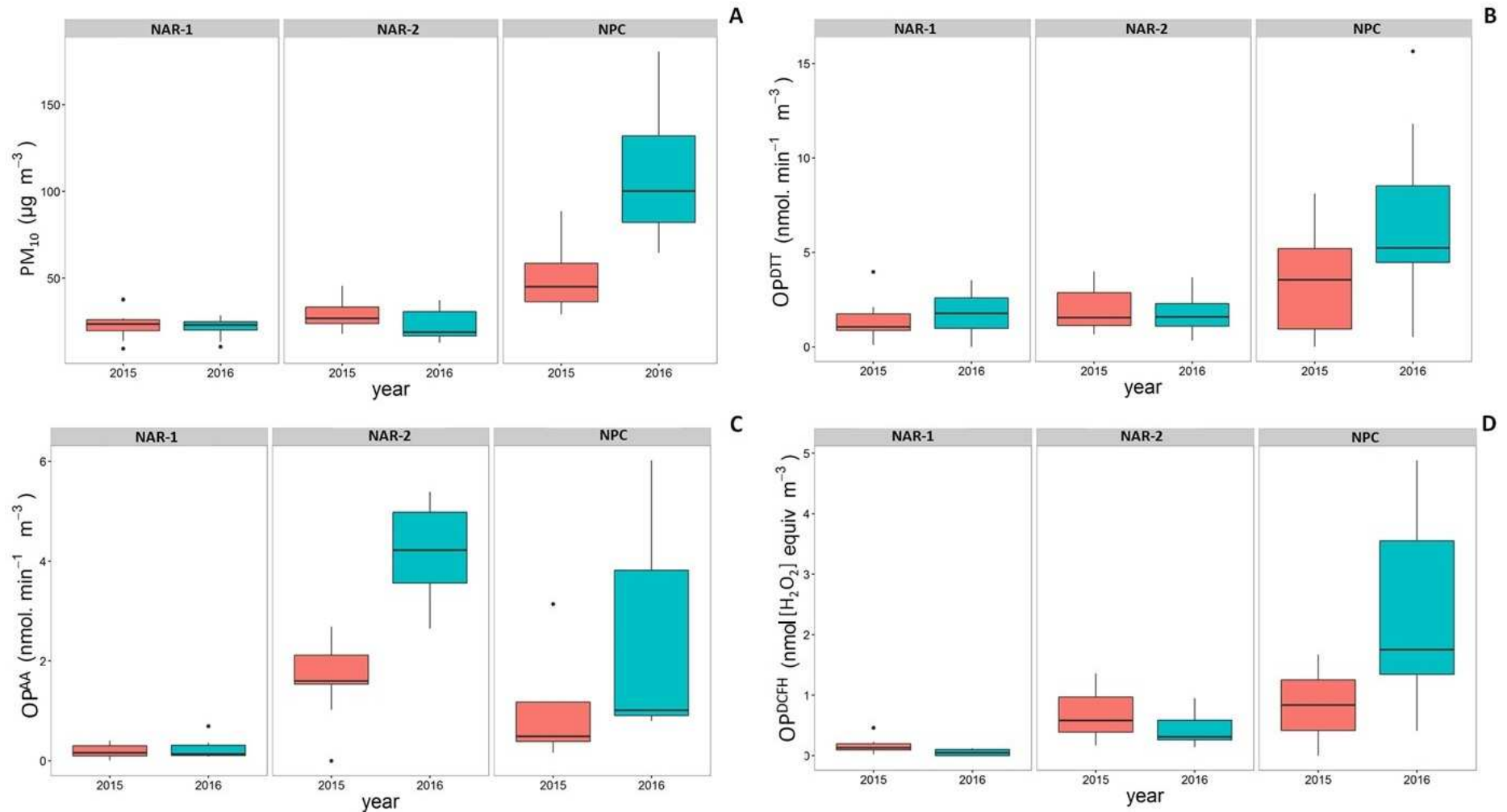
504 Results of OP from monthly  $\text{PM}_{10}$  filters (10 to 12 filters per year for NAR stations and up to 23  
 505 for NPC) measured by three different assays are shown in Fig. 3.

506 Among all sampling sites, NPC presents the highest ROS generation potential for all OP  
 507 assays, followed by NAR-2 and NAR-1. An increase in OP in 2016 matched an increase of  
 508  $\text{PM}_{10}$  in 2016 at NPC.

509 For NAR-2,  $\text{OP}^{\text{DCFH}}$  and  $\text{OP}^{\text{DTT}}$  provided similar information, whereas  $\text{OP}^{\text{AA}}$  displayed a  
 510 noticeable difference between 2015 and 2016.

511 Annual  $\text{OP}^{\text{DTT}}$  in both NAR locations was below  $1.2 \text{ nmol DTT min}^{-1} \text{ m}^{-3}$ , whereas it was three-  
 512 fold higher in NPC. The  $\text{OP}^{\text{DCFH}}$  exhibited a similar trend in NAR ( $< 1 \text{ nmol [H}_2\text{O}_2\text{] eq. m}^{-3}$  in  
 513 NAR-1), being three-fold higher in NPC. The lowest values were measured in NAR-1, with  
 514  $\text{OP}^{\text{AA}}$  below  $0.5 \text{ nmol AA min}^{-1} \text{ m}^{-3}$ .

