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This thesis is dedicated to my father,

…for his words of wisdom, which I discover more certain as my years go by

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It's very real the phrase *"Choose well who inspires you, and see what they have done with their lives»*. I'd like to thank those compatriots who inspired me to continue every day in this adventure, although these words would never reach their ears: to Inty Gronneberg, Glenda Morejon, and in my village, to Roberto Guachi for being my main motivation.

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To my parents, for their silent and unconditional support. I have always wanted to transcribe down my dad's words written for my high school graduation; I've re-read them each time I felt disappointed and discouraged. I'd like to keep them forever here, in my Thesis:

"El objetivo de aprender es entender porque las máquinas y las personas funcionan como lo hacen; cuando entiendas lo primero te sorprenderás de lo fascinante de las soluciones dadas a grandes problemas, entendiendo lo segundo te responderás porqué aún subsisten problemas enormes con

soluciones relativamente simples. Entendiendo los dos, conocerás el mundo.
Y verás porque aquellos que alimentan al mundo son minimizados y aquellos que usan discursos elocuentes para manipular a sus semejantes se dicen superiores. Verás que una sonrisa no necesariamente es de amistad ni de acogida.
Entenderás porqué consideramos siempre más verde el prado ajeno y verás que sólo es un espejismo, y entenderás que la gente que sabe más de biología no necesariamente sabe más de humanidad, y descubrirás con asombro que los derechos humanos son relativos y no absolutos.
Aprenderás que no todas las formas de violencia y dominio están necesariamente ligadas a las armas ni a los golpes, que las protestas y revoluciones, también se hacen sin fuego y sin palabras.
Que para muchos tener una religión y para otros no tenerla, es sólo cliché social para decirse buenos o más letrados; encontrarás verdades en lo que muchos decían ser falso... y falsedades en lo que se grita como verdad.
Descubrirás que quien viaja contigo o te habla de amistad no es que sea un compañero ni un amigo, de ésos cuídate!
Quien te habla de salud puede ser que esté muriendo...y no por eso siente que su vida se termina!
Quien dice saber,.. talvez ignora más que tú….y verás que las almas pobres son las que se piensan superiores y alimentan su sentido de grandeza subrayando y poniendo en evidencia los defectos y los errores de los otros... y descubrirás con asombro y hasta con repudio como la ambición, los prejuicios y el ego hablan más fuerte que los libros...y aunque hablarás de Tesla, de Gandhi, de Einstein, de Luther King; y aunque recordarás a Fernando Daquilema, Dolores Cacuango, Matilde Hidalgo, José Rodríguez Labandera... también deberás conocer y te verás obligado por deber moral a no olvidar a Edison, Hitler ni Hopenheimer.
Pero sobre todo, deberás entender y ver que nada se termina hasta que tú lo decidas, así que continua siempre…."

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In the next lines more than a scientific work, an adventure…. a long adventure that has witnessed many changes in my life. Enjoy it!

Résumé (FR)

L'activité pétrolière en Équateur pose le problème des conditions indispensables au développement durable du pays dont une partie repose sur l'exploitation des géoressources tout en préservant l'environnement et le bien-être des populations sans compromettre les conditions de vie des générations futures, ni la biodiversité. L'Équateur est le 4ème producteur de pétrole en Amérique du Sud et un des pays possédant la plus grande biodiversité.

Ce travail de thèse s'insère dans le cadre du programme MONOIL (ANR 2014-2018) dont l'objectif principal est d'améliorer la compréhension et le suivi des impacts de l'exploitation pétrolière sur l'environnement et la société, en termes de dommages et de vulnérabilités.

Plusieurs campagnes d'échantillonnage d'eaux (de pluie, de surface et souterraine) et de sédiments ont été réalisées dans des bassins versants situés dans des zones d'exploitation pétrolière (Amazonie) et de raffinage (côte Pacifique); pour contrôle, d'autres prélèvements ont été effectués en amont de ces zones exploitées ainsi qu'en aval, jusqu'à la frontière péruvienne.

Des HAPs (hydrocarbures aromatiques polycycliques) et BTEX (benzène, toluène, éthylbenzène et xylènes) ont été analysés par Gas Chromatography Mass Spectrometry (GC-MS), des métaux associés aux activités pétrolières (Ni, V, Cd, As, Mn, Pb) ont été déterminées par Inductively Coupled Plasma Mass Spectrometry (ICP-MS); la spectrométrie de fluorescence atomique (AFS) a été utilisée pour le Hg. Un comptage microbiologique et une analyse sociale ont été réalisés. Le logiciel ©Rstudio 3.5.1 a été utilisé pour l'analyse statistique (normalité, corrélation, analyse en composantes principales-PCA et analyse de cluster hiérarchique-HCA). Des valeurs toxicologiques de référence (TRV) ont été utilisées afin de déterminer la qualité environnementale et celle de l'eau de consommation, ainsi que le HCA et le PCA pour tracer les sources de contamination. Une évaluation des risques pour la santé humaine par ingestion et contact dermique a été effectuée sur les sources d'eau potable.

Les résultats montrent que les eaux de surface des bassins versants présentent des niveaux de HAPs en conformité avec les TRV et sont caractérisées par des molécules organiques de faible masse molaire. Les alkyl-naphtalènes représentent 70 à 96 % de la charge aromatique totale dissoute dans 90 % des échantillons. Les molécules alkylées représentent plus de 50% de la charge aromatique total (TAC) dans 91% des sédiments.

Résumé

Le traçage des sources indique que le diméthyl et le triméthyl-phénanthrène ainsi que le méthyl-chrysène caractérisent la TAC. Sur la côte Pacifique, les effluents de la raffinerie montrent une nature similaire aux fosses de déchets non restaurés. Les sédiments des rivières Napo et Aguarico dans la zone d'exploitation pétrolière présentent certaines valeurs de HAPs correspondant à une empreinte similaire à celle des sables bitumineux et de certaines fosses de déchets pétroliers.

Dans l'eau de consommation des populations locales, les concentrations d'ions majeurs, d'éléments trace, de HAPs et de BTEX sont conformes aux recommandations nationales et internationales, sauf pour le Mn, le Zn et l'Al. Les concentrations de toluène analysées dans des puits profonds près des camps pétroliers étaient plus élevées que le fond naturel. L'analyse microbiologique a révélé un niveau élevé de coliformes représentant des risques importants pour la santé.

L'évaluation des risques sanitaires a montré que l'ingestion représente 99 % des voies d'exposition aux éléments cancérigènes et non cancérigènes chez les adultes et les enfants, tandis que 20 à 49 % de l'index de risque sanitaire est causé par l'arsenic. Cependant, l'indice de risque sanitaire (HI) indique des effets chroniques acceptables. La plupart (72 %) des familles interrogées connaissent les risques sanitaires, cependant un écart a été observé entre leurs connaissances et leurs actions pour faire face à ces risques.

Abstract (EN)

Oil industry activities in Ecuador face up the problem of necessary conditions for a sustainable development that permits the exploitation of resources and preserves the environment and the wellbeing of people, without compromising the living conditions of future generations, or the biodiversity. Ecuador is the 4th largest oil producer in South America, and the country with the highest biodiversity.

This thesis work is part of the MONOIL program (ANR 2014-2018) which main objective is to improve the understanding and monitoring of oil impacts on society and environment in terms of damage and vulnerabilities.

Several water (rain, surface and underground) and sediment sampling campaigns were conducted in dry and wet seasons in watersheds located in oil-extracting (Amazon) and refining (Pacific coast) areas; for control, other samples were taken upstream of these exploited areas as well as downstream until the Peruvian border.

Analyses of PAHs (polycyclic aromatic hydrocarbons) and BTEX (benzene, toluene, ethylbenzene and xylenes) as well as heavy metals associated with oil activities (Ni, V, Cd, As, Mn, Pb and Hg) were carried out. PAHs were analyzed by Gas Chromatography Mass Spectrometry (GC-MS); Atomic fluorescence spectrometry (AFS) was used for Hg analyses while other heavy metals were analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Carbon, Sulphur and sediment particle size were determined; a microbiological count and social analysis were applied.

The software ©Rstudio 3.5.1 was used for the statistical analysis; various tests (normality, correlation, principal component analysis-PCA and hierarchical cluster analysis-HCA) were performed. Toxicological reference values (TRVs) were used to determine the environmental and drinking-water quality, as well as HCA and PCA were used to trace sources of contamination. A human health risk assessment by ingestion and dermal contact was conducted on drinking water sources.

The results show that the studied watersheds have PAH levels in compliance with TRVs and that the aquatic environment is characterized by molecules of low molecular weight. Alkyl-naphthalenes accounted for 70 to 96% of the total dissolved aromatic load in 90% of the samples. Alkylated molecules represent more than 50% of the total aromatic charge (TAC) in 91% of sediments.

Source tracing indicates that dimethyl and trimethylphenanthrene as well as methyl-chrysene

characterize the TAC. On the Pacific coast, the refinery effluent showed a similar nature to ancient-oil waste pools. The Napo and Aguarico River basins had points with a fingerprint similar to the oil sands and waste pits, with only two points related to crude oil.

In drinking water; the concentrations of major ions, trace elements, PAHs and BTEX were in compliance with national and international guidelines, except for Mn, Zn and Al. Toluene concentrations from deep wells near oil camps were higher than the natural background. Microbiological analysis revealed a high level of coliforms representing significant health risks.

Human health risk assessment showed that ingestion represents 99% exposure to carcinogens and non-carcinogens (e. g. zinc) in adults and children, while 20-49% of THI was caused by arsenic. The hazard index (HI) indicates acceptable chronic effects. Most (72%) of interviewed families knew sanitary risks, but a discrepancy was observed between knowledge and action.

Resúmen (ES)

La actividad petrolera en Ecuador plantea la el problema de las condiciones adecuadas para un desarrollo sostenible que permita la explotación de recursos con una adecuada preservación del medio y el bienestar de las poblaciones, sin comprometer las condiciones de vida de las generaciones futuras ni la biodiversidad. Ecuador es el cuarto mayor productor de petróleo de Sudamérica y el país con mayor biodiversidad.

Este trabajo de tesis se enmarca dentro del programa MONOIL (ANR 2014-2018) cuyo objetivo principal es mejorar la comprensión y el seguimiento de los impactos de la industria petrolera en la sociedad y el medio ambiente en términos de daños y vulnerabilidad.

Se realizaron varias campañas de muestreo de aguas (pluviales, superficiales y subterráneas) y sedimentos en cuencas de captación ubicadas en áreas petroleras (Amazonas) y de refinación (costa del Pacífico); para fines de control, se tomaron otras muestras aguas arriba de estas áreas explotadas, así como aguas abajo hasta la frontera con Perú.

Se realizaron análisis de HAPs (hidrocarburos aromáticos policíclicos) y BTEX (benceno, tolueno, etilbenceno y xilenos), así como de metales pesados asociados a actividades petroleras (Ni, V, Cd, As, Mn, Pb y Hg). Los HAPs se analizaron mediante espectrometría de masas-cromatografía de gases (GC-MS). Se utilizó la espectrometría de fluorescencia atómica para los análisis de Hg, mientras que los otros metales pesados se analizaron mediante ICP-MS (espectrometría de masas- plasma de acoplamiento inductivo). Se determinaron el carbono, azufre y la granulometría de sedimentos. También se realizaron un recuento microbiológico y un análisis social.

Para el análisis estadístico se utilizó el software ©Rstudio 3.5.1. Se realizaron varias pruebas (normalidad, correlación, análisis de componentes principales-PCA y análisis de conglomerados-HCA). Se utilizaron valores toxicológicos de referencia (TRVs) para determinar la calidad ambiental y la calidad del agua potable, así como HCA y PCA para rastrear las fuentes de contaminación. Se realizó una evaluación del riesgo para la salud humana por ingestión y contacto dérmico en fuentes de agua potable.

Los resultados muestran que las cuencas hidrográficas tienen niveles de HAP que cumplen con los TRVs y que el medio acuático se caracteriza por moléculas de bajo peso molecular. Los alquilnaftalenos representaron entre el 70 y el 96% de la carga aromática total disuelta en el 90% de las muestras. Las moléculas alquiladas representan más del 50% de la carga aromática total (TAC) en el 91% de los sedimentos.

Resúmen

El análisis de las fuentes de HAPs indica que el di y trimetilfenantreno, así como el metilcriseno, caracterizan la TAC. En la costa del Pacífico, el efluente de la refinería mostró una naturaleza similar a la de los pozos de desechos no reparados. Las cuencas de los ríos Napo y Aguarico mostraron sitios con una huella similar a las arenas bituminosas y los residuos una piscina desechos, y sólo dos puntos mostraron conexión con el petróleo crudo.

En el agua potable, las concentraciones de los principales iones, elementos trazas, HAP y BTEX cumplen las directrices nacionales e internacionales, excepto en el caso de Mn, Zn y Al. Las concentraciones de tolueno de los pozos profundos cerca de los campos petroleros fueron más altas que las del fondo natural. Los análisis microbiológicos revelaron un alto nivel de coliformes que representa riesgos significativos para la salud.

La evaluación de riesgos para la salud mostró que la ingestión representa el 99% de la exposición a agentes carcinógenos y no carcinógenos (por ejemplo, el zinc) en adultos y niños, mientras que el 20-49% del THI fue causado por el arsénico. El índice de peligrosidad (HI) indica efectos crónicos aceptables. La mayoría (72%) de las familias encuestadas eran conscientes de los riesgos para la salud, pero se observó una discrepancia entre el conocimiento y la acción.

Abbreviations

A: Anthracene
Ac: Acenaphthylene
Ace: Acenaphthene
AG: 5 de Agosto
BaA: Benzo[a]anthracene
BaP: benzo(a)pyrene
BaP: Benzo[a]pyrene
BB: Bomboiza
BbjkF: Benzo[bjk]fluoranthene
BeP: Benzo[e]pyrene
BPe: Benzo[ghi]perylene
BTEX: Benzene, toluene, ethylbenzene, xylenes
CC: Carlos Concha
CFU: Colony-forming Units
Ch: Chrysene+Triphenylene
DBA: Dibenzo[ah]anthracene
DBT: Dibenzothiophene
DU: Dureno
DY: Dayuma
EF: Enrichment Factor
ERL: Effect Range Low
ERM: Effect Range Median
Fa: Fluoranthene
Fl: Fluorene
GC-MS: Gas Chromatography–Mass Spectrometry
HCA: Hierarchical Cluster Analysis
HIing: Ingestion Hazard Index
HI: Hazard Index
HMW: High Molecular Weight
HRA: Health Risk Assessment
(i): Interferences
ICP-MS: Induced Coupled Plasma-Mass Spectrometry
IP: Indeno[123-cd]pyrene
JS: Joya de los Sachas
LD:Limit of Detection
LI: Limoncocha
LM: Lumbaqui
LMW: Low Molecular Weight
LOEL: Lowest Observed Effect Level
LQ: Limit of Quantification
MA: 2-Methylanthracene
MAE: Ecuadorian Ministry of the Environment
MCh: ΣMethylchrysene
MDBT: Methyldibenzothiophene
MPhMA: 1Methylanthracene+[9,4]Methylphenanthrene+[45]Methylenephenanthrene
mSQGQ: Mean-SQG-Quotient
N : Naphthalene
NEAR: Northern Ecuadorian Amazon Region

Abbreviations

NEPC: Northern Ecuadorian Pacific Coast
NOEL: No Observed Effect Level
NR: Nuevo Rocafuerte
PAHs: Polycyclic Aromatic Hydrocarbons
PCA: Principal Component Analysis
PEL: Probable Effect Level
Ph: Phenanthrene
PK: Pacayacu
PN: Puerto Napo
PO: Puerto Francisco de Orellana
Py: Pyrene
RAOHE: Reglamento Ambiental de las Operaciones hidrocarburiferas del Ecuador
REE: Esmeraldas Refinery
S: Santiago
SC: San Sebastian del Coca
SEAR: Southern Ecuadorian Amazon Region
SEPC: Southern Ecuadorian Pacific Coast
SF: Shushufindi
SJ: San José
SOTE: Sistema de Oleoducto Transecuatoriano (Trans-Ecuadorian Oil Pipeline System)
SQG: Sediment Quality Guidelines
SR: San Roque
TAC: Total Aromatic Charge
TEF: Toxic Equivalent Factor
TEL: Threshold Effect Level
TEQ: Toxic Equivalent Quantity
THI: Total Hazard Index
TI: Tiputini
TM: Trace metal(oid)s
TOC: Total Organic Carbon
TRV: Toxicity Reference Values
TU: Toxic Units
TUA: Toxic Units Accumulated
TULSMA: Texto Unico de Legislación Secundaria del Ministerio del Ambiente
US EPA: Unites States Environmental Protection Agency
VL: Vuelta Larga
WHO: World Health Organization
WQG: Water Quality Guidelines
1MN: 1-Methylnaphthalene
1MPh: 1-Methylphenanthrene
1-OHP: 1-hydroxypyrene
2MN: 2-Methylnaphthalene
2MPh: 2-Methylphenanthrene
3MPh: 3-Methylphenanthrene
∑DMPh: Sum of dimethylphenanthrene
∑TMPh: Sum of trimethylphenanthrene

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CHAPTER 1

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INTRODUCTION (VERSION FRANÇAISE)

I.1. CONTEXTE DU PROJET

La forêt amazonienne est la plus grande richesse naturelle d'Amérique Latine. Elle est aussi au centre de nombreux débats économiques, écologiques et socioculturels. Le bassin amazonien équatorien, bien qu'ayant une très faible densité de population, dévoile un important registre de conflits socio-environnementaux, principalement dus à l'exploitation pétrolière.

I.1.1. Production et raffinage du pétrole en Équateur : contexte historique, économique et législatif

L'extraction du pétrole en Équateur a débuté sur la côte Pacifique en 1911 et s'est centralisée sur cette région pendant près de 60 ans (BCE, 1990). Actuellement, cette région produit moins de 1% du pétrole du pays, tandis que 99% sont concentrés dans la région amazonienne nord équatorienne (North Ecuadorian Amazon Region, NEAR), principalement dans les provinces d'Orellana et de Sucumbíos (Bustamante and Jarrín, 2005; EP Petroecuador, 2013). Les activités d'extraction dans la NEAR ont débuté en 1967 avec le forage du premier puits du pétrole par Texaco Gulf, et sont devenues économiquement importantes dès 1972, avec initialement une production de 300 000 barils par jour pour atteindre 522 000 barils en 2017 (BCE, 2018; EP Petroecuador, 2013). L'exportation de pétrole brut a été la principale source de revenus de l'économie équatorienne, représentant plus du 50% des exportations totales de 2004 à 2014 (**Figure I**) puis s'réduisant à 37% en 2017 (BCE, 2010; Calderón et al., 2016; MCE, 2017). En Amérique du Sud, l'Équateur est désormais le 4ème plus gros producteur de pétrole, et le 3ème en volume de réserves (OPEC, 2017).

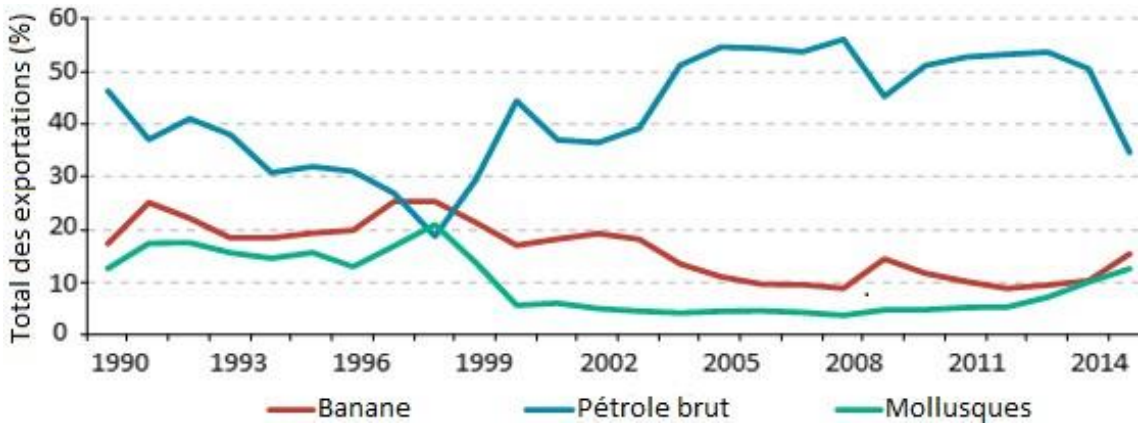


Figure I. Pourcentage des exportations totales des principaux produits équatoriens de 1990 à 2015 (Calderón et al., 2016).

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Le raffinage du pétrole en Équateur est, depuis le début de l'exploitation en 1926, centré sur la côte Pacifique. Actuellement le pays compte trois usines de raffinage: la raffinerie « Shushufundi », la seule située en Amazonie et cumulant 10% du raffinage total national; la raffinerie de «La Libertad » et celle « Esmeraldas », situées sur la côte pacifique et produisant la presque totalité des dérivés raffinés du pays. La raffinerie d'Esmeraldas (REE), construite en 1977, représente 63% de la capacité totale de raffinage du pays (EP Petroecuador, 2013).

Les infrastructures de production pétrolière situées en Amazonie et les installations de raffinage de la côte Pacifique ont engendré la construction de nombreux systèmes de stockage et de transport de pétrole brut et de leurs produits dérivés: notamment l'oléoduc trans-équatorien (SOTE), l'oléoduc San Miguel-Lago Agrio (OSLA), l'oléoduc du pétrole lourd (OCP) et la tuyauterie Eden Yuturi-Villano qui collectent et transportent le pétrole brut depuis la NEAR, traversent la cordillère des Andes, et arrivent jusqu'au port maritime d'Esmeraldas à Balao (EP Petroecuador, 2013).

Ainsi, suite à ce développement important des activités pétrolières, dans ce contexte historique et économique, des pratiques environnementales peu soucieuses du respect de la Nature ont vu le jour. Cependant, ces pratiques environnementales en Équateur sont restées méconnues jusqu'en 1972: les premiers rapports bibliographiques remontent à peine au début des années 70 en lien avec l'affaire Texaco (1990-2010). Certains auteurs ont signalé des documents de 1972 expliquant aux employés que seuls les incidents environnementaux déjà connus par la presse ou par le gouvernement doivent être signalés, les autres devant être passés sous silence et les enregistrements existants effacés (Andrade, 2008; Buccina et al., 2013). Par ailleurs, il apparait que le gouvernement équatorien n'a appliqué aucune réglementation environnementale au cours des 28 années d'exploitation pétrolière par la compagnie Texaco Gulf Company, en lien également avec les 12 autres compagnies pétrolières impliquées dans la région NEAR (BCE, 1990; Narváez, 2000).

