

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

Laurence Maurice, Fausto López, Sylvia Becerra, Hala Jamhoury, Karyn Le Menach, Marie-Hélène Devier, Hélène Budzinski, Jonathan Prunier, Guilhem Juteau-Martineau, Valeria Ochoa-Herrera, et al.

▶ To cite this version:

Laurence Maurice, Fausto López, Sylvia Becerra, Hala Jamhoury, Karyn Le Menach, et al.. Drinking water quality in areas impacted by oil activities in Ecuador: Associated health risks and social perception of human exposure. Science of the Total Environment, 2019, 690, pp.1203-1217. 10.1016/j.scitotenv.2019.07.089. hal-02337023

HAL Id: hal-02337023

https://hal.science/hal-02337023

Submitted on 25 Oct 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Drinking water quality in areas impacted by oil activities in Ecuador:

2 associated health risks and social perception of human exposure

- 4 Laurence Maurice^{1,2*}, Fausto López¹, Sylvia Becerra¹, Hala Jamhoury³, Karyn Le Menach⁴,
- 5 Marie-Hélène Dévier⁴, Hélène Budzinski⁴, Jonathan Prunier^{5,1}, Guilhem Juteau-Martineau⁶,
- 6 Valeria Ochoa-Herrera^{7,8}, Diego Quiroga⁷, and Eva Schreck¹
- 8 ¹ Géosciences Environnement Toulouse (GET), Observatoire Midi Pyrénées, Toulouse
- 9 University, CNRS, IRD, 31400 Toulouse, France
- ² Universidad Andina Simón Bolívar, Área de Salud, Toledo N22-80, P.O. Box 17-12-569,
- 11 Quito, Ecuador

1

3

7

15

- 12 ³ Swiss Federal Institute of Technology in Zurich, Master Génie de l'Environnement,
- 13 Switzerland.
- ⁴ Bordeaux University CNRS, EPOC UMR 5805, LPTC, F-33400 Talence, France.
- ⁵ Laboratoire des Sciences du Bois, UMR EcoFoG, CNRS, Campus Agronomique de
- 17 Kourou, 97387 Kourou, France
- 18 ⁶ Centre d'Études et de Recherches Travail Organisation Pouvoir (CERTOP), Maison de la
- 19 Recherche, Université de Toulouse, 31058 Toulouse, France
- ⁷ Universidad San Francisco de Quito, Diego de Robles y Vía Interoceánica, P.O. 17-0901,
- 21 Quito, Ecuador
- 22 8 Department of Environmental Sciences and Engineering, Gillings School of Global Public
- 23 Health, University of North Carolina at Chapel Hill, NC 2759, USA

- 25 *Corresponding author : Laurence Maurice^{1,2}
- 26 Permanent address: ¹Géosciences Environnement Toulouse (GET), Observatoire Midi
- 27 Pyrénées, Université de Toulouse, CNRS, IRD, 31400 Toulouse, France
- E-mail address: laurence.maurice@ird.fr; phone number: +33 626121211

29

30 Highlights

- A punctual enrichment in volatile hydrocarbons is observed in several private wells.
- Low mineralization of drinking waters is a special health issue in the Amazon
- region.
- The bacterial contamination of waters needs more attention by public policy.
- Local stakeholders are unable to provide effective water supply and water treatment
 systems.
- 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
- 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

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

65

64

48

49

50

51

52

53

54

55

56

57

58

59

60

61

62

63

Graphical abstract

67

68

66

Keywords (max. 6)

69 Oil activities; Domestic waters; Hydrocarbons; Metal(loid)s; Demineralized waters; Social

70 risk perception.

1. Introduction

71

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. 90 Oil hydrocarbons, in particular PAHs and BTEX, are considered a high environmental and 91 health concern since most of them are persistent and carcinogenic (Amiard, 2017; 92 Jørgensen and Fath, 2010). Certain PAHs and their metabolites can induce leukemia, 93 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 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

118 stomach cancers); they can also affect nervous, immune and reproductive systems and can 119 induce abortions, anemia, and teratogenic effects (Fry, 2015). 120 Released in the environment, hydrocarbons, metals and metalloids can reach aquifers and 121 surface waters throughout all the phases of petroleum production. These pollutants can 122 integrate the dissolved phase or be sorbed onto sediment and particles as their speciation 123 and distribution depend on the physicochemical characteristics of aquatic environments 124 (US-EPA, 2000; Amiard, 2017; Boehler et al., 2017). 125 Extensive information has been compiled in relation with the signs and symptoms of health 126 problems in oil extraction areas in Ecuador (Arana and Arellano, 2007; Hurtig and San 127 Sebastián, 2005; O'Callaghan-Gordo et al., 2016; San Sebastian, 2001). However, to our 128 knowledge, there is no quantitative determination of the risks involved by drinking water 129 exposure, nor epidemiological studies that connect water quality to suspected cancer and 130 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

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

2. Materials and Methods

160 2.1 Study area

142

143

144

145

146

147

148

149

150

151

152

153

154

155

156

157

158

- 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

Ecuadorian Ministry of Environment (PRAS Program, 2010) as the most affected socially and environmentally due to oil activities. The second area is located in the Northern Ecuadorian Pacific Coast (NEPC) between 79°39'27"-79°42'18"W and 00°53'52.00"-00°56'41"N in the Esmeraldas province where most of the crude oil refining is performed. During four decades, these zones were associated to a historic record of oil production and many environmental disasters (Buccina et al., 2013). Both regions were compared with two 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 province (80°19'59"-80°20'57"W; 1°12'57"S-1°13'32" S) Pacific Coast (SEPC), where neither oil nor mining activities has taken place.