515



516  
517  
518  
519

**Fig. 3. A)** PM<sub>10</sub> mass concentration ( $\mu\text{g m}^{-3}$ ) *versus* **B)** oxidative potential (OP,  $\text{m}^{-3}$ ) measured by Dithiothreitol (DTT) assay; **C)** ascorbic acid (AA) assay and **D)** dichlorofluorescein (DCFH) assay in NAR-1 (Auca in Orellana), NAR-2 (Shuara in Sucumbios), both in NAR and NPC (La Florida in Esmeraldas) for 2015 and 2016.

## 520 4. Discussion

521

### 522 4.1 PM<sub>10</sub> mass reconstruction

523 Species contribution to PM<sub>10</sub> mass balance for each site is shown in Fig. 4. Even if NAR-1 and  
524 NAR-2 are located in two different provinces, Orellana and Sucumbíos, respectively, both  
525 sampling sites display similar mass contributions. Small villages in the NAR of Ecuador  
526 appeared as a consequence of the roads opening into the rainforest to establish oil activities  
527 (Lessmann et al., 2016). Hence, in rural sites like these, OM rates might be dominated by  
528 biogenic emissions from the remaining forest (soils and plants) and by episodes of biomass  
529 burning related to agricultural practices or deforestation (Medeiros et al., 2006). In both  
530 provinces, the deforestation rates calculated for 2013 ranged from 10 to 15% of the primary  
531 forest (RAISG, 2015). Even so, the contribution of OM to the PM<sub>10</sub> mass in NAR was 32 to  
532 37% and major elements (accounting for 47% PM<sub>10</sub>) may have originated from soil dust  
533 resuspension (Fig. 4).

534 In contrast, NPC displays a more urban and industrial profile. Esmeraldas is a coastal city with  
535 scattered patches of tropical rainforest and dry forest. Oil refining, thermoelectric stations,  
536 vehicular traffic and sea salts are the main sources of ambient particles in this area. The OM  
537 contribution was 5%, about six times lower than in NAR. Soil elements and sea salts accounted  
538 for 40 and 27%, respectively. EC also exhibited higher percentages in NPC than in NAR, i.e.,  
539 9% vs 3–5% of total PM<sub>10</sub> mass (Fig. 4).

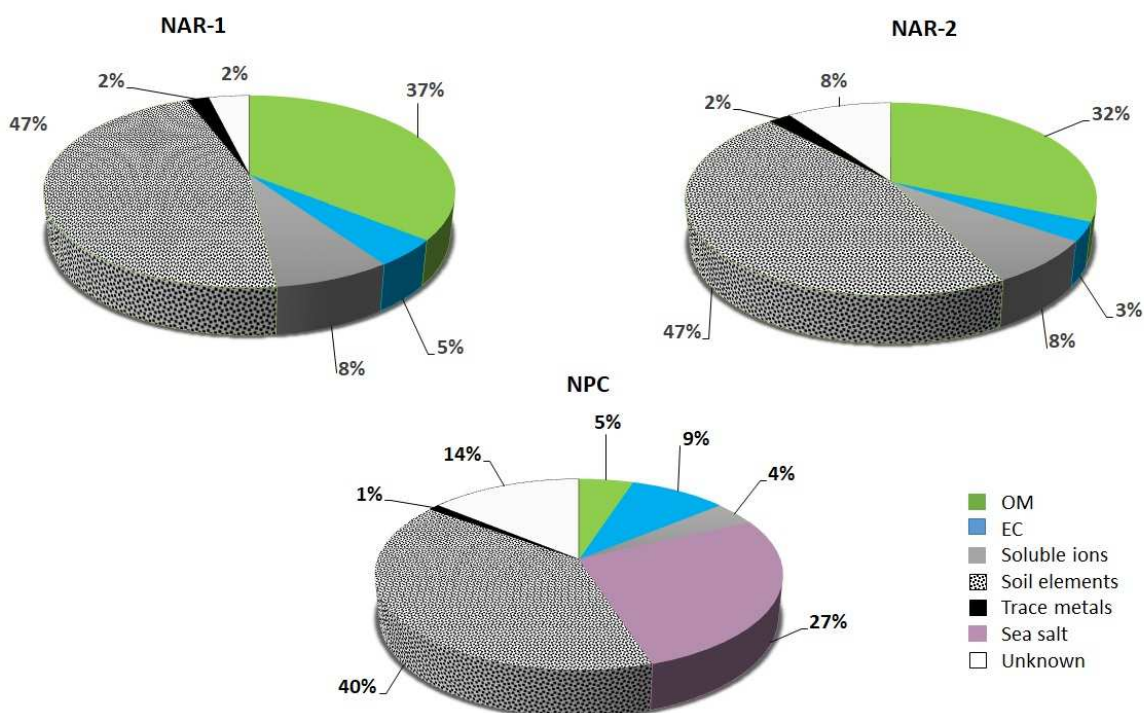
540 Soluble ions accounted for 4.5 and 8% in NPC and NAR, respectively, while trace elements in  
541 both areas represented less than 2%.

