

Drinking water quality in areas impacted by oil activities in Ecuador: Associated health risks and social perception of human exposure

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1	Drinking water quality in areas impacted by oil activities in Ecuador:
2	associated health risks and social perception of human exposure
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30	Highlights
31	• A punctual enrichment in volatile hydrocarbons is observed in several private wells.
32	• Low mineralization of drinking waters is a special health issue in the Amazon
33	region.
34	• The bacterial contamination of waters needs more attention by public policy.
35	• Local stakeholders are unable to provide effective water supply and water treatment
36	systems.
37	• Social and economic constraints lead people to choose the risks they have to face.
38	
39	Abstract
40	The unregulated oil exploitation in the Northern Ecuadorian Amazon Region (NEAR),
41	mainly from 1964 to the 90's, led to toxic compounds largely released into the
42	environment. A large majority of people living in the Amazon region have no access to
43	drinking water distribution systems and collects water from rain, wells or small streams.
44	The concentrations of major ions, trace elements, PAHs (polycyclic aromatic
45	hydrocarbons) and BTEX (benzene, toluene, ethylbenzene, xylenes) were analyzed in
46	different water sources to evaluate the impacts of oil extraction and refining. Samples were
47	taken from the NEAR and around the main refinery of the country (Esmeraldas Oil

48 Refinery/State Oil Company of Ecuador) and were compared with domestic waters from 49 the Southern region, not affected by petroleum activities. In most of the samples, 50 microbiological analysis revealed a high level of coliforms representing significant health 51 risks. All measured chemical compounds in waters were in line with national and 52 international guidelines, except for manganese, zinc and aluminium. In several deep-water 53 wells, close to oil camps, toluene concentrations were higher than the natural background 54 while PAHs concentrations never exceeded individually 2 ng.L⁻¹. Water ingestion represented 99% of the total exposure pathways for carcinogenic and non-carcinogenic 55 56 elements (mainly zinc) in adults and children, while 20% to 49% of the Total Cancer Risk 57 was caused by arsenic concentrations. The health index (HI) indicates acceptable chronic 58 effects for domestic use according the US-EPA thresholds. Nevertheless, these limits do not 59 consider the cocktail effects of metallic and organic compounds. Furthermore, they do not 60 include the social determinants of human exposure, such as socio-economic living 61 conditions or vulnerability. Most (72%) of interviewed families knew sanitary risks but a 62 discrepancy was observed between knowledge and action: religious beliefs, cultural 63 patterns, information sources, experience and emotions play an important role front to 64 exposure.

65

66 Graphical abstract

67

68 Keywords (max. 6)

69 Oil activities; Domestic waters; Hydrocarbons; Metal(loid)s; Demineralized waters; Social
70 risk perception.

71 **1. Introduction**

72 Since decades, the petroleum industry has become a significant component of the global economy, but with strong environmental and social impacts (WEC, 2016). A high record of 73 74 accidents occurring throughout the history of oil production demonstrates the devastating 75 effects and the risks involved for exposed populations (Amiard, 2017; Levy and Nassetta, 76 2011). In Ecuador, crude oil exportation represents the country's main source of income, exceeding 50% of the total exportations from 2004 to 2014, and settling down at 37% in 77 78 2017 (Banco Central del Ecuador (BCE), 2010; Calderon et al., 2016; MCE, 2017). On the 79 other hand, Ecuadorian oil industry is characterized by a long-term history of social and 80 environmental conflicts (Fontaine, 2007).

81 The oil industry exerted with inadequate environmental standards is strongly suspected of 82 polluting surface and ground waters, particularly in Orellana and Sucumbíos provinces 83 where 80% of total oil spills and 97% of waste pits were recorded (MAE, 2015). During 84 the Texaco oil extraction period (1964-1992), formation waters were directly released into the environment, in forests and rivers (Buccina et al., 2013; Narváez, 2000). However, 85 86 since the 2000's the Ecuadorian legislation prohibited these practices, binding oil 87 companies to redirect these waters into ancient oil wells (Decree 1215, 2001). Nevertheless, 88 local inhabitants testified that illegal polluting discharges are still released punctually and 89 mainly during the night.

Oil hydrocarbons, in particular PAHs and BTEX, are considered a high environmental and
health concern since most of them are persistent and carcinogenic (Amiard, 2017;
Jørgensen and Fath, 2010). Certain PAHs and their metabolites can induce leukemia,
hepatitis and immunotoxicity; they can also affect the reproductive system and cause

94 genotoxic and carcinogenic effects (IARC, 2010). Twelve PAHs and BTEX have been 95 classified as probable or suspected carcinogens in humans but only benzo(a)pyrene (BaP) 96 and benzene are confirmed as carcinogenic (ATSDR, 2007; IARC, 2018). Despite their 97 high toxicity, volatility and solubility in water, BTEX are not commonly studied; noting 98 that they are responsible for acute and chronic effects including eyes and throat irritation, 99 headaches, tachycardia, leukemia, affections to nervous system, cancer and death (Leusch 100 and Bartkow, 2010; Mitra and Roy, 2011; Neghab et al., 2015). Previous epidemiological 101 studies reported numerous chronic effects including psychological disorders, endocrine and 102 reproductive affections and cases of cancers (Hurtig and San Sebastián, 2002; Levy and 103 Nassetta, 2011; Ramirez et al., 2017; Clinica Ambiental, 2017; Webb et al., 2018). 104 Genotoxic analyses on individuals from the NEAR showed that the exposure to 105 hydrocarbons has caused DNA damage and increased the risk of developing cancer (Paz-y-106 Miño et al., 2008).

107 Although hydrocarbons constitute the main fraction (75%) of crude oil, petroleum is a 108 complex mixture of elements, such as sulfur, major cations, anions, trace metal(oid)s 109 (TME) and organic molecules. Major elements (potassium (K), magnesium (Mg), sodium 110 (Na) and calcium (Ca)), and trace elements (nickel (Ni), vanadium (V), iron (Fe) and 111 cooper (Cu)), are naturally present as salts or organometallic compounds in crude and 112 formation waters, while barium (Ba), cobalt (Co), arsenic (As) and lead (Pb) salts are added 113 during the extraction, transportation or storage (Amiard, 2017). Though certain metallic 114 elements are essential for biological functions, most of them could be highly toxic, even at 115 low concentrations, and can cause hazardous effects due to their tendency to bio-116 accumulate (Jørgensen and Fath, 2010). In 2017, IARC listed cadmium (Cd), As, Cr and Ni 117 as probed carcinogenic elements for humans (lungs, prostate, bladder, kidney, liver and

stomach cancers); they can also affect nervous, immune and reproductive systems and caninduce abortions, anemia, and teratogenic effects (Fry, 2015).

Released in the environment, hydrocarbons, metals and metalloids can reach aquifers and surface waters throughout all the phases of petroleum production. These pollutants can integrate the dissolved phase or be sorbed onto sediment and particles as their speciation and distribution depend on the physicochemical characteristics of aquatic environments (US-EPA, 2000; Amiard, 2017; Boehler et al., 2017).

Extensive information has been compiled in relation with the signs and symptoms of health problems in oil extraction areas in Ecuador (Arana and Arellano, 2007; Hurtig and San Sebastián, 2005; O'Callaghan-Gordo et al., 2016; San Sebastian, 2001). However, to our knowledge, there is no quantitative determination of the risks involved by drinking water exposure, nor epidemiological studies that connect water quality to suspected cancer and non-cancer risks.

131 In Ecuador, access to a water supply network has increased in recent years but the 132 percentages of the supplied population are very heterogenous over the territory; in the 133 studied cantons, it varies from 26,6% in Aguarico, to 33,7% in Shushufindi, 41,6% in Joya 134 de Los Sachas and 57,5% in Orellana (SENPLADES, 2014). Nevertheless, in the NEAR, the use of unreliable water sources for domestic purposes (drinking, cooking, bathing and 135 136 washing clothes) is still a high-risk factor of exposure to toxic pollutants either by dermal 137 contact or ingestion. In Esmeraldas city, along the Pacific coast, where refining activities 138 take place, the water distribution system reaches most of the households but is unreliable 139 supply and safety wise. Therefore, Amazonian and Esmeraldas inhabitants rely on different 140 water sources such as rivers, springs, streams, rainwater, or private wells; sources that are 141 not always safe. Most of the dug wells, in general deep wells (≥ 8 m), were drilled by oil

142 companies as compensation for the disturbance caused by their activities. However, 143 inhabitants dig private shallow wells (<8 m) given that they don't trust the groundwater 144 quality. Then, in this context of extended oil activities in a precarious environment, the 145 presence of pollutants can reach the groundwater, as well as superficial waters 146 (Wernersson, 2004; Webb et al., 2018), highlighting a serious health concern for local 147 populations of the NEAR and Esmeraldas areas. But, in Ecuador, similar to most of 148 countries, effective regulations for drinking waters do not exist or are still inadequate 149 (Kayser et al., 2015; Pinto et al., 2012), mainly because they define thresholds for 150 individual elements and not for the mixture of metallic and organic compounds present in 151 water.