2.2 Water sample collection

From 2012 to 2016, we realized five sampling campaigns of surface and drinking waters in the whole study area: two during the low water stage, two during the flood and one during the falling water stage of the Napo River and tributaries. A total of 83 samples of domestic water were collected from local communities from 7 different sources: 15 samples from 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 households tap water. Among these water samples, 15 were collected from the Pacific coast coming mainly from the water distribution system.

Water sampling was performed in Teflon bottles, using ultra-clean procedures. River waters were filtered (0.45 μm 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.

2.3 Analytical methods

2.3.1 Major and trace elements concentrations

Analysis of fluorides, chlorides, sulfates and nitrates were performed by Ion Chromatography (Dionex® ICS 200). The cations Ca, K, Mg, Na and Si were determined by Optical Emission Spectrometry-Inductively Coupled Plasma (ICP-OES, Horiba® Jobin Yvon Ultima2). The determination of trace metal(loid)s elements (TME) was performed by Mass Spectrometry-Inductively Coupled Plasma (ICP-MS, Agilent 7500CE). Total Hg analysis were performed according to the US EPA Methods 1631 (US Environmental Protection Agency (US EPA), 2002) using oxidation-reduction with BrCl and SnCl₂, and finally analyzed by cold-vapor atomic fluorescence spectrometer (CV-AFS, Brooks Rand®). The quantification limits were calculated as 10 times the reagent blanks standard deviation (SD) and listed in the table SI_1. The recoveries were calculated from different River Water Certified Reference Standards; the percentages obtained for anions, trace metal(loid)s and cations were 104±5% (ION-915), 96±10 % (SLRS-5) and 105±4 % (SLRS-5 and EPOND) respectively. The average recovery for total Hg analysis reached 92±9 % (ORMS-5).

2.3.2 PAHs and BTEX concentrations

210 Solid-phase microextraction (SPME) was used in immersion mode in combination with gas 211 chromatography-mass spectrometry (SPME-GC/MS) for the analysis of parent and 212 alkylated PAHs and BTEX in water samples (8 mL and 10 mL for PAHs and BTEX, 213 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)

233 was used as the carrier gas at a flow rate of 1.3 mL.min⁻¹. Analytes were separated on a HP-234 5MS-UI column (30 m x 0.25 mm, 0.25 µm film thickness; Agilent Technologies, J&W 235 Scientific). The column oven program was as follows: 50°C (2 min) to 300°C (5 min) at 236 10°C.min⁻¹. The MSD was operated with electron impact ionization (70 eV) in selected ion 237 monitoring (SIM) mode. The transfer line, source and quadrupole temperatures were 280, 238 300 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 3MTM 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.

2.4 Sociological methods

"Risk culture" refers to the oil contamination risks awareness, behaviours and social practices to cope with it in everyday life, considering another set of risks (social, 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 parishes of the NEAR, Dayuma (Orellana Province) and Pacayacu (Sucumbíos Province). We studied how people perceived and managed their environment and the associated contamination risks. Water resources were not the only issue considered in the interviews, while it appeared as the main concern. We focused on both mestizo 1 and indigenous communities. Primary sociological data were collected during five field surveys between 2012 and 2016, most of them during the water sampling campaigns. Our study is novel in interdisciplinary scope, from inception though application, combining faster environmental monitoring with slower-paced sociological studies that facilitate trust-based relationships 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

278

279

280

281

282

283

284

2.5 Health risk assessment

287 Risk assessments were carried out according risk management measures proposed by the 288 WHO (2014). Since human exposure to multiple chemical mixtures is ubiquitous (polluted 289 air, soil and water), we used US-EPA guidelines (Callahan and Sexton, 2007) for assessing 290 the cumulative risk related to these chemical cocktails and considering different pathways 291 for toxic compounds into the body, with ingestion and dermal contact as main exposure 292 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 in the Amazon region. Values of HI higher than 1 means that adverse health effects can occur. The TCR is the accumulation of cancer risk values (CR) calculated for carcinogenic elements (As, Cd, Cr, Ni) and PAHs by the product of slope factor (SF) and LADD. The TCR is then compared with the guidelines given by the US EPA meaning the probability of providing cancer risks of 10⁻⁴ (1 in 10 000) or 10⁻⁶ (1 in 1 000 000).

Software ©Rstudio (Version 3.5.1) was used for statistical analysis and box plots figures.

One sample t-test was used when data showed a normal distribution (Shapiro-Wilcoxon test). In other cases, variables were log-transformed to follow a normal distribution. A confidence level of 0.95 was chosen. Pearson coefficient correlations were calculated to check the significance of the correlations between the parameters.

313

314

3. Results

3.1 Physico-chemical parameters

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

323 and the rainwater (pH of 4.84±1.02). The only neutral sources were stream and distribution 324 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±12.9 µS.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 µS.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

341

342

343

344

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 WHO 346 guidelines (Fig. 2). 347 Regarding Al concentrations, all the water sources sampled in the Amazon region (SEAR 348 and NEAR) showed values in a similar and acceptable range (WHO, 2005). While in the 349 public water system (Fig. 3), these concentrations exceeded regularly 200 µg.L⁻¹, explained 350 by the utilization of aluminum sulfate as flocculent during the water treatment. A similar 351 behavior was observed with Fe concentrations, both elements presenting a common origin 352 from the soil weathering; tropical, ferralitic soils are characterized by elevated Al and Fe 353 contents (Mainville et al., 2006). 354 Manganese concentrations in drinking water sources ranged between 0 and 2373 µg.L⁻¹, 355 and averaged 72 µg.L⁻¹; the highest concentrations being measured in a deep well close to 356 Pacayacu village in a private property (Pichincha 11, Libertador oil camp). In the majority 357 of private water wells, Mn concentrations exceeded the recommended values by Ecuador 358 (100 μg.L⁻¹), and a fortiori France and Canada (50 μg.L⁻¹), while in rivers, springs and 359 water systems, they were acceptable (Fig. 3). 360 The Zn concentrations in samples collected from rainwater tanks were significantly higher 361 than other sources (Fig. 3). Even though high concentrations of this element are not of health concern, a limit of 500 µg/L was considered as WQG in France, being the most 362 363 restrictive value among the legislations consulted; all rain waters exceeded this limit. In 364 isolated areas of the Amazon basin, people collect rainwater from their home's roof. The 365 acidic rain water passing through the roofs leached, dissolved and transported dissolved Zn 366 to water tanks. 367 The elements As, Cd, Cr, Ni and Pb and Co are considered carcinogenic (group 1 and 2A), 368 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.