Sans aucune mesure de protection de l'environnement, l'extraction du pétrole opérée en Amazonie Equatorienne par l'entreprise Texaco aurait causé le déversement d'environ 65 milliards de litres de pétrole, le rejet de 76 milliards de litres d'eau de formation dans les rivières et la combustion de 7 millions de m^3 de gaz. Plus de 1000 piscines de déchets toxiques ont été abandonnées (Narváez, 2000). En 1992, Texaco-Gulf transféra toutes ses installations à l'entreprise publique Petroecuador ; et encore, sans aucune contrôle de la remédiation imposée par le gouvernement, les pratiques industrielles sont demeurées les mêmes pendant de nombreuses années (Kashinsky, 2008).

Sur la côte Pacifique, aucun incident n'avait été répertorié avant la publication du document de Narváez (2000) présentant une liste des incidents liés au transport par oléoducs et aux incendies ayant touché les rivières Esmeraldas et Teaone depuis 1997.

Le CEPAL (1990) indique que l'obsolescence des infrastructures a contribué à la pollution chronique de l'air, de l'eau et du sol ; et à la génération de scénarii favorables aux conflits socio-environnementaux, comme par exemple, le cas des effluents liquides de la REE dilués et dispersés dans les rivières Teaone et Esmeraldas. Récemment, Chachalo (2016) a signalé que la REE a produit plus de 30 000 tonnes de sous-produits dangereux en août 2014 et que de nouveaux procédés remplaçaient les anciens depuis 2015. Des améliorations similaires avaient déjà été mises en place en 1987, 1995 et 1997 afin d'augmenter la capacité de raffinage de 55 000 à 110 000 barils par jour; mais ces ajustements techniques n'ont en rien amélioré l'impact de la raffinerie sur l'environnement (Cevallos, 2015).

En 2015, le Ministère équatorien de l'environnement (MAE) a répertorié 3 raffineries, 2 oléoducs majeurs, 6383 puits d'extraction et 1190 plates-formes, tandis que les passifs environnementaux étaient estimés à 1170 accidents de fuites de pétrole et 2489 fosses à déchets (MAE, 2015a). Ces éléments ont induit des impacts environnementaux et sociaux importants; plusieurs communautés autochtones ont été forcées de migrer (Buccina et al., 2013). La pollution des eaux de surface et des eaux souterraines dans les provinces d'Orellana et de Sucumbíos a affecté cette zone dont la biodiversité est particulièrement riche (Bustamante and Jarrín, 2005; Marx, 2010; Wernersson, 2004). Selon le MAE (2015), 97% du total des passifs environnementaux (fosses et déversements d'hydrocarbures) se situent dans la NEAR. Et l'eau est le milieu que les populations locales considèrent comme le plus affecté par les activités pétrolières (Clinica Ambiental and CSS, 2017).

Les activités de l'industrie pétrolière sont regroupées en cinq phases: (1) exploration, (2) exploitation ou production, (3) stockage et transport, (4) raffinage et (5) commercialisation ; toutes ces activités affectent l'environnement et particulièrement les sources d'eau, mais les phases de production et de transport sont les plus critiques en raison des volumes importants d'eaux de formation rejetées (liquide très salé contenant des hydrocarbures et des éléments métalliques), des boues de forage, des eaux de traitement et des risques de déversement (Avellaneda, 2005; Fontaine, 2013). En Equateur, l'exploration et l'exploitation du pétrole sont sous la responsabilité de l'entreprise publique Petroamazonas tandis que les activités de raffinage, de transport et de vente sont sous le contrôle de Petroecuador travaillant également avec certaines entreprises internationales (chinoises, canadiennes, etc.).

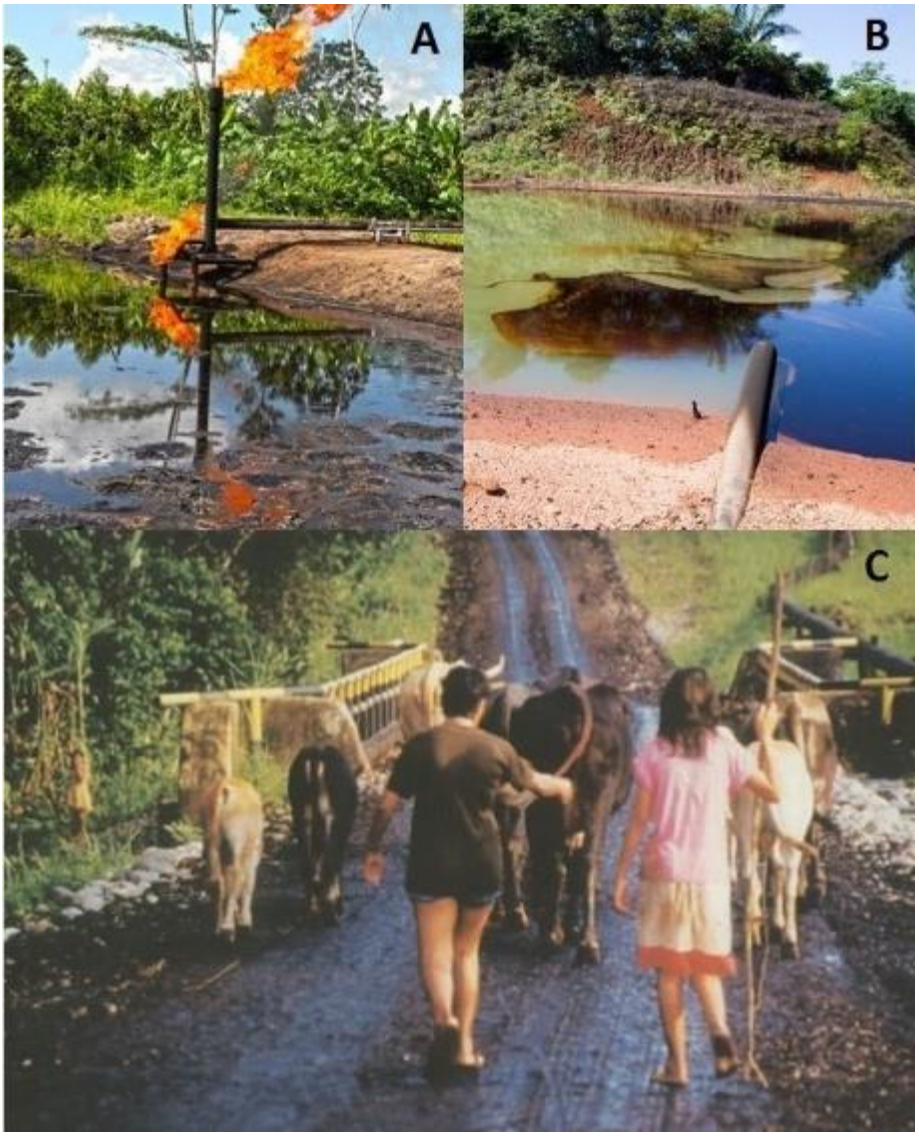


Figure II. Élimination des déchets pétroliers dans la NEAR: A. Torchères et fosse des déchets. B. Déversement des déchets liquides. C. Pétrole brut répandu sur une route de terre. (Crédit photos: A et B de MONOIL, 2015 ; C de IESC, 2004).

Certains auteurs ont listé des variables « cause-effet » de la pollution pétrolière dans la région amazonienne équatorienne (Buccina et al., 2013; IESC, 2004; Narváez, 2000; Widener, 2007). Parmi ces causes de pollution signalées durant la période 1972-1993 (**Figure II**), et affectant le système aquatique, nous pouvons énumérer:

- la construction de fosses à proximité des puits de pétrole pour recueillir les déchets (une à trois fosses par puits),
- les déchets solides et liquides eux-mêmes, ayant été accumulés dans les piscines ou déversés dans les cours d'eau,
- les déchets accumulés qui ont été incinérés ou récupérés pour être épandus sur des chemins de terre,
- les résidus de pétrole ayant été souvent emportés par les eaux de ruissellement vers les

cours d'eau,

- le gaz brûlé sur place (environ 200 torchères brulaient 2 millions de m^3 de gaz par jour).

Les mauvaises pratiques pétrolières en Equateur représentent depuis plusieurs décennies un cas rare de pollution chronique où l'adoption d'une réglementation environnementale est arrivée tardivement et avec une applicabilité biaisée. Ainsi, le TULSMA ou «Texto Unico de Legislación Secundaria del Ministerio del Ambiente» (MAE, 2015; MAE, 2003) fixe désormais des seuils pour la préservation de la vie aquatique. Parallèlement, le «Reglamento Ambiental de las operaciones hidrocarburiferas» (RAOHE, 2001), consacré à la surveillance des effluents et des émissions des activités pétrolières, présente des seuils différents, mettant en évidence de fortes disparités entre ces deux réglementations.

Les seuils donnés par le RAOHE n'ont pas changé depuis près de 20 ans et sont toujours utilisés pour le contrôle des effluents de l'industrie pétrolière, tandis que la réglementation du TULSMA, qui inclut les directives de l'Organisation Mondiale de la Santé (WHO, 2017), a été modifié plusieurs fois avec une réduction du nombre de paramètres surveillés (MAE, 2015). La législation RAOHE présente des seuils pour seulement quatre éléments métalliques toxiques (baryum, chrome, plomb et vanadium), pour les hydrocarbures totaux (TPH) et les hydrocarbures aromatiques polycycliques totaux (HAPs) dans l'eau et les effluents liquides provenant de tous les procédés de l'industrie pétrolière. Mais aucune de ces normes ne contrôle la qualité des sédiments alors que la plupart des contaminants sont hydrophobes. Le RAOHE propose de surveiller le risque pour la vie aquatique en suivant deux critères : les teneurs au niveau du point de décharge des effluents industriels ou en aval dans la masse d'eau douce qui les recueille. De son côté, le TULSMA contrôle la qualité des eaux selon leur

Table I. Seuils relatives à la qualité de l'eau ($mg.L^{-1}$) pour Ba, Cr, Pb, V, TPH et PAHs d'après RAOHE et TULSMA

ÉLÉMENT	RAOHE[1] Point de décharge	RAOHE[2] Point de contrôle	TULSMA Préservation de la vie aquatique	TULSMA Vers le réseau d'égout
Baryum	<5	--	1.0	--
Chrome	<0.5	--	0.032	0.5 as Cr(VI)
Plomb	<0.5	--	0.001	0.5
Vanadium	<1	--	--	--
TPH	<0.5	<0.5	0.5	20.0
HAPs	<0.0003	<0.0003	--	--

D'après: Table 4 de RAOHE (2001); Table 2 et Table 8 de TULSMA-2015 (MAE, 2015)

1.- Point de décharge des effluents après traitement

2.- Au moins 300 mètres en aval du point de décharge

objectif d'utilisation (consommation, préservation de la vie aquatique, etc.) (**Table I**).

Mais, les effluents sont-ils destinés à s'écouler directement dans un cours d'eau douce ? Affectent-ils la vie aquatique ? Et si les eaux de formation atteignent les principales sources d'eau utilisées par les populations, existe-t-il un risque pour la santé humaine ?

Ces quelques questions permettent de prendre conscience de l'ambiguïté de ces deux règlementations équatoriennes en matière de surveillance de l'environnement et de contrôle des activités pétrolières.

I.1.2. Contexte social et sanitaire dans les zones d'activités pétrolières en Équateur

La production pétrolière en Équateur constitue un cas d'étude intéressant car elle reflète l'évolution historique de l'utilisation des ressources naturelles, elle permet de visualiser les relations économie-société-environnement et d'identifier un groupe de quatre acteurs de cette dynamique: 1) les habitants métisses et indigènes, 2) les entreprises extractives, 3) les organisations locales et internationales et enfin, 4) l'État équatorien (Juteau-Martineau, 2012). Ce dernier a été le principal acteur (positivement ou négativement) parmi les autres éléments lors des étapes du développement du pays depuis la pré-réforme agraire, la réforme agraire (1964-1979) et jusqu'à l'ère d'exploitation pétrolière à partir de 1973 (Juteau-Martineau et al., 2014).

Avant la réforme agraire, les relations entre les habitants autochtones de l'Amazonie et la nature étaient basées sur une agriculture itinérante à petite échelle ainsi que d'autres pratiques productives qui préservaient l'équilibre écologique et la conservation des ressources à long terme (Varea et al., 1995). L'économie équatorienne était basée sur l'exportation de produits agricoles de la région côtière (bananes et cacao notamment) et la population rurale servait généralement de main-d'œuvre agricole (Acosta, 2006). Pendant la première période de la réforme agraire (1964-1972), les provinces de Pichincha, Esmeraldas et Morona Santiago sont devenus de nouvelles zones de colonisation (Gondard and Mazurek, 2001) et l'industrie pétrolière, concentrée sur la côte Pacifique, restait minimale (EP Petroecuador, 2013). Cependant, une forte colonisation est apparue lors de la deuxième réforme agraire du pays, qui a coïncidé avec le début de la production pétrolière dans la NEAR (1972) et la construction de la raffinerie (1975) dans la province d'Esmeraldas (Wasserstrom and Southgate, 2013). À la suite de ces événements et des activités minières également en expansion, la colonisation des provinces amazoniennes et d'Esmeraldas a augmenté de manière exponentielle (**Figure III**), alors qu'elle est restée linéaire dans le reste du pays

(Gondard and Mazurek, 2001).

La route Quito-Lago Agrio (construite en 1972) a rendu la NEAR accessible, la colonisation de zones considérées jusque-là comme inhabitées (malgré la présence de populations autochtones) a avancé amplement, et les compagnies pétrolières ont construit de nombreuses routes et ponts (Wasserstrom and Southgate, 2013). L'exploitation des ressources naturelles (bois, pétrole, etc.) avec le soutien de l'état a forcé la migration des différents groupes ethniques ainsi que la confrontation entre les « colons» et les peuples « originaires » (Jarrín et al., 2016). Les entreprises étaient gérées sur le principe d'investissement minimal; les « colons » sont devenus la main-d'œuvre principale et on assistait en parallèle à l'expansion de l'agriculture pour l'autoconsommation ou pour le marché local (Gondard and Mazurek, 2001; Varea et al., 1995). Dans ces schémas de production, ni les aspects environnementaux ni les aspects socioculturels n'ont été pris en compte. Les nouveaux arrivants (appelés en Amazonie les «colonos»), sans assistance technique ni ressources financières, ont commencé à déforester et à appliquer leurs propres techniques agricoles, générant dès lors une importante dégradation des sols. Les pratiques

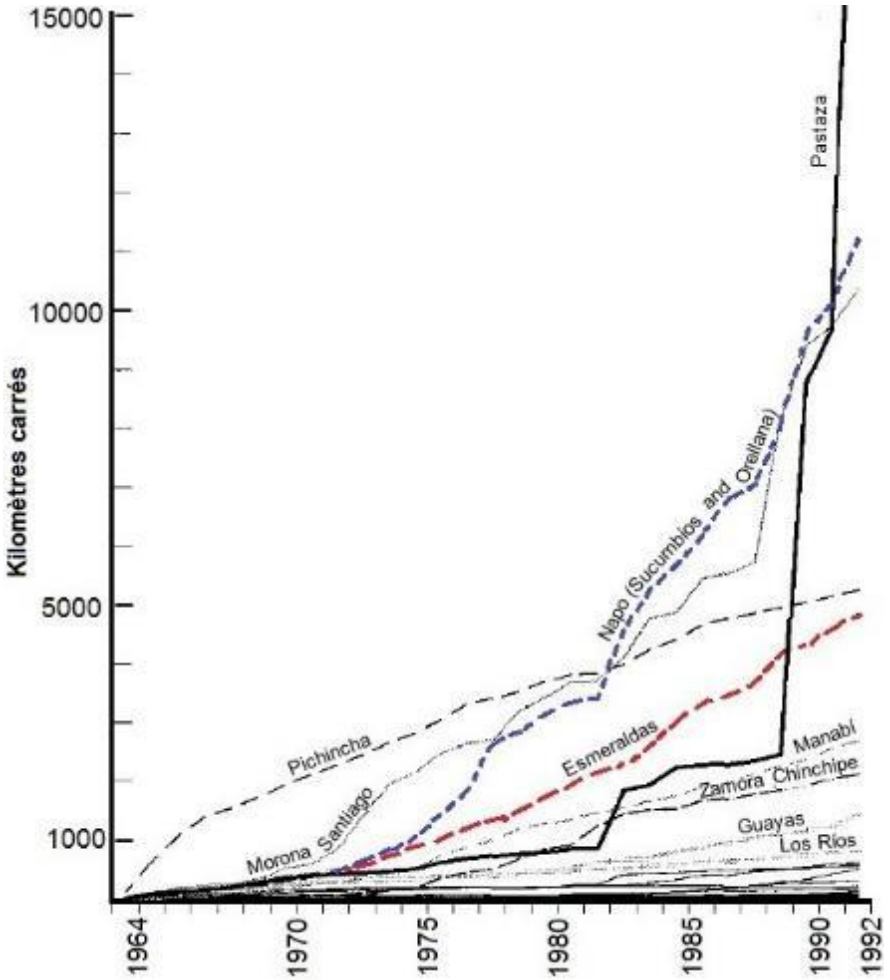


Figure III. Colonisation en Equateur: surface accumulée en km^2 (Gondard et Mazurek, 2001).

ancestrales telles que l'agriculture itinérante ont été perdues ou sédentarisées. L'économie est devenue dépendante des exportations de pétrole (Acosta, 2006) et les effets visibles de sa production sur les populations et l'environnement se sont multipliés (voir la section I.1.1).

Dans ce contexte, d'un point de vue sanitaire, plusieurs études épidémiologiques dans des communautés situées à proximité d'infrastructures pétrolières ont mis en évidence des affections de la santé humaine en raison d'une exposition chronique au pétrole brut et/ou à ses déchets toxiques. Ces études ont signalé des maladies respiratoires, des symptômes et des lésions cutanées ainsi que des effets chroniques, notamment des troubles psychologiques, des troubles endocriniens et reproductifs. Certaines études ont mis en évidence une génotoxicité de ces produits avec notamment des cas de leucémies, fausses couches et différents types de cancer (Arana and Arellano, 2007; Hurtig and San Sebastián, 2005; IESC, 2004; Kelsh et al., 2009; San Sebastián and Hurtig, 2005). L'eau est alors apparue comme le principal vecteur des contaminants (O'Callaghan-Gordo et al., 2016; Ramirez et al., 2017; Levy and Nassetta, 2011).

Hurtig and San Sebastian (2002) ont signalé que les taux de cancer dans les communautés équatoriennes vivant près des zones d'exploitation pétrolière étaient plus élevés que dans le reste du pays, et probablement liés, comme le proposent différents auteurs dans les années 2000, à des hydrocarbures tels que le benzo(a)pyrène, déversé dans les zones de production pétrolière (Buccina et al., 2013; Hurtig and San Sebastian, 2002). Cependant, aucune donnée sérieuse sur les impacts environnementaux des activités pétrolières sur la qualité de l'eau et du sol n'a été publiée à ce jour pour confirmer cette hypothèse. Plus récemment, Webb et al. (2016) ont analysé le mercure et le 1-hydroxypyrène (1-OHP) dans l'urine d'individus vivant dans les zones de production du pétrole au Pérou et en Équateur. Ils ont constaté que les femmes qui utilisent des eaux de surface pour se laver et se baigner présentent des teneurs plus élevées en mercure et HAPs; par ailleurs les concentrations en Hg étaient plus élevées chez les hommes au Pérou et chez les ouvriers travaillant pour la mise en place des dispositifs de remédiation des déversements de pétrole.

Cependant, la question de la santé est plus complexe puisque, en épidémiologie environnementale, il n'y a pas de relation directe entre les causes (émissions de déchets pétroliers) et les effets sur la santé (incidences du cancer), même si les habitants des zones pétrolières présentent des signes et des symptômes d'une exposition aiguë et/ou chronique au pétrole brut et aux composés volatiles. En 2008, des analyses génotoxiques sur des individus de la NEAR ont toutefois confirmé que l'exposition aux hydrocarbures avait causé

des dommages à l'ADN et augmenté le risque de développer un cancer (Paz-y-Miño et al., 2008).

I.1.3. Contexte socio-scientifique du projet MONOIL

Dans ce contexte de production pétrolière et de mise en évidence d'impacts sur l'environnement et la santé des habitants, l'Équateur a mis en place en 2008 une nouvelle constitution qui reconnaît le droit de la Nature à être restaurée, le droit des personnes à vivre dans un environnement sain et l'action de l'État pour garantir la santé et la restauration des écosystèmes en cas de catastrophes environnementales (AC, 2008). Ainsi, le gouvernement équatorien a mis en place le "Programa de Reparación Ambiental y Social" (PRAS). Ce programme inclut la politique publique de réparation des dégâts ou des passifs environnementaux comme une nécessité de l'État équatorien (Bissardon et al., 2013a; MAE, 2012).

En 2010, la "Secretaría Nacional de Ciencia y Tecnologia" (SENESCYT) et la compagnie pétrolière EP-Petroecuador ont demandé à l'Institut français de recherche pour le développement (IRD) de les aider à mieux comprendre toutes les conséquences sociales et environnementales des activités pétrolières en Equateur, et ce depuis la première période d'exploitation du pétrole dans la région amazonienne équatorienne. A partir de 2010, et en collaboration directe avec des partenaires académiques et institutionnels français et équatoriens, une équipe de l'IRD, du CNRS et de l'Université de Toulouse, au GET, a développé et mis en œuvre un projet de recherche binational d'évaluation des impacts des activités pétrolières en Equateur. Il s'agit du programme MONOIL (Monitoring environnemental, santé, société et pétrole en Equateur) qui a pour but d'améliorer les connaissances transdisciplinaires sur les impacts sociaux et environnementaux des activités pétrolières en Equateur (ANR, 2013). Ce programme a été financé par l'Agence Nationale de la Recherche (ANR, 2014-2018) et des aides supplémentaires ont été offertes en France par l'IRD et le CNRS, et en Équateur par les universités USFQ, EPN et UASB et le Secrétariat d'Etat à l'Education Supérieure, la SENESCYT (dont 2 bourses doctorales).

Cette thèse s'inscrit dès lors dans le deuxième objectif principal de ce projet, et notamment au sein de la tâche 3 du programme MONOIL qui a pour but de mesurer les impacts et les risques des mélanges chimiques des hydrocarbures aromatiques polycycliques (HAPs et des métaux et métalloïdes (TM) associés aux activités extractives sur la qualité des eaux, des sédiments et de la chaîne trophique aquatique.

Dans ce vaste programme pluridisciplinaire, un des objectifs vise à déterminer les sources et les niveaux de pollution causés par les activités pétrolières sur l'environnement dans la région amazonienne équatorienne (centre de production pétrolière) et sur la côte équatorienne (principale zone de raffinage). La zone d'étude est ainsi présentée avant de décrire les différents objectifs de cette thèse.