Then, this study aims to measure the drinking water quality level (by determining trace metal(loid)s and hydrocarbons contents) and the associated human health risk in areas influenced by oil industry (production and refining activities) in Ecuador. The two major questions that motivated our research were: i) are the punctual and local wastewater discharges by oil companies in the Ecuadorian Amazon traceable by chemical analysis? and ii) what are the social responses of local communities to face the perceived contamination of drinking water?

159 2. Materials and Methods

160 2.1 Study area

161 Two oil areas were selected for this study (Fig. 1). The first area is located in the Northern 162 Ecuadorian Amazon Region (NEAR) between 76°30'20"-77°12'00"W and 00°05'01"N-163 00°55'11"S covering the Orellana and Sucumbíos provinces. This area was defined by the 164 Ecuadorian Ministry of Environment (PRAS Program, 2010) as the most affected socially 165 and environmentally due to oil activities. The second area is located in the Northern 166 Ecuadorian Pacific Coast (NEPC) between 79°39'27"-79°42'18"W and 00°53'52.00"-167 00°56'41"N in the Esmeraldas province where most of the crude oil refining is performed. 168 During four decades, these zones were associated to a historic record of oil production and 169 many environmental disasters (Buccina et al., 2013). Both regions were compared with two 170 control areas located in the Morona-Santiago province (77°53'12"-78°34'51"W; 2°58'48"-3°31'20"S) in the Southern Ecuadorian Amazon Region (SEAR) and in the Manabí 171 172 province (80°19'59"-80°20'57"W; 1°12'57"S-1°13'32" S) Pacific Coast (SEPC), where 173 neither oil nor mining activities has taken place.

174

175 2.2 Water sample collection

176 From 2012 to 2016, we realized five sampling campaigns of surface and drinking waters in 177 the whole study area: two during the low water stage, two during the flood and one during 178 the falling water stage of the Napo River and tributaries. A total of 83 samples of domestic 179 water were collected from local communities from 7 different sources: 15 samples from 180 deep wells (≥ 8 m depth), 8 from shallow wells (< 8 m depth), 10 from rainwater stored in plastic or concrete tanks, 18 from springs, 10 from rivers, 5 from streams, and 17 of 181 182 households tap water. Among these water samples, 15 were collected from the Pacific coast 183 coming mainly from the water distribution system.

Water sampling was performed in Teflon bottles, using ultra-clean procedures. River waters were filtered (0.45 μ m porosity) in the field on Teflon and cellulose acetate precleaned membranes. Each sample was conditioned by addition of nitric acid (for major and trace elements analysis) and hydrochloric acid (for Hg analysis) and kept cooled (4°C) until
analysis. For PAHs determination, samples were collected in glass vials (10 and 20 mL)
previously calcined at 450°C overnight and kept frozen (-18°C) until analysis. Temperature
(T), potential Hydrogen (pH), electrical conductivity (EC), oxide reduction potential (ORP)
and dissolved oxygen (DO) were measured *in situ* by ®YSI probes.

192

193 2.3 Analytical methods

194 2.3.1 Major and trace elements concentrations

195 Analysis of fluorides, chlorides, sulfates and nitrates were performed by Ion 196 Chromatography (Dionex® ICS 200). The cations Ca, K, Mg, Na and Si were determined 197 by Optical Emission Spectrometry-Inductively Coupled Plasma (ICP-OES, Horiba® Jobin 198 Yvon Ultima2). The determination of trace metal(loid)s elements (TME) was performed by 199 Mass Spectrometry-Inductively Coupled Plasma (ICP-MS, Agilent 7500CE). Total Hg 200 analysis were performed according to the US EPA Methods 1631 (US Environmental 201 Protection Agency (US EPA), 2002) using oxidation-reduction with BrCl and SnCl₂, and 202 finally analyzed by cold-vapor atomic fluorescence spectrometer (CV-AFS, Brooks 203 Rand®). The quantification limits were calculated as 10 times the reagent blanks standard 204 deviation (SD) and listed in the table SI 1. The recoveries were calculated from different 205 River Water Certified Reference Standards; the percentages obtained for anions, trace 206 metal(loid)s and cations were 104±5% (ION-915), 96±10 % (SLRS-5) and 105±4 % 207 (SLRS-5 and EPOND) respectively. The average recovery for total Hg analysis reached 208 92±9 % (ORMS-5).

209 2.3.2 PAHs and BTEX concentrations

Solid-phase microextraction (SPME) was used in immersion mode in combination with gas
chromatography-mass spectrometry (SPME-GC/MS) for the analysis of parent and
alkylated PAHs and BTEX in water samples (8 mL and 10 mL for PAHs and BTEX,
respectively).

214 An Agilent Technologies 7890A/5975C GC/MS (Palo Alto, CA, USA) was used for the 215 analysis of BTEX. A MPS2XL autosampler (Gerstel®) was used to hold the 65 µm 216 PDMS/DVB SPME fibre (Supelco) during extraction and injection. After the addition of 217 perdeuterated surrogate standards, the fibre was immersed into the 10 mL water sample 218 with agitation (250 rpm) at 40 °C during 30 min. After extraction, the fiber was thermally 219 desorbed for 3 min into the liner of the GC injector port at 220°C in pulsed splitless mode 220 (25 psi, 1.5 min). Helium (6.0) was used as the carrier gas at a flow rate of 2 mL.min⁻¹. 221 Analytes were separated on a DB-624 column (30 m x 0.32 mm, 1.8 µm film thickness; 222 Agilent Technologies, J&W Scientific). The column oven program was as follows: 0°C (5 223 min) (liquid nitrogen) to 150°C (1 min) at 5°C.min⁻¹ and then to 260°C (8 min) at 224 30°C.min⁻¹. The MSD was operated with electron impact ionization (70 eV) in selected ion 225 monitoring (SIM) mode. The transfer line, source and quadrupole temperatures were 260, 226 230 and 150°C, respectively. Parent and alkylated PAHs were analyzed using an Agilent 227 Technologies 7890A/5973 GC/MS (Palo Alto, CA, USA) (Kanan et al., 2012). A GC 228 Sampler 120 (Agilent Technologies) was used to hold the 100 µm PDMS SPME fibre fibre 229 (Supelco) during extraction and injection. After the addition of perdeuterated surrogate 230 standards, the fibre was immersed into the 8 mL water sample with agitation (250 rpm) at 231 40 °C during 60 min. After extraction, the fiber was thermally desorbed for 3 min into the 232 liner of the GC injector port at 270°C in pulsed splitless mode (25 psi, 1 min). Helium (6.0)

was used as the carrier gas at a flow rate of 1.3 mL.min⁻¹. Analytes were separated on a HP-5MS-UI column (30 m x 0.25 mm, 0.25 μ m film thickness; Agilent Technologies, J&W Scientific). The column oven program was as follows: 50°C (2 min) to 300°C (5 min) at 10°C.min⁻¹. The MSD was operated with electron impact ionization (70 eV) in selected ion monitoring (SIM) mode. The transfer line, source and quadrupole temperatures were 280, 300 and 180°C, respectively.

239 PAHs and BTEX were quantified by their perdeuterated surrogate standards using their 240 molecular ions (SIM mode). Analyzed compounds (and acronyms) and their limits of 241 quantification (LQs) are listed in Table SI_2 and Table SI_4, respectively. A fiber blank 242 was measured before each water sample by exposing the SPME fiber in an empty vial 243 under the same conditions as the samples. A blank sample (reagents and surrogate 244 standards) and a control sample (blank sample spiked with model compounds) were 245 performed for each batch of experiments in order to check the background contamination 246 and the analytical performance. Whole-method accuracy was determined on spiked water samples (at 10 ng.L⁻¹ in Milli-Q water and 50 ng.L⁻¹ in Vittel water for PAHs and BTEX, 247 248 respectively) and remained between 100-105% (CV < 10%) for parent and alkylated PAHs 249 and 89-98% (CV < 10%) for BTEX. Limits of quantification (LQs) were determined from a 10 signal to noise ratio (SNR) observed in low-spiked samples (Table SI_4), except for 250 251 compounds present in blanks. For these latter compounds, LQs were determined using 252 blank levels, assuming at least a factor three between the analyte mass in the sample and 253 that found in the blank. LQs are in the range 0.3 - 5.0 ng.L⁻¹ for parent and alkylated PAHs, and 2 - 9 ng.L⁻¹ for BTEX, except for benzene (100 ng.L⁻¹). 254

255 2.3.3 Microbiological analysis

Water samples were collected in sterile flasks, refrigerated and analyzed within 12 hours of collection. One mL of raw sample was plated onto selective $3M^{TM}$ PetrifilmTM 6404/6414/6444 plates (3M Microbiology Products, St. Paul, MN) and incubated following manufacturer instructions. The concentrations of total coliforms and *E. coli* were determined within 24-48 h of incubation time at 30°C. Confirmed coliforms are red or blue colonies with associated gas bubbles. Confirmed *E. coli* are blue colonies with associated gas bubbles. Results are accurate between 25-250 colonies of total coliforms per plate.