3.3 PAHs concentrations

All aromatic organic compounds (PAHs and BTEX) concentrations measured in the analyzed drinking waters (Table SI_4) were in line with the WQGs, even in the NEAR. The benzo(a)pyrene considered as carcinogenic (group 1) was under the quantification limit in all the samples. However, high values of toluene (2000 to 6000 ng.L⁻¹) were measured in 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 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 not detected in 2017. The results of 2016 can be due to the contamination of the water stored by residents in plastic or metallic tanks as a solution for the frequent water network shortages. Our results show that there is a risk of accidental and local contamination of drinking water by benzene in collection tanks from traffic or industrial emissions in Esmeraldas city.

3.4 Bacteriological results

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

3.5 Human health risks assessment

For both adults and children (Table 2), the ingestion hazard index (Hling) 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

414 from a pumping and storage station in front of the discharge channel of the main refinery of 415 the 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. 429 For both, adults and children, water from a deep well located in the stadium of Dayuma 430 (NEAR) presented the highest contribution (93%) of carcinogenic molecules in the dermal-431 HI, while regarding the ingestion risk contribution, system water from the pumping station 432 close to the refinery exhibited a contribution of 88% to the total HI. 433 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 μg.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

440

441

442

443

444

445

446

447

448

449

450

451

452

453

454

455

456

457

458

459

4. Discussion

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 compounds that can trace oil activities impacts in the hydrological system, due to their high contents in the Ecuadorian Amazon crude oil (Table SI_6). High concentrations of V $(305\pm36 \text{ mg.kg}^{-1})$, Ba $(133\pm5 \text{ mg.kg}^{-1})$, Ni $(99\pm11 \text{ mg.kg}^{-1})$, Co $(1.82\pm0.04 \text{ mg.kg}^{-1})$, and Mo (0.93±0.02 mg.kg⁻¹) were measured in a topsoil sampled in a waste pool (from the Auca 08 oil well, NEAR). These values were slightly higher than the concentrations measured in fresh crude oil from the same oil camp (Auca 03), except for barium (7±1 mg.kg⁻¹). However, the crude from the national oil pipeline showed slightly lower values of toxic compounds than these in the waste pool soil except for PAHs (Table SI_6). Barium is then considered as a relevant element to trace oil activities since barite (barium sulfate) is commonly used in drilling activities. This element in surface and groundwaters mainly comes from the soil drainage, as in Ecuador these sources are defined as calcium bicarbonate waters where barium salts may precipitate easily (Kabata-Pendias and Szteke, 2015). All the Ba values measured in the study drinking waters were in line with the WQGs. The only elements that exceeded the WQGs thresholds were Al, Fe, Mn, Cu and Ba; these elements mainly originate from the natural soil erosion and are not of health concern at observed concentrations except for Mn. The water sample from Pacayacu (Pichincha 11 oil camp) presented concentrations in most of the analyzed elements and compounds 10 to 100 times higher than the sampling points average. Manganese

concentrations were higher than 50, 100 and 500 µg.L⁻¹ in 11%, 9% and 4% of the samples, respectively. The highest concentrations were all observed in private or public deep wells. Manganese can be related with agriculture practices, as it is one of the main components in fertilizers, animal food, and pesticides. As proposed by Van Wendel de Joode et al. (2016), drinking water risk assessment should consider Mn as a health hazard. Several studies have shown a negative association between elevated Mn concentrations in drinking waters and children's neurodevelopment, behavior and academic achievement (Bouchard et al., 2011; Van Wendel de Joode et al., 2016). Regarding organic toxic compounds, no pollution by hydrocarbons was found in the study water samples. The unique concern highlighted in drinking water sources which can originate from the oil activities, was the toluene and the sum of methylnaphthalene concentrations measured in several deep wells in the San Carlos community (located on oil camps managed by the Rio Napo Company), nevertheless without exceeding individually, national and international guidelines. Individual alkylated PAHs have been observed to have potentially mutagenic, tumor-promoting, or carcinogenic activity and their toxic potential may easily surpass that of the parent compounds (Andersson and Achten, 2015). However, the concentrations of di- and tri-methylnaphthalenes were very low, but except for 1- and 2-methylnaphthalene, insufficient toxicity data is available to quantify cancer risk from chronic exposure to individual or mixtures of alkylated PAHs. Considering the concentrations ranges of carcinogenic PAHs, we may suppose that direct ingestion of water and dermal contact are probably not the main exposure routes. This hypothesis was confirmed by the Total Cancer Risk indexes calculated for parents and alkylated-PAHs (section 3.5).