542 In NPC, total contribution of SO<sub>4</sub><sup>2-</sup> (sea salt and non-sea salt) for PM<sub>10</sub> mass balance was  
543 around 8%. Regarding the OM fraction, only 4% of the compounds were identified:  
544  $\Sigma(\text{monosaccharide anhydrides, polyols+glucose})$  and  $\Sigma(\text{PAHs} + \text{oxy-PAHs} + \text{nitro-PAHs})$   
545 accounted for 90 and 10%, respectively.

546

547 In the NAR, between 2 and 3% of the OM compounds were identified with a difference, in that  
548 PAHs contributed less than 1% and the rest came from monosaccharides, polyols and sugars.  
549 In both areas, the contribution of polyols (from biogenic emissions) to OM was higher than the  
550 tracers of biomass burning. Chemical balance closure for NPC and NAR was satisfactory with  
551 a range of non-identified compounds within 2 to 14%.

552



553

554 Fig. 4. PM<sub>10</sub> mass balance for NAR-1 (Auca in Orellana) and NAR-2 (Shuara in Sucumbíos)  
 555 stations in the Ecuadorian NAR and NPC (La Florida in Esmeraldas).

556 OM stands for organic matter and EC for elementary carbon.

557

558 Waked et al. (2014) showed that in Lens (France), a region with many petrochemical,  
 559 metallurgic and non-metallurgic industries, OM, EC, SO<sub>4</sub><sup>2-</sup>, NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup> and other compounds  
 560 (Cl<sup>-</sup>, major and trace elements) accounted for almost 30, 5, 12, 8, 21 and 9% of PM,  
 561 respectively. In the same study, the non-identified fraction was about 14%, whereas more than  
 562 5% of the compounds in the OM were identified: 56% corresponding to levoglucosan, 24% to  
 563  $\Sigma$ polyols, 9% to mannosan, 3% to galactosan and 8% to glucose.

564 It should be noted that several organic compounds that contribute to the OM fraction were not  
 565 quantified in our study. These compounds include: carboxylic acids, naturally present in plant  
 566 waxes (Santos et al., 2014); humic-like substances (HULIS) (Graber and Rudich, 2006; Zhao  
 567 et al., 2016) and volatile organic compounds (VOCs), such as BTEX (benzene, toluene,  
 568 ethylbenzene and xylene) issued from biogenic and anthropogenic sources (Baltrenas et al.,  
 569 2011; Zhang et al., 2017).

570 The remaining mass ("unknown" fraction) could also be assigned to water bound to particles,  
 571 measurement errors (i.e., weighting samples), volatilization of species due to sampling time  
 572 and local meteorological conditions or constraints in choosing an appropriate mass balance  
 573 equation as suggested by Chow et al. (2015) and Malm et al. (2011).

574

## 575 4.2 PM<sub>10</sub> composition and identification of potential sources

576 Recent literature published data on PM<sub>10</sub> mass concentrations for two cities in Ecuador (Quito  
577 and Cuenca), both located in the Andes mountains, and influenced by industry, thermoelectric  
578 stations and traffic. Concentrations ranged from 24 and 77 µg m<sup>-3</sup> for Quito (Raysoni et al.,  
579 2016) and between 32 and 46 µg m<sup>-3</sup> for Cuenca (Palacios and Espinoza, 2014). Even if these  
580 results are not comparable to both regions of our study, PM<sub>10</sub> concentrations were within such  
581 ranges, except for the substantial increase observed in NPC in 2016. This is mainly explained  
582 by the downtime, renovation and restart of the oil refinery in Esmeraldas with twice its initial  
583 capacity (Table 1 and Fig. SI-1).

584 In the NAR, PM<sub>10</sub> mass concentrations ranged from 9.39 to 45 µg m<sup>-3</sup> (Fig. SI-1), with an  
585 increase in the wet season, but only in NAR-1. Our results were higher than those found in the  
586 Brazilian Western Amazon in Manaus (annual mean of 5 µg m<sup>-3</sup> in a forest reserve in pristine  
587 condition) (Artaxo et al., 2013); similar to those found in Porto Velho by De Oliveira Alves et  
588 al. (2015)(13.38 to 30.20 µg m<sup>-3</sup> depending on season) in an area highly impacted by land use  
589 change and biomass burning.

590  
591 Regarding elements associated with soil dust, Artaxo et al. (2013) found that concentrations  
592 of Al, Ca, Fe, Si and Ti in Manaus were less than 300 ng m<sup>-3</sup>, supported by the fact that soil  
593 was covered by plant debris, reducing natural emissions and resuspension. By contrast, in  
594 Porto Velho these concentrations were about eight times higher, but still lower than those  
595 recorded in the Ecuadorian NAR (Table 1).