263

264 2.4 Sociological methods

265 "Risk culture" refers to the oil contamination risks awareness, behaviours and social 266 practices to cope with it in everyday life, considering another set of risks (social, 267 economic), and the capacity to think the building of future projects at both individual and territorial scale (Becerra et al., 2015). The sociological study was centred on two rural 268 269 parishes of the NEAR, Dayuma (Orellana Province) and Pacayacu (Sucumbíos Province). 270 We studied how people perceived and managed their environment and the associated 271 contamination risks. Water resources were not the only issue considered in the interviews, 272 while it appeared as the main concern. We focused on both mestizo¹ and indigenous 273 communities. Primary sociological data were collected during five field surveys between 274 2012 and 2016, most of them during the water sampling campaigns. Our study is novel in 275 interdisciplinary scope, from inception though application, combining faster environmental 276 monitoring with slower-paced sociological studies that facilitate trust-based relationships 277 with study participants. Were realized 160 qualitative interviews, according various levels

¹ In other words, the individuals who consider that they don't belong to any ethnic group or native nationality because their parents have different geographical and cultural characteristics.

of exposure, living next to possible sources of contamination. Various generations as well as both genders were represented. Around 30 interviews were conducted with elected officials and community leaders. Interviews were built around 4 general topics: 1) History of life; 2) Living conditions (economic incomes), perceptions of oil activities impacts (positive and/or negative), perception of their regulation by local or national authorities; 3) Attitude towards the future (quality of life, future projects); and 4) Biographical data (age, nationality, education level, etc.).

285

286 2.5 Health risk assessment

Risk assessments were carried out according risk management measures proposed by the WHO (2014). Since human exposure to multiple chemical mixtures is ubiquitous (polluted air, soil and water), we used US-EPA guidelines (Callahan and Sexton, 2007) for assessing the cumulative risk related to these chemical cocktails and considering different pathways for toxic compounds into the body, with ingestion and dermal contact as main exposure routes (Barraza et al., 2018; US EPA, 2015a,b).

293 Mathematical equations of the Probabilistic Risk Assessment (as published by Barraza et 294 al., 2018) allow us to evaluate the Hazard Index (HI) and the Total Cancer Risk (TCR), 295 which are defined as the addition of individual quotients of non-carcinogenic (HQ) and 296 carcinogenic (CR) elements respectively, obtained from the average daily dose (ADD), the 297 lifetime average daily dose (LADD) and the references doses (RfD) (US Environmental 298 Protection Agency (US EPA), 2015a, 2015b). For drinking water, we supposed a daily 299 consumption rate of 3 L and 1.5 L for adults and children, respectively and an annual 300 exposure frequency of 350 days per year, assuming that people moved 15 days every year 301 in the Amazon region. Values of HI higher than 1 means that adverse health effects can

302 occur. The TCR is the accumulation of cancer risk values (CR) calculated for carcinogenic

303 elements (As, Cd, Cr, Ni) and PAHs by the product of slope factor (SF) and LADD. The

304 TCR is then compared with the guidelines given by the US EPA meaning the probability of

305 providing cancer risks of 10^{-4} (1 in 10 000) or 10^{-6} (1 in 1 000 000).

306

307 2.6 Statistical analysis

308 Software ©Rstudio (Version 3.5.1) was used for statistical analysis and box plots figures. 309 One sample t-test was used when data showed a normal distribution (Shapiro-Wilcoxon 310 test). In other cases, variables were log-transformed to follow a normal distribution. A 311 confidence level of 0.95 was chosen. Pearson coefficient correlations were calculated to 312 check the significance of the correlations between the parameters.

313

314 **3. Results**

315 3.1 Physico-chemical parameters

316 Physico-chemical parameters of drinking waters (Table 1) were compared with the 317 different water quality guidelines (WQGs) reported in the Supplementary Information 318 (Table SI_3).

In the drinking water sources of the Amazon region, the pH values ranged from 3.5 to 8.7 (average of 5.8±1.3) with an extreme minimum value of 2.5 in a forest spring (Shuara 09 oil camp). Most pH values (73%) were in the range of the Ecuadorian quality guidelines. Several water sources were found to be acidic: the river water from the SEAR (4.80±1.47), and the rainwater (pH of 4.84±1.02). The only neutral sources were stream and distribution
system waters (7.02±1.38 and 7.16±0.51, respectively).

The EC range (3-1479 µS.cm⁻¹; average: 122±204 µS.cm⁻¹) showed that all the samples 325 326 were lower than the maximum recommended value (1100 µS.cm⁻¹), except in a deep well 327 (26 m) in Pacayacu (NEAR). Only 19% of the samples were in line with the WQG used in 328 France (200-1100 µS.cm⁻¹): most of the water samples (78%) showed conductivity lower 329 than 200 µS.cm⁻¹, and can be considered as demineralized waters. In the Amazon Region, rainwaters showed the lowest conductivity in both, the oil $(11.9\pm12.9 \ \mu\text{S.cm}^{-1})$ and control 330 area (5.21 µS.cm⁻¹). Only the deep wells (272.2±348.5 µS.cm⁻¹) and system waters 331 332 $(224.3\pm152.2 \ \mu\text{S.cm}^{-1})$ in the NEAR, and river surface water $(237.7\pm139.2 \ \mu\text{S.cm}^{-1})$ in the 333 SEAR showed conductivity higher than the recommended value (200 μ S.cm⁻¹). However, in Esmeraldas, the tap water conductivity never reached the minimum WQG (200 µS.cm⁻¹). 334 335 Concerning the total dissolved salts (TDS) content of the samples, it was found to be very low falling below the minimum concentration of 100 mg. L⁻¹ and the optimal range of 250-336 500 mg. L⁻¹ set by WHO. Only water from deep wells and the distribution system met the 337 338 minimum recommended value.

339

340 3.2 Major and TME concentrations

The analyzed anions (Table 1) are present in concentrations compliant to the local and international standards but lower than the recommended WHO guidelines. For example, all analyzed sources were deficient in fluoride based on the minimum level of 0.5 mg.L⁻¹ recommended by WHO (2005) for dental health. Similarly, most of the major cations' 345 concentrations (for example Ca and Mg) were lower than the minimum 2005 WHO346 guidelines (Fig. 2).

Regarding Al concentrations, all the water sources sampled in the Amazon region (SEAR and NEAR) showed values in a similar and acceptable range (WHO, 2005). While in the public water system (Fig. 3), these concentrations exceeded regularly 200 μ g.L⁻¹, explained by the utilization of aluminum sulfate as flocculent during the water treatment. A similar behavior was observed with Fe concentrations, both elements presenting a common origin from the soil weathering; tropical, ferralitic soils are characterized by elevated Al and Fe contents (Mainville et al., 2006).

Manganese concentrations in drinking water sources ranged between 0 and 2373 μ g.L⁻¹, and averaged 72 μ g.L⁻¹; the highest concentrations being measured in a deep well close to Pacayacu village in a private property (Pichincha 11, Libertador oil camp). In the majority of private water wells, Mn concentrations exceeded the recommended values by Ecuador (100 μ g.L⁻¹), and *a fortiori* France and Canada (50 μ g.L⁻¹), while in rivers, springs and water systems, they were acceptable (Fig. 3).

The Zn concentrations in samples collected from rainwater tanks were significantly higher than other sources (Fig. 3). Even though high concentrations of this element are not of health concern, a limit of 500 μ g/L was considered as WQG in France, being the most restrictive value among the legislations consulted; all rain waters exceeded this limit. In isolated areas of the Amazon basin, people collect rainwater from their home's roof. The acidic rain water passing through the roofs leached, dissolved and transported dissolved Zn to water tanks.

The elements As, Cd, Cr, Ni and Pb and Co are considered carcinogenic (group 1 and 2A), while oxides of Sb, V and Mo are defined as possibly carcinogenic (2B) by the IARC. System water and (deep and shallow) wells presented the highest values of As, Ni, Cr, Pb, Sb, and V without exceeding the WQGs. Chromium concentrations were very low (average of $0.56\pm5.44 \ \mu g.L^{-1}$) and the maximum value (10.57 $\ \mu g.L^{-1}$), lower than the WQGs, was measured in the Dayuma tap water. The increase of these carcinogenic elements may come from the pipework quality of the water distribution system. Antimony in rainwater presented also a mean concentration ($0.087\pm0.097 \ \mu g.L^{-1}$) higher than in the other sources, but lower than the recommended limits.

376

377 3.3 PAHs concentrations

378 All aromatic organic compounds (PAHs and BTEX) concentrations measured in the 379 analyzed drinking waters (Table SI_4) were in line with the WQGs, even in the NEAR. The 380 benzo(a)pyrene considered as carcinogenic (group 1) was under the quantification limit in 381 all the samples. However, high values of toluene (2000 to 6000 ng.L⁻¹) were measured in 382 deep wells of the "12 de Febrero" community in San Carlos village located on the Sacha oil field. Benzene (also classified as carcinogenic group 1) was present in the water from the 383 384 distribution system in Esmeraldas (NEPC) and Portoviejo (SEPC) sampled in 2016 but these significant concentrations (490 to 710 ng.L⁻¹) close to the WQG (1000 ng.L⁻¹), were 385 386 not detected in 2017. The results of 2016 can be due to the contamination of the water 387 stored by residents in plastic or metallic tanks as a solution for the frequent water network 388 shortages. Our results show that there is a risk of accidental and local contamination of 389 drinking water by benzene in collection tanks from traffic or industrial emissions in 390 Esmeraldas city.