460

461

462

463

464

465

466

467

468

469

470

471

472

473

474

475

476

477

478

479

480

481

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

490

491

492

493

494

495

496

497

498

499

500

501

502

503

504

505

483

484

485

486

487

4.2 Drinking water risks due to low mineralization

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

morbidity and mortality from cardiovascular disease (CVD) compared to hard water and water high in Mg (Kozisek, 2005). Epidemiological studies of an ecologic design among Russian populations supplied with water varying in TDS suggested that low-mineral drinking water may be a risk factor for hypertension and coronary heart disease, gastric and duodenal ulcers, chronic gastritis, goiter, pregnancy complications and several complications in newborns and infants, including jaundice, anemia, fractures and growth disorders (Turnlund, 2002). The intake of low water-content in Ca, is associated with a higher risk of fracture in children, certain neurodegenerative diseases, pre-term birth and low weight at birth and some types of cancer (Kozisek, 2005). The WHO established in 1980 minimum and optimum levels of minerals and recommended that demineralized water contains: for Mg and Ca, a minimum of 10 and 20 mg.L⁻¹, respectively, and an optimum 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 water source for Amazonian communities, the Mg and Ca average concentrations were less than 0.01 and 1.28 mg.L⁻¹, respectively. Average concentration of Na in rainwater was 0.12 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. It appears that the health risk tied to the chronic exposure to low mineralized water can be as important or in some cases, more important than the health risk related with current oil activities. Though, it is necessary to pay attention to specific sampling points (deep wells)

506

507

508

509

510

511

512

513

514

515

516

517

518

519

520

521

522

523

524

525

526

527

528

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.

4.3 Limits of Ecuadorian Regulations

- We suggest three types of limits in the National environmental regulations: legal, technical
- and political.
- *4.3.1 Legal limits*
- In Ecuador, two regulations have been set up: the INEN 1-108 and the TULSMA (Texto Unificado de Legislación Secundaria del Ministerio del Ambiente). The Ecuadorian regulation INEN 1-108 is related to treated water for human consumption, and certain parameters, such as pH, conductivity or oxygen percentage were omitted from the 2014 latest version compared to the 2006 version (Table SI_3). Regarding the inorganic compounds, from 34 parameters considered in the 2006, only 18 were proposed in 2014. For example the Mn threshold values increased from 0.1 mg.L⁻¹ in 2006 to 0.4 mg.L⁻¹ in 2011, to completely be removed in 2014. From 5 PAHs regulated in 2006, INEN reduced to one molecule in 2014, the Benzo(a)Pyrene, with a maximum permissible value (MPV)

553 higher than in the 2006 version. For BTEX molecules, toluene MPV became more 554 permissive, and ethylbenzene regulation disappeared. A restriction of the maximum 555 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 556 557 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

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

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

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

4.4 Social perception of the risk and human exposure

599

600

601

602

603

604

605

606

607

608

609

610

611

612

613

614

615

616

617

618

619

620

621

Perceived environment and perceived exposure to health risks

In the Amazon basin, traditionally, indigenous and mestizo use water sources close to their home, from rivers, streams, rainwater or shallow wells. But in the oil Amazon basin, the lack of access to drinking water is the major concern expressed by communities living close to oil infrastructures (Fig. 5), not only for inhabitants but also for cattle. The social experience of the environmental pollution is stable with time and the general resentment is that "everything is polluted and oil companies are lying". Contamination is mainly perceived empirically, directly from the farms or indirectly from a decrease in aquatic biodiversity. The interviews conducted in the NEAR showed 2 main social responses to perceived contamination of local water resources, *Exit* and *Voice* (as proposed by Hirschman, 2011): Exit means leaving the current water supply. At the household level, harvesting rainwater is today perceived as the safest and most effective way to collect water even if in fact various sources are combined (rainwater, wells, rivers or spring). Harvesting rainwater has undergone a rapid development thanks to the social compensation programs systematically implemented by the National oil Company, Petroecuador, since the 2000's. During oil exploration campaigns or when opening new platforms, the public company offered zinc plates to cover the roofs of many communities' houses and water tanks to store the clean water. Later filtration systems were offered by NGOs to specific families involved in the protestation against oil activities. At the community scale, collective action took place: for instance, two communities close to the urban centre of Pacayacu developed their own 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 technical and financial maintenance.

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

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

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

The role of religious beliefs, cultural ideals, experience and emotions were evaluated in order to understand why people resist to change their practices to face supposed polluted 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. Cultural ideals and practices. Change to prevent sanitary risk depends first on social perceptions of the risks, and secondly on a cultural process, but also depends on the existence of other available alternative ways and on adequate financial resources. In the Amazon forest, Shuar and Kishwa communities have a strong reliance on nature and surface waters because of their ancestral culture. Their spirituality is based on the principle of Mother Earth as well as deities of the jungle, the agricultural garden "chacra" and the water. They usually leave far from towns or oil infrastructures. Even if these groups tend to evolve toward a cultural hybridism (for instance integrating modern food to their diet), they prefer natural food and water from the farm, rivers or mountains (Beguet, 2015). Furthermore, in indigenous groups, environmental pollution is unequally perceived. We observed in Shuar and Kischwa groups that generally, this perception by women is less noticeable than by men: maybe because women usually don't work for oil company (Racines, 2017). Sensitive experience. Danger is learned by sensitive experiences which could be traduced by: "the kick warns you and the damage teaches you". Since health effects of environmental exposure are not immediate, people tend not to change their practices and

644

645

646

647

648

649

650

651

652

653

654

655

656

657

658

659

660

661

662

663

664

665

666

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. *Chronic and historical distrust of oil companies*.

Due to numerous social liabilities between oil companies and Amazonian communities,

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

5. Conclusion and recommendations

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

691

692

693

694

695

696

697

698

699

700

701

702

703

704

705

706

707

708

709

710

711

712

713

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

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

Acknowledgements

This work was supported by the French National Research Agency (ANR-13-SENV-0003-01) and realized in the frame of the French-Ecuadorian MONOIL Program "Monitoring of social and environmental impacts and vulnerabilities in an oil country, Ecuador". We are very grateful to the technical teams of the two laboratories where chemical analyses were performed (OMP-GET and EPOC in France). We would like to sincerely thank the local populations from the Amazon and Pacific coast regions, especially from Dayuma, Joya de los Sachas and Pacayacu villages and in Esmeraldas for their kind cooperation during the

- 739 field work, to the farmers for sharing their knowledge, and the IRD in Quito for its
- cooperation to the field trips. This work has been possible thanks to the financial support of
- the PhD grant of Fausto Lopez by the Ecuadorian Secretary of Higher Education, Science
- and Technology (SENESCYT).