596 Gilardoni et al. (2011) reported that trace elements (Cr, Cu, Ni, Pb, V, Ti, Sb and Zn) in Porto  
597 Velho (pristine rainforest) in the coarse fraction were 8 to 28 times lower than the  
598 concentrations reported in our study (except for Pb and Sb which are in the same range) (Table  
599 1). All these findings may suggest that anthropogenic activities in NAR greatly affect the air  
600 quality in comparison to pristine Amazon forests in Brazil.

601  
602 Trace elements such as Ba, Mo, Ni and V have been reported as air pollutants commonly  
603 emitted during oil refining operations (Islam et al., 2010), whereas Ni and V are proxies for the  
604 combustion of heavy oil being ubiquitous for shipping emissions and petroleum industry  
605 (Moreno et al., 2010). Ni and V displayed higher concentrations in NAR than in Quito, but in  
606 PM<sub>2.5</sub> (Raysoni et al., 2017). Similar contents of Ni and V in NPC (Table 1) were found in La  
607 Linea/Algeciras, the main shipping area and petrochemical complex of Spain (Moreno et al.,  
608 2010). As a rough comparison (assuming that the chemical composition of PM<sub>10</sub> and PM<sub>2.5</sub>  
609 differs), Ba and Mo in NAR and in NPC reached concentrations from 2 to 7 and from 200 to  
610 1000 times higher than those reported by Raysoni et al.(2017) for PM<sub>2.5</sub> in Quito.

611

612 Literature is scarce about Mo in the air, but concentrations between 10 and 30 ng m<sup>-3</sup> are  
613 commonly reported in urban areas and between 1 and 3.2 ng m<sup>-3</sup> in rural areas (ATSDR, 2017).  
614 This is in disagreement with our study because the mean Mo concentration in NAR and NPC  
615 reached 47.5 and 126 mg m<sup>-3</sup>, respectively, by far higher than those reported in the US or  
616 Europe (Alleman et al., 2010; Fernández-Olmo et al., 2016; Hama et al., 2018). Molybdenum  
617 is used as a catalyzer during refining of heavy crude oil (Mironenko et al., 2017; Pradhan et  
618 al., 2013), as a friction reduction additive (Humood et al., 2019) and as a weighting agent in  
619 drilling fluids (McDaniel and Jamison, 2014). Concentrations of Mo in PM<sub>10</sub> collected in a  
620 heavily industrialized site located adjacent to one of the largest petrochemical complexes in  
621 the US and related to the combustion of crude oil (in association with Ni, V and Sc)(Bozlaker  
622 et al., 2013) were 73 to 1000 times lower than the concentrations measured in NPC.

623 Similar results occur with Ba. Despite it not being regulated, its concentration in the air should  
624 remain below 8 ng m<sup>-3</sup> (ATSDR, 2007). Even if Ba in PM<sub>10</sub> originates from crustal dust, it is  
625 commonly used as a weighting agent in drilling fluids (Do Amaral Sobrinho et al., 2018;  
626 Oskarsson, 2015). The PM<sub>10</sub> collected between the Mediterranean and Atlantic coasts showed  
627 daily concentrations of Ba varying from 0.8 to 49.1 ng m<sup>-3</sup>, associated with crustal and  
628 anthropogenic sources such as shipping fuel and oil combustion (Moreno et al., 2010).

629 Therefore, high Ba, Mo, V and Ni concentrations may evidence the impact of oil extraction and  
630 refining on the atmospheric composition in both regions. These four elements can be  
631 considered as specific tracers of oil activities in the Ecuadorian environment.

632  
633 Total mean cation concentrations in NAR (Table 1) were double compared to those reported  
634 by Gilardoni et al. (2011)—20 to 80 ng m<sup>-3</sup> in the coarse mode—in a pristine rainforest located  
635 in northern Manaus, where they were mainly associated with biogenic emissions.

636 Yamasoe et al. (2000) found SO<sub>4</sub><sup>2-</sup> to be the most important inorganic ion in biomass burning  
637 aerosols in Amazonia. Its percentage varied as a function of the burning phase, smoldering  
638 *versus* flaming, reaching mean values of 0.35–0.72% and 0.39–0.90% of the PM<sub>10</sub> mass,  
639 respectively.

640 In the Ecuadorian Amazon, sulfate concentrations represent between 3 and 5% of the total  
641 PM<sub>10</sub> mass in NAR-2 and NAR-1, respectively, suggesting that other sources might contribute  
642 to SO<sub>4</sub><sup>2-</sup> contents. Likewise, chemical analyses of rain and fog water samples collected in the  
643 mountainous rain forest of southern Ecuador showed frequent episodes of high sulfate and  
644 nitrate emissions, assigned to biomass burning from areas upwind of the Amazon basin  
645 (Fabian et al., 2005). Sulphates can also be secondary products from oil and gas extraction  
646 procedures (Sarnela et al., 2015; Tuccella et al., 2017).