I.2. ZONE D'ETUDE

I.2.1 Les spécificités de la région amazonienne

La région amazonienne en Équateur représente 45% de la surface totale du pays et est placée sur une zone sédimentaire comprenant des plaines, des zones à forte pente, des aires marécageuses et sableuses; elle est formée de sols latéritiques issus de couches volcaniques présentant une teneur élevée en oxydes de fer et d'aluminium (**Figure IV**); cette région se trouve entre 200 et 1 200 m d'altitude, le climat y est humide et pluvieux avec une température moyenne de 25 °C et des précipitations annuelles de l'ordre de 500 à 4 000 millimètres (Narváez, 2000; Schlesinger, 2000). Au cours de l'année, les pluies sont abondantes et constantes sans saisonnalité marquée (Foucault, 2016); mais il y a deux périodes où les précipitations ont une influence majeure: la première de décembre à avril et la seconde de septembre à novembre, avec des valeurs maximales de mars à avril et en octobre. Les précipitations minimales sont généralement enregistrées de juin à août (Armijos et al., 2013; Gualpa et al., 2001). Les précipitations annuelles moyennes diminuent du nord au sud, elles sont en moyenne de 3100 mm dans le bassin du Napo et de 2000 mm dans le bassin du Santiago (Laraque et al., 2007; USDA, 2005)..

Des sables saturés de pétrole brut lourd et d'asphalte émergent le long des rives des rivières Hollin, Jodachi et Napo; les champs pétrolifères datent du Crétacé et la roche réservoir se compose de grès provenant des formations Hollin, Napo et Tena (Baby et al., 2014). Environ 68 200 km^2 (soit 68%) de l'Amazonie équatorienne sont recouverts de blocs pétroliers (**Figure IV**); avec 8,3 milliards de barils de réserves et une production journalière d'environ 550 000 barils (EP Petroecuador, 2013; Lessmann et al., 2016; OPEC, 2018).

Les précipitations, les températures et l'humidité dans la région amazonienne constituent des conditions idéales pour le développement de la forêt tropicale humide, un des écosystèmes offrant la plus grande biodiversité sur Terre. Près de 50% des espèces de mammifères amazoniens se trouvent en Amazonie équatorienne; 1 100 espèces d'arbres, 270 espèces d'amphibiens (150) et de reptiles (121), 500 espèces d'oiseaux, 300 espèces de mammifères,

382 espèces de poissons et 35 000 espèces d'insectes (sur un rayon de 3 km) ont été détectées dans le parc Yasuni (Bass et al., 2010; Dangles et al., 2009; Hettler et al., 1996). Ce parc national appartient à un groupe de dix zones protégées au sein de la région amazonienne équatorienne dans le cadre du programme «Sistema Nacional de Areas protegidas» (Système national d'aires protégées) (MAE, 2015b).

En dépit d'être une zone d'une biodiversité extrêmement riche, et avec des ressources naturelles importantes (pétrole, bois et agriculture), la région amazonienne présente le pourcentage de pauvreté le plus élevé du pays : 71% contre 45% au niveau national (INEC, 2010a).

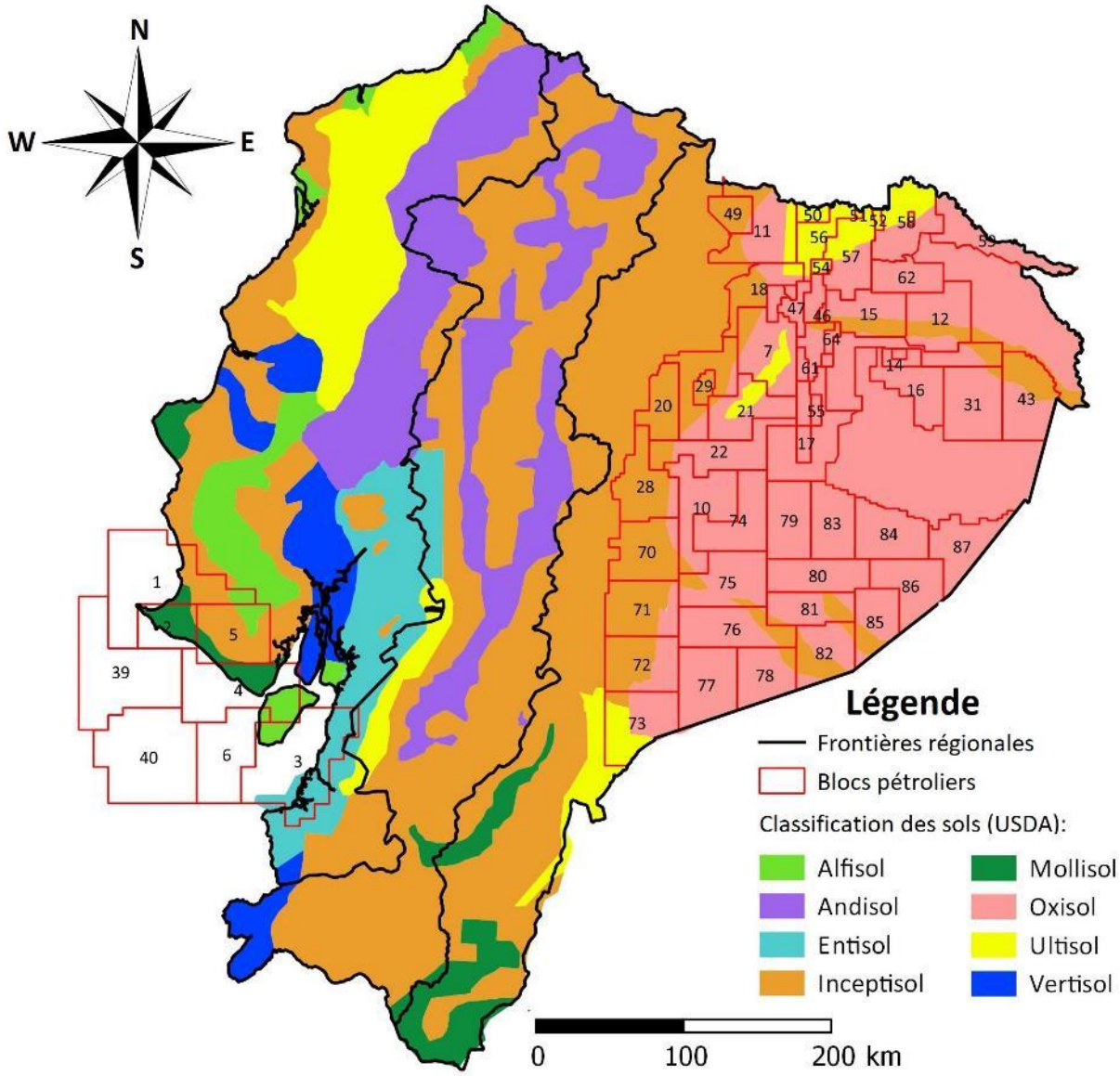


Figure IV. Classification des sols et distribution des blocs pétroliers en Équateur (modifié d'après USDA, 2005 et MAE-PRAS, 2015).

Avec près de la moitié du territoire national et seulement 5% de sa population totale, l'Amazonie équatorienne présente une riche diversité culturelle; 2 populations sont en isolement volontaire et 11 autres groupes de populations indigènes vivent dans le bassin amazonien équatorien (López, 2016; Oberem, 1980; Vallejo and Ávila, 2017). L'UNESCO (2010) a ainsi enregistré 9 langues autochtones en Amazonie équatorienne, toutes en danger d'extinction. Les autochtones représentent 30% de la population de cette région, les « blancs » 10% et les «métis» 60% (Juteau-Martineau, 2012).

En plus de l'exploitation pétrolière, la région amazonienne présente d'autres stratégies de production locale: 1) petit élevage et agriculture (cacao, café), 2) agriculture industrielle (palmier africain), 3) extraction de bois et de minéraux, 4) main d'œuvre technique pour différents travaux et 5) services touristiques ; ces activités sont secondaires par rapport à la capacité d'investissement de l'industrie pétrolière (SENPLADES and ECORAE, 2016; Varea et al., 1995).

I.2.2 Les spécificités de la côte Pacifique

La région Pacifique équatorienne (Costa) couvre 26% de la superficie du pays; elle s'insère entre l'océan Pacifique et les Andes occidentales. Les principaux bassins versants côtiers de l'Équateur sont les bassins du Guayas et d'Esmeraldas, qui s'écoulent d'est en ouest, dans l'océan Pacifique (Buckalew et al., 1998). Cette région présente une saisonnalité marquée avec une saison des pluies intense de février à mai et une saison sèche de juillet à novembre (Armijos et al., 2013).

La province d'Esmeraldas est située au nord-ouest de l'Équateur avec une superficie de 16 155,97 km² en plateau avec de petites collines formées par sols ferralitiques rouges fortement acides. Elle se caractérise par un climat tropical subhumide à très humide, et une température moyenne de 23 °C ; les rivières Teaone et Esmeraldas constituent le principal système hydrologique de la zone. Cette zone s'inscrit dans la microrégion de Choco présentant l'un des taux de biodiversité les plus élevés au monde (Espinosa et al., 2017; Sierra et al., 2009)

La population d'Esmeraldas représente 3% de la population équatorienne totale et se définit comme afro-descendante et métisse «mestizo» (INEC, 2010b). Malgré les activités industrielles (centrale thermique, raffineries, etc.), cette région est considérée comme l'une des plus pauvres de l'Équateur (SENPLADES, 2015). Une grande partie de son économie dépend du tourisme, de la production de crevettes, de bananes et de cacao et de l'élevage et la vente de bétail (PUCE-Esmeraldas, 2017).

I.3. OBJECTIF GENERAL DE LA THESE

L'objectif principal de ce travail est d'étudier les impacts des activités pétrolières actuelles et passées sur la qualité de l'eau du bassin amazonien équatorien (zone de production pétrolière) et du bassin versant de la rivière Esmeraldas (zone de raffinage) en déterminant les concentrations en HAPs dans les eaux de surface et les sédiments. L'étude spécifique des teneurs en HAPs et éléments inorganiques (métaux et métalloïdes) dans les sources d'eaux utilisées pour la consommation humaine fournira des informations sur les niveaux d'exposition des populations vivant dans ces zones.

I.4. OBJECTIFS SPECIFIQUES

Plus précisément, cette étude a pour objectif de :

- Mesurer les concentrations en HAPs dans les sédiments et eaux de surface (phase dissoute et particulaire) des rivières situées en zone d'exploitation pétrolière et de raffinage
- Mesurer les concentrations des TM et HAPs dans les eaux de consommation humaine en zone d'exploitation pétrolière et de raffinage
- Comparer les résultats avec une zone de contrôle située dans le bassin amazonien et non affectée par les activités extractives
- Identifier les potentielles sources de contaminants organiques et métalliques dans les eaux de surface et de consommation
- Comparer les résultats avec les normes nationales et internationales de régulation environnementale
- Calculer des indices de risque sanitaire pour les éléments cancérigènes et non cancérigènes mesurés dans les eaux de consommation
- Proposer des recommandations pour réduire le risque d'exposition des populations locales.

Le présent manuscrit est divisé en deux grands chapitres présentés sous la forme de publications scientifiques, l'un portant que la qualité environnementale des eaux de surface et des sédiments associées dans les zones impactées par les activités pétrolières et l'autre se focalisant sur la qualité sanitaire des eaux de consommation en Equateur. Les informations supplémentaires sont incluses dans chaque chapitre, et autres informations complémentaires sont presentés comme annexe à la fin de ce manuscrit de thèse.

Le **Chapitre 1** correspond à un article en préparation intitulé *"Polycyclic aromatic*

hydrocarbons (PAHs) in surface water and sediments at oil exploration and refining sites in Ecuador: concentrations and source distribution". Dans cet article, les hydrocarbures aromatiques polycycliques sont spécifiquement étudiés : les concentrations en HAPs dans les eaux de surface et dans les sédiments du bassin amazonien équatorien sont comparées entre les zones contaminées par le pétrole et une région non perturbée par les activités extractives, tout en tenant compte des recommandations nationales et internationales pour préserver la vie aquatique. Le quotient SQG moyen a été utilisé pour définir la priorité par rapport au niveau de toxicité. Le facteur de toxicité équivalente au benzo(a)pyrène (TEF) a été utilisé pour définir le risque cancérogène, et un important traçage des sources de ces polluants est proposé via la méthode des ratios isomériques.

Le **Chapitre 2** intitulé *" Drinking water quality in areas impacted by oil activities in Ecuador: associated health risks and social perception of human exposure*" traite des concentrations en HAPs et TM dans les eaux consommées sur la côte Pacifique et en Amazonie équatorienne. Les concentrations sont comparées aux directives équatoriennes et internationales relatives à la qualité de l'eau de consommation ; et une évaluation du risque sanitaire est proposée en considérant un scénario mis en œuvre sur deux populations (adultes et enfants) et en considérant deux voies d'exposition aux polluants (contact cutané et ingestion). En effet, en utilisant différentes sources d'eau brute comme source d'eau domestique, les populations équatoriennes peuvent mettre leur santé en danger, car les polluants émis par les activités pétrolières peuvent rapidement atteindre les systèmes aquatiques. Certaines recommandations sont également proposées. Ce chapitre 2 correspond à un article récemment publié dans le journal *Science for The Total Environment* (STOTEN) en juillet 2019.

Enfin, ce manuscrit de thèse s'achève par une partie de conclusions générales et de perspectives proposées pour ce travail.

La version anglaise de cette partie introductive est présentée en suivant.

INTRODUCTION (ENGLISH VERSION)

I.1. PROJECT CONTEXT

The Amazon rainforest is considered as the largest natural capital in Latin America due to the richness of its natural resources; this place has become the center of debates related with the economic, ecologic, and socio-cultural sustainability. The Ecuadorian Amazon basin, with a very low population density and only 2% of the total Amazon Rainforest, has an important register of socio-environmental conflicts, mainly due to oil production.

I.1.1. Oil production and refining in Ecuador: Historic, economic and legislative context

Oil production in Ecuador began inshore on the Pacific coast in 1911, and lasted concentrated in this region for 60 years (BCE, 1990); at present, this region produces less than 1%, while 99% is concentrated in the Ecuadorian Amazon region, mainly in the provinces of Orellana and Sucumbíos (Bustamante and Jarrín, 2005; EP Petroecuador, 2013). Extraction crude activities in the Northern Ecuadorian Amazon Region (NEAR) began in 1967 with the drilling of the first oil well by Texaco Gulf, becoming economically important in 1972, with a daily production of 300,000 barrels reaching 522,000 barrels in 2017 (BCE, 2018; EP Petroecuador, 2013). Since 1972, crude oil exportation has represented the main source of income for the Ecuadorian economy, exceeding 50% of total exportations from 2004 to 2014 (**Figure I**), and settling down at 37% in 2017 (BCE, 2010; Calderón et al., 2016; MCE, 2017). In South America, Ecuador is the 4th larger oil producer and the 3rd country with the largest oil reserves (OPEC, 2017).

Oil refining processes in Ecuador have been centered on the Pacific coast since their origin (1926); this region possesses 90% of the total refining production. The country has three refineries: “Esmeraldas”, "Libertad" and the industrial complex “Shushufindi”. The Esmeraldas

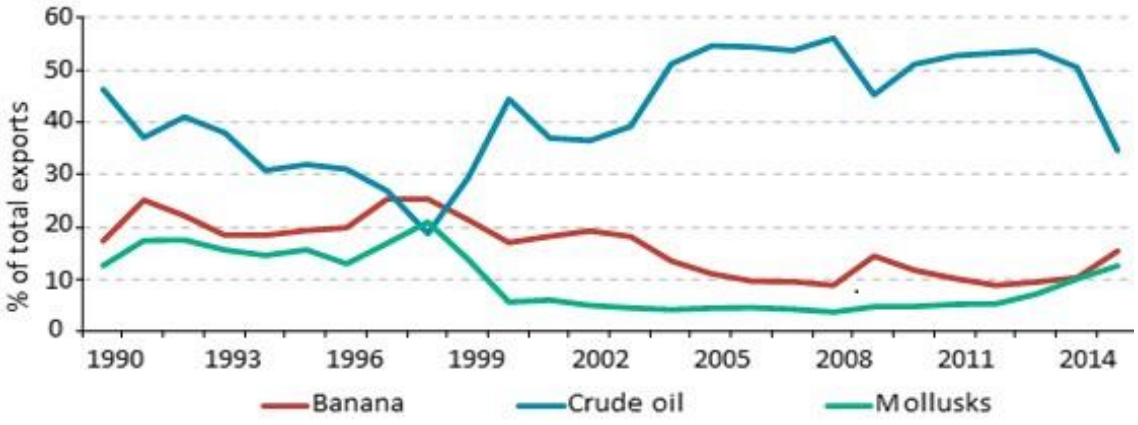


Figure I. Percentage of total exportations for the main Ecuadorian exporting products from 1990 to 2015. (Modified from: Calderón et al., 2016).

refinery (built in 1977) represents 63% of the total refining capacity (EP Petroecuador, 2013). La Libertad and Esmeraldas are refineries situated on the coast, whereas the Shushufundi refinery is located in the Northern Amazon area.

The oil production infrastructures concentrated in the NEAR and the refining facilities on the Pacific coast have generated many systems of storage and transport of crude oil and derivatives: the Trans-Ecuadorian pipeline (SOTE), the San Miguel-Lago Agrio pipeline (OSLA), the heavy-crude Pipeline (OCP) and the Eden Yuturi-Villano Pipeline. These pipelines collect and transport crude oil from the NEAR, crossing the Andean Cordillera, until the Balao seaport in Esmeraldas (EP Petroecuador, 2013).

Environmental practices related with oil industry in Ecuador remained unregistered until 1972: the first bibliographic reports dated back to the early 1970s and appeared because of the importance of Texaco trial in the last two decades (1990-2010). Some authors pointed out documents from 1972 which explained to employees that only environmental incidents already known by the press or the government should be reported, otherwise they do not have to be registered and the existing reports must be destroyed (Andrade, 2008; Buccina et al., 2013).

Through the 28 years that Texaco Gulf Company with other 12 private oil companies operated in the NEAR, no environmental regulation was enforced by Ecuador Government (BCE, 1990; Narváez, 2000). Oil production in a context of non-environmental policies caused almost 65 billion liters of crude oil spills, 76 billion liters of formation water discharged in the environment, and the burning of 7 million cubic meters of gas. And more than 1000 pools of toxic waste were abandoned (Narváez, 2000). In 1992, Texaco-Gulf transferred all its goods to the state company Petroecuador, without any remediation obligations imposed by the government at that time, and industrial practices remained similar for several years (Kashinsky, 2008).

The historic of the environmental practices related with the refining zones in the Pacific coast since the beginning has not been published; (Narváez, 2000) presents a record (1997-2000) of oil spills, pipeline and fire incidents that affected the Esmeraldas and Teaone rivers since 1997, but not previous information exists. CEPAL (1990) indicates that the obsolescence of infrastructures contributed to chronic pollution of the air, water and soil leaving a favorable scenario for socio-environmental conflicts; in the case of liquid effluents of the REE, they used to be diluted and dispersed in the Teaone and Esmeraldas rivers.

Chachalo (2016) signaled that Esmeraldas refinery (REE) generated more than 30000 tons of

dangerous byproducts in August 2014, and that new treatment processes are replacing the old ones since the last renovation in 2015. These kind of improvements were already realized in the refinery facilities in 1987, 1995 and 1997 allowing to increase the refining capacity from 55000 to 110000 barrels per day; but, these technical adjustments have not improved the refinery's impact on the environment (Cevallos, 2015).

In 2015, the Ecuadorian Ministry of Environment (MAE) inventoried 3 refineries (2 in the Pacific coast and 1 in the NEAR), 2 main oil pipelines, 6383 wells and 1190 platforms while the environmental liabilities were estimated at 1170 oil spills and 2489 waste pits (Ministerio del Ambiente (MAE), 2015a). These liabilities have induced important environmental and social impacts; several indigenous communities were forced to migrate (Buccina et al., 2013) and the pollution of surface and ground waters in Orellana and Sucumbíos provinces affected this rich biodiverse area (Bustamante and Jarrín, 2005; Marx, 2010; Wernersson, 2004).

According to the MAE-PRAS (2015), 97 % of the total environmental liabilities (waste pits and oil spills) is located in the NEAR being the water the abiotic component that local people claim as the most affected by oil activities (Clinica Ambiental and CSS, 2017).

The activities involved in the oil industry are grouped into five main phases: (1) exploration, (2) exploitation or production, (3) storage and transport, (4) refining and (5) commercialization. These activities impacts on the environment mainly affect water sources. However, production and transport phases are the most critical due to the high volumes of formation water (very salty liquid that contains hydrocarbons and metallic elements), drilling mud, process water and the risk of spills (Avellaneda, 2005; Fontaine, 2013). The activities of exploration-exploitation are now in charge of the Petroamazonas public company while the activities of refining, transport and sale are under the control of the Petroecuador public company. Some international-private companies (Chinese, Canadian, etc.) work together with the national enterprises.

Some authors have listed many of the cause-effect variables in the case of oil pollution in the Ecuadorian Amazon region (Buccina et al., 2013; IESC, 2004; Narváez, 2000; Widener, 2007). Some of the current practices mentioned by these authors for the 1972-1993 period, and that can affect negatively the aquatic system are shown in the **Figure II**, and listed below:

- One to three waste pools were built in the vicinity of oil wells to collect byproducts formed by drilling mud, water, oil residues and formation water.

- Solid and liquid wastes were accumulated in pools or discharged directly into rivers and

streams.

- Once waste was accumulated in pools, it was incinerated or recovered to be spread on local dirt roads.

- Crude oil residues were often released by runoff into rivers and estuaries.

- Gas was burned; about 200 flares continuously burned 2 million cubic meters of gas per day.