743

744

References

- 745 Agency for Toxic Substances & Disease Registry (ATSDR), 2007. Priority List of
- Hazardous Substances. https://www.atsdr.cdc.gov/spl/previous/07list.html.
- Amiard, J.C., 2017. Les risques chimiques environnementaux : méthodes d'évaluation et
- impacts sur les organismes, 2nd ed. Tec & Doc Lavoisier, Paris, France.
- Andersson, J.T., Achten, C., 2015. Time to Say Goodbye to the 16 EPA PAHs? Toward an
- Up-to-Date Use of PACs for Environmental Purposes. Polycycl. Aromat. Compd. 35,
- 751 330–354.
- 752 Arana, A., Arellano, F., 2007. Cancer incidence near oilfields in the Amazon basin of
- Ecuador revisited. Occup. Environ. Med. 64, 490.
- Auyero, J., Swistun, D., 2007. Confused because exposed: Towards an ethnography of
- 755 environmental suffering. Ethnography 8, 123–144.
- 756 https://doi.org/10.1177/1466138107078630
- Baird, S.J.S., Bailey, E.A., Vorhees, D.J., 2007. Evaluating Human Risk from Exposure to
- Alkylated PAHs in an Aquatic System. Hum. Ecol. Risk Assess. Int. J. 13, 322–338.
- 759 Banco Central del Ecuador (BCE), 2010. La Economía Ecuatoriana Luego de 10 Años de
- 760 Dolarización
- 761 https://contenido.bce.fin.ec/documentos/PublicacionesNotas/Notas/Dolarizacion/Dolariz
- acion10anios.pdf.

- Barraza, F., Maurice, L., Uzu, G., Becerra, S., López, F., Ochoa-Herrera, V., Ruales, J.,
- Schreck, E., 2018. Distribution, contents and health risk assessment of metal(loid)s in
- small-scale farms in the Ecuadorian Amazon: An insight into impacts of oil activities.
- 766 Sci. Total Environ. 622–623, 106–120.
- 767 Becerra S., Sagalli M., Gangneron F., Dia H. A., 2015. Everyday vulnerabilities and "social
- dispositions" in the Malian Sahel, an indication for evaluating future adaptability to
- water crises? Regional environmental change (DOI: 10.1007/s10113-015-0845-7)
- Becerra, S., Juteau-Martineau, G., Maestripieri, N., Maurice Bourgoin, L., 2016. Vivre avec
- 771 le risque sanitaire environnemental et les activités pétrolières en Amazonie
- fquatorienne: une culture d'urgence, in: Becerra, S., Lalanne, M., Weisbein, J., Gilbert,
- 773 C. (Eds.), Faire face aux risques dans les sociétés contemporaines. Octarès Editions,
- 774 Toulouse, France, pp. 199–221.
- 775 Beguet E., 2015. Alimentation et contamination en Amazonie équatorienne : Ethnographie
- des comportements de subsistance et des réseaux trophiques Shuar. Master Report,
- 777 Université Paris Ouest Nanterre La Défense, France.
- Boehler, S., Strecker, R., Heinrich, P., Prochazka, E., Northcott, G.L., Ataria, J.M., Leusch,
- F.D.L., Braunbeck, T., Tremblay, L.A., 2017. Assessment of urban stream sediment
- 780 pollutants entering estuaries using chemical analysis and multiple bioassays to
- characterise biological activities. Sci. Total Environ. 593–594, 498–507.
- Bouchard, M.F., Sauvé, S., Barbeau, B., Legrand, M., Brodeur, M.-È., Bouffard, T.,
- Limoges, E., Bellinger, D.C., Mergler, D., 2011. Intellectual Impairment in School-Age
- Children Exposed to Manganese from Drinking Water. Environ. Health Perspect. 119,
- 785 138–143.

- Buccina, S., Chene, D., Gramlich, J., 2013. Accounting for the environmental impacts of
- 787 Texaco's operations in Ecuador: Chevron's contingent environmental liability
- 788 disclosures. Account. Forum 37, 110–123. https://doi.org/10.1016/j.accfor.2013.04.003
- 789 Bundschuh, J., Litter, M.I., Parvez, F., Román-Ross, G., Nicolli, H.B., Jean, J.-S., Liu, C.-
- W., López, D., Armienta, M.A., Guilherme, L.R.G., Cuevas, A.G., Cornejo, L., Cumbal,
- L., Toujaguez, R., 2012. One century of arsenic exposure in Latin America: A review of
- history and occurrence from 14 countries. Sci. Total Environ. 429, 2–35.
- 793 Callahan, M.A., Sexton, K., 2007. If Cumulative Risk Assessment Is the Answer, What Is
- the Question? Environ. Health Perspect. 115, 799–806.
- 795 Clínica Ambiental, 2017. Informe de Salud.
- https://www.clinicambiental.org/docs/publicaciones/informe_salud_tex.pdf.
- 797 Calderón A., Dini, M., Stumpo, G. (Eds), 2016. Los desafíos del Ecuador para el cambio
- 798 estructural con inclusión social, 1st ed. Naciones Unidas, Santiago.
- 799 Decree 1215, 2001. Executive Decree 1215 from Gustavo Noboa Bejarano. Reglamento
- 800 sustitutivo del Reglamento Ambiental para las Operaciones Hidrocarburiferas en el
- Ecuador (RAHOE). http://extwprlegs1.fao.org/docs/texts/ecu79497.doc
- 802 Fontaine G. 2007. El precio del petróleo: conflictos socio-ambientales y gobernabilidad en
- la región amazónica. Ed. FLACSO-IFEA (Ecuador).
- 804 Fry, R.C. (Ed.), 2015. Systems biology in toxicology and environmental health, 1st ed.
- Academic Press, Amsterdam, Netherlands.
- Hirschman, A.O., Besseyrias, C., Delwit, P., 2011. Exit, voice, loyalty: défection et prise de
- parole. Ed. de l'Université de Bruxelles, Bruxelles, Belgique.
- 808 Hurtig, A., San Sebastián, M., 2005. Epidemiology vs epidemiology: the case of oil
- exploitation in the Amazon basin of Ecuador. Int. J. Epidemiol. 34, 1170–1172.