647 Sulphate is also a prevalent tracer of sea salt sources that should be considered in the NPC  
648 area. In this site, SO<sub>4</sub><sup>2-</sup> reached annual mean concentrations of 2556 and 3120 ng m<sup>-3</sup> in 2015

649 and 2016, respectively (Table 1), evidencing both industrial and seawater emissions. These  
650 values were within the range of concentrations found in coastal industrial cities in Europe like  
651 Barcelona, Porto and Athens, which also have petrochemical plants (Amato et al., 2016).  
652 Moreover, Ecuadorian oil is known to contain high-sulfate contents, between  $0.99\pm 0.08$  and  
653  $1.34\pm 0.27\%$  (samples collected from the National Oleoduct and an oil camp) that may also  
654 explain a part of the sulfate fraction.

655  
656 Among organic compounds, levoglucosan (main pyrolysis product from cellulose), galactosan  
657 and mannosan (derived from hemicellulose) lead to tracers for biomass burning episodes with  
658 concentrations that vary depending on region and season (Chen et al., 2017; Cheng et al.,  
659 2013; Li et al., 2017). As a general trend, concentrations of these compounds in NAR and  
660 NPC, were much lower in comparison to the literature about wood burning and deforestation  
661 in the Amazonian region (De Oliveira Alves et al., 2015), suggesting that the Amazon region  
662 in Ecuador is nowadays less impacted by land use change and biomass burning.

663 On the other hand, total mean concentrations of levoglucosan, mannosan and galactosan in  
664 NPC were within the range of those in Barcelona obtained by Reche et al. (2012), but in  $PM_{2.5}$   
665 as related to agricultural waste burning and long-distance transport of aerosols from forest  
666 fires. However, the levoglucosan concentration in NPC was four times lower than those  
667 recorded by Oliveira et al. (2007) in the coarse fraction in Oporto (Portugal) and probably  
668 originated from wood burning ovens and fireplaces. Thus, the NPC area could be impacted by  
669 similar sources.

670 Ratios of 11 to 18 for OC/EC recorded in Porto Velho by De Oliveira Alves et al. (2015) were  
671 two to three times higher than those calculated for NAR (Table 1, Fig. SI-2). This suggests that  
672 biomass burning is of a lesser impact in our rural sampling sites and probably related to  
673 limitations in our methodology (section 2.3.4).

674 Esmeraldas (NPC sampling site) with over 500 000 inhabitants, showed OC/EC ratios similar  
675 to those found in urban and industrial site profiles similar to sites in Spain and Portugal, ranging  
676 from  $1.8\pm 0.8$  to  $2.8\pm 1.3$  (Oliveira et al., 2007; Reche et al., 2012).

677  
678 In regards to organic compounds, PAH concentrations were different between the two  
679 sampling sites located in NAR (Table 1, Fig. 2). Since air samplers at both sites were located  
680 an equal distance from open flares and similar  $PM_{10}$  concentrations were observed, differences  
681 in PAH content could be due to the size of open flares (bigger in NAR-1), to the number of  
682 flares (one in NAR-1, four in NAR-2) and to the close environment (wooded area in NAR-1).  
683 Total PAH (PM+gas phase) concentrations in NAR were two to five times higher than oxy-  
684 PAHs, while nitro-PAHs were 90 to 224-fold lower. Similarly, French sites such as Marseille

685 (shipping+oil activities) or alpine valleys display the same order of magnitude for PAHs and  
686 oxy-PAHs (Albinet et al., 2008, 2007).

687 Total PAHs (PM+gas phase) in NPC (Table 1, Fig. 2) were on the order of magnitude of  
688 concentrations recorded in Porto (30 ng m<sup>-3</sup> in a shipping and oil activities areas) (Albuquerque  
689 et al., 2016) or in the Amazonian forest in Brazil (35 ng m<sup>-3</sup>) as reported by Krauss et al.,  
690 (2005).

691 Concentrations of 0.13±0.04 ng m<sup>-3</sup> and 6.54±0.88 ng m<sup>-3</sup> in NPC for nitro-PAHs and oxy-  
692 PAHs, respectively (PM<sub>10</sub>+gas phase), are in the lowest range of the main French shipping  
693 and oil activities area of Marseille or Athens, Greece (Albinet et al., 2007; Andreou and  
694 Rapsomanikis, 2009). Conversely, in NAR, values of total nitro-PAHs in the range of 0.01 to 0  
695 0.05 ng m<sup>-3</sup> was low as observed in rural sites in North China (0.013–3.70 ng m<sup>-3</sup>) or in a  
696 remote area of Chile (0.001 ng m<sup>-3</sup>)(Li et al., 2015; Scipioni et al., 2012).

697 In the particulate phase, nitro-PAHs ranged between 1–5 pg m<sup>-3</sup> for the three sampling sites  
698 and must be considered in the lowest range of available literature: 9–19 pg m<sup>-3</sup> in Paris in  
699 summer (Ringuet et al., 2012) and 18–1546 pg m<sup>-3</sup> in Sao Paulo in summer (De Castro  
700 Vasconcellos et al., 2008).

701 Thus, the low concentrations recorded for particulate PAHs can be explained by volatilization  
702 due to high temperatures and an extended sampling period (as well as for levoglucosan, see  
703 section 2.2).