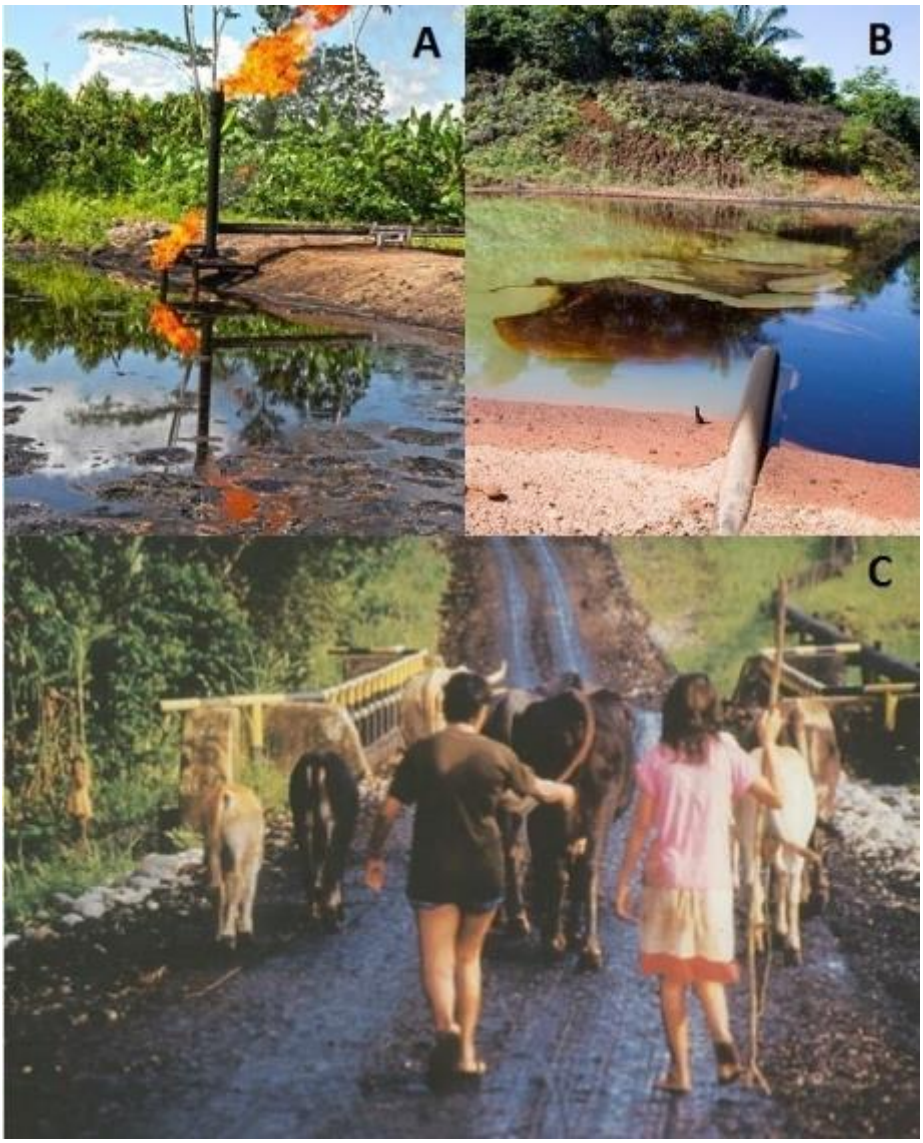


Figure II. Oil waste disposal in the NEAR: A. Waste earthen pool and open flares. B. Dumping or liquid waste. C. Crude oil spread on local dirt road. (Credit photos: A and B from MONOIL, 2015; C from IESC, 2004).

The bad industrial practices during oil production in the Ecuadorian Amazon region for several decades, represents a rare case of long-term chronic pollution where the adoption of environmental regulation arrived late and with a biased applicability. To ensure a legislative basis to the environmental protection and water quality, the TULSMA or "*Texto Unico de Legislación Secundaria del Ministerio del Ambiente*" (MAE, 2015; MAE, 2003) was

implemented by setting quality guidelines for water and liquid effluents in Ecuador but these thresholds were seriously reduced by the "*Reglamento Ambiental de las operaciones hidrocarburiferas*" (RAOHE, 2001) dedicated to the monitoring of oil activities effluents and emissions. There are high disparities between them.

Quality guidelines given by the RAOHE have no changed since their publication almost 20 years ago and are still considered for the effluents and emissions from oil industry, while TULSMA that is more accurate as it includes the guidelines given by the World Health Organization (WHO, 2017); it has been modified several times but reducing the number of monitored parameters (MAE, 2015). RAOHE legislation presents thresholds for only four toxic metallic elements (barium, chromium, lead and vanadium), for the Total Hydrocarbons (TPH) and Total PAHs in water and liquid effluents from the oil industry processes. But in any normative, river sediments control is considered while most of contaminants are hydrophobic.). These both two Ecuadorian regulations are presented in the **Table I.**

Table I. RAOHE and TULSMA water guidelines ($mg.L^{-1}$) for Ba, Cr, Pb, V, TPH and PAHs

ELEMENT	RAOHE[1] Discharge point	RAOHE[2] Control point	TULSMA Preservation of aquatic life	TULSMA Input to sewer system
Barium	<5	--	1.0	--
Chromium	<0.5	--	0.032	0.5 as Cr(VI)
Lead	<0.5	--	0.001	0.5
Vanadium	<1	--	--	--
TPH	<0.5	<0.5	0.5	20.0
PAHs	<0.0003	<0.0003	--	--

Source: Table 4 from RAOHE (2001); Table 2 and Table 8 from TULSMA-2015 (MAE, 2015)
1.- Point where effluents are discharged after treatment

According to the RAOHE normative, which proposed to monitor the risk for aquatic life, two criteria for choosing the sampling points are proposed: directly into the discharge point of the industrial effluent or downstream in the freshwater body receiving the effluent. In the TULSMA normative, effluents quality to freshwater body is controlled regarding the water uses (drinking water, preservation of aquatic life, etc.)

Are these effluents allowed to flow directly into a freshwater body? Do they affect aquatic life? And if formation waters reach the main sources of water used by the populations, is there any risk to human health?

Some questions that allows to visualize the ambiguity of the two Ecuadorian regulations regarding the oil activities monitoring and control.

I.1.2. Social and health context in oil activities zones in Ecuador

The petroleum production zones in Ecuador constitute an interesting case of study because it reflects the historical evolution of the land and natural resources use. It is possible to visualize the relations economy-society-environment and identify a group of four actors that define this dynamic: 1) the native inhabitants 2) the extractive companies, 3) the local and international organizations and 4) the Ecuadorian State (Juteau-Martineau, 2012). This latter has been the main integrator (positively or negatively) among the other actors during the stages of the development of the country before the agrarian reform (Juteau-Martineau et al., 2014), during the first and second agrarian reform period (1964-1979) and in the petroleum era (since 1973).

Before the agrarian reform, in the Amazon rainforest, the relationships between the native inhabitants and Nature were based in an itinerant small-scale agriculture and other productive practices preserving the ecological equilibrium and the conservation of natural resources in the long term (Varea et al., 1995). The Ecuadorian economy was based on the exportation of raw agriculture products coming from the coastal region (banana and cocoa) and the rural population generally served as workforce in these activities (Acosta, 2006).

During the first agrarian reform period (1964-1972), only Pichincha and Esmeraldas (where access roads existed) and Morona Santiago (where roads were built to encourage migration to the Southern Amazon) showed important new areas of colonization (Gondard and Mazurek, 2001). During this period, the petroleum industry, centered on the Pacific coast, was minimal (EP Petroecuador, 2013). But, a strong colonizing boom occurred since the issuance of the second agrarian reform law, which coincided with the start of oil production in the NEAR (1972) and the construction of the refinery (1975) in the Esmeraldas province (Wasserstrom and Southgate, 2013). As a consequence of these events and of the mining activities, the colonization of Amazonian provinces and Esmeraldas increased exponentially (**Figure III**).

When the road Quito-Lago Agrio was completed (1972), the NEAR became more accessible. The Ecuadorian government advanced with the colonization of zones considered uninhabited (ignoring the right of original groups regarding the land occupation) and the oil companies were asked to build complementary facilities (roads and bridges) (Wasserstrom, 2013). The companies that exploited natural resources (wood, petroleum, etc.) with the complicity of the government forced the displacement of ethnic groups, and the confrontation between “colonos” and indigenous people became usual (Jarrín et al., 2016). The petroleum, logging or agro-industrial companies were based on economic interests extracting the natural resources

with the minimum investment in workforce and technology; the "colonos" who became the main local workforce in the companies, expanded the agriculture for their self-consumption or to supply the local market (Gondard and Mazurek, 2001; Varea et al., 1995). In these productive schemes, neither environmental nor socio-cultural aspects were considered.

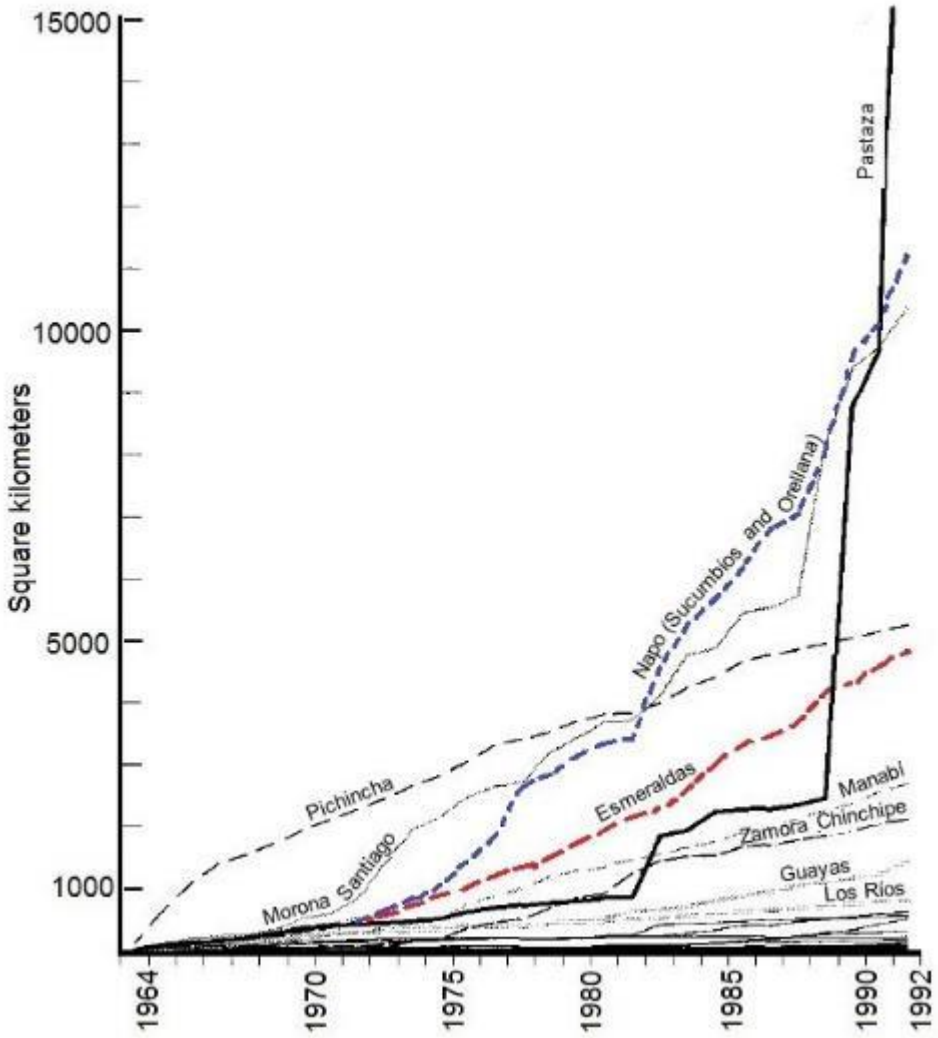


Figure III. Colonization in Ecuador: accumulated surface in km2 (from: Gondard and Mazurek, 2001).

The new settlers ("*colonos"*), without technical assistance or financial resources, cut down the forest and applied the same techniques from his place of origin generating important soil degradation; some ancestral practices such as the itinerant agriculture were lost or modified. The economy became dependent of petroleum exportations (Acosta, 2006). But the effects of oil production on populations and the environment were multiple (See Section I.1.1)

In a health context, several epidemiological studies assigned human health affections in communities based near oil infrastructures due to chronic exposure to crude oil and its toxic byproducts. These studies reported respiratory diseases, skin symptoms and lesions, and chronic effects including psychological disorders, endocrine and reproductive affections and

genotoxicity with leukemia, miscarriages and different sort of cancers (Arana and Arellano, 2007; Hurtig and San Sebastián, 2005; IESC, 2004; Kelsh et al., 2009; San Sebastián and Hurtig, 2005) with water being one of the main vectors of contaminants (O'Callaghan-Gordo et al., 2016; Ramirez et al., 2017; Levy and Nassetta, 2011).

Hurtig and San Sebastian (2002) reported that cancer rates in Ecuadorian communities living close to oil exploitation areas were higher than in the rest of the country, possibly linked, as proposed by different authors in the 2000's, to oil-based pollutants such as benzo(a)pyrene discharged into oil production areas (Buccina et al., 2013; Hurtig and San Sebastian, 2002). But any serious data on environmental impacts of oil activities on the water and soil quality were published to confirm this hypothesis.

More recently, Webb et al. (2016) analyzed mercury and 1-hydroxypyrene(1-OHP) in urine samples from humans living in the Amazonian oil production zones in Peru and Ecuador, and determined that women using surface water for washing and bathing showed higher contents of mercury and PAHs; this author found also that men exposed to mercury concentrations were higher in Peru and in individuals involved in oil spill remediation activities.

But the health issue is more complex since, in environmental epidemiology, there is no direct relationship between causes (oil by-products emissions in the environment) and health effects (cancer incidences), even if inhabitants living in oil areas show different signs and symptoms of an acute and/or chronic exposure to crude oil and gas compounds. For example, in 2008, genotoxic analyses on individuals from the NEAR confirmed that the exposition to hydrocarbons has produced DNA damage and increased the risk of developing cancer (Paz-y-Miño et al., 2008).

I.1.3. Socio-scientific context of the MONOIL project

In this general context of oil production and impacts on Amazon rainforest environment and inhabitant's health, in 2008, Ecuador established a new Constitution which recognizes the right of Nature to be restored, the rights of people to live in a healthy environment, and the action of the State to guarantee the health and the restoration of the ecosystems in the case of environmental disasters (AC, 2008). The Ecuadorian Government has established the "Programa de Reparación Ambiental y Social" (PRAS). This program includes the public policy of repairing damages or environmental liabilities as a necessity of the Ecuadorian State (Bissardon et al., 2013a; Ministerio del Ambiente (MAE), 2012).

In 2010, the "Secretaría Nacional de Ciencia y Tecnologia" (SENESCYT) and the oil company

EP-Petroecuador requested the French Institute of Research for the Development (IRD) to help them in understanding better all the social and environmental consequences of oil activities since the first period of oil exploitation in the Ecuadorian Amazon region. From 2010, in straight collaboration with French and Ecuadorian academic and institutional partners, IRD's team developed and implemented a binational research project for evaluating the impacts of oil activities in Ecuador, the MONOIL program which aims to improve transdisciplinary knowledge on the social and environmental impacts related with the oil activities in Ecuador (ANR, 2013). This Program has been funded by the French National Research Agency (ANR, 2014-2018) and some additional helps have been offered in France by the IRD and the CNRS, and in Ecuador by the USFQ, the EPN and the UASB Universities; and the SENESCYT (2 PhD grants).

This Thesis is part of the second main objective and the task 3 of the MONOIL program: "Monitoring of oil activities in Ecuador: a cross-disciplinary approach between Environment, Health and People", that aims to measure the impacts and risks of chemical mixtures of polycyclic aromatic hydrocarbons (PAH) and trace metal(oid)s (TM) associated with extractive activities on waters, sediments and aquatic food chains.

In the large and pluridisciplinary MONOIL program, this specific work aims to determine the origins and the levels of pollution caused by oil activities on the environment in the Ecuadorian Amazon Region as the center of oil production and in the Ecuadorian Pacific coast, where the main refinery of the country is located. The study area is thus presented before describing the different objectives of this work thesis.

I.2. STUDY AREA

I.2.1 Amazon Region: specificities

The Amazon Region in Ecuador represents 45% of the total surface of the country and is placed over a sedimentary zone that includes plains, areas with steep slopes, swampy and sandy areas; this region is mainly formed by lateritic soils of volcanic coats that are characterized by their high content of iron and aluminium oxides (**Figure IV**); it is located between 200 and 1 200 m.a.s.l and the climate is defined as wet and rainy with an average temperature of 25 °C and an annual precipitation of 500 to 4 000 millimeters (Narváez, 2000; Schlesinger, 2000). During the year, the presence of abundant rains tends to be constant without a marked seasonality (Foucault, 2016); but there are two periods in which precipitation has a major influence: the first from December to April, and the second from September to November,

with maximum values in March–April and in October. The minimum rainfall is registered from June to August (Armijos et al., 2013; Gualpa et al., 2001). The mean annual precipitation decreases from the North to the South, from 3100 mm in the Napo basin, and 2000 mm in the Santiago basin (Laraque et al., 2007; USDA, 2005)..

Sands saturated with heavy-crude oil and asphalt emerge along the banks of the Hollin, Jodachi and Napo rivers; the oilfields date from the Cretaceous and the reservoir rock consists of sandstone from Hollin, Napo and Tena formations (Baby et al., 2014). 68 200 km^2 (68%) of the Ecuadorian Amazon is covered by oil blocks from the Andean piedmont till the Peruvian border (**Figure IV**); with 8.3 billion barrels of proved reserves and an average daily production of ~550000 barrels (EP Petroecuador, 2013; Lessmann et al., 2016; OPEC, 2018).

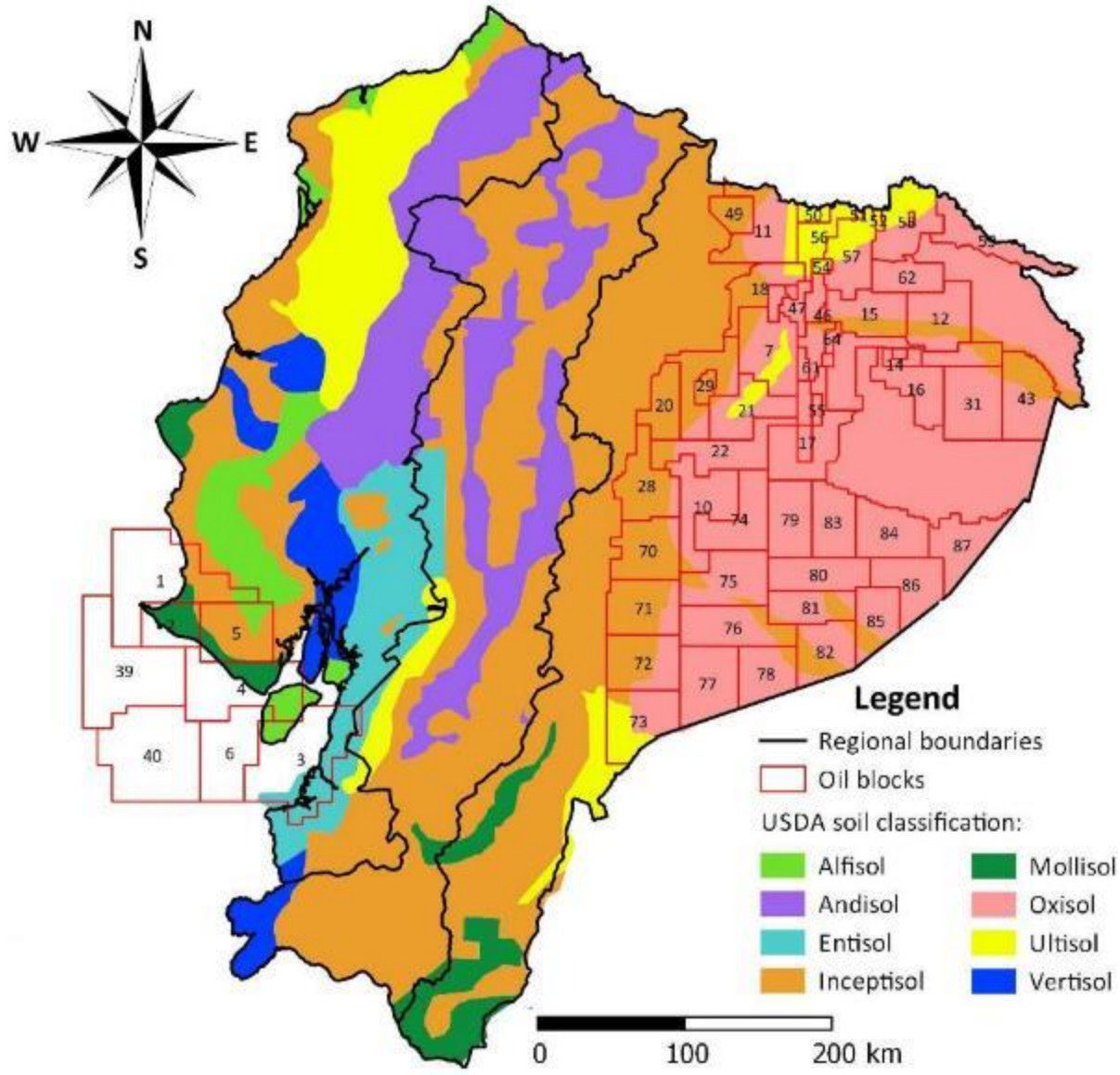


Figure IV. USDA soil classification and oil blocks distribution in Ecuador (modified from: USDA, 2005 and MAE and PRAS, 2015).

Precipitation, temperature and humidity in the Ecuadorian Amazon Region constitute ideal conditions for the development of the tropical humid forest that is among the ecosystems with the greatest biodiversity on Earth. Almost 50% of all Amazonian mammal species are found in the Ecuadorian Amazon; 1 100 species of trees, 270 species of amphibians (150) and reptiles (121), 500 species of birds, 300 species of mammals, 382 species of fish and 35 000 species of insects (in a 3 km radius) have been detected in the Yasuni Park (Bass et al., 2010; Dangles et al., 2009; Hettler et al., 1996). This National Park belongs to a group of ten protected areas that exist in the Ecuadorian Amazon Region as part of the "*Sistema Nacional de Areas protegidas*" (National protected areas system) (MAE), 2015b).

In despite of being a zone extremely rich in biodiversity with important natural resources (petroleum, wood and agriculture), the Amazon region present the highest percentage of poverty: 71% compared with the national level of 45% (INEC, 2010a).

With nearly half of the national territory and only 5% of the total population, the Amazon region presents a rich cultural diversity; 2 populations in voluntary isolation and 11 other groups of native populations live in the Ecuadorian Amazon basin (López, 2016; Oberem, 1980; Vallejo and Ávila, 2017); UNESCO (2010) registered 9 native languages in the Ecuadorian Amazon, all of them in danger of extinction. The natives represent 30 % of the population in this region, the whites, 10% and the "*mestizos*" 60% (Juteau-Martineau, 2012).

In addition to oil production, the Amazonian region presents other basic production strategies: 1) small scale livestock and agriculture (cocoa, coffee), 2) industrial agriculture (African palm), 3) extraction of wood and minerals, 4) sale of force-work and 5) tourism services, activities considered secondary compared with the investment capacity of petroleum industry(SENPLADES and ECORAE, 2016; Varea et al., 1995).

I.2.2 Pacific Coast: specificities

The Ecuadorian Pacific Coast (Costa) covers 26% percent of the country surface; it is located between the Pacific Ocean and the western Andes. The coastal major watersheds in the Ecuador are the Guayas and the Esmeraldas which drains to the west into the Pacific Ocean (Buckalew et al., 1998). This region presents a marked seasonality with a wet season from February to May and a dry season from July to November (Armijos et al., 2013).