- Hurtig, A.-K., San Sebastián, M., 2002. Geographical differences in cancer incidence in the
- Amazon basin of Ecuador in relation to residence near oil fields. Int. J. Epidemiol. 31,
- 812 1021–1027.
- 813 International Agency for Research on Cancer (IARC), 2018. IARC Monographs-
- Classifications http://monographs.iarc.fr/ENG/Classification/latest_classif.php.
- 815 International Agency for Research on Cancer (IARC), 2010. Some non-heterocyclic
- polycyclic aromatic hydrocarbons and some related occupational exposures, IARC
- 817 monographs on the evaluation of carcinogenic risks to humans. World Health
- 818 Organization, Lyon, France.
- 819 Juteau-Martineau G. (2019). Quand les instruments de participation reconduisent
- l'incapacité politique : Le cas de la régulation sociale et environnementale des activités
- pétrolières en Equateur. Thèse de doctorat de sociologie de l'Université de Toulouse.
- Jørgensen, S.E., Fath, B.D. (Eds.), 2010. Ecotoxicology: a derivative of Encyclopedia of
- ecology, 1st ed. Elsevier/Academic Press, Amsterdam, The Netherlands.
- Kabata-Pendias, A., Szteke, B., 2015. Trace Elements in Abiotic and Biotic Environments,
- 1st ed. CRC Press, Florida, United States.
- 826 Kayser, G.L., Amjad, U., Dalcanale, F., Bartram, J., Bentley, M.E., 2015. Drinking Water
- Quality Governance: A Comparative Case Study of Brazil, Ecuador, and Malawi.
- 828 Environ. Sci. Policy 48, 186–195.
- 829 Kozisek, F., 2005. Health Risk from Drinking Demineralized Water, in: Nutrients in
- Drinking Water. World Health Organization, Geneva, Switzerland, pp. 148–163.
- Larrea C. and Camacho G., 2013. Atlas de las desigualidades del Ecuador. SENPLADES,
- Quito, Ecuador.

- 833 Leusch, F., Bartkow, M., 2010. A short primer on benzene, toluene, ethylbenzene and
- 834 xylenes (BTEX) in the environment and in hydraulic fracturing fluids.
- https://www.ehp.qld.gov.au/management/coal-seam-gas/pdf/btex-report.pdf.
- 836 Levy, B.S., Nassetta, W.J., 2011. The Adverse Health Effects of Oil Spills: A Review of
- the Literature and a Framework for Medically Evaluating Exposed Individuals. Int. J.
- 838 Occup. Environ. Health 17, 161–168.
- Mainville, N., Webb, J., Lucotte, M., Davidson, R., Betancourt, O., Cueva, E., Mergler, D.,
- 840 2006. Decrease of soil fertility and release of mercury following deforestation in the
- 841 Andean Amazon, Napo River Valley, Ecuador. Sci. Total Environ. 368, 88–98.
- 842 MCE, 2017. Informe Mensual de Comercio Exterior Diciembre 2017. Ministerio de
- 843 Comercio Exterior e Inversiones, Quito, Ecuador.
- 844 Ministerio del Ambiente (MAE), 2015. Explotación Hidrocarburífera.
- http://pras.ambiente.gob.ec/fr/web/siesap/explotacion-hidrocarburifera.
- Mitra, S., Roy, P., 2011. BTEX: A Serious Ground-water Contaminant. Res. J. Environ.
- 847 Sci. 5, 394–398. https://doi.org/10.3923/rjes.2011.394.398
- Narváez, I., 2000. Aguas de formación y derrames de petróleo. La dimensión política en la
- problemática socioambiental petrolera, 1st ed. Quito, Ecuador.
- Neghab, M., Hosseinzadeh, K., Hassanzadeh, J., 2015. Early Liver and Kidney Dysfunction
- Associated with Occupational Exposure to Sub-Threshold Limit Value Levels of
- Benzene, Toluene, and Xylenes in Unleaded Petrol. Saf. Health Work 6, 312–316.
- https://doi.org/10.1016/j.shaw.2015.07.008
- Nerbrand, C., Agréus, L., Lenner, R.A., Nyberg, P., Svärdsudd, K., 2003. The influence of
- calcium and magnesium in drinking water and diet on cardiovascular risk factors in