704

#### 705 **4.3 Identification of PM<sub>10</sub> chemical components generating ROS**

706

707 Saffari et al. (2014) reported OP<sup>DTT</sup> between 1.4 nmol min<sup>-1</sup> m<sup>-3</sup> for urban background up to 3.3  
708 nmol min<sup>-1</sup> m<sup>-3</sup> for a highway traffic place. Total mean values for OP<sup>DTT</sup> over a two-year  
709 sampling period were two-fold higher in NPC (Fig. 3), displaying an important oxidative burden.  
710 Conversely, in the NAR, total mean OP<sup>DTT</sup> varied between 1.63 and 1.83 nmol min<sup>-1</sup> m<sup>-3</sup>.

711 Concerning the DCFH assay, Hedayat et al. (2015) reported DCFH oxidation rates up to 3.81  
712 nmol [H<sub>2</sub>O<sub>2</sub>] eq. m<sup>-3</sup> for urban sites which are in agreement with NPC values (Fig. 3). As  
713 observed for OP<sup>DTT</sup>, OP<sup>DCFH</sup> remained lower for both NAR sites.

714 In spite of almost equivalent PM<sub>10</sub> mass concentrations for the two-year sampling period in  
715 NAR-1 and NAR-2, OP<sup>AA</sup> was different between 2015 and 2016. OP<sup>AA</sup> is known to be highly  
716 sensitive to metals (Hedayat et al., 2015; Szigeti et al., 2015). Being the concentration of trace  
717 elements was higher in NAR-2 than in NAR-1, it is not surprising that OP values reached higher  
718 values at the former site. However, this increase of OP<sup>AA</sup> in 2016 at NAR-2 is not totally  
719 understood considering that PM<sub>10</sub> and its composition were stable over 2015-2016.



720 Taken together, these three complementary OP assays highlight the importance of ROS  
721 exposure for NPC residents, a polluted and industrial site as compared to an acceptable  
722 exposure in the rural or urban background in NAR.

723  
724 Several studies have already indicated that ROS formation as measured by OP assays is  
725 strongly driven by PM reactivity and redox compounds (Calas et al., 2018; Charrier et al., 2015;  
726 Eiguren-Fernandez et al., 2010; Yang et al., 2014). To determine which particulate compounds  
727 were responsible for ROS formation in NAR and NPC, a correlation matrix according to  
728 Spearman's test (chosen because of the non-normal data distribution) was calculated (Fig. 5).  
729 In the oil extraction area,  $OP^{DTT}$  was correlated with Ba, Ni,  $NH_4^+$ , Si and Zn ( $r \sim 0.8$ ); moderately  
730 with OC, TC and polyols ( $r \sim 0.5$ ); and had a negative correlation with benzanthrone,  
731 fluoranthene and perylene ( $r_s > -0.8$ ).  $OP^{AA}$  was strongly correlated to EC, mannosan and  
732 galactosan ( $r_s 0.7-0.8$ ) and inversely correlated with Al, Co and Zn ( $r_s > -0.7$ ) in NAR-1. In NAR-  
733 2,  $OP^{DCFH}$  was either low or not positively correlated to any of the investigated chemical  
734 compounds; the same for  $OP^{DTT}$ .

735 However,  $OP^{AA}$  was strongly correlated ( $r_s > 0.8$ ) with Ba, moderately correlated with some oxy-  
736 PAHs (i.e., naphthoquinone) and PAHs (i.e., BaP) and polyols, and inversely correlated with  
737 Al, Cr,  $NO_3^-$  and Sn.  $OP^{DCFH}$  was not correlated with any compound.

738 In the oil refining area (NPC),  $OP^{DTT}$  was moderately correlated with As, Ba, Ni, Zn and  $NH_4^+$   
739 and inversely correlated with Cl,  $Ca^{2+}$  and  $\sum$ oxy-PAHs.  $OP^{AA}$  was strongly correlated with Ba  
740 and  $NH_4^+$  ( $r_s > 0.7$ ), but inversely to metals (Co, Cr, Fe, Sn). Finally,  $OP^{DCFH}$  was moderately  
741 correlated to MSA,  $NH_4^+$ , Ba, Ni and Zn and strongly correlated to levoglucosan, MSA and  
742  $NH_4^+$ .

743 Our results showed that  $OP^{AA}$  and  $OP^{DCFH}$  were correlated with Ba (oil tracer) for all sites.  
744 Perrone et al. (2013) reported that Ba in  $PM_{2.5}$  and  $PM_1$  may induce cytotoxicity in human  
745 alveolar cells. It has been reported that exposure to Ba can produce oxidative stress in  
746 mammals and impair cellular antioxidant defense systems like glutathione (Elwej et al., 2017).

747  
748 Nevertheless, there is not conclusive information about Ba redox activity in lung cells, but it is  
749 probable that its emission during oil activities is bound to other compounds that are redox  
750 active.

751 Despite high concentrations of Mo in  $PM_{10}$ , this element shows a low to moderate correlation  
752 with OP results. In contrast, Ni and V were moderately to strongly correlated with OP assays  
753 in NPC as they are supposed to be tracers of shipping traffic and oils activities (Pey et al.,  
754 2013). It has been observed that both elements are able to generate hydroxyl radicals when  
755 they come into contact with biological cells (Verma et al., 2009).