Esmeraldas Province is located in the northwestern corner of Ecuador and covers a land area of 16 155.97 km². The territory is flat, with small hills formed by highly desaturated and acid red ferralitic soils (Espinosa et al., 2017). The climate of Esmeraldas is tropical from sub humid

to very humid, with an average temperature of 23 °C. The Teaone and Esmeraldas Rivers make up the hydrological system of the province. Esmeraldas is part of the Choco microregion that has one of the highest rates of biodiversity in the world (Sierra et al., 2009)

The population in Esmeraldas represents 3% of the total Ecuadorian population and is defined as afrodescendant and "mestizo" (INEC, 2010b). Despite of the industrial activities (thermal plant, refineries, etc.), this region is considered as one of the poorest in Ecuador (SENPLADES, 2015). Much of its economy depends on tourism, the production of shrimp, banana and cocoa; and livestock (PUCE-Esmeraldas, 2017).

I.3. GENERAL OBJECTIVE

The main objective of this work is to study the impacts of current and past oil activities on water quality of the Ecuadorian Amazon basin (oil production area) and the Esmeraldas River watershed (refining zone) by the determination of the concentrations of polycyclic aromatic hydrocarbons (PAHs) in surface water and sediments. The specific study of metal(loid)s and PAHs contents in water sources used for the human consumption will provide information on exposure levels of populations living in these areas.

I.4. SPECIFIC OBJECTIVES

- Measure the concentrations of PAHs in sediments and surface waters (dissolved and particulate phase) from petroleum production and refining areas.
- Measure the concentrations of trace metal(oid)s and PAHs in human consumption waters from petroleum production and refining areas
- Compare the results with a control watershed located in the Southern Amazon basin and unaffected by extractive activities.
- Identify the sources of contaminants in surface and/or drinking waters.
- Compare the results with national and international environmental guidelines.
- Calculate health risk indices for carcinogenic and non-carcinogenic elements in drinking waters
- Propose recommendations for local populations to reduce the risk of exposure to contaminants.

The present manuscript is divided into two big chapters presented in scientific publication format, one dealing with environmental quality of surface waters and sediments, in areas impacted by oil activities; and the other focusing on health quality of drinking waters in

Ecuador. The Supplementary information is also included in each chapter, and other additional information is presented as an appendix at the end of the manuscript thesis.

The **Chapter 1** is a draft version of a scientific article entitled "*Polycyclic aromatic hydrocarbons (PAHs) in surface water and sediments at oil exploration and refining sites in Ecuador: concentrations and source distribution*". In this draft article, polycyclic aromatic hydrocarbons are specifically studied; PAHs contents in surface waters and sediments are compared in oil impacted areas with a pristine region not disturbed by extractive activities taking into count the current national and international quality guidelines to preserve the aquatic life. The mean SQG quotient was used to define the priority relative to the level of toxicity; the toxicity-equivalent benzo(a)pyrene factor (TEF) was employed to define the carcinogenic risk, and an important source tracing was done by using the isomeric-ratios method.

The **Chapter 2** entitled "*Drinking water quality in areas impacted by oil activities in Ecuador: associated health risks and social perception of human exposure*" deals with concentration data for PAHs and metal(oid)s in drinking waters from the Pacific coast and the Amazon region. Results were compared to Ecuadorian and International quality guidelines and an assessment of health risks involved by the two exposition pathways (dermal and ingestion) is proposed considering a scenario on two populations (adults and children).Actually, by using different raw water sources as domestic water supplies, Ecuadorian populations can endanger their health since oil pollutants can reach aquatic systems. Some recommendations are also proposed. This Chapter 2 corresponds to an article published in *Science for The Total Environment* (STOTEN) in July 2019.

And finally, a last part of general **discussions** and **perspectives** is presented at the end of the manuscript.

CHAPTER 1. Tracing oil activities sources by PAHs distribution in surface water and sediments of the Amazonian and coastal regions of Ecuador

Forewords

"Je découvre que l'absence a une consistance. Peut-être celle des eaux sombres d'un fleuve, on jurerait du pétrole, en tout cas un liquide gluant, qui salit, dans lequel on se débattrait, on se noierait. Ou alors une épaisseur, celle de la nuit, un espace indéfini, où l'on ne possède pas de repères, où l'on pourrait se cogner, où l'on cherche une lumière, simplement une lueur, quelque chose à quoi se raccrocher, quelque chose pour nos guider. Mais l'absence, c'est d'abord, évidement, le silence, ce silence enveloppant, qui appuie sur les épaules, dans lequel on sursaute dès que se fait entendre un bruit imprévu non identifiable, ou la rumeur de dehors." *-Phillipe Besson, 2017*

"I discover that absence has a consistency. Perhaps that of the dark waters of a river, we would swear oil, at least a sticky liquid, which dirties, in which we would struggle, we would drown. Or maybe it's a thickness, the thickness of the night, an indefinite space, where we don't have any landmarks, where we could hit each other, where we look for a light, just a glow, something to hold on to, something to guide us. But absence, of course, is first; and the silence, that surrounding silence that presses on the shoulders, and in which one jumps as soon as an undefined and unexpected noise is heard; or the rumour from outside." *-Phillipe Besson, 2017*

Polycyclic aromatic hydrocarbons (PAHs) are considered as ubiquitous contaminants in the environment; they are formed by three or more benzene rings in its structure **(Figure V)**; but the molecules with four to seven rings are considered particularly toxic. PAHs are generated by the incomplete combustion of organic materials (wood or fossil fuels); in general PAHs of high molecular weight (e.g., fluoranthene, benzo(a)pyrene) are considered issued of combustion while the molecules of low molecular weight (e.g., naphthalene, fluorene) and the alkylated ones are associated to unburned petroleum (Crane and Hennes, 2007).

Environmental quality has been traditionally based on specific water and sediment thresholds developed and adopted by different countries. These thresholds or guidelines are developed since toxicity tests on benthic environments and recommended for protecting the aquatic life from adverse effects (CCME, 1999). In the case of sediments Keshavarzi et al. (2015) classified the different sediment quality guidelines (SQG) as follows:

-Effect range low (ERL) and threshold effect level (TEL) are thresholds below which adverse effects are not expected;

-Effect range median (ERM) and probable effect level (PEL) are thresholds related with concentrations where adverse effects are more probable to be manifested.

A description of TEL, PEL and different effect ranges are presented in the **Figure VI**.

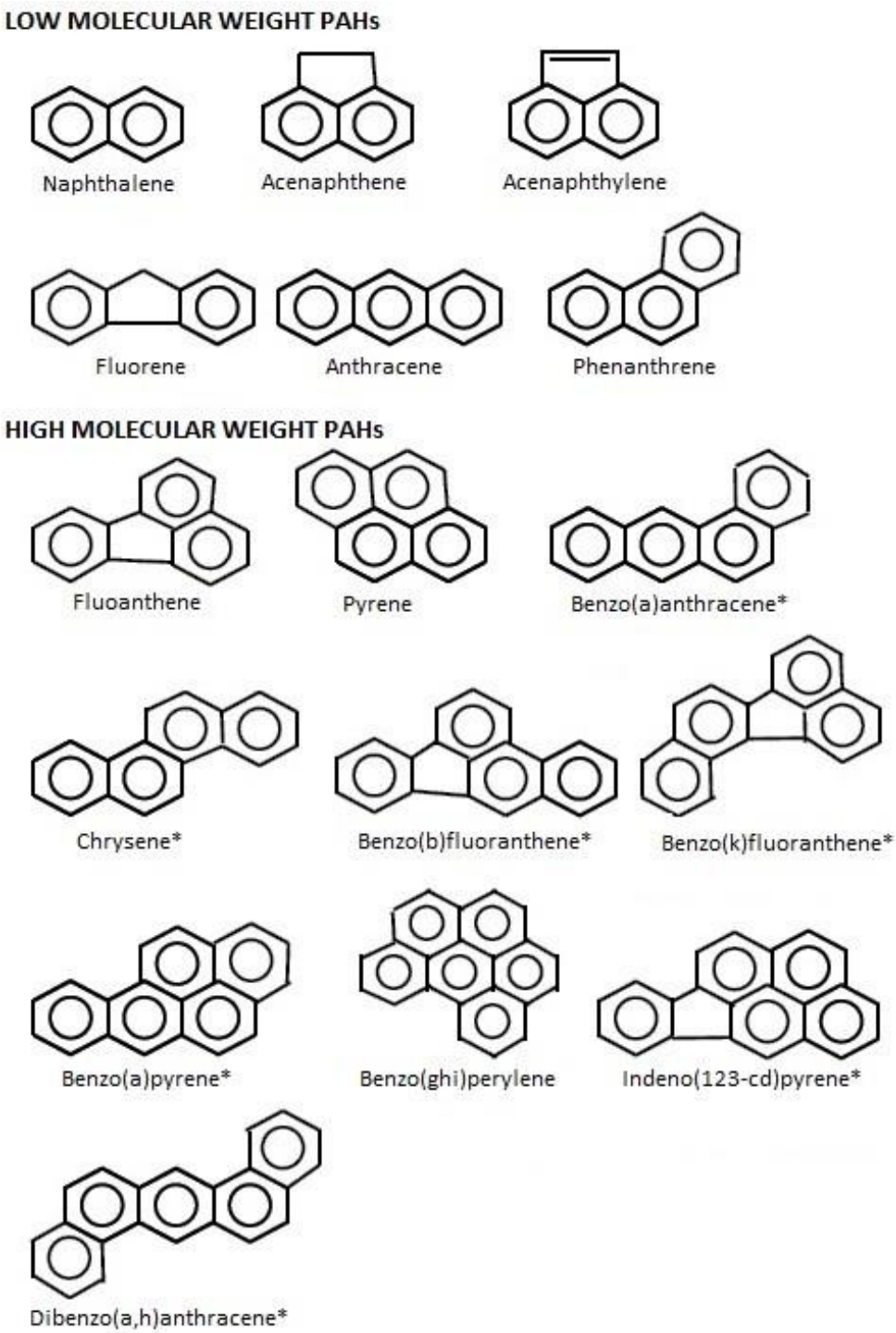


Figure V. Structure of sixteen US-EPA parent PAHs. (*) Molecules considered as possibly carcinogenic (modified from CCME,2010).

Other values like the “no observed effect level” (NOEL) and the “lowest observed effect level” (LOEL) are also important thresholds used for developing specific sediment quality guidelines (CCME, 1999).

Although many environmental quality guidelines (water and sediments) have been proposed by different countries, the criteria given by the NOAA (2008) and CCME (2018) have become

the most frequently employed to assess environmental quality based on the charge of pollutants in sediments (Hübner et al., 2009; Kwok et al., 2014). These SQG are nearly similar since they both are based in the rapports developed by Long and Morgan (1990) and compiled by Swartz (1999). Not being deeply modified since then, they are considered as the most accurate sediment quality criteria for aquatic ecosystems (Burton, Jr., 2002; de Deckere et al., 2011; Ugwu and Ukoha, 2018).

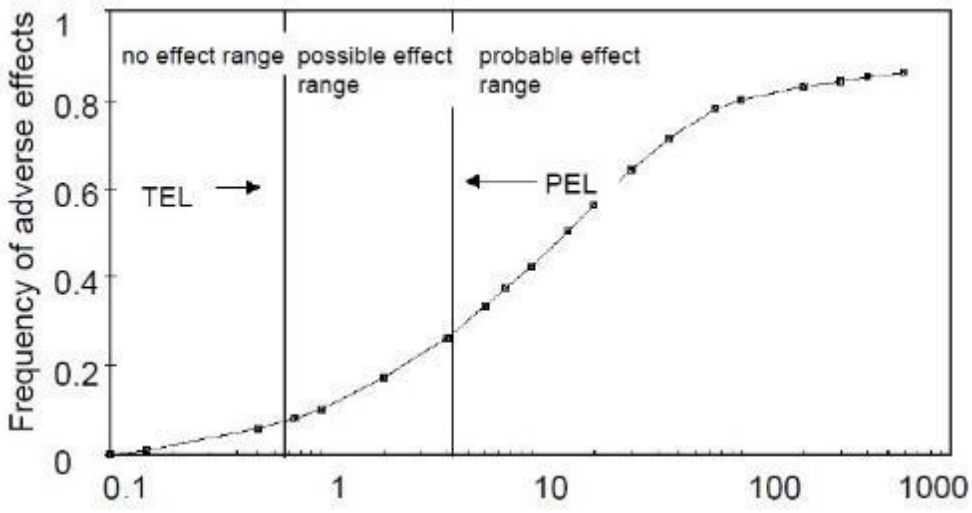


Figure VI. Conceptual example of threshold effect level (TEL) and Probable effect level (PEL).Source: CCME (1999).

Some chemicals are harmless individually and/or at low doses, but can be harmful when they interact. Amiard (2017) defines four ways in which chemicals can interact (synergy, antagonism, inhibition and potentiation). It is called "the cocktail effect" and cannot be evaluated by the individual toxicity thresholds, because they do not take into account the different interactions. The identification of these conjugated effects constitutes a major scientific challenge and some methods has been proposed (Choudhury et al., 2000; European Commission, 2012).

There are many aspects where environmental conclusions based on GC and GCMS data may be unclear, or inadequate, in general as a result of weathering processes (evaporation, photo oxidation, water washing, and biodegradation: they change the distribution of components in the spilled material making it very different from the original sample. The possibility of incorporating the isotopic analysis (carbon and/or hydrogen isotopic analysis) can eliminate many of these uncertainties because stable isotopes have the ability to permit a better correlation between original and weathered samples; but even with isotopic chemistry an individual compound from oil spills would be nearly useless for trace sourcing (Baskaran, 2012). The fingerprinting of the n-alkane fraction in crude oils and refined products combined

with isotopic analysis of carbon from individual homologues is also useful to tracing sources of sediment contamination. But the principal aim of the different hydrocarbon fingerprint identification techniques is to distinguish biogenic, petrogenic and pyrogenic sources (Wang and Fingas, 2003) .

Measuring and defining environmental risk and tracing sources of oil pollutants (PAHs) are the main topics in our first chapter developed in the lines below.

Polycyclic aromatic hydrocarbons (PAHs) in surface water and sediments at oil exploration and refining sites in Ecuador: concentrations and source distribution

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Highlights

- PAHs concentrations in surface waters were in range with levels measured in control zones.
- Punctual pollution was found in few streams of the refining and extraction areas.
- The perylene predominance highlights the biogenic fingerprint in the sediment's PAHs content.
- Sedimentary and dissolved phases are in compliance with quality guidelines.
- Cluster analysis applied to Isomeric ratios showed the fingerprint of ancient pollution.

Abstract

Polycyclic aromatic hydrocarbons (PAHs) are compounds of environmental and health concern due to their toxicity. In rivers, PAHs can accumulate in sediments and suspended materials increasing the risk of exposition and damage to aquatic flora and fauna. In Ecuador, several natural (volcanism, organic matter decomposition) and anthropogenic sources (slash and burn, incomplete combustion of wood and fossil fuels, oil refining and production, oil spills, etc.) are suspected to have an important effect on the distribution and transport of PAHs in rivers. In the present study, concentrations of 39 PAHs containing the sixteen parent PAHs recommended by the U.S. Environmental Protection Agency (US EPA) and their alkylated forms were determined in surface water and sediments of the crude oil production zone (Napo and Aguarico river basins) and the refining zone (Esmeraldas river basin). Their distribution has been compared to rivers located in non-extractive sites.

Alkyl-naphthalenes represented the most important fraction of total aromatic charge in the dissolved phase. With PAHs concentrations below the international quality guidelines for the preservation of the aquatic life, surface waters are not at risk in the different basins except in the national refinery effluent and in one point located in an oil field (Auca 22).

The total aromatic charge in sediments showed in most of the sampling sites an important biogenic fingerprint due to the predominance of perylene. The alkylated-low-molecular weight compounds were the most abundant fraction in all sites, which indicates a petrogenic origin. By considering the non-alkylated PAHs in sediments, significant correlations were found between the Auca-oilfield sampling points and the crude oil showing that sediments collected from Rumiyacu and Tiputini Rivers are directly affected by oil extraction activities. Similar results were obtained along the Aguarigo River in the parishes of Dureno, Pacayacu and Shushufindi.

In the Amazon region, oil activity is considered by local communities as the main source of environmental pollution and health risk. Even if there is evidence that natural petrogenic sources are meaningful, we found that pyrolytic and biogenic sources are not negligible.

Keywords: polycyclic aromatic hydrocarbons, sources, environmental quality, surface water, sediments, risk

1. Introduction

Ecuador is affected from east to west by all the petroleum-industry stages, most of which are centered in two areas the Northeast Amazonian region (NEAR), focused on crude extraction and characterized for having the totality (99.8% of oil rigs) of crude extraction facilities, and the Northeast Pacific Coast (NEPC), related with refining process, where 155000 barrels per day (90 % of the total refining capacity) are treated, with the majority (110000 barrels per day) being processed in the Esmeraldas refinery (BCE, 2018; EP Petroecuador, 2013).

Petroleum activities executed in Ecuador during the last four decades, in particular during the period from 1970 to 1993, are related with many environmental and social problems.

As a consequence of the lack of environmental policies, crude-waste byproducts were directly released in the environment, polluting waters, air and soils, affecting humans health, as well as the local flora and fauna (Clínica Ambiental, 2017; Jochnick and Normand, 1994; Paz-y-Miño et al., 2008; San Sebastián and Hurtig, 2005). The dumping of oil-waste and crude oil in the Ecuadorian Amazon region is considered among the most extreme cases of pollution in the world, with 18 billion gallons of formation-water and 16 million gallons of spilled crude, approximately 50% more than the crude dumped by the Exxon Valdez in Prince William Sound, Alaska, in 1989 (Buccina et al., 2013; Narváez, 2000; Skinner and Reilly, 1989). The "Centro de Estudios para America Latina y el Caribe", CEPAL (1990), noted that the infrastructural obsolescence of the Esmeraldas Refinery contributed to chronic environmental pollution in the nearby of the Esmeraldas Refinery (REE), where the liquid effluents used to be diluted and dispersed in the Teaone and Esmeraldas rivers.

Since hydrocarbons constitute the main fraction of crude oil, many organic molecules, in particular the polycyclic aromatic hydrocarbons (PAHs) have been widely used to trace the petrogenic origin of pollution (Benlahcen et al., 1997; Chen et al., 2015; Li et al., 2014; Speight, 2002). PAHs are molecules formed by multiple (2 to 6) fused aromatic rings and distributed in the different environmental compartments as function of their solubility and vapor pressure, these physicochemical properties (**Table SI-1**) are inversely correlated with the molecular weight and the alkylated substituents (Jørgensen and Fath, 2010). Therefore, low molecular weight species (2-3 benzene rings) are mostly found in water and high molecular weight species (4-6 benzene rings) are dominant in particulate matter and sedimentary bed.

As other persistent organic pollutants (POPs), most PAHs can resist to environmental

degradation resulting in their bioaccumulation and increasing the probability of exposure and the risk of acute and chronic toxic effects on human health and the environment (Abdel-Shafy and Mansour, 2016). Though non-metabolized PAHs are suspected to produce toxic effects (i. e. ingested or inhaled naphthalene is related with the destruction of red-blood cells), a higher concern is given to the produced metabolites, such as epoxides and dihydrodiols, since these molecules present probed genotoxic and carcinogenetic properties (Rengarajan et al., 2015).

PAHs with alkylated substituents, commonly present in crude oils and ancient sediments, are known to be more abundant, persistent ant toxic than parent PAHs; hence including the alkylated PAHs along with the parent PAHs concentrations is thus important in a risk assessment (Budzinski et al., 1995; Casal et al., 2014)

Once in the human body, PAHs are easily absorbed in the intestine, and metabolized by the liver. A study done on aquatic species after a marine oil spill, showed that PAHs in fish and crustaceans can contribute from 2 to 7% in human exposure by ingestion pathway (Amiard, 2017).

For their carcinogenic and mutagenic properties, 16 molecules have been considered as priority pollutants by the US-EPA; this list includes seven molecules (benzo(a)anthracene, chrysene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k) fluoranthene, dibenz(a,h)anthracene, and indeno(1,2,3-cd)pyrene) considered as carcinogenic for humans (Bojes and Pope, 2007; US EPA, 2015a). Amiard, (2017) claims that PAHs in humans can induce hematological, immunological, hepatic and reproductive disorders, with 4-5 aromatic rings being the most carcinogenic, in particular the Benzo(a)pyrene.

Despite the concerning health issue, till now, no precise data on PAHs contents and distribution in the aquatic systems of the Ecuadorian oil exploration and refining sites were available. This work is based on the analysis of polycyclic aromatic hydrocarbons (PAHs) in surface water and sediments from the main basins of two Ecuadorian regions affected by oil activities in order to: (i) analyze the influence of oil activities on environmental quality (PAHs concentrations) of waters and sediments by comparing the zones of crude extraction and refining areas with control zones; (ii) compare PAH concentrations in water and sediments with different quality guidelines and (iii) Asses the fingerprint of the PAHs origins by using statistical methods as Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA).

2. Materials and methods

2.1 Study Area

Extraction zone

The Ecuadorian Amazon region represents 116 588 km^2 (2% of the total Amazonian rainforest) and covers nearly half of the Ecuadorian territory (Ríos and Oliveira-Miranda, 2015). The oil extraction facilities are located in the northern part of the Ecuadorian Amazon region (NEAR); this zone is known as a hot spot of biodiversity, being even considered as the richest place on Earth in terms of biodiversity (Dangles et al., 2009). Average precipitation levels can reach 4000 mm annually with air temperatures nearly constant and a not very differentiate seasonality during the year (Armijos et al., 2013; Schlesinger, 2000). Along the Napo and Aguarico Rivers, seven sub-basins were selected between 75°12'0"-77°47'58"W and 0°3'25"N-1°2'50"S. This area covers the parishes of Dayuma and Pacayacu considered as the main hot spots of oil extraction in Ecuador (Bustamante and Jarrín, 2005) and for comparison a control area was chosen in the Southern Amazon (Morona-Santiago province) between 77°41'00"-78°34'51"W and 2°53'00"-3°31'20"S (**Figure 1-1**) considered free of anthropogenic sources of hydrocarbons, heavy metals and with geographical, geomorphological, ecological and hydrological characteristics similar to those of the NEAR. And with a population density (6 people.km^2) lower than Orellana (6.3) and Sucumbios (10) provinces (INEC, 2010).

Refining zone

In the refining study zone, the Teaone and the Esmeraldas river basins were considered. This study area is located between 79°36'60"- 79°42'1"W and 0°42'26"- 0°57'35"N (**Figure 1-1**) close to Esmeraldas city where the biggest refinery of the country (63% of the total national refining capacity) is located. The Esmeraldas Province is part of the Choco micro-region, a hot spot of biodiversity characterized by a marked seasonality with a wet season from February to May, a dry season from July to November and an annual average precipitation of 368 mm (Armijos et al., 2013; Sierra et al., 2009). A specific site (1°11'38.53"S; 80°19'50.91"W) at the South, in the Portoviejo basin (Manabi Province) was considered as the reference point of the NEPC.