- 856 individuals living in hard and soft water areas with differences in cardiovascular
- 857 mortality. BMC Public Health 3, 21. https://doi.org/10.1186/1471-2458-3-21
- Nevels, D., 2013. The effects of oil operations on the Pacayacu and Sacha river watersheds
- in the Ecuadorian Amazon. Univ. Wash. Bothell Policy J. 19–30.
- 860 O'Callaghan-Gordo, C., Orta-Martínez, M., Kogevinas, M., 2016. Health effects of non-
- 861 occupational exposure to oil extraction. Environ. Health 15.
- 862 https://doi.org/10.1186/s12940-016-0140-1
- 863 Paz-y-Miño, C., López-Cortés, A., Arévalo, M., Sánchez, M.E., 2008. Monitoring of DNA
- Damage in Individuals Exposed to Petroleum Hydrocarbons in Ecuador. Ann. N. Y.
- 865 Acad. Sci. 1140, 121–128.
- Pinto, V.G., Heller, L., Bastos, R.K.X., 2012. Drinking water standards in South American
- countries: convergences and divergences. J. Water Health 10, 295.
- 868 Racines D., 2017. Cultura de riesgo: Impacto social de la actividad petrolera en
- comunidades shuar y kichwa de la parroquia de Dayuma, Francisco de Orellana.
- 870 Informe de PosGrado, Master en Ecología, mención en Estudios Amazónicos.
- Universidad San Francisco de Quito, Ecuador.
- 872 Ramirez, M.I., Arevalo, A.P., Sotomayor, S., Bailon-Moscoso, N., 2017. Contamination by
- oil crude extraction Refinement and their effects on human health. Environ. Pollut.
- 874 231, 415–425.
- 875 San Sebastian, M., 2001. Exposures and cancer incidence near oil fields in the Amazon
- basin of Ecuador. Occup. Environ. Med. 58, 517–522.
- 877 SENPLADES, 2014. Agua potable y alcantarillado para erradicar la pobreza en el Ecuador.
- 878 Turnlund, J., 2002. Molybdenum Metabolism and Requirements in Humans, in: Sigel, A.,
- Sigel, H. (Eds.), Metals Ions in Biological System. CRC Press, pp. 727–739.

- United States Environmental Protection Agency (US EPA), 2015a. Exposure Assessment
- Tools by Routes-Dermal. https://www.epa.gov/expobox/exposure-assessment-tools-
- routes-dermal.
- United States Environmental Protection Agency (US EPA), 2015b. Exposure Assessment
- Tools by Routes-Ingestion. https://www.epa.gov/expobox/exposure-assessment-tools-
- routes-ingestion.
- United States Environmental Protection Agency (US EPA), 2002. Method 1631 Mercury in
- Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence
- Spectrometry. (No. EPA-821-R-02-019). US Environmental Protection Agency, Office
- of Water, Washington, DC.
- van Wendel de Joode, B., Barbeau, B., Bouchard, M.F., Mora, A.M., Skytt, Å., Córdoba,
- L., Quesada, R., Lundh, T., Lindh, C.H., Mergler, D., 2016. Manganese concentrations
- in drinking water from villages near banana plantations with aerial mancozeb spraying
- in Costa Rica: Results from the Infants' Environmental Health Study (ISA). Environ.
- 894 Pollut. 215, 247–257.
- Webb, J., Coomes, O.T., Mergler, D., Ross, N.A., 2018. Levels of 1-hydroxypyrene in
- urine of people living in an oil producing region of the Andean Amazon (Ecuador and
- Peru). Int. Arch. Occup. Environ. Health 91, 105–115.
- 898 Webb, J., Coomes, O.T., Ross, N., Mergler, D., 2016. Mercury concentrations in urine of
- amerindian populations near oil fields in the peruvian and ecuadorian amazon. Environ.
- 900 Res. 151, 344–350.
- 901 Weiss, K., Girandola, F., Colbeau-Justin, L., 2011. Les comportements de protection face
- au risque naturel: de la résistance à l'engagement. Prat. Psychol. 17, 251-262.
- 903 https://doi.org/10.1016/j.prps.2010.02.002

904 World Energy Council (WEC), 2016. World Energy Resources 2016. 905 https://www.worldenergy.org/publications/2016/world-energy-resources-2016/ 906 Wernersson, A.-S., 2004. Aquatic ecotoxicity due to oil pollution in the Ecuadorian 907 Amazon. Aquat. Ecosyst. Health Manag. 7, 127–136. 908 Widener, P., 2007. Oil Conflict in Ecuador: A Photographic Essay. Organ. Environ. 20, 84-909 105. https://doi.org/10.1177/1086026607300321 910 World Health Organization (WHO), United Nations Children's Fund (UNICEF), 2014. 911 Progress on sanitation and drinking-water: 2014 update. World Health Organization, Geneva, Switzerland. 912 913

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).

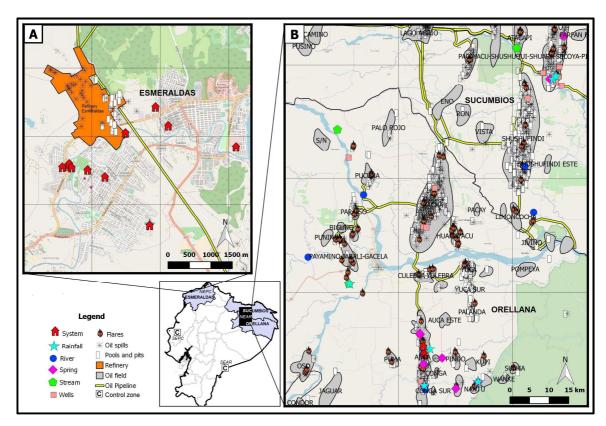


Figure 1. Hazards description (flares, oil spills, pools and pits, refinery, oil fields and pipelines) and sampling points of drinking waters (from various sources: rainfall, river, spring, stream, well) in four study areas: A) Northern Ecuadorian Pacific Coast (NEPC), B) Northern Ecuadorian Amazon Region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