392 3.4 Bacteriological results

393 One of the main health concerns was the presence of Escherichia Coli and total coliforms 394 in water sources sampled in the Amazon region which could reach in deep wells up to 40 395 and 700 CFU.100 mL⁻¹, respectively, except in the public water distribution systems. 396 According to international regulations on drinking water quality, Escherichia Coli and total 397 coliforms must be absent in drinking water. Untreated wastewaters, agricultural runoffs, 398 migration and development of microorganisms in wells and shallow surface waters exposed 399 to light and high temperatures can contribute to the development of coliforms. Therefore, it 400 would be crucial to disinfect (e.g. boiling, chlorination) any kind of water sources in the 401 Amazon region prior to consumption to prevent any risk of water-borne diseases.

402

403 3.5 Human health risks assessment

For both adults and children (Table 2), the ingestion hazard index (HIing) showed a contribution of 99 to 100% to the non-carcinogenic total health risk (THI). Compared to the reference value (US EPA, 2015), 7% and 27% of the THI obtained for deep well water sources was higher for adults and children, respectively.

For adults, the HI values ranged from 3.4×10^{-02} to 2.6 and from 1.4×10^{-04} to 2.0×10^{-02} for ingestion and dermal routes, respectively. From the sites that shows HQ values > 1 (Table SI_5), two samples came from the NEAR, with the highest value (THI=2.6) in Dayuma due to high aluminum concentrations (HQ=1.8) in the system water, and in a deep well (HI=1.1) with an elevated hazard quotient in Mn (HQ=0.75). Along the Pacific coast (NEPC), only one sample showed a HQ value > 1, corresponding to a tap water collected from a pumping and storage station in front of the discharge channel of the main refinery ofthe country; this elevated HI (1.8) is mainly explained by the Cd content (HQ=1.5).

416 For children, no contribution of dermal exposure was found in the total hazard index. The ingestion route in the THI ranged from 7.5×10^{-02} to 5.5. From all the samples, 9 (11%) were 417 418 higher than the reference value (US EPA, 2015). The highest THI values were found in 419 deep wells waters of the NEAR, two in Pacayacu (HI =1.6 and 0.61 due to Mn 420 concentrations), and two in Dayuma (HI=1.32 and 1.38 explained by As concentrations), in 421 a private well and in the stadium, respectively. Individually, hazard quotients >1 in 422 rainwater were found in the whole Amazon region, being Zn the element that contributed to 423 most of the total hazard index (HQ of Zn=1.01 and 1.06, in the NEAR and SEAR 424 respectively). Finally, in the system water from Dayuma (NEAR), we found one point with 425 a high concentration of Al in Auca 09 field corresponding to THI equal to 3.9. In the 426 NEPC, the highest risk explained by Cd (HI=3.13) and As (HI=0.38) concentrations were 427 found in Esmeraldas, in the potable water pumping station and in a particular house, 428 respectively.

For both, adults and children, water from a deep well located in the stadium of Dayuma
(NEAR) presented the highest contribution (93%) of carcinogenic molecules in the dermalHI, while regarding the ingestion risk contribution, system water from the pumping station
close to the refinery exhibited a contribution of 88% to the total HI.

It is interesting to notice that, the hazard quotient of arsenic represents between 20% and 434 49% of the total ingestion HI (Fig. 4), while As concentrations never exceeded 3 μ g.L⁻¹. In 435 the Total Cancer Risk (TCR) calculated for carcinogenic elements (As, Cd, Cr and Ni), 436 arsenic contributes with 51% to 100% in 65 points (78% of the total sampling points). In 437 Esmeraldas, Cd contributes with 56% to 94% of the TCR in 4 system water samples.

439 **4. Discussion**

440 4.1 Impacts of oil activities on drinking water quality

Vanadium, Ba, Ni, Co, Mo and PAHs (except AC, IP, and Pe) are the main elements and 441 442 compounds that can trace oil activities impacts in the hydrological system, due to their high 443 contents in the Ecuadorian Amazon crude oil (Table SI_6). High concentrations of V 444 (305±36 mg.kg⁻¹), Ba (133±5 mg.kg⁻¹), Ni (99±11 mg.kg⁻¹), Co (1.82±0.04 mg.kg⁻¹), and Mo (0.93±0.02 mg.kg⁻¹) were measured in a topsoil sampled in a waste pool (from the 445 446 Auca 08 oil well, NEAR). These values were slightly higher than the concentrations 447 measured in fresh crude oil from the same oil camp (Auca 03), except for barium (7±1 448 mg.kg⁻¹). However, the crude from the national oil pipeline showed slightly lower values of 449 toxic compounds than these in the waste pool soil except for PAHs (Table SI_6). Barium is 450 then considered as a relevant element to trace oil activities since barite (barium sulfate) is 451 commonly used in drilling activities. This element in surface and groundwaters mainly 452 comes from the soil drainage, as in Ecuador these sources are defined as calcium 453 bicarbonate waters where barium salts may precipitate easily (Kabata-Pendias and Szteke, 454 2015). All the Ba values measured in the study drinking waters were in line with the 455 WQGs. The only elements that exceeded the WQGs thresholds were Al, Fe, Mn, Cu and 456 Ba; these elements mainly originate from the natural soil erosion and are not of health 457 concern at observed concentrations except for Mn. The water sample from Pacayacu 458 (Pichincha 11 oil camp) presented concentrations in most of the analyzed elements and 459 compounds 10 to 100 times higher than the sampling points average. Manganese

460 concentrations were higher than 50, 100 and 500 µg.L⁻¹ in 11%, 9% and 4% of the samples, 461 respectively. The highest concentrations were all observed in private or public deep wells. 462 Manganese can be related with agriculture practices, as it is one of the main components in 463 fertilizers, animal food, and pesticides. As proposed by Van Wendel de Joode et al. (2016), 464 drinking water risk assessment should consider Mn as a health hazard. Several studies have 465 shown a negative association between elevated Mn concentrations in drinking waters and children's neurodevelopment, behavior and academic achievement (Bouchard et al., 2011; 466 467 Van Wendel de Joode et al., 2016).

468 Regarding organic toxic compounds, no pollution by hydrocarbons was found in the study 469 water samples. The unique concern highlighted in drinking water sources which can 470 originate from the oil activities, was the toluene and the sum of methylnaphthalene 471 concentrations measured in several deep wells in the San Carlos community (located on oil 472 camps managed by the Rio Napo Company), nevertheless without exceeding individually, national and international guidelines. Individual alkylated PAHs have been observed to 473 474 have potentially mutagenic, tumor-promoting, or carcinogenic activity and their toxic 475 potential may easily surpass that of the parent compounds (Andersson and Achten, 2015). 476 However, the concentrations of di- and tri-methylnaphthalenes were very low, but except 477 for 1- and 2-methylnaphthalene, insufficient toxicity data is available to quantify cancer 478 risk from chronic exposure to individual or mixtures of alkylated PAHs. Considering the 479 concentrations ranges of carcinogenic PAHs, we may suppose that direct ingestion of water 480 and dermal contact are probably not the main exposure routes. This hypothesis was 481 confirmed by the Total Cancer Risk indexes calculated for parents and alkylated-PAHs 482 (section 3.5).

On the other hand, we observed just two significant correlations between toxic compounds and oil activities impacts. These moderate and positive correlations were found between the number of pits in the vicinity area of the sampling points and MA (2-methylanthracene; r=0.43) and total dissolved Hg (r=0.47) concentrations. However, no correlation was found with the oil spills frequency, nor with the number of flares or oil waste pools.

488

489 4.2 Drinking water risks due to low mineralization

490 In the whole Ecuadorian Amazon Region and along the Pacific Coast, the study water 491 sources presented very low mineralization levels, till 10 to 100 times lower than the 492 WHO's minimum recommended concentrations (WHO, 2006), with certain exceptions in 493 deep wells. Although high concentrations of certain major elements can affect the human 494 health (Nerbrand et al., 2003), it is very important to pay attention to acid and low 495 mineralized water sources as well. Acid pH water can accelerate the leaching of toxic 496 metals and other compounds from roofs or distribution pipes and modify the taste. Acidic 497 pH is characteristic of rainwaters which feed spring and shallow groundwater and is the 498 main source of drinking water for local people. The percolation of rain waters in tropical 499 soils of the Amazonian plain does not change the water pH as these soils are acidic and 500 highly weathered. Additionally, the lack of minerals can cause direct health effects like 501 tooth caries due to the lack of fluoride, malfunction of the intestines, reduction of calcium 502 and magnesium intake and other essential elements as well as an increase of intake of toxic 503 elements, due to their dissolution in acid waters during the cooking for example (WHO, 504 2006). For about 50 years, epidemiological studies in many countries all over the world 505 have reported that soft water (i.e., water low in Ca and Mg) is associated with increased

506 morbidity and mortality from cardiovascular disease (CVD) compared to hard water and 507 water high in Mg (Kozisek, 2005). Epidemiological studies of an ecologic design among 508 Russian populations supplied with water varying in TDS suggested that low-mineral 509 drinking water may be a risk factor for hypertension and coronary heart disease, gastric and 510 duodenal ulcers, chronic gastritis, goiter, pregnancy complications and several 511 complications in newborns and infants, including jaundice, anemia, fractures and growth 512 disorders (Turnlund, 2002). The intake of low water-content in Ca, is associated with a 513 higher risk of fracture in children, certain neurodegenerative diseases, pre-term birth and 514 low weight at birth and some types of cancer (Kozisek, 2005). The WHO established in 515 1980 minimum and optimum levels of minerals and recommended that demineralized water 516 contains: for Mg and Ca, a minimum of 10 and 20 mg.L⁻¹, respectively, and an optimum 517 range of 20-30 and 40-80 mg.L⁻¹, respectively. For total water hardness, the sum of Ca and Mg should be 2 to 4 mmol.L⁻¹ (Kozisek, 2005). In rainwater, the most important drinking 518 519 water source for Amazonian communities, the Mg and Ca average concentrations were less 520 than 0.01 and 1.28 mg.L⁻¹, respectively. Average concentration of Na in rainwater was 0.12 521 mg.L⁻¹, 2000 less than the minimum recommended value (WHO, 1980).