756

757 PAHs can induce oxidative stress indirectly if they are oxidized to polar compounds including  
758 quinones and possibly nitro-PAHs, which are redox active compounds (Cho et al., 2005; Li et  
759 al., 2002; Squadrito et al., 2001). OP assays were strongly correlated with some individual oxy-  
760 PAHs or nitro-PAHs compounds (e. g. 1,4 naphthoquinone; 9, 10 antraquinone, benzenthron  
761 with  $r > 0.7$  in NAR-2; 9, 10 antraquinone with  $r > 0.8$  in NPC).

762 Polyols were moderately correlated with ROS generation in both NAR sites where biogenic  
763 emissions are prevalent and recently shown to contribute to OP values (Samaké et al., 2017).

764

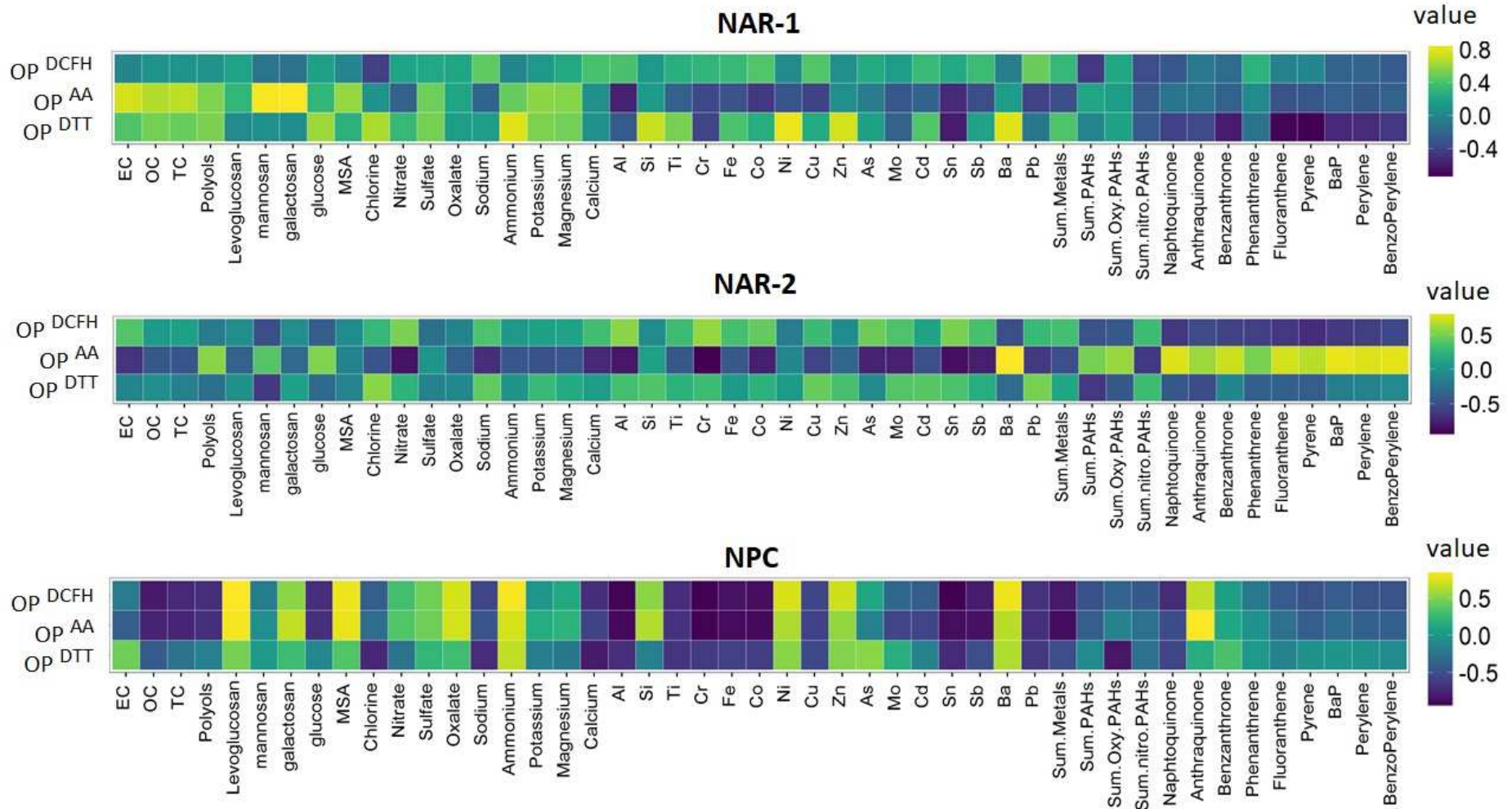
765 Such correlations provide interesting information about sources of emission possibly involved  
766 in ROS exposure from PM: (i) in NAR-1,  $OP^{DTT}$  is mainly correlated with oil extraction tracers  
767 and anthropogenic emissions from biomass burning; (ii) in NAR-2,  $OP^{AA}$  is associated with oil  
768 extraction proxies (Ba and oxy-PAHs) and (iii) in NPC,  $OP^{AA}$  and  $OP^{DCFH}$  assays agree in  
769 pointing to oil refining and thermoelectric industrial tracers (Ni, Ba), and possibly road traffic.