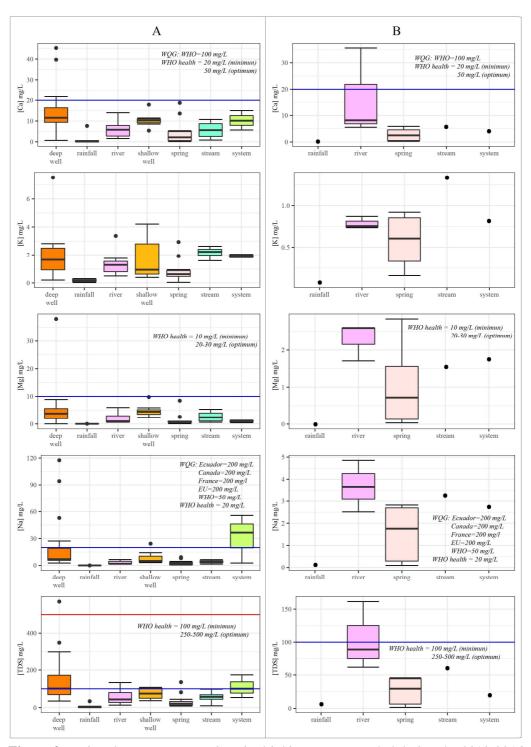


Figure 2. Major element concentrations in drinking water sampled during the 2012-2016 period, in (A) the Northern Ecuadorian Amazon Region (NEAR) and in (B) the control zone in the Southern Ecuadorian Amazon Region (SEAR); the red and blue lines report maximum and minimum values recommended by the World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

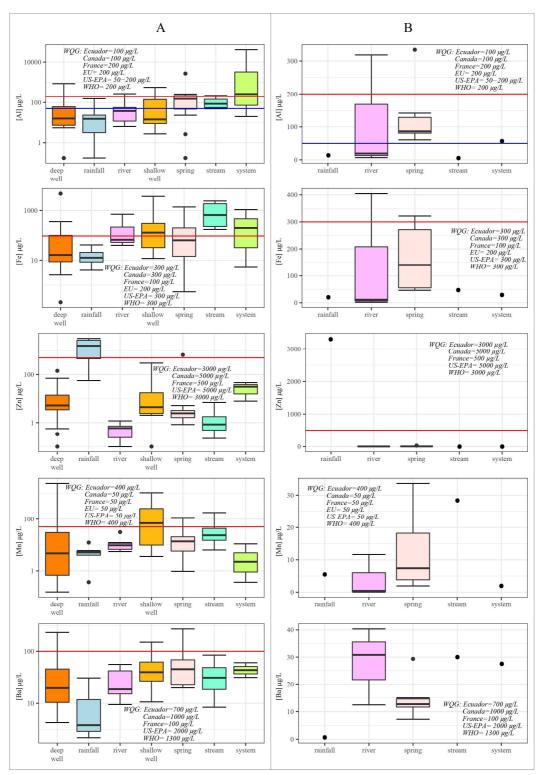


Figure 3. Al, Fe, Mn, Zn and Ba concentrations in drinking water sampled during the 2012-2016 period, in (A) the Northern Ecuadorian Amazon Region (NEAR) and in (B) the control zone in the Southern Ecuadorian Amazon Region (SEAR). The red and blue lines report maximum and minimum

values recommended by the World Health Organization for drinking water (2005), respectively; international quality guidelines (WQG) are reported.

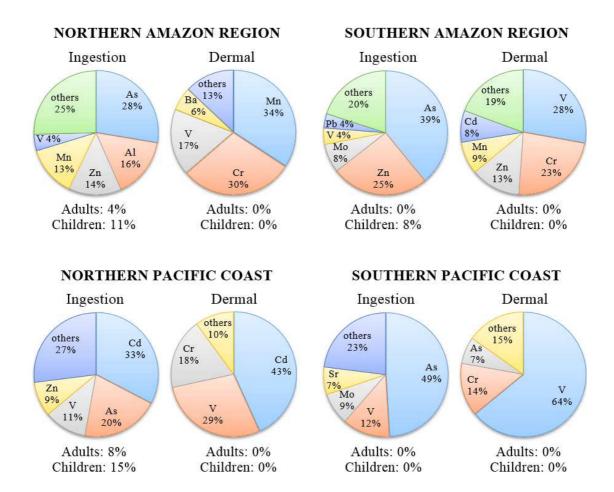


Figure 4. Distribution of ingestion and dermal contact Hazard Index (HI) for the Amazon and Pacific Ecuadorian regions, followed by the percentage of samples that overcome the Total HI reference value (US EPA, 2015) in children and adults.



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

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 Region (NEAR and SEAR, respectively) and in the Northern and Southern Ecuadorian Pacific Coast (NEPC and SEPC, respectively).

Elevation# 2	deep well 281±17 27±3	rainfall 276±18	river	shallow			<u> </u>						T			
		276±18		well	spring	stream	system	rainfall	river	spring	stream	system	rainfall	system	system	shallow well
T## 2	27±3		264±10	264±6	283±12	293±36	266±6	321*	301±22	497±278	850*	303*	108*	32±25	65*	74*
-		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*
pH	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 2	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*
$\mathbf{K}^{\mathbf{b}}$	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*
Hg^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
V ^e	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*
Coe	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*

Nie	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*
Cue	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*
Zne	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*
See	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*
Sre	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*
Sbe	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*
$\mathbf{P}\mathbf{b}^{\mathbf{e}}$	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*
Ue	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); ##=°C; * single value (n=1); **Ca+Mg (mmol.L⁻¹); a=μS.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 (HIing and HIder), Total Hazard Index (THI), Cancer Risk for ingestion and dermal exposure pathways (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).

POPULATION	RISK INDEX	NEAR							SEAR					NEPC		SEPC	
		deep well	rainfall	river	shallow well	spring	stream	system	rainfall	river	spring	stream	system	rainfall	system	system	shallow well
ADULTS	HIing	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	1.21×10^{-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	2.68×10^{-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
	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%
	HIing	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%
CHILDREN	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
	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%

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