Another issue caused by the regular domestic use of low mineralized water is the loss of essential minerals from food during the cooking, mainly of Mg and Ca and in a less extent of essential microelements (Cu, Mn and Co). A low diversified diet due to precarious living conditions coupled to the domestic use of demineralized water reduce the nutrients intake by local populations and participate to the child undernutrition.

527 It appears that the health risk tied to the chronic exposure to low mineralized water can be 528 as important or in some cases, more important than the health risk related with current oil 529 activities. Though, it is necessary to pay attention to specific sampling points (deep wells) were the total hazard index and total cancer risk denote that inorganic elements related with oil production (as V or Mo in surface water, Table SI_5) can contribute significantly to the sanitary risk.

However, the quality of rainwater may subsequently deteriorate during harvesting, storage and household use (WHO, 2011). In the Amazon region, many families collect rainwater from their house' roof, explaining the very high concentrations of Zn measured in this water source. Later, they store it in large plastic or metallic tanks without any cover where wind-blown dirt, leaves, insects, fecal particles, or particles from the atmosphere or from burning materials (e.g. trash or oil flares) can contaminate the stored rainwater.

539

540 4.3 Limits of Ecuadorian Regulations

541 We suggest three types of limits in the National environmental regulations: legal, technical542 and political.

543 4.3.1 Legal limits

544 In Ecuador, two regulations have been set up: the INEN 1-108 and the TULSMA (Texto 545 Unificado de Legislación Secundaria del Ministerio del Ambiente). The Ecuadorian 546 regulation INEN 1-108 is related to treated water for human consumption, and certain 547 parameters, such as pH, conductivity or oxygen percentage were omitted from the 2014 548 latest version compared to the 2006 version (Table SI_3). Regarding the inorganic 549 compounds, from 34 parameters considered in the 2006, only 18 were proposed in 2014. 550 For example the Mn threshold values increased from 0.1 mg.L⁻¹ in 2006 to 0.4 mg.L⁻¹ in 551 2011, to completely be removed in 2014. From 5 PAHs regulated in 2006, INEN reduced 552 to one molecule in 2014, the Benzo(a)Pyrene, with a maximum permissible value (MPV) higher than in the 2006 version. For BTEX molecules, toluene MPV became more permissive, and ethylbenzene regulation disappeared. A restriction of the maximum permissible limit for microbiological parameters was also observed, reducing the MPV for fecal coliforms from 2 NMP.100 ml⁻¹ in 2006 to 1.1 NMP.100 ml⁻¹ currently, and eliminating total coliforms guidelines.

558 The second Ecuadorian regulation, TULSMA, is applicable to natural water sources for 559 human consumption prior to any treatment. In its last version (November 2015), this regulation only considered treated-clean waters and raw water that needed a physical 560 561 treatment and presented a lower number of parameters than the former text. The MPV of 562 some elements, such as Cd, increased from 0.003 mg.L⁻¹ in February, 2015 to 0.02 mg.L⁻¹ 563 in November, 2015. Concentrations of PAHs and BTEX in drinking water sources are not 564 regulated. The current version for fecal coliforms set up a lower concentration (1000 565 NMP.100 ml⁻¹) than the previous ones (2000 NMP/100 ml) but it still remains very high.

566 Then, during the last decade, both Ecuadorian regulations, INEN and TULSMA, have not 567 just reduced the number of control parameters but also proposed less restrictive values 568 without considering international recommendations. Since international regulations (Santé-569 Canada, WHO, US-EPA and European Union) are based on epidemiological and risk 570 assessment studies, we considered them in this study as more adequate water quality 571 references for the health risk assessment discussion. Nevertheless, concentrations 572 thresholds are related to individual elements or molecules, or for groups of specific metal or 573 organic contaminants but not for chronic exposure to cocktails of both categories of toxic 574 elements and compounds.

575 4.3.2. Technical limits

576 These limits are mainly due to the weakness of technical capacities of local stakeholders. In 577 the different visited communities, we found collective water supply systems installed by 578 local autonomous governments that were often ineffective. Many of these systems were 579 abandoned because of the lack of water availability, and/or of pump maintenance. This 580 ineffectiveness reflects two realities combined in the Amazon region: i) the lack of 581 technical ability of the projects managers and ii) lack of proper management of public 582 resources (Juteau-Martineau, 2019). Sometimes, under the pretext of public utility projects, 583 public funds can be redirected to non-public matters.

584 *4.3.3. Political limits: political ability to relay the social demands*

585 People in charge of community relationships between public oil companies and local 586 inhabitants have always negated the link between river's contamination and oil activities. 587 According to them and policy makers, water quality degradation is mainly due to the 588 presence of total and fecal coliforms, given that wastewater treatment is not available in the 589 country, except in big cities. They don't constitute any opposition force that would set up a 590 water quality monitoring or at least the compliance of safety regulations. The latter does not 591 reflect the social experience of inhabitants of the oil region, with what they observed in 592 their own farm or in the close river, this experience leads them to ask for remediation, 593 compensation and indemnity. The local political ability to relay the social demands varies 594 from place to place. For example, in the Management Plan of Pacayacu, oil activities are 595 not accounted as responsible for the poor water quality, in contrast to the Dayuma Plan that 596 holds oil companies responsible for the contamination of water resources, even during environmental remediation activities. 597

599 4.4 Social perception of the risk and human exposure

600 Perceived environment and perceived exposure to health risks

601 In the Amazon basin, traditionally, indigenous and mestizo use water sources close to their 602 home, from rivers, streams, rainwater or shallow wells. But in the oil Amazon basin, the 603 lack of access to drinking water is the major concern expressed by communities living close 604 to oil infrastructures (Fig. 5), not only for inhabitants but also for cattle. The social 605 experience of the environmental pollution is stable with time and the general resentment is 606 that "everything is polluted and oil companies are lying". Contamination is mainly 607 perceived empirically, directly from the farms or indirectly from a decrease in aquatic 608 biodiversity.

609 The interviews conducted in the NEAR showed 2 main social responses to perceived 610 contamination of local water resources, *Exit* and *Voice* (as proposed by Hirschman, 2011): 611 *Exit* means leaving the current water supply. At the household level, harvesting rainwater is 612 today perceived as the safest and most effective way to collect water even if in fact various 613 sources are combined (rainwater, wells, rivers or spring). Harvesting rainwater has 614 undergone a rapid development thanks to the social compensation programs systematically implemented by the National oil Company, Petroecuador, since the 2000's. During oil 615 616 exploration campaigns or when opening new platforms, the public company offered zinc 617 plates to cover the roofs of many communities' houses and water tanks to store the clean 618 water. Later filtration systems were offered by NGOs to specific families involved in the 619 protestation against oil activities. At the community scale, collective action took place: for 620 instance, two communities close to the urban centre of Pacayacu developed their own 621 drinking water supply system within a "minga", an indigenous practice of cooperative and

voluntary work for the common good. One of them has failed due to the lack of technicaland financial maintenance.

624 Voice: In the centre of Pacayacu village, most of the inhabitants contrary to the position of 625 the leaders, do not trust the quality of the drinking water system and choose the « voice » 626 thanks to the help of the NGO "Acción Ecológica". The mobilization, coordinated by this 627 same NGO, operates in different ways: creation in 2009 of the "environmental clinic" as an 628 alternative program to restore the environment and livelihoods of about 30 families living 629 in the oil impacted area; in 2011, opening of a defense committee of families that perceived 630 a local contamination of their water resources, and organization of "Toxic-tours" in Atacapi 631 and Libertador oil camps.

632 *Facing the risk but to which risk high priority is given?*

633 The perception of the contamination risk was largely shared in the interviewed families as 634 72% of them knew about sanitary risks linked to bad water quality. But there was a discrepancy between knowledge and action, as social investigations underlined for other 635 636 risks (Weiss et al., 2011): existence of the first (knowledge) does not guarantee the second 637 (action). It is important to distinguish between the drinking water supplies: primarily public 638 water system in urban centres and rain, river or private wells in rural areas. Paradoxically to 639 the perceived sanitary risk, the adopted strategy is not always to reduce the exposure. An 640 oil spill in a private farm is generally conserved as a proof of oil activities damages and 641 used to ask for material compensation (job or material good) or money (Becerra et al., 642 2016). Similarly, a riparian who saw his water resource damaged by an oil spill for 643 example, won't necessary look for other water sources for domestic use.

644 The role of religious beliefs, cultural ideals, experience and emotions were evaluated in 645 order to understand why people resist to change their practices to face supposed polluted 646 water sources.