2.2 Sample Collection

A total of 90 water and 85 sediment samples (**Table C-1**) were collected between 2012 and 2016 during the dry and rainy seasons (**Figure SI-1**) considering the location of oil facilities

throughout the Napo and Aguarico Rivers' basins, the refining zone in Esmeraldas and 2 control areas at the South (Morona, Santiago and Portoviejo Rivers).

Water samples were collected in 2L amber glass bottles, filtered a couple of hours after the sampling on glass-fiber membranes (0.7 µm) and kept frozen (-18°C) in 10 ml SPME (solid phase micro extraction) glass vials until analysis. All the material was previously calcined at 550°C.

Sediment samples were obtained by scraping the top 1-3 cm of the surface sediment at the riverbanks according to USEPA considerations given in the SW-846 (US EPA, 2014): a metallic sampler was used and the collected samples were placed in aluminum boxes. In addition to sediment river samples, a natural bituminous sandstone from the Andean headwater (Napo) and a residual soil from an ancient waste pool close to Auca 08 oil pit were collected. Two samples of crude oil (national pipeline and Auca 03 oilfield) were also collected. All the samples were kept frozen at -18◦C until analysis.

2.3 Chemical analysis

Parent HAPs and their alkylated forms in the dissolved phase were determined by Solid-phase microextraction (SPME) coupled to gas chromatography-mass spectrometry (Agilent Technologies:7890GC-5975MS) according to the methodology developed by Kanan et al. (2012). The quantification limits were calculated as 10 times the reagent blanks standard deviation (SD) and quality control analysis was performed by using supra-pure water enriched with 10µl of a reference solution (MIX PAH45, Dr Ehrenstorfer) containing 18 native PAHs. In addition, 15 µl of a solution containing a mixed of 19 deuterated PAHs (Cambridge Isotope Laboratories, Inc) was added in each sample to correct losses due to manipulations as reported in de-Perre et al. (2014). The recoveries obtained in the enriched water was equal to 101±7 %.

The freeze sediments were freeze-dried and subsequently treated by microwave extraction (StartE, Millestone®). The extracts were pre-concentrated using a RapidVap vacuum evaporation system (Labconco) and purified in column using dichloromethane and pentane in two steps; the first one using active copper and alumina as stationary phase; and the second one using silica in order to separate the aliphatic from the aromatic compounds. Purified extracts containing the aromatic charge were re-concentrated to 300 µl of isooctane solution under a gentle stream of nitrogen. Finally, total-PAHs concentrations of individual molecules were determined by gas chromatography-mass spectrometry (Hewlett-Packard series: 5890 GC-5972MS).

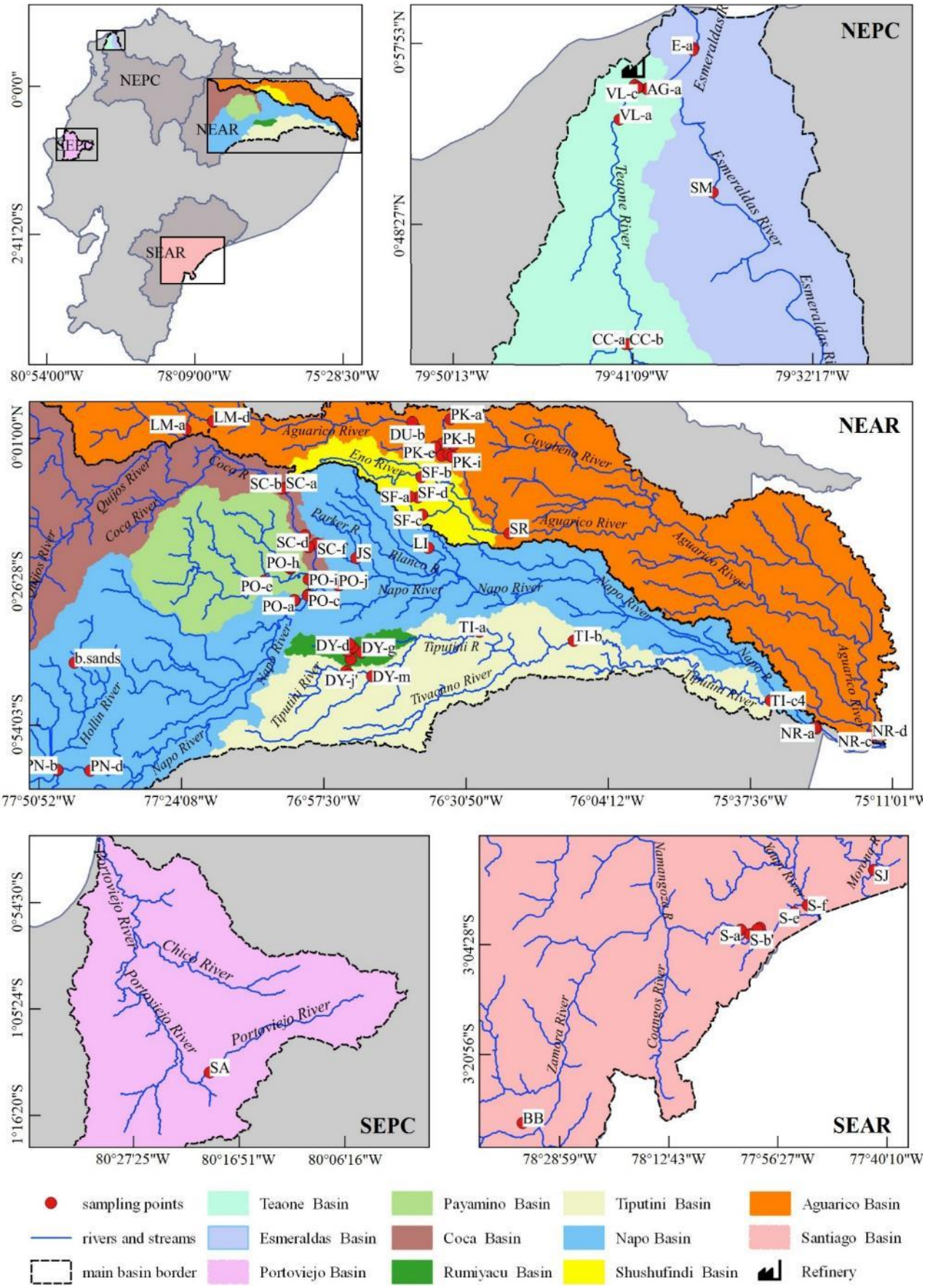


Figure 1-1. Location of study drainage basins and sampling points: Northern Ecuadorian Pacific Coast (NEPC), Northern Ecuadorian Amazon Region (NEAR), Southern Ecuadorian Amazon Region (SEAR) and Southern Ecuadorian Pacific Coast (SEPC).

Reagent blanks and certified materials were analyzed altogether with the sediment samples. The Fontainebleau sandstone (1-3 g) embedded with 100 µl of a reference solution (MIX PAH45, Dr Ehrenstorfer) as well as 0.5 g of a marine sediment (SRM® NIST1941b) were used to determine the recovery. A reference solution (Cambridge Isotope Laboratories, Inc) containing 19 deuterated PAHs was diluted to obtain 2 $mg.L^{-1}$ of each molecule, 30 µl of this solution was added into each sample before extraction to calculate the response factors. The average recovery of certified materials was 91±10 %.

As complementary analysis, nitrogen, carbon and sulfur (FLASH 2000 CHNS/O Analyzer; ThermoScientific™); and the grain size distribution (LA-950 Laser Particle Size Analyzer) were determined in most of the sediment samples.

Different series of analysis were needed for the same year, so different quantification limits were considered for each molecule.

2.4 Statistical analysis

In the complete database, the 50% of the annual-average limit of quantification was replaced in all the values detected under the LQ. Values under the limit of detection were reported as non-detected (nd). Excel and the complement RStudio from the software R were used for the statistical analysis. Different basic statistic tests (normality, correlation, PCA and HCA) were performed. Hierarchical Cluster and PCA were applied separately to the relative abundances and isomeric ratios in order to differentiate the PAHs sources (natural and due to oil activities).

2.5 Environmental and human risk assessment

Many tools are proposed to evaluate the risk of PAHs distribution in the environment. All these tools are based on different "toxicity reference values" (TRVs) like the quality guidelines/reference concentrations, reference doses, toxic units and toxic equivalent factors(Anses, 2018; European Commission, 2012).

Environmental quality guidelines, as defined by the US Environmental Protection Agency, are the highest concentrations of contaminants in a specific compartment (water, sediments, soil, air) that are expected not to pose a significant risk to most of the species in a given environment (US EPA, 2015b, 2018a). Different water quality guidelines (WQG) for PAHs have been developed at local and international levels; among them, the Canadian (CCME, 2018) and European (European Commission, 1998) guidelines seem the most complete, and propose quality guidelines for individual components, while Ecuadorian (RAOHE) and US-EPA guidelines are defined by the sum of different molecules. A compilation of different surface

water regulations is presented in **Table SI-2**.

The sediment quality guidelines (SQG) are defined as numerical limits from which toxicity tests on benthic environments ensure the protection of the aquatic life from adverse effects (CCME, 1999); Keshavarzi et al. 2015) sets SQG in several ranges : "Effect range low" (ERL) and "threshold effect level" (TEL) defined by concentrations below which adverse effects are improbable and infrequently expected; "effect range median" (ERM) and "probable effect level" (PEL) that define the concentration at which adverse effects are more probable to occur. Other values like NOEL (no observed effect level) and LOEL (lowest observed effect level) are also considered in Canadian sediment quality guidelines (CCME, 1999). In the case of Ecuador, there is no regulation for PAHs contents in river sediments, but a recent amendment (TULSMA, 2015) allows the use of international SQGs except for oil activities monitoring (where RAHOE applies). We used the ERL/TEL and PEL/ERM for assessing the environmental quality of the different basins.

References doses (RfD), According to the Environmental Protection Agency (US EPA, 2019) RfD is a numerical estimate of a daily oral exposure to the human population that is not likely to cause harmful effects during a lifetime. This concept is extrapolated for other exposure pathways as dermal or inhalation, and can be used for evaluating acute or chronic human risk (A human risk analysis based on reference doses related to water by dermal and ingestion pathways is presented in the Chapter 2).

Toxic units (TU) is defined as concentration of a chemical divided by a standard measure of its toxicity TEL, PEL , ERL and ERM are typical values used as standard measures of toxicity (US EPA, 2019). The addition of the individual TUs (accumulated toxicity) is considered as the toxic units accumulated (TUA), and the mean is known as the " mean SQG quotient" (mSQGQ) .We used the approach developed by Soliman et al. (2015) in assessing the Ecological Risk to obtain two mSQG quotients based on the TEL and ERM, respectively; and estimate the potential acute toxicity of the PAHs.

Toxic equivalent Factor (relative potency factors) this method allows to represent a group of molecules with similar mechanisms of action as the concentration of a single molecule with a well characterized toxicity. In the case of PAHs, multiplying the measured concentration of the individual hydrocarbon by its corresponding TEF gives the concentration of the molecule in terms of BaP, since BaP is considered the most well defined in terms of carcinogenicity and toxicity; the addition of individual concentrations results in a total concentration of BaP defined as the toxic equivalent quantity (TEQ) (Keshavarzi et al., 2015; Nisbet and LaGoy, 1992)

Alternatively, *cartographic methods* are also of current use for mapping hazards and risks

(Baynard et al., 2013; Cuba et al., 2014; Durango-Cordero et al., 2018; Finer et al., 2008). To determine the hydrocarbon pollution hazard we combined the surface runoff estimated with the IRIP (Intensive Rainfall Runoff) method(Cadot et al., 2016). Since this method is based on the environmental characteristics (geology, nature of soils, relief, land use, etc.) and takes into account the multiplicity of sources, it was used only for the NEAR. In addition, the software Qgis and Arcmap 10.4 were used to define the number of oil facilities (oilwells and flares) and pollution sources (pits and pools, and oil spills) affecting each one of the sampling sites. These results were integrated to our database and used for analyzing the correlation with the molecules analyzed.

2.6 Identification of PAHs sources

From the main anthropogenic sources of PAHs, we can distinguish the pyrogenic PAHs originated from the incomplete combustion of coal, petroleum and biomass, and the petrogenic PAHs presented in petroleum products found in fossil fuels and crude-oil spills (Amiard, 2017; Sun et al., 2017). The use of molecular ratios of isomeric PAHs in bottom sediments allow to reduce the misinterpretation due to volatility, water solubility, adsorption, etc; this method has been developed and widely used for source identification of PAHs contamination (Budzinski et al., 1997; Sun et al., 2017, 2010, Yunker et al., 2014, 2002). This method is based on the fact that low molecular weight (LMW) and alkylated PAHs are mainly present in petrogenic sources, while pyrogenic sources are mostly formed by high molecular weight (HMW) parent PAHs (Raza et al., 2013).

The ratios Phe-A and Fa-Py has been traditionally used to distinguish petrogenic and pyrolytic sources; Phenanthrene is considered as the most thermodynamically stable among the LMW-PAHs (Budzinski et al., 1997) and the presence of Phe, Flu and Py is related with a pyrolytic origin of the pollution (Stogiannidis and Laane, 2015). Since naphthalene, is highly volatile and hydrophilic (Douben, 2003) it is relatively unstable in sediments, thus it was not considered in the analysis of sources.

For each site, different isomeric ratios were calculated and we considered that samples from a common origin present similar isomeric ratios, they were used in a Hierarchical Cluster Analysis (HCA) and PCA in order to trace de different sources in function of its nature. This is a new approach proposed here that allows to treat all the isomeric ratios in an only one analysis, instead of using the traditional bi-plot analysis.

3. Results and discussion

3.1 Distribution of PAHs concentrations in surface freshwater

All the PAHs acronyms are presented in the **Table SI-1**.

3.1.1 Dissolved individual PAHs and total aromatic charge

Among the parent-PAHs with two or three aromatic rings (LMW), Ph (0.3-141 ng.L^{-1}), Fl(0.3-212 ng.L^{-1}) and N (2.5-1830 ng.L^{-1}) were present over the LQ in 87%, 56% and 40% of samples, respectively. The other LMW-PAHs were present in 8% to 27% of the samples (Anthracene=8%, acenaphthylene =13% and acenaphthene=27 %). In the parent-PAHs from tetra to hexa-aromatics molecules (HMW), the concentrations of BaA, BbjkF, BaP, IP, DBA and BPe were under the limit of quantification (LQ) with most of non-detected data in 45, 56, 88, 97, 98 and 90% of sites, respectively. Pyrene concentrations ranged from 0.3 to 79 ng.L^{-1} distributed on 47 % of the sampling sites, followed by Fa (0.2-5 ng.L^{-1}) in 39% of the samples and BeP concentrations (07-2.4 ng.L^{-1}) detected in 18 % of the samples where the only value over the LQ was measured in the Teaone river (2.5 ng.L^{-1}) at the REE channel outlet (VL-d4). Perylene was detected (>LD) in 35% of the samples, but only the Tiputini river (point TI-b4) in the Napo basin presented a value over the LQ (1.8 ng.L^{-1}); this river is a black water river draining a large forest basin without any Andean sources. The less frequently detected PAH was Ch (0.3-8 ng.L^{-1}) in only 10% of the sites.

Alkyl-PAHs were present (>LQ) in most of the samples: mono-methyl phenanthrenes (mMPh) were found in 63 to 71% of water samples and methyl-naphthalenes were present in nearly all the sites and ∑DMN in all the sampling points. In fact, in 90% of samples alkyl-naphthalenes (nMN) represent the most important fraction (70-96 %) of the total aromatic charge (TAC) followed by the mMPh (0.6 to 6% to TAC). The remaining alkylated-compounds were detected with a frequency inferior to 33%. The ranges of the different molecules and the respective percentages of sites with values over LQ are presented in the **Table SI-7** and in the **Figure 1-2**.

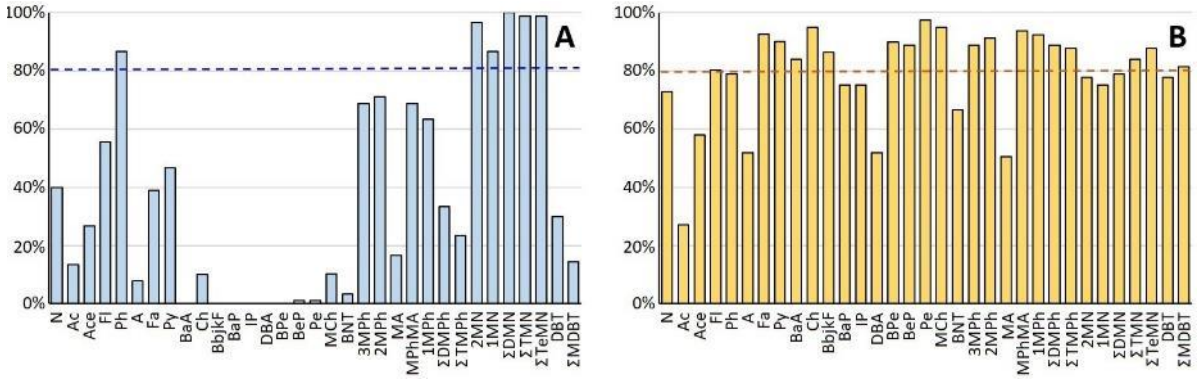


Figure 1-2. Percentage of samples quantified in A) waters and B) Sediments.

The TAC analyzed along the Pacific Coast Rivers ranged from 129 ng.L^{-1} in the Portoviejo basin to 1803 ng.L^{-1} in the outflow of the refinery channel (VL-b6). This range is similar to the extreme values found in the Amazon region (31-1134 ng.L^{-1}) excluding the DY-j4 sampling point (Auca 22) that reached 131726 ng.L^{-1}. In the NEAR, we found two points with a TAC similar to the point VL-e6 (1517 ng.L^{-1}) in the Teaone river downstream the refinery. One of these points was located in Auca 22 (1032 ng.L^{-1} in DY-k2), and the other one close to Atacapi 03 oil well in the Aguarico basin (1134 ng.L^{-1} in DU-c3, Dureno parish) upstream of the Libertador oil field. The average concentrations of all the analyzed molecules in each sub-basin are reported in the **Table 1-1**.

Comparing the different sampling points, the site DY-j4 (Tiputini River located in the Auca 22 oil well influence zone, close to Dayuma) presented the maximum concentrations for 26 molecules (79%) from the 33 analyzed; this point showed a TAC (131,726 ng.L^{-1}) 73 times the second highest value (1803 ng.L^{-1}) measured in the refinery channel (VL-b6). These both sites can be considered as the most contaminated from the whole study area; the Auca 22 (DY-j4) point presented an aromatic charge 2278 times the value obtained in the upstream-cleanest point from the Tiputini River and 1333 times the average from the Morona Santiago basin, non-affected by extractive activities. The TAC in the effluents of the refinery (VL-b6) reached 10 and 14 times the average aromatic charge found in the same River upstream (CC-a6, CC-b4 and VL-a3) and in the reference basin (SA6), respectively. This site also revealed the presence of phenanthrene, anthracene, methyl-anthracene and methyl-phenanthrenes in concentrations that the analysis method did not allowed to determine individually due to important peak interferences between molecules. Although the results (**Figure SI-2**) of TAC and $_{16}$PAH are underestimated for the refinery effluents, even so this site presented the highest PAHs concentrations measured in the NEPC, placing the Teaone River as the most contaminated Ecuadorian River in relation to aromatic hydrocarbons.

The TAC trends to grow in urbanized places and in points close to oil facilities (**Figure 1-3**). We can consider that a TAC lower than 100 ng.L^{-1} is representative of non-contaminated sites in Ecuador since these values were found in points non-directly influenced by human activities, in particular in the Amazon Region upstream, without agricultural and oil activities. From the total of the sites, 30% of the samples belongs to this category. Comparable ranges of TAC in the control areas (Al-Agroudy et al., 2017; Farooq et al., 2011; Manoli et al., 2000; Montuori et al., 2016; Ross and Oros, 2004) were found in surface water from Northern countries with better environmental practices, in the Chesapeake Bay, and Missisipi (US) or the Seine

(France) Rivers (Fernandes et al., 1997; Gustafson and Dickhut, 1997; Zhang et al., 2007).