770

771 Finally, these results indicate that the population living in the vicinity of the Esmeraldas National  
772 Oil Refinery and the Thermoelectric plant (in NPC) has a significant exposure to ROS and are  
773 potentially impacted by oxidative stress due to PM inhalation more than those living in the oil  
774 extraction area of the Amazonian region (NAR).

775 All these trends must be confirmed by a source apportionment to assign PM emission sources  
776 to their overall ROS contribution (Weber et al., 2018), but that would involve a more intensive  
777 sampling that would be difficult to maintain under the sampling conditions described in section

778 .



779

780 **Fig. 5.** Correlation matrix according to Spearman's coefficient for a subset of chemical species determined in PM<sub>10</sub> and the three OP assays for  
 781 NAR-1 (Auca in Orellana), NAR-2 (Shuara in Sucumbíos) and NPC (La Florida in Esmeraldas) sampling stations.

782 **5. Conclusions**

783 The chemical composition of PM<sub>10</sub> in oil producing and refining areas in Ecuador not only  
784 depends on the type of oil activity but also on other anthropogenic sources as well as on the  
785 natural environment. Even if no seasonality was evidenced in NAR-2, more pronounced  
786 variations with time and between sampling years have been observed for some compounds,  
787 especially for sugars and PAHs, mainly in NPC and probably due to the shutdown and  
788 rehabilitation of the refinery in 2015.

789 In the NAR area, OM and soil elements were the dominant fractions of PM<sub>10</sub> composition,  
790 indicating that biogenic and soil dust emissions are the main sources of atmospheric particles.  
791 By contrast, in NPC, sea salts and soil elements were the major compounds. Contribution of  
792 EC to the PM<sub>10</sub> mass balance in the NPC area was significant, highlighting industrial emissions  
793 due to oil refining processes. PAHs also contributed to a higher percentage of OM in NPC  
794 (10%) than in NAR (less than 2%). Trace elements like Ba and Mo, both widely used in oil  
795 production and refining, and not usually reported in studies on air quality, showed higher  
796 concentrations than those recorded in urban-industrialized sites in Quito, US or Europe. Thus,  
797 Ba, Mo, Ni and V can be considered as relevant tracers of oil activities in Ecuador.

798 ROS formation depends on the airborne chemical composition and was specific to each region.  
799 The PM from NPC exhibited a very high ROS generation capacity, representative of industrials  
800 sites, whereas PM from both NAR stations presented an overall OP attributed to rural sites.  
801 Additionally, OP assays in combination with PM detailed composition evidenced that oil  
802 activities in combination with biogenic emissions in NAR and with other industrial emissions in  
803 NPC, are responsible for the PM capacity for ROS generation. Finally, this study reported that  
804 elevated concentrations of PM chemical constituents previously associated with adverse  
805 human health (Barraza et al., 2018) were identified at the three sampling sites. The present  
806 study opens the way for further investigations in epidemiology and risk assessment in the areas  
807 presented here, but also in other Latin America and African countries where oil activities are  
808 widely developed without relevant environmental and health policies.

809

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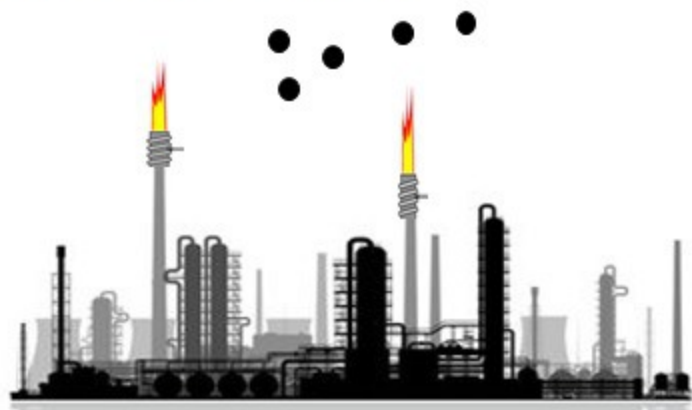
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# Oil Ecuadorian environment



Oil extraction



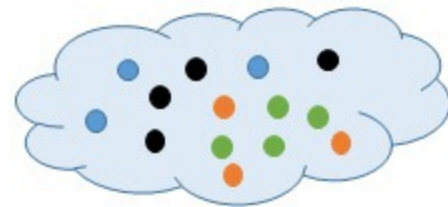
Oil refining



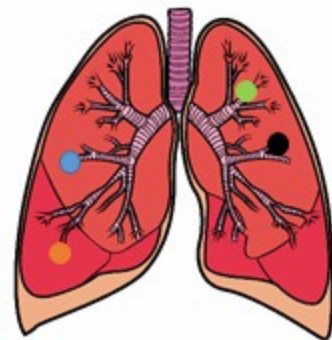
Biogenic emissions



Deforestation & Biomass Burning



PM<sub>10</sub> chemical composition?



ROS generation and oxidative stress?