Religious beliefs. Data collected from interviews with mestizo people showed that culture risk is highly influenced by religious beliefs in at least two ways. First, faith can bring a certain form of fatalism towards one's own existence. Some individuals could also stop worrying about the future since God decides for them. Data collected gave numerous references to biblical scriptures.

652 Cultural ideals and practices. Change to prevent sanitary risk depends first on social 653 perceptions of the risks, and secondly on a cultural process, but also depends on the 654 existence of other available alternative ways and on adequate financial resources. In the 655 Amazon forest, Shuar and Kishwa communities have a strong reliance on nature and 656 surface waters because of their ancestral culture. Their spirituality is based on the principle 657 of Mother Earth as well as deities of the jungle, the agricultural garden "chacra" and the 658 water. They usually leave far from towns or oil infrastructures. Even if these groups tend to 659 evolve toward a cultural hybridism (for instance integrating modern food to their diet), they 660 prefer natural food and water from the farm, rivers or mountains (Beguet, 2015). 661 Furthermore, in indigenous groups, environmental pollution is unequally perceived. We 662 observed in Shuar and Kischwa groups that generally, this perception by women is less 663 noticeable than by men: maybe because women usually don't work for oil company 664 (Racines, 2017).

665 *Sensitive experience*. Danger is learned by sensitive experiences which could be traduced 666 by: *"the kick warns you and the damage teaches you*". Since health effects of 667 environmental exposure are not immediate, people tend not to change their practices and

the collective action stops to the suspicion or denunciation. Social determinants such as the high rates of unemployment and poverty (Larrea and Camacho, 2013) explain the difficulty to get out from this situation of "environmental suffering". People respond to the contamination of water in a confused way. As explained by Auyero and Swistun (2007) often people under these conditions have "toxic confusion", as awareness of their situation is distorted by lack of knowledge of the real causes which leads to inappropriate behaviors.

674 *Chronic and historical distrust of oil companies.*

675 Due to numerous social liabilities between oil companies and Amazonian communities, 676 health issues related to water contamination are attributed by inhabitants to the impact of oil 677 activities which obscure the complexity of the causes neglecting all the historical and 678 political context that is responsible for poor human health, limits the perception of their 679 own responsibilities and inhibits practices changes. Because of this situation that despite 680 the awareness of rivers and water being contaminated, people are not changing their daily 681 practices based on the hope that finally, there will be some recognition and retribution due 682 to the damage caused by the oil companies during the last decades. Each emergence of 683 cancer cases, whatever its origins, nourished the proofs list against oil companies' 684 activities. The social liability acts as a psychological lock that convinces inhabitants and 685 NGOs that only oil companies are responsible of the environmental and sanitary hazards of 686 the region.

687 **5. Conclusion and recommendations**

688 Contrarily to the common prejudices, this study showed for the first time that the health 689 risks due to drinking water exposure could be more impacted by the precarious living 690 conditions than by the oil activities in the Ecuadorian Amazon region. Local people routinely chose the water sources based on the end-use, availability and some of themregarding their perception of contamination risks especially after an accident (oil spill).

693 International and national regulations are generally based on maximum acceptable 694 concentrations of inorganic and organic compounds because water may contain elements 695 and molecules that are undesirable. Main of the different water sources sampled in Ecuador 696 can be considered as suitable for human consumption. It is important to control the quantity 697 of aluminum sulfate in the system during the water treatment as well as the way of 698 collecting and storing rainwater. Regarding Mn, a well-known neurotoxin, the high 699 concentrations observed in private wells can also be related to agriculture (use of 700 pesticides; van Wendel de Joode et al., 2016). Arsenic which contributes from 20% to 49% 701 to the ingestion health index, is naturally present in high concentrations in soils and waters 702 of most of Latin America regions (Bundschuh et al., 2012). But the novelty of this study is 703 the low mineralization of the drinking water sources which could be an important health 704 issue due to the deficiency in essential minerals like Ca, Mg and F. The addition of salt 705 enriched with fluoride and iodine into the cooking water is a common practice, but not used 706 everywhere in Ecuador, especially in remote areas. Most of the symptoms as fatigue, 707 stomachaches or dizziness, often signaled by the population can be related with the low 708 concentrations of minerals in their domestic water.

In Ecuador, agricultural runoffs and discharges of household effluents into water bodies without previous waste treatment seems to be the main source of microbiological pollution, confirmed by the presence of fecal coliforms in almost all the drinking water samples. It appears primordial before consumption, to disinfect or boil any kind of water sources before use in areas where there is no access to treated clean water. At the national level, public policies should address this problem by extending rural potable water supply and

715 waste water treatment systems to the communities living in remote areas of the Amazon716 region.

717 Although no toxic compounds in drinking water samples exceeded the international water 718 quality guidelines, human co-exposure to low mineralized water and volatile organic 719 molecules needs more attention in oil impacted areas. Local people living in these areas 720 still endure the insufficient recognition of historical impacts of oil exploitation by the 721 Ecuadorian government, confirming that information can be considered as a sort of power 722 that should be shared. Till now, without any satisfactory processing of the historical 723 impacts of the oil activities in the country, inhabitants of the NEAR focus their problems on 724 oil companies ignoring other possible sources, such as agriculture practices or the lack of 725 water treatment. The belief held by many of the inhabitants that oil companies are the only 726 reason for water pollution is part of a symbolic process by which water pollution 727 crystallizes the set of social and environmental claims in front of oil industry. Water quality preservation is the most shared argument that can become a symbol of the oil companies' 728 729 environmental debt and of the government to solve this issue.

730

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Figures captions

Figure 1. Hazards description (flares, oil spills, pools and pits, refinery, oil fields and pipelines) and sampling points of drinking waters (from various sources: rainfall, river, spring, stream, well) in four study areas: A) Northern Ecuadorian Pacific Coast (NEPC), B) Northern Ecuadorian Amazon Region (NEAR) and C) in two control zones (Southern Ecuadorian Amazon Region (SEAR) and Southern Ecuadorian Pacific Coast (SEPC)).

Figure 2. Major element concentrations in drinking water sampled during the 2012-2016 period, in (A) the Northern Ecuadorian Amazon Region (NEAR) and in (B) the control zone in the Southern Ecuadorian Amazon Region (SEAR); the red and blue lines report maximum and minimum values recommended by the World Health Organization for drinking water (2005) respectively; international water quality guidelines (WQG) are reported.

Figure 3. Al, Fe, Mn, Zn and Ba concentrations in drinking water sampled during the 2012-2016 period, in (A) the Northern Ecuadorian Amazon Region (NEAR) and in (B) the control zone in the Southern Ecuadorian Amazon Region (SEAR). The red and blue lines report maximum and minimum values recommended by the World Health Organization for drinking water (2005), respectively; international quality guidelines (WQG) are reported.

Figure 4. Distribution of ingestion and dermal contact Hazard Index (HI) for the Amazon and Pacific Ecuadorian regions, followed by the percentage of samples that overcome the Total HI reference value (US EPA, 2015b) in children and adults.

Figure 5. The 20 most cited words in Spanish by local people living in Dayuma and Pacayacu villages (©NVivo simulation).



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Start-----Table 1

Table 1. Local metrics^{#,##,b,c}, inorganic major element ^b and metal(oid)s average concentrations (±Standard Deviation)^{d,e} in different sources of domestic water in the Northern and