In Ecuador, urban sewage treatment is only processed in the two main cities (Quito and

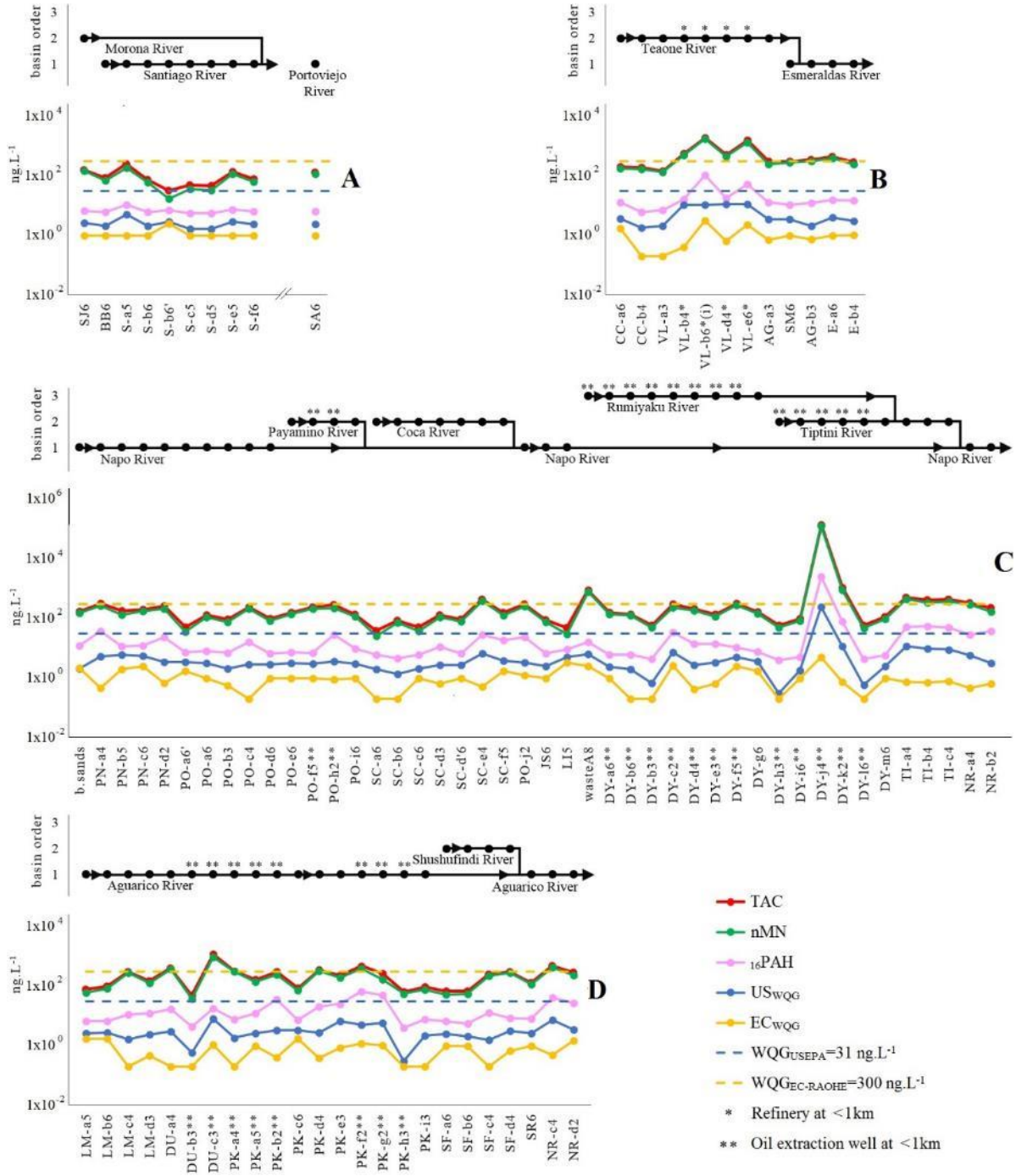


Figure 1-3. Concentration (ng.L-1, log-scale) of different aromatic groups in water samples from upstream to downstream in the sub-basins from the reference zones (A), NEAR (B and C) and NEPC (D). TAC=total aromatic charge, nMN=Sum of methyl-naphthtalenes, 16PAH=∑USEPA-PAHs; US_{WQG}=B[bjk]Fa+B[ghi]Pe+IP; EC_{WQG} =Fa+B[bjk]Fa+B[a]P+B[ghi]Pe+IP. The two first initials indicate the name of the closest city, village or parish: PN=Puerto Napo, PO=Puerto Francisco de Orellana, SC=San Sebastian del Coca, JS=Joya de los Sachas, LI=Limoncocha, DY=Dayuma, TI=Tiputini, NR=Nuevo Rocafuerte, A8=Auca08, LM=Lumbaqui, DU=Dureno, PK=Pacayacu, SF=Shushufindi, SR=San Roque, SJ=San José, BB=Bomboiza, S=Santiago, CC=Carlos Concha, VL=Vuelta Larga, AG=5 de Agosto, SM=San Mateo, E=Esmeraldas, SA=Santa Ana; (i)= GC-MS interferences. The number at the end of the site's code indicates the year of sampling (2:2012, 3:2013, 4:2014, 5:2015 and 6: 2016) and the lowercase letter indicates the location of the sampling points from upstream (a) to downstream (d) from a same parish, village or city.

Guayaquil), while oil wastewaters are censed to be treated before their discharges in the environment, according to the legislation. The presence of cities and oil infrastructures with non-manifested impacts showed TAC-values between 100 and 500 ng.L^{-1}, corresponding to 62% of the sampling points; these concentrations tends to increase from upstream to downstream in each sub-basin **(Figure 1-3).** The TAC values in the Teaone River vary from 100 to 196 ng.L^{-1} upstream the Refinery and reaches 293 ng.L^{-1} before the confluence with the Esmeraldas River (285-426 ng.L^{-1}). Similar values were also found in the NEAR, in the city of San Sebastian del Coca (127-421 ng.L^{-1}) Coca river downstream, in Puerto Francisco de Orellana (293 ng.L^{-1}) under the main bridge of the village; in Puerto Napo (upstream of Napo Basin, 197-300 ng.L^{-1}) and along the Payamino River (152-281 ng.L^{-1}), part of the latest river being located in active-oil camps. From all the other basins, the Tiputini River downstream presents the highest value of the TAC range (400-499 ng.L^{-1}), even though this part of the Tiputini River is isolated and sparsely populated. This river is usually employed to reach the Napo River by motor-boats, which could explain the local TAC values. This values are similar to the ones determined in other studies for example, in San Francisco Estuary, Suez Canal, Tiber River, and in the Aliakmon Basin **(Table 1-2**). In these regions, TAC is suspected to come from (sub)urban, industrial and agricultural activities (Al-Agroudy et al., 2017; Farooq et al., 2011; Manoli et al., 2000; Montuori et al., 2016; Ross and Oros, 2004).

Only 8% of our study sites showed a TAC over 500 ng.L^{-1}; in all these places, there is at least one active source of oil emissions. Along the Pacific Coast, we recorded values from 551 to 1803 ng.L^{-1} that came from points directly influenced by the discharge of liquid effluents from oil-refining processes that are dumped into the Teaone River. In the NEAR, two points (1032-131726 ng.L^{-1}) close to Auca 22 oilwell in the Tiputini sub-basin are affected by the presence of a waste pool and occasional oil spills. Another point (WasteA8,TAC= 869 ng.L^{-1}) close to Auca08 oil well, is also influenced by an abandoned waste pit covered by soil where rainwater can percolate. The last point (1134 ng.L^{-1}) is close to Atacapi 03 oil well; water comes from a swamp that belongs to the Aguarico basin in Dureno parish. In this site there is a waste pool under remediation process. Higher values like the last ones are typically found in places categorized as polluted (Table 2) like the Gao-ping River and in channels from Hangzhou City in China (Chen et al., 2004; Doong and Lin, 2004).

Other similar studies also reported high TAC values in coastal waters affected by highly industrialized areas (Gorleku et al., 2014) and in rivers where municipal sewage waste is discharged directly without any treatment (Nekhavhambe et al., 2014).

Table 1-1. Average concentration ± standard deviation of dissolved organic carbon ($mg.L^{-1}$), total suspended solids ($mg.L^{-1}$) and PAHs ($ng.L^{-1}$) in surface water from different basins in the Northern oil extraction and Southern Ecuadorian Amazon Region (NEAR and SEAR, respectively) and in the Northern and Southern Ecuadorian Pacific Coast (NEPC and SEPC, respectively)

VARIABLE	NEAR							SEAR	NEPC		SEPC
	Napo	Payamino	Coca	Rumiyacu	Tiputini	Aguarico	Shushufindi	Santiago	Teaone	Esmeraldas	Portoviejo
DOC	8.7±15.4	10.7±15.3	7±14.1	44.5±86.1	25.1±51.8	19.2±37.1	2.9±1.6	28.6±38.1	5.2±3.9	2.2±0.4	2.5*
TSS	66±59	14±7	41±52	16±15	46±34	126±337	14±4	44±100	36±40	66±74	137*
N	6.4±7.0	4.7±2.9	5.6±5.2	3.9±2.3	216.4±605.4	7.8±7.8	4.2±3.5	<3.0	5.6±6.8	5.6±2.5	<3.0*
Ac	0.65±0.33	<0.67	0.69±0.58	<0.67	26.43±48.45	0.68±0.48	0.74±0.5	<0.67	0.69±0.53	<0.67	<0.67*
Ace	1.0±1.0	1.5±2.1	<0.6	1.2±1.9	19.7±48.2	1.4±2.5	0.6±0.3	<0.6	1.7±2.5	0.9±0.8	<0.6*
Fl	3.8±7.0	2.7±4.7	1.6±2.4	1.9±2.8	30.8±69.8	5.3±9.5	<0.42	0.5±0.4	1.2±1.2	1.2±0.6	<0.4*
Ph	2.2±1.4	2.1±1	1.5±1.5	2.1±2	19.6±45.9	2.3±1.9	1.1±0.5	0.9±1.2	2.6±2.1(i)	1.9±0.5	0.43*
A	<0.4	<0.4	<0.4	<0.4	3.6±6.5	<0.4	<0.4	<0.4	0.5±0.3(i)	<0.4	<0.4*
Fa	0.5±0.5	0.4±0.4	0.3±0.2	0.5±0.8	1.0±1.5	0.5±0.4	0.3±0.2	<0.3	0.5±0.3	0.5±0.4	<0.3*
Py	0.6±0.5	0.4±0.4	0.3±0.3	1.0±1.6	1.3±2.2	0.6±0.7	0.4±0.2	<0.3	11.8±27.2	1.3±1.1	<0.3*
BaA	<0.40	<0.40	<0.40	<0.40	<0.40*	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40*
Ch	<0.40	<0.40	<0.40	0.63±0.75	0.89±1.25	0.72±1.43	<0.40	<0.40	3.58±3.62	<0.40	<0.40*
BbjkF	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0*
BaP	<1.0	nd	<1.0	<1.0	nd	<1.0	nd	<1.0	<1.0	nd	nd
IP	<1.0	nd	nd	<1.0	nd	nd	nd	nd	nd	nd	nd
DBA	<1.0	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BPe	<1.0	nd	<1.0	<1.0	nd	<1.0	nd	<1.0	<1.0	nd	nd
$_{16}$PAH	16.1±10.7	13±10.2	11.5±8.7	12.2±8.8	298.3±802.5	19±16.7	8.2±3.2	6.7±1.5	27.9±32.9	12.9±2.1	6.3*
US_{WQG}	3.7±1.4	3.1±0.3	3±1.7	3.7±2.2	31.9±78.4	3.3±2	2.3±0.6	2.5±1	6.7±4.3	3.1±0.8	2.3*
EC_{WQG}	1.2±0.9	0.9±0.03	0.7±0.5	1.3±1.0	1.1±1.5	0.8±0.6	0.7±0.4	1.1±0.5	1.1±1.1	0.9±0.1	1.0*
BeP	<1.0	<1.0	nd	<1.0	<1.0	<1.0	nd	<1.0	1.1±0.8	nd	<1.0*
Pe	<1.0	<1.0	<1.0	<1.0	1.1±0.6	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0*
MCh	<0.52	<0.52	<0.52	1.2±0.75	4.3±5.67	4.06±5.33	<0.52	<0.52	4.72±2.23	3.63*	<0.52*
3MPh	0.8±0.6	0.8±0.5	0.4±0.3	0.9±0.8	15.5±43.5	1.0±1.4	0.4±0.3	0.8±1.6	2.4±3.3(i)	1.2±0.3	<0.3*
2MPh	0.9±0.8	0.8±0.6	0.5±0.5	1.0±0.9	7.7±18.9	0.8±0.9	0.5±0.3	0.8±1.6	2.5±3.5(i)	1.3±0.6	<0.3*
MA	0.4±0.4	0.4±0.4	<0.3	0.9±1.7	<0.3	0.3±0.4	<0.3	<0.3	0.5±0.7(i)	<0.3	<0.3*
MPhMA	0.9±0.8	1.1±0.6	0.4±0.4	1.1±1.1	16.0±43.9	1.1±1.8	0.5±0.4	0.6±1.2	2.9±3.9(i)	1.4±0.4	<0.3*
1MPh	0.8±0.7	0.9±0.5	0.4±0.4	0.8±0.9	31.6±91.1	1±1.7	0.3±0.2	0.5±0.8	2.1±2.9(i)	1.0±0.5	<0.3*
mMPh	3.3±2.9	3.7±2	1.7±1.6	3.8±3.5	70.8±197.3	3.9±5.7	1.7±1.2	2.7±5.1	9.9±1 (i)	4.9±1.7	<0.6*
∑DMPh	4.9±3.7	7.9±8.9	<3.0	6.9±7.7	87.4±240.7	7.1±14.8	3.2±1.4	4.4±5.6	19.5±25.8	8.2±4.2	<3.0*
∑TMPh	3.7±2.5	4.5±4.1	<3.0	6.2±5.7	39.4±94.7	8.1±18.5	3.3±1.7	3.3±2.3	17.1±16.3	6±2.8	<3.0*
2MN	9±4	9±3	8±6	8±2	511±1496	12±10	8±5	6±3	17±21	18±10	10*
1MN	5±3	5±1	5±4	6±5	832±2469	9±9	6±4	3±3	14±21	12±7	5.3*
∑DMN	47±27	41±20	37±38	59±52	190±340	73±53	42±32	24±14	107±91	85±27	43*
∑TMN	57±35	67±28	44±55	88±75	9442±27976	78±71	55±43	26±20	204±198	116±15	25*
∑TeMN	32±19	46±10	23±20	63±89	3290±9675	54±114	38±34	21±20	230±338	69±24	30*
nMN	149±83	167±51	117±120	225±220	14265±41951	227±200	149±113	79±55	572±586	301±61	113*
BNT	<0.4	<0.4	<0.4	<0.4	<0.4	0.4±0.4	<0.4	<0.4	0.8±1.1	<0.4	<0.4*
DBT	<0.4	<0.4	<0.4	0.6±0.9	52.6±154.8	0.6±0.7	<0.4	<0.4	1.1±1.3	0.6±0.2	<0.4*
∑MDBT	1.6±1.2	2±1.3	1.3±0	2.8±4.3	122.6±360.4	2.8±5.8	1.3±0	1.8±1.8	5.2±8.1	3.0±2.0	1.3*
TAC	179±94	199±70	137±131	257±243	14933±43798	267±243	167±118	99±68	648±646	338±64	129*
nMN/TAC	0.81±0.08	0.85±0.06	0.81±0.08	0.87±0.05	0.86±0.04	0.85±0.06	0.85±0.08	0.77±0.11	0.88±0.04	0.89±0.03	0.88*
16PAH/TAC	0.09±0.04	0.06±0.03	0.10±0.04	0.06±0.03	0.08±0.04	0.08±0.04	0.07±0.03	0.09±0.06	0.04±0.01	0.04±0.01	0.049*

NEAR=North Ecuadorian Amazon Region; SEAR= South Ecuadorian Amazon Region; NEPC= North Ecuadorian Pacific Coast; SEPC= South Ecuadorian Pacific Coast; DOC=dissolved organic carbon ; TSS=total suspended solids; N=naphthalene; Ac=acenaphthylene; Ace=acenaphthene; Fl=Fluorene; Ph=phenanthrene; A=anthracene; Fa=Fluoranthene; Py=pyrene; BaA=benzo[a]anthracene; Ch= chrysene + triphenylene; BbjkF=benzo[bjk]fluoranthene; BaP=benzo[a]pyrene; IP=indeno[1,2,3-cd]pyrene; DBA=dibenzo[ah]anthracene; BPe=benzo[ghi]perylene; $_{16}$PAH=∑US-EPA PAHs; US_{WQG}=B[bjk]Fa+B[ghi]Pe+IP; EC_{WQG} =Fa+B[bjk]Fa+B[a]P+B[ghi]Pe+IP;BeP=benzo[e]Pyrene; Pe= perylene; MCh=methylchrysene; 3MPh=3Methylphenanthrene; 2MPh=2methylphenanthrene; MA=2methylanthracene; MPhMA=[9+4]methylphenanthrene+1methylanthracene+ 4,5methylenephenanthrene; 1MPh=1methylphenanthrene; mMPh=∑mono-methyl phenanthrenes ; ∑DMPh=∑dimethylphenanthrene; ∑TMPh=∑trimethylphenanthrene; 2MN=2methylnaphthalene; 1MN=1methyl- naphthalene; ∑DMN=∑dimethylnaphthalene; ∑TMN=∑trimethylnaphthalene; ∑TeMN=∑tetramethylnaphthalene; nMN= ∑methylnaphthalenes; BNT=2,1benzonaphtothiophene; DBT=dibenzothiophene; ∑MDBT=∑methyldibenzothiophene; TAC=total aromatic charge; *= single value (n=1); nd=non detected (<LD); ---=non measured data; (i)=interference; #= percentage of analyzed samples (all sites) over the quantification limit(LQ).

The weathering (physicochemical and biological processes) altogether with the local hydrodynamics in both studied areas should be responsible of a fast reduction in the TAC from

the punctual source. In the Teaone River it is not possible to differentiate urban/agricultural activities from industrial ones, we hypothesize that aromatic charge downstream of the Esmeraldas Refinery is a mixed of both.

Table 1-2. Ranges of total aromatic charge (TAC) in ng.L^{-1} in surface freshwater of our study and around the world, in oil producer countries or in urban areas.

SITE	NUMBER#	TAC (phase)	REFERENCE
NEAR	33 parents+alkyl	37-1134 (d)	(present study)
NEAR(Auca22)	33 parents+alkyl	131725 (d)	(present study)
SEAR	33 parents+alkyl	31-244 (d)	(present study)
NEPC	33 parents+alkyl	142-1803 (d)	(present study)
SEPC	33 parents+alkyl	129 (d)	(present study)
Seine River and Estuary, France	11 parents	4-36 (d)	(Fernandes et al., 1997)
Harbour Line, India	15 parents	9-47 (d)	(Dhananjayan et al., 2012)
Hartbeespoort Dam, South Africa	16 USEPA	30-52 (d)	(Amdany et al., 2014)
Chesapeake Bay, USA	17 parents	20-66(d) 24-91 (d+p)	(Gustafson and Dickhut, 1997)
Mississippi river, USA	16 USEPA	63-145 (d+p)	(Zhang et al., 2007)
Amazon Region, Ecuador	33 parents+alkyl	29-184 (d) drinking water network	(Maurice et al,2019)
North Sea, Norway	+50 parents+alkyl	25-350 (d) at 1km from oil platform 4-8 (d) background sea level	(Durell et al., 2006)
Amazon Region, Ecuador	33 parents+alkyl	52-324 (d) rainfall	(Maurice et al,2019)
Suez Canal, Egypt	16 USEPA	12-500 (b)	(Al-Agroudy et al., 2017)
Tiber River and Estuary, Italy	16 USEPA	2-607 (d)	(Montuori et al., 2016)
Tehran, Iran	16USEPA	33-733 (d), drinking water network	(Karyab et al., 2013)
San Francisco Estuary, USA	25 parents+alkyl	1-847 (d+p), total range 7-120 (d+p), median range	(Ross and Oros, 2004)
Aliakmon basin, Greece	16 USEPA	184-856 (b), surface water) 143-954 (b), precipitation	(Manoli et al., 2000)
Xiamen Harbour, China	16USEPA	106-945 (d)	(Zhou, 2000)
Chenab River, Pakistan	17 parents	888–1140 (d+p), urban 87–703 (d+p), suburban 473–522 (d+p), agricultural	(Farooq et al., 2011)
Gao-ping River, Taiwan	16USEPA	10-9400 (d)	(Doong and Lin, 2004)
Hangzhou City, China	10 parents	989-9663 (d)	(Chen et al., 2004)
Tianjin, China	16 USEPA	1800-35000(d)	(Cao et al., 2005)
Sergipe, Brazil	11 parents	37500 produced water < 40-52430 coastal areas	(Dórea et al., 2007)
Tema Harbour, Ghana	20 parents	33200-84500 (b)	(Gorleku et al., 2014)
Limpopo, South Africa	6 parents	100-137000(b)	(Nekhavhambe et al., 2014)
Luleå, Sweden	16 USEPA	700-340000 (d), gully pots	(Karlsson and Viklander, 2008)
Mvudi and Nzhele River, South Africa	16 USEPA	13174000–26382000 (b)	(Edokpayi et al., 2016)

d= dissolved phase
p=particulate phase
b=brut, if not specified we assumed non-filtered water
#=number of compounds analyzed in the study

3.1.2 Environmental quality risk related with dissolved aromatic charge

By comparing PAH-concentrations with the different quality guidelines compiled in the **Table SI-2** we found that PAHs in surface water (**Figure 1-3**) from the ***Amazon region*** matched with Ecuadorian and international guidelines, except in a spring (DY-j4) from the Napo basin (sub-basin of Tiputini river) at the edge of Auca-22 oil well in Dayuma parish. This oil well is still active and the spring water crosses a waste pool just covered with soil and oil waste poured on the forest hill; this point presents the highest naphthalene (1830 ng.L^{-1}) and anthracene

(13 ng.L^{-1}) concentrations measured in the Amazon Region exceeding the Canadian regulations (CCME, 2018). The sum of Ac, BaA, BaP; BbjkF, BPe, Ch, DBA, IP and Ph (244 ng.L^{-1}) reached eight times the US-EPA recommendation (US EPA, 2018b) at this same sampling point. The last updated version of Ecuadorian regulation (MAE, 2015c) does not present limits for PAHs in surface water; only RAOHE (2001) sets a value of 300 ng.L^{-1} for the sum of six molecules (Fa+BbjbkF+BaP+BPe+IP). In none of our sampling points, this sum exceeded the national quality criteria for oil activities areas.

Along the ***Pacific Coast***, all water samples are in compliance with the regulations, except the refining effluent point (VL-b6), which presented the highest concentration of pyrene (79 ng.L^{-1}) overpassing the Canadian recommended value (CCME: 25 ng.L^{-1}). The peak interferences found in phenanthrene and anthracene did not allow to define their relation with the WQGs.

Since environmental water quality guidelines we observed that there is not risk for aquatic environments in most of the basins analyzed in the present study. Punctual pollution does not show an important contribution to the aromatic charge in the dissolved phase further than one kilometer from the source. This punctual contamination was found in sampling points directly related with oil activities, but only in 8% of samples.

3.2 Concentrations of PAHs in bottom sediments

3.2.1 Sedimentary aromatic charge

Nearly all the analyzed PAHs were detected in sediment samples (**Figure 1-2**), representing 99.6 % of the database. The average concentrations in dried weight are presented in the **Table 1-3**. Ac, A, DBA and MA are the molecules with the lowest percentages of samples with concentrations over the LQ (27 %, 52 %, 52 and 71%, respectively), being Ac the molecule that present the highest number of values inferior to LQ with concentrations ranging from 0.1 to 70 ng.g^{-1}. In parent PAHs, total PAH_{16} concentrations ranged from 1.3 to 1677 ng.g^{-1} with Ch (0.1-448 ng.g^{-1}) and Pe (0.1-556 ng.g^{-1}) measured in 95% and 98 % of the samples, respectively. While in methylated PAHs, the alkyl-phenanthrenes were present in 88-93 % of sites altogether with MCh (95%; 0.1-1420 ng.g^{-1}), alkyl naphthalenes from 75% for 1MN (0.1-1241 ng.g^{-1}) to 87 % for the ΣTeMN (0.5-34440 ng.g^{-1}); and ∑MDBT (81%; 0.1-2475 ng.g^{-1}). The percentages of sites with values over LQ in the different molecules are presented in the **Figure 1-2**.

The distribution of the total aromatic charge (TAC) analyzed in sediments is represented in the

Table 1-3. Average ± standard deviation of pollution hazard, grain size (%) and concentration (ng.g^{-1} dry weight) of PAHs in sediments from different basins 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).