Southern Ecuadorian Amazon Regio	n (NEAR and SEAR,	respectively) and in the Nor	rthern and Southern Ecuadorian	Pacific Coast (NEPC	and SEPC, respectively).
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	NEAR							SEAR					NEPC		SEPC	
PARAMETER	deep well	rainfall	river	shallow well	spring	stream	system	rainfall	river	spring	stream	system	rainfall	system	system	shallow well
Elevation [#]	281±17	276±18	264±10	264±6	283±12	293±36	266±6	321*	301±22	497±278	850*	303*	108*	32±25	65*	74*
T ##	27±3	28±4	25*	26±1	26±2	27±1	29±3	24*	25±1	25±2	23*	25*	23*	27±2	29*	29*
EC ^a	272±349	12±13	82±91	156±59	60±67	86±66	224±152	5*	238±139	31±28	60*	49*	17*	144±63	210*	1319*
рН	6.11±1.03	4.84±1.02	6.12±2.06	5.61±0.42	5.2±1.43	7.02±1.38	7.16±0.51	7.11*	4.80±1.47	5.64±1.17	7.26*	6.69*	7.11*	7.01±0.19	6.82*	6.7*
OD ^b	3.25±2.42	4.89±2.34	5.37±1.99	3.33±2.68	5.24±1.9	5.97±2.78	5.96±1.76	2.56*	5.57±1.87	2.82±2.13	2.02*	2.05*		3.62±0.92	4.34*	3.12*
OD ^c	43.9±27	63±28	68.4±17.6	42.4±33.7	66.8±22.3	71.5±28.5	77.9±19.4	29.9*	66.6±22.6	33.6±24.8	23.8*	24.8*		46.9±10.9	57.5*	42.9*
CaCO ₃ ^b	75.5±49.7	5.76±7.69	29.2±22.2	45.7±14.8	23.9±27.2	34.2±24.5	46.1±21.7	4.42*	47.2±29.3	13.9±13.2	28*	23.3*	2.14*	30.9±18.5	66*	239.2*
Bicarbonates ^b	92.1±60.7	7.03±9.38	35.7±27.1	55.7±18.1	29.2±33.2	41.8±29.9	56.2±26.5	5.4*	57.6±35.8	16.9±16.1	34.2*	28.5*	2.61*	37.8±22.6	80.5*	291.8*
Fluorides ^b	0.12±0.17	< 0.02	0.04 ± 0.04	0.03±0.02	0.03±0.04	0.06 ± 0.04	0.07 ± 0.04	<0.02*	0.08 ± 0.02	0.04±0.03	0.07*	0.07*	<0.02*	0.08±0.03	0.17*	0.36*
Chlorides ^b	25.28±83.48	0.19±0.11	0.96±0.83	10.65±11.29	0.92±1.39	0.55±0.43	36.61±32.95	0.19*	1.64±1.74	0.09±0.03	0.65*	0.09*	3.18*	4.22±2.06	6.09*	18.6*
Sulfates ^b	1.13±1.26	0.62±0.33	1.88±3.06	2.5±2.67	0.46±0.75	0.36±0.11	2.56±3.32	0.11*	7.38±7.35	0.27±0.25	0.34*	0.19*	2.07*	20.99±6.12	14.76*	253.81*
Nitrates ^b	5.38±4.71	0.81±0.52	1.32±1.23	5.18±5.51	1.69±2.2	0.31±0.22	0.74±1.13	0.17*	0.13±0.19	0.35±0.19	0.16*	0.47*	0.06*	2.3±1.61	0.56*	22.17*
Ca ^b	15.27±12.22	1.28±2.81	6.1±4.34	10.55±3.79	4.53±5.8	5.71±4.52	10.30±4.69	0.06*	16.42±16.63	2.71±2.45	5.53*	3.94*	0.56*	12.02±7.76	21.19*	104.13*
K ^b	1.99±1.73	0.18±0.11	1.41±0.96	1.77±1.48	0.86±0.81	2.17±0.43	1.93±0.1	<0.08*	0.79 ± 0.07	0.58±0.33	1.34*	0.81*	0.5*	2.18±0.54	3.57*	7.6*
Mg ^b	6.04±9.23	<0.01	2.1±1.99	4.83±2.49	1.38±2.32	2.66±2.15	0.95±0.5	<0.01*	2.3±0.52	1.02±1.11	1.55*	1.76*	0.08*	2.87±0.84	5.61*	34.9*
Na ^b	24.05±35.88	0.12±0.05	3.25±2.08	8.75±7.81	3.09±2.86	4.07±2.07	31.68±26.85	<0.12*	3.68±1.17	1.54±1.33	3.27*	2.74*	0.64*	7.37±3.13	8.48*	68.79*
Si ^b	18.65±8.18	0.44±0.72	13.85±11.25	11.88±3.85	11.47±7.63	19.79±12.14	7.46±3.87	0.02*	8.45±4.53	6.19±4.66	10.69*	9.44*	0.10*	13.74±0.55	15.64*	39.73*
SiO ₂ ^b	39.90±17.50	0.95±1.54	29.64±24.07	25.41±8.23	24.54±16.32	42.35±25.98	15.96±8.29	0.04*	18.07±9.7	13.23±9.98	22.87*	20.2*	0.21*	29.4±1.18	33.45*	85.01*
Hardness**	0.63±0.62	0.03±0.07	0.24±0.19	0.46±0.10	0.17±0.24	0.25±0.20	0.30±0.11	<0.01*	0.51±0.39	0.11±0.10	0.20*	0.17*	0.02*	0.42±0.19	0.76*	4.03*
TDS ^b	211±155	8±12	82±58	125±33	64±62	100±64	157±94	6*	108±50	37±31	70*	59*	7*	119±43	174*	887*
$\mathbf{H}\mathbf{g}^{d}$	2.1±3.5	1.9±1.1	1.7±0.7	0.8±0.7	2.6±2.5	1.5±1.5	8.0*				1.6*					
Ale	110±230	32±55	64±93	126±202	340±755	113±79	13693±23475	14*	115±177	132±103	5.43*	55*	129*	318±249	168*	6.93*
Ti ^e	0.91±1.26	0.27±0.26	1.17±1.53	5.84±10.65	10.71±32.78	4.15±3.96	29.47±50.68	0.11*	0.32±0.35	1.11±0.56	0.03*	0.30*	0.23*	2.31±2.64	1.82*	<0.02
Ve	1.79±2.25	0.35±0.34	2.37±2.68	0.84±0.71	1.26±1.44	3.11±2.89	4.87±6.95	0.06*	2.06±0.4	0.9 ± 0.95	0.49*	1.12*	19.8*	4.96±3.14	4.9*	9.13*
Cr ^e	0.62±1.42	0.23±0.18	0.26±0.34	0.14±0.2	0.61±0.7	0.21±0.1	3.67±5.98	0.05*	0.32±0.21	0.18±0.1	0.06*	0.11*	2.14*	0.7±1.47	0.16*	0.46*
Mn ^e	230.4±635.1	5.3±3.6	11.9±8.8	231.8±366.7	21.8±29.5	57.2±79.1	4.5±5.6	5.3*	4±6.6	12.5±12.5	28.3*	1.8*	6.7*	7±9.7	11*	0.7*
Fe ^e	392±1223	17±13	208±258	669±1362	255±430	1146±1115	432±579	18*	139±230	165±127	47*	30*	69*	290±630	64*	10*
Co ^e	0.23±0.5	0.04 ± 0.04	0.11±0.13	0.6±0.53	0.32±0.31	0.38±0.32	0.09±0.09	0.03*	0.09±0.14	0.13±0.1	0.19*	0.03*	0.1*	0.1±0.09	0.06*	0.01*

Ni ^e	0.57±0.93	0.26±0.1	0.18±0.13	0.38±0.54	0.77±0.6	0.54±0.68	0.82±0.56	0.78*	0.26±0.4	0.25±0.21	0.2*	0.18*	6.55*	0.92±1.04	0.57*	6.78*
Cu ^e	7.76±12.63	1.52±1.62	0.36±0.29	8.87±15.31	1.07 ± 1.28	0.71±0.86	6.82±9.15	0.61*	2.56±2.8	8.66±13.34	0.51*	2.01*	0.65*	3.9±2.86	15.42*	7.76*
Zn ^e	20.3±38.1	1629±1249	0.5 ± 0.4	49.9±111.5	57.5±190.9	2.2±3.2	28.5±19.3	3316.8*	3.5±1.2	8.5±11	0.2*	4*	999.3*	144.7±338	14.3*	25.5*
Ase	0.87±1.46	0.03±0.03	0.22±0.11	0.41±0.56	0.17±0.13	0.62±0.6	1.19±1.51	<0.02*	0.61±0.55	0.34±0.28	0.5*	0.85*	0.04*	0.51±0.3	1.03*	1.36*
Se ^e	1.66±5.61	0.27±0.36	0.36±0.44	1.23±1.96	0.44 ± 0.42	0.3±0.45	0.21±0.19	<0.06*	0.08 ± 0.09	<0.06	0.07*	<0.06*	0.07*	0.21±0.14	0.31*	2.06*
Sr ^e	206.6±197.1	3.8±5.3	70.9±52.8	125.6±62.5	73.7±96.4	75.5±50.3	67.6±27.4	0.3*	56.5±18.8	24.2±21.2	58.7*	26.4*	2.3*	80.4±33.8	126.6*	569.9*
Mo ^e	2.59 ± 5.48	0.03±0.03	0.55 ± 1.04	0.07 ± 0.05	0.07±0.19	0.19±0.13	0.32±0.39	<0.02*	5.5±9.42	0.02 ± 0.02	0.12*	<0.02*	0.14*	1.25 ± 1.08	0.27*	6.59*
Cd ^e	0.036 ± 0.046	0.022 ± 0.014	0.019 ± 0.023	0.085 ± 0.078	0.042 ± 0.035	0.040 ± 0.064	0.015 ± 0.012	0.036*	0.089 ± 0.147	0.039 ± 0.076	0.003*	0.001*	0.02*	1.381±4.711	0.006*	0.071*
Sb ^e	0.024 ± 0.029	0.087 ± 0.097	0.013 ± 0.009	0.028 ± 0.028	<0.011	0.023 ± 0.022	0.055 ± 0.03	0.23*	0.028 ± 0.026	0.017 ± 0.013	0.033*	<0.011*	0.163*	0.279 ± 0.312	0.152*	0.076*
Ba ^e	54.7±74.2	9.4±10.2	28.4±18.3	54.1±46.6	62.7±68.4	39.3±32.9	44.9±14.6	0.5*	27.9±14.2	14.8±7.6	29.8*	27.5*	0.5*	23.9±7.9	33.1*	24.2*
Pb ^e	0.509 ± 0.639	1.169±1.994	0.084±0.15	1.536±2.796	0.247 ± 0.293	0.129 ± 0.117	0.948 ± 0.846	0.151*	0.246±0.101	0.808 ± 1.023	0.003*	0.090*	0.146*	0.453 ± 0.684	0.768*	0.451*
U ^e	0.071±0.116	0.004 ± 0.009	0.027 ± 0.021	0.022±0.019	0.068 ± 0.077	0.069 ± 0.089	0.396±0.639	0.001*	0.042 ± 0.068	0.008 ± 0.004	0.009*	0.004*	0.001*	0.052 ± 0.092	0.083*	0.977*

NEAR=North Ecuadorian Amazon Region; SEAR= South Ecuadorian Amazon Region; NEPC= North Ecuadorian Pacific Coast; SEPC= South Ecuadorian Pacific Coast; #=masl (meters above sea level); $\#\#=^{\circ}C$; * single value (n=1); **Ca+Mg (mmol.L⁻¹); a= μ S.cm⁻¹; b= mg.L⁻¹; c=%saturation; d=ng.L⁻¹.

End-----Table 1

Start---Table 2

Table 2. Health Index for ingestion and dermal exposure pathways (Hling and Hlder), Total Hazard Index (THI), Cancer Risk for ingestion and dermal exposure pathways

	RISK INDEX	z NEAR						SEAR				NEPC		SEPC			
POPULATION		deep well	rainfall	river	shallow well	spring	stream	system	rainfall	river	spring	stream	system	rainfall	system	system	shallow well
	Hling	3.17x10 ⁻¹	2.88x10 ⁻¹	8.34x10 ⁻²	2.29x10 ⁻¹	1.09x10 ⁻¹	1.69x10 ⁻¹	9.27x10 ⁻¹	5.27x10 ⁻¹	1.92x10 ⁻¹	1.01x10 ⁻¹	1.05x10 ⁻¹	1.51x10 ⁻¹	3.58x10 ⁻¹	3.45x10 ⁻¹	4.52x10 ⁻¹	2.67x10 ⁻¹
	HIder	2.16x10 ⁻³	8.03x10 ⁻⁴	7.23x10 ⁻⁴	1.69x10 ⁻³	9.79x10 ⁻⁴	1.12x10 ⁻³	3.77x10 ⁻³	1.15x10 ⁻³	8.05x10 ⁻⁴	4.77x10 ⁻⁴	3.94x10 ⁻⁴	4.14x10 ⁻⁴	5.06x10 ⁻³	3.13x10 ⁻³	2.13x10 ⁻³	1.21x10 ⁻³
	THI	3.20x10 ⁻¹	2.89x10 ⁻¹	8.41x10 ⁻²	2.31x10 ⁻¹	1.10x10 ⁻¹	1.70x10 ⁻¹	9.30x10 ⁻¹	5.29x10 ⁻¹	1.93x10 ⁻¹	1.02x10 ⁻¹	1.06x10 ⁻¹	1.51x10 ⁻¹	3.63x10 ⁻¹	3.48x10 ⁻¹	4.54x10 ⁻¹	2.68x10 ⁻¹
	> 1	7%	0%	0%	0%	0%	0%	33%	0%	0%	0%	0%	0%	0%	8%	0%	0%
	CRing	2.46x10 ⁻⁵	9.53x10 ⁻⁷	6.28x10 ⁻⁶	1.17x10 ⁻⁵	4.83x10 ⁻⁶	1.77x10 ⁻⁵	3.38x10 ⁻⁵	2.35x10 ⁻⁷	1.72x10 ⁻⁵	9.71x10 ⁻⁶	1.42x10 ⁻⁵	2.42x10 ⁻⁵	1.27x10 ⁻⁶	1.45x10 ⁻⁵	3.87x10 ⁻⁵	2.93x10 ⁻⁵
ADULIS	CRder	6.52x10 ⁻⁹	2.52x10 ⁻¹⁰	1.66x10 ⁻⁹	3.10x10 ⁻⁹	1.33x10 ⁻⁹	4.70x10 ⁻⁹	8.95x10 ⁻⁹	6.22x10 ⁻¹¹	4.56x10 ⁻⁹	2.57x10 ⁻⁹	3.76x10 ⁻⁹	6.40x10 ⁻⁹	3.35x10 ⁻¹⁰	3.84x10 ⁻⁹	1.02x10 ⁻⁸	7.75x10 ⁻⁹
	TCR	2.46x10 ⁻⁵	9.53x10 ⁻⁷	6.28x10 ⁻⁶	1.17x10 ⁻⁵	4.83x10 ⁻⁶	1.77x10 ⁻⁵	3.38x10 ⁻⁵	2.35x10 ⁻⁷	1.72x10 ⁻⁵	9.71x10 ⁻⁶	1.42x10 ⁻⁵	2.42x10-5	1.27x10 ⁻⁶	1.45x10 ⁻⁵	3.87x10 ⁻⁵	2.93x10 ⁻⁵
	>10 ⁻⁴	13%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%
	10-6-10-4	73%	29%	100%	86%	100%	100%	100%	0%	100%	100%	100%	100%	100%	100%	100%	100%
	<10 ⁻⁶	13%	71%	0%	14%	0%	0%	0%	100%	0%	0%	0%	0%	0%	0%	0%	0%
	Hling	6.88x10 ⁻¹	6.24x10 ⁻¹	1.81x10 ⁻¹	4.97x10 ⁻¹	2.37x10 ⁻¹	3.65x10 ⁻¹	2.01x10 ⁻⁰	1.14 x10 ⁻⁰	4.16x10 ⁻¹	2.19x10 ⁻¹	2.28x10 ⁻¹	3.27x10 ⁻¹	7.75x10 ⁻¹	7.47x10 ⁻¹	9.79x10 ⁻¹	5.78x10 ⁻¹
	HIder	3.75x10 ⁻⁴	1.39x10 ⁻⁴	1.25x10 ⁻⁴	2.93x10 ⁻⁴	1.70x10 ⁻⁴	1.94x10 ⁻⁴	6.53x10 ⁻⁴	1.99x10 ⁻⁴	1.40x10 ⁻⁴	8.27x10 ⁻⁵	6.82x10 ⁻⁵	7.18x10 ⁻⁵	8.78x10 ⁻⁴	5.42x10 ⁻⁴	3.69x10 ⁻⁴	2.10x10 ⁻⁴
	THI	6.88x10 ⁻¹	6.24x10 ⁻¹	1.81x10 ⁻¹	4.97x10 ⁻¹	2.37x10 ⁻¹	3.65x10 ⁻¹	2.01x10 ⁻⁰	1.14x10 ⁻⁰	4.16x10 ⁻¹	2.20x10 ⁻¹	2.28x10 ⁻¹	3.27x10 ⁻¹	7.76x10 ⁻¹	7.48x10 ⁻¹	9.79x10 ⁻¹	5.78x10 ⁻¹
	> 1	27%	14%	0%	0%	0%	0%	33%	100%	0%	0%	0%	0%	0%	17%	0%	0%
CHII DDEN	CRing	1.07x10 ⁻⁵	4.13x10 ⁻⁷	2.72x10 ⁻⁶	5.08x10 ⁻⁶	2.09x10 ⁻⁶	7.69x10 ⁻⁶	1.47x10 ⁻⁵	1.02x10 ⁻⁷	7.46x10 ⁻⁶	4.21x10 ⁻⁶	6.16x10 ⁻⁶	1.05x10 ⁻⁵	5.49x10 ⁻⁷	6.28x10 ⁻⁶	1.68x10 ⁻⁵	1.27x10 ⁻⁵
CHILDREN	CRder	2.82x10 ⁻⁹	1.09x10 ⁻¹⁰	7.19x10 ⁻¹⁰	1.34x10 ⁻⁹	5.53x10 ⁻¹⁰	2.03x10 ⁻⁹	3.87x10 ⁻⁹	2.69x10 ⁻¹¹	1.97x10 ⁻⁹	1.11x10 ⁻⁹	1.63x10 ⁻⁹	2.77x10-9	1.45x10 ⁻¹⁰	1.66x10 ⁻⁹	4.42x10 ⁻⁹	3.35x10 ⁻⁹
	TCR	1.07x10 ⁻⁵	4.13x10 ⁻⁷	2.72x10 ⁻⁶	5.08x10 ⁻⁶	2.09x10 ⁻⁶	7.69x10 ⁻⁶	1.47x10 ⁻⁵	1.02x10 ⁻⁷	7.46x10 ⁻⁶	4.21x10 ⁻⁶	6.16x10 ⁻⁶	1.05x10 ⁻⁵	5.49x10 ⁻⁷	6.28x10 ⁻⁶	1.68x10 ⁻⁵	1.27x10 ⁻⁵
	>10 ⁻⁴	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%
	10-6-10-4	53%	0%	100%	71%	75%	100%	100%	0%	100%	100%	100%	100%	0%	100%	100%	100%
	<10 ⁻⁶	47%	100%	0%	29%	25%	0%	0%	100%	0%	0%	0%	0%	100%	0%	0%	0%

(CRing and CRder), Total Cancer Risk (TCR), and percentage of samples (%) higher than the reference value for non-cancer risk (THI:1) and for cancer risk (TCR:10⁻⁶-10⁻⁴).

NEAR=North Ecuadorian Amazon Region; SEAR= South Ecuadorian Amazon Region; NEPC= North Ecuadorian Pacific Coast; SEPC= South Ecuadorian Pacific Coast; HIing=hazard index for ingestion exposition; Hider= hazard index for dermal exposition; THI=total hazard index.

End-----Table 2