VARIABLE	NEAR							SEAR	NEPC		SEPC
	Napo	Payamino	Coca	Rumiyacu	Tiputini	Aguarico	Shushufindi	Santiago	Teaone	Esmeraldas	Portoviejo
hazard	1.3±10	2.4±0.8	1.9±0.2	2.8±0.5	2.6±0.8	2.4±0.6	2.8±0.8	0.0	--	--	--
≤ 4 µm	12±7	12±6	7±5	14±2	19±7	13±8	16±6	23±13	12±3	12±1	12*
4-63 µm	55±10	50±9	34±22	47±8	51±10	50±15	50±4	48±4	56±11	53±10	44*
≤ 63 µm	66±13	62±13	41±26	61±10	71±15	63±21	66±10	71±15	69±14	65±10	57*
> 63µm	34±13	38±13	59±26	39±10	29±15	37±21	34±10	29±15	31±14	35±10	43*
TC (%)	1.1±0.7	3.8±4.0	0.6±0.4	1.1±0.7	2.0±1.1	1.4±1.3	2.2±0.8	1.6±1.0	1.9±0.9	1.4±0.6	0.8*
OC (%)	0.9±0.6	3.6±4.0	0.5±0.4	0.9±0.7	1.7±0.9	1.3±1.3	2.0±0.8	1.0±0.8	1.5±0.8	1.0±0.2	0.5*
N	3±2	11±13	2±1	<1.15	13±21	3±3	2±3	<1.2	23±41	<1.2	<1.2*
Ac	<0.1	14.3±31.4	<0.1	<0.1	2.2±6.0	0.3±0.8	<0.1	<0.1	1.6±4.7	0.2±0.1	<0.1*
Ace	0.3±0.4	28.6±57.3	0.1±0.1	<0.1	2.8±6.2	0.3±0.6	<0.1	<0.1	9.5±24.1	<0.1	<0.1*
Fl	0.6±0.6	86.0±182.5	0.3±0.2	0.2±0.1	10.3±27.0	0.6±1.1	<0.2	0.2±0.2	21.0±40.5	0.4±0.4	<0.2*
Ph	4.3±4.1	38.8±52.0	3.2±2.3	0.8±0.5	19.7±39.2	4.5±7.9	0.9±0.1	2.6±5.0	101.7±196.9	1.9±1.1	<0.7*
A	0.2±0.3	1.2±1.4	0.1±0.1	<0.1	0.5±1.2	0.2±0.6	<0.1	<0.1	8.8±18.3	0.210.2	<0.1*
LMW	9±7	180±326	6±4	2±1	48±93	8±12	4±3	4±6	165±312	4±2	1*
Fa	2.0±4.9	30.7±38.6	0.5±0.4	0.4±0.5	20.0±39.3	3.5±13.5	0.5±0.4	0.5±0.7	54.9±152.9	1.2±0.6	0.2*
Py	2.1±3.8	18.1±27.4	1.0±0.7	0.8±0.9	13.8±27.0	3.0±9.8	0.6±0.5	1.2±2.1	68.0±133.4	1.9±1.2	<0.2*
BaA	0.6±0.8	4.2±4.9	0.4±0.2	0.2±0.3	2.7±7.5	0.4±0.6	0.3±0.1	0.3±0.7	12.1±25.3	0.5±0.4	<0.1*
Ch	1.6±1.0	31.2±52.6	1.6±1.3	1.1±1.5	51.5±148.8	2.8±3.1	0.6±0.4	2.4±5.6	41.8±91.3	1.2±0.7	0.2*
BbjkF	0.9±0.6	6.2±5.5	0.7±0.6	0.7±0.7	9.4±25.1	1.1±1.0	1.1±0.5	1.4±2.7	10.0±17.6	1.0±0.3	<0.3*
BaP	0.4±0.4	2.5±2.4	0.3±0.2	0.4±0.3	0.4±0.6	0.4±0.5	0.3±0.2	0.3±0.6	8.9±18.9	0.6±0.4	<0.2*
IP	0.9±2.3	1.3±0.8	0.3±0.3	0.4±0.4	1.7±3.5	0.3±0.3	0.6±0.3	<0.2	2.0±2.2	0.7±0.4	<0.2*
DBA	0.3±0.4	1.0±1.1	<0.2	<0.2	2.7±7.3	0.2±0.2	<0.2	<0.2	2.0±3.8	<0.2	<0.2*
BPe	1.2±0.9	3.6±3.5	0.9±0.8	1.0±1.3	4.7±10.2	1.2±1.7	0.8±0.3	1.3±2.9	6.9±10.7	1.1±0.6	1.2*
$_{16}$PAH	18±16	278±417	12±8	7±6	155±344	21±38	8±4	12±22	372±685	12±7	3*
BeP	1.1±0.5	10.7±12.1	1.2±1.0	0.9±1.4	16.2±43.1	2.2±3.0	0.5±0.3	2.6±6.7	17.2±34.8	0.8±0.5	<0.2*
HMW#	11±10	109±106	7±5	6±7	123±294	15±28	5±3	10±22	224±398	9±5	2*
Pe	58±120	211±180	24±16	29±24	42±48	58±127	91±27	8±14	33±27	329±22	3*
MCh	3.9±2.1	89.1±146.0	4.1±3.8	4.4±7.8	162.0±471.7	7.1±9.1	3.6±3.8	4.7±9.9	180.9±414.6	4.4±5.2	<0.3*
3MPh	1.4±1.0	183.5±389.4	1.5±1.4	0.3±0.3	47.8±140.9	1.7±2.2	0.3±0.1	1.1±2.3	119.1±273.3	0.9±0.5	<0.1*
2MPh	1.9±1.4	215.5±454.8	1.9±1.7	0.4±0.4	60.3±177.0	2.4±3.1	0.4±0.2	1.4±2.8	148.8±370.1	1.1±0.7	<0.1*
MA	0.3±0.3	14.4±28.7	0.2±0.1	<0.1	5.6±16.0	0.2±0.3	<0.1	0.1±0.1	15.6±32.7	0.2±0.1	<0.1*
MPhMA	2.7±1.9	278.0±586.9	2.7±2.5	0.5±0.6	99.0±277.9	2.6±3.1	0.6±0.3	2.0±4.6	106.7±253.9	1.0±0.7	<0.1*
1MPh	2.2±1.5	316.4±677.2	2.6±2.4	0.5±0.6	99.5±279.3	1.9±2.2	0.6±0.4	1.6±3.9	90.4±213	0.7±0.5	<0.1*
∑DMPh	15±9	1803±3858	17±13	8±8	920±2738	16±18	4±2	9±18	1075±2545	17±21	<1*
∑TMPh	15±9	1614±34501	18±13	7±10	1213±3614	19±30	4±2	6±13	1041±2461	21±30	<1*
2MN	4.0±2.7	274.8±565.0	4.2±2.5	0.8±0.7	39.6±84.7	10.6±19.3	0.3±0.3	0.8±1.3	81.1±188.9	0.4±0.3	<0.3*
1MN	3.5±2.3	265.9±546.0	3.7±2.2	0.6±0.6	33.3±73.8	9.05±17.14	0.3±0.2	1.2±2.5	65.2±153.6	0.3±0.2	<0.3*
∑DMN	17±10	2859±6120	17±11	3±2	423±1207	26±33	2±2	6±13	3190±8990	3±3	<1*
∑TMN	28±17	5366±11460	31±22	4±3	1174±3494	21±22	4±2	10±22	5936±16880	8±11	<1*
∑TeMN	17±11	3270±6980	16±12	6±5	1227±3655	16±18	8±3	9±16	4034±11416	12±17	<1*
MPAH	111±63	16550±35259	121±85	36±35	5482±16190	133±146	28±13	53±109	16085±44133	70±89	3*
BNT	0.4±0.3	14.5±29.1	0.5±0.5	0.3±0.4	26.0±77.2	0.6±0.7	0.1±0.1	0.5±0.9	12.7±26.3	0.1±0.1	<0.1*
DBT	1.5±1.2	67.7±142.1	0.8±0.6	0.3±0.3	34.0±98.8	0.9±1.2	<0.1	0.4±0.6	38.8±75.8	0.3±0.2	<0.1*
PASH	1.9±1.5	82.2±171.1	1.2±1.0	0.5±0.5	60.0±176.0	1.5±1.7	0.2±0.1	0.8±1.4	51.5±101.0	0.4±0.2	0.1*
∑MDBT	2.7±2.9	501.6±1103.2	2.4±2.1	1.0±1.0	210.6±628.3	2.2±2.3	0.5±0.2	0.6±0.9	178.5±415.2	1.0±0.8	0.2*
TAC	193±103	17633±36988	161±112	74±49	5965±17364	218±188	129±15	76±139	16738±45122	117±90	9*
TAC#	135±76	17422±36944	137±96	45±42	5924±17371	160±168	37±17	68±139	16704±45117	85±97	6*
Pe/TAC	0.25±0.31	0.3±0.31	0.19±0.11	0.44±0.3	0.4±0.37	0.24±0.3	0.7±0.15	0.15±0.22	0.26±0.37	0.38±0.23	0.30*

NEAR=North Ecuadorian Amazon Region; SEAR= South Ecuadorian Amazon Region; NEPC= North Ecuadorian Pacific Coast; SEPC= South Ecuadorian Pacific Coast; N=naphthalene; Ac=acenaphthylene; Ace=acenaphthene; Fl=Fluorene; Ph=phenanthrene; A=anthracene; LMW=low molecular weight; Fa=Fluoranthene; Py=pyrene; BaA=benzo[a]anthracene; Ch= chrysene + triphenylene; BbjkF=benzo[bjk]fluoranthene; BaP=benzo[a]pyrene; IP=indeno[1,2,3-cd]pyrene; DBA=dibenzo[ah]anthracene; BPe=benzo[ghi]perylene; BeP=benzo[e]Pyrene; HMW=high molecular weight Pe= perylene; MCh=methylchrysene; 3MPh=3Methylphenanthrene; 2MPh=2methylphenanthrene;MA=2methylanthracene; MPhMA=[9+4]methylphenanthrene+1methylanthracene+ 4,5methylenephenanthrene; 1MPh=1methylphenanthrene; ∑DMPh=∑dimethylphenanthrene; ∑TMPh=∑trimethylphenanthrene; 2MN=2methylnaphthalene; 1MN=1methyl- naphthalene; ∑DMN=∑dimethylnaphthalene; ∑TMN=∑trimethylnaphthalene; ∑TeMN=∑tetramethylnaphthalene; BNT=2,1benzonaphtothiophene; DBT=dibenzothiophene; ∑MDBT=∑methyldibenzothiophene; #=Pe excluded; *= single value (n=1)
Detected molecules with an average concentration between LD and LQ are reported as <LQ; Data non meausured=--

(**Table A-1**), but in these samples, the levels of Fa and Py were higher than our method allowed to analyze. Perylene was detected in all the sediments in a range of 0.1 to 852 $ng.g^{-1}$ (**Table SI-8**), in higher concentrations upstream and/or downstream the study rivers, but not close to main villages or oil facilities.

Perylene is a derivative molecule of perylenequinones, and its presence confirms its biogenic origin explained by the transformation of the biomass particularly important in the tropical forest (Zamani et al., 2015).This natural process allows us to use Pe as an indicator of the environmental quality of uncontaminated sites with a high primary productivity. The highest proportion of Pe correspond to Joya de los Sachas (435 $ng.g^{-1}$) and Pacayacu (555 $ng.g^{-1}$) representing 98% of the total aromatic charge in both sites. The average charge of Pe in relation to the total aromatic charge (Pe/TAC) ranged from 20% in the Coca basin to 70% in the Shushufindi Basin. The Coca basin drains basin through two of the most populated cities (Sas Sebastian del Coca and Francisco de Orellana) in the Amazon Region. While Rumiyacu and Tiputini basins are characterized by less populated areas.

Since our main objective is tracing oil contamination and considering that Pe is a compound tied to the natural biogenic origin, from all the variables analyzed (**Figure SI-3** and **Figure SI-4**) we decided to exclude Pe from the relative abundance of the aromatic charge in the following analysis. These results represented in the **Figure 1-5** show that the methylated compounds from low molecular weight molecules (M-LMW) are the dominant ones in nearly all the samples (30% to 97% of TAC). In the two crude oils analyzed this fraction represents the 92% and 94 % of aromatic charge; a similar abundance (>90%) was found in all the basin versants at the points closest to active oil wells (Coca 08, Auca22, Carabobo and Shuara 24), at the discharge channel of the Refinery (97%) and in the Payamino river in the point of drinking water abstraction used to the villages Shushufindi, Sacha and Coca.

In sediments, no one of the variables showed a normal distribution (Shapiro-Wilk test) of the concentrations; the results of these normality tests are presented in the **Table SI-4**. Two supplementary normality test were done using the relative abundance of each PAH molecule related with the totality of analyzed hydrocarbons, and to the sum of parent PAHs, respectively; these methodology allows to consider the crude oil samples and the bituminous together with the sediment samples in the subsequent analysis.

Spearman correlation analysis ($p<0.05$) showed that only nitrogen presents a significant correlation with total carbon ($r=0.96$) and organic carbon ($r=0.90$); the organic carbon represents more than 75% of total carbon in 65%of the samples which explains these

correlations with nitrogen and shows that most of the carbon found in our samples belongs to organic matter from the forest instead of hydrocarbons from oil activities. No correlation was found between TAC and organic carbon (**Table SI-3**); it coincides with other studies (Cavalcante et al., 2009; Farias et al., 2008; Raza et al., 2013) claiming that only polluted sites shows correlations between total-PAHs and TOC (Simpson et al., 1996). TAC presented the strongest correlations with HMW molecules (r=0.84) and with $_{16}$PAH (r=0.86), the lattest is mainly represented by molecules of HMW, in particular the fluoranthene and chrysene.

3.2.2 Environmental quality risk related with sedimentary aromatic charge

Individual parent-PAHs showed a general compliance with the TEL and PEL (**Table SI-5**). Three specific exceptions existed in (1) the Payamino River (Coca oilfield: PO-g and PO-h) for the LMW-molecules Py and Ch; (2) the upstream of Tiputini River in Dayuma Parish in an specific oil well (Auca22: DY-j, DY-k and DY-l) for all the LMW-molecules, and certains HMW (Py, Ch and DBA). And (3) in the Teaone River at the refinery channel (VL-b and VL-c), where at least 66% of parent-PAHs regulated by the NOAA/CCME were over the TEL. Among all the places that overcome the TEL, there is only one point (Payamino river, PO-g, Coca8 oilwell) with concentrations over the PEL for Ace (1.5 times the PEL) and Fl (3 times the PEL).

The only methylated molecule with defined TEL and PEL by NOAA/CCME is the 2-methylnaphthalene, the concentrations of this hydrocarbon confirmed the punctual pollution manifested beforehand since the parent-PAHs, in particular the points close to the oil wells Coca 8 (PO-g, Payamino River), Auca 22 (DY-j, Tiputini River) and the refinery channel (VL-b, Teaone River), where 2MN overpass the PEL with 6, 1.3 and 3 times, respectively. In addition, 2MN showed that Aguarico river in three points from Pacayacu parish (PK-b, PK-f and PK-g) is also affected by anthropogenic activities, since these points shows values between the TEL and the PEL, even though this points do not overpass the PEL. These concentrations could possibly be the result of fresh crude oil presence as alkylated naphthalenes are characteristic of crude oil profile (Hawthorne et al., 2006).

The NOAA/CCME does not present TEL-PEL values for the TAC in sediments from freshwater, but ERL and ERM are reported among the SQG. We considered TAC as the sum of all quantified parent and alkyl PAHs (Stogiannidis and Laane, 2015) to compare it with the ERL and the ERM. We determined that only 5 % of the sites (4 points: VL-b, VL-c, PO-g, DY-j) are over the ERL, among them; only one (VL-c) is inferior to the ERM.

Since the TEL/PEL analysis, we observed that only 12% (10 samples) shows at least one

individual compound over the TEL; among them only 3 samples (4% of the total) manifested values over the PEL of 2MN and only one sample showed concentrations over the PEL for Ace and Fl. 88% of individual sites studied here do not present a risk for aquatic populations, since these samples are under the TEL-value in all individual compounds. It was confirmed with the analysis of the TAC compared with the ERL and ERM. And finally, we can affirm that the Teaone Basin in the refinery channel and the Payamino River close to Coca08 oilwell are the most affected by oil activities, followed by the Tiputini River in Auca 22 and Teaone River downstream of the dump of the Refinery channel. According to (CCME, 1999) these points overcome a threshold value (ERM) above which adverse effects on most species are frequently or always observed. The TEQ expressed as concentration of BaP was also compared with the TEL, PEL, ERL and ERM and confirmed that 93% of the sampling sites are under the TEL, but 100% are in compliance with PEL, ERL and ERM.

The quotients mERMQ and mPELQ allow to define a relative level of priority related to toxicity (Soliman et al., 2015); applying these method to our analysis (**Table SI-5**), only three points (refinery channel, Coca8 and Auca 22) are defined as slightly toxic, requiring a low medium priority in order to correct or modify the sources of pollution. The same level of priority was present in the bituminous sands. The only point determined as “high priority site” and highly toxic is the residual soil (wasteA8) from an ancient waste pool close to Auca08 oilwell. These points are dirty references for assessing the sources of PAHs.

The results exposed beforehand are in accord with the cartographic method (**Figure 1-6**) developped by Cadot in the frame of the MONOIL program. This method also found wasteA8 (Auca08) as the place with the highest oil pollution hazard. But, since this method takes into count the main sources of pollution (cause), it is usefull to evaluete the risk tied to the density of infraestructures and the presence of oilspils based on historical registres or database, but not directly tied to chemical concentrations as the mERMQ and mPELQ. we could not relate directly our results with the hazard values. It is confirmed with the Spearman’s correlation where none of the variables presented a relation with the oil pollution hazards.

In spite of the high concentration of oil infrastructures and the risk that these may present, it does not necessarily imply the presence of pollutants in the surrounding environment. This can be explained by the improvement in environmental practices due to local actions, in particular since 2008 in which the Ecuadorian State recognized Nature as a “subject of rights” and impel to repair and prevent environmental damages in order to waranty the protection of nature.

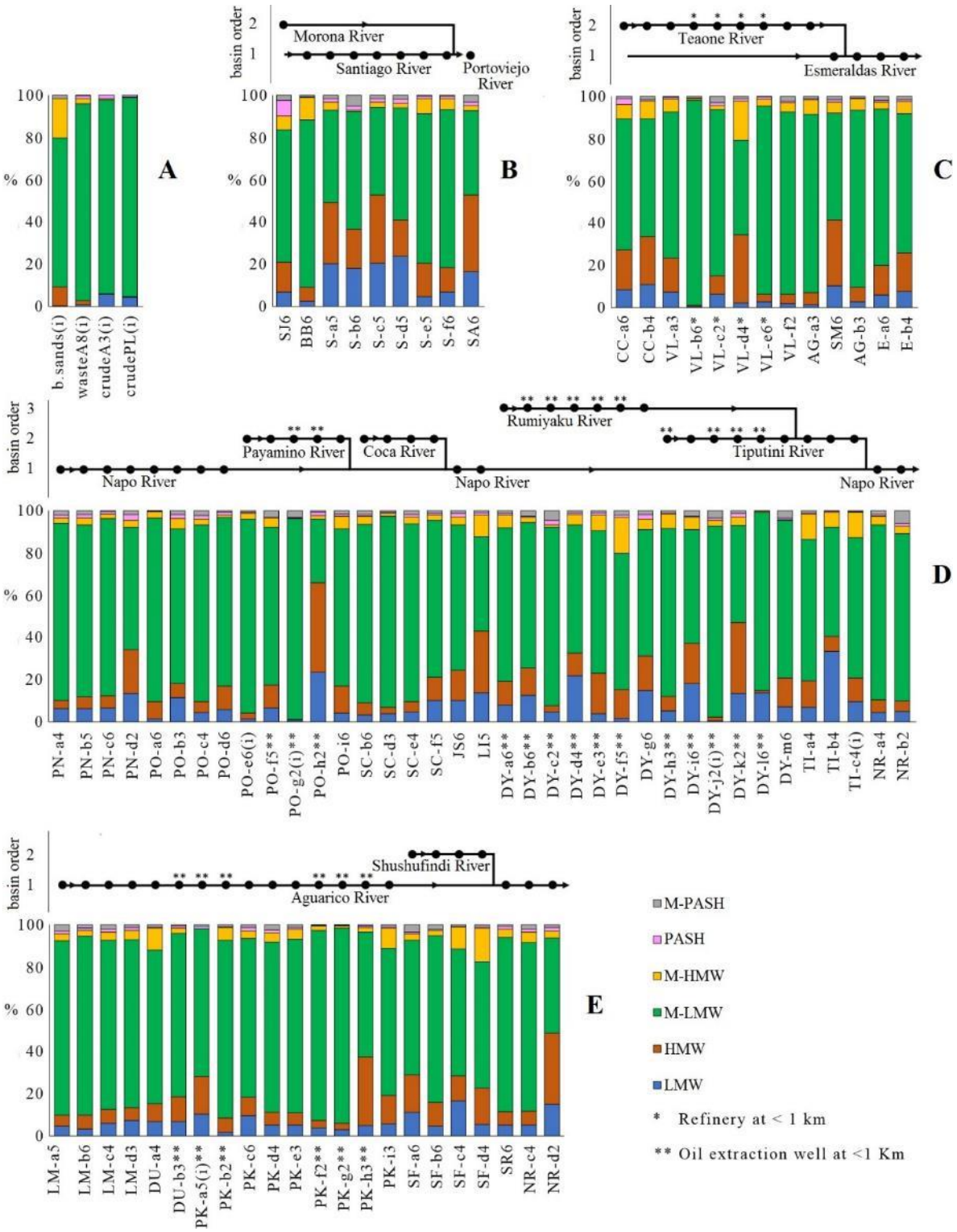


Figure 1-4. Distribution of PAHs as relative abundance of total aromatic charge in sediments from upstream to downstream of the different basins. LMW=Low molecular weight, HMW=high molecular weight, PASH= Polycyclic aromatic sulfur heterocycles, M=methylated molecules, Perylene is excluded; (i)= GC-MS interferences. The two first initials indicate the name of the closest city, village or parish: PN=Puerto Napo, PO=Puerto Francisco de Orellana, SC=San Sebastian del Coca, JS=Joya de los Sachas, LI=Limoncocha, DY=Dayuma, TI=Tiputini, NR=Nuevo Rocafuerte, A8=crude waste pit, A3=Crude Auca oilfield, PL= LM=Lumbaqui, DU=Dureno, PK=Pacayacu, SF=Shushufindi, SR=San Roque, SJ=San José, BB=Bomboiza, S=Santiago, CC=Carlos Concha, VL=Vuelta Larga, AG=5 de Agosto, SM=San Mateo, E=Esmeraldas, SA=Santa Ana. The number at the end of the site's code indicates the year of sampling (2:2012, 3:2013, 4:2014, 5:2015 and 6: 2016) and the lowercase letter indicates the location of the sampling points from upstream (a) to downstream (d) from a same parish, village or city.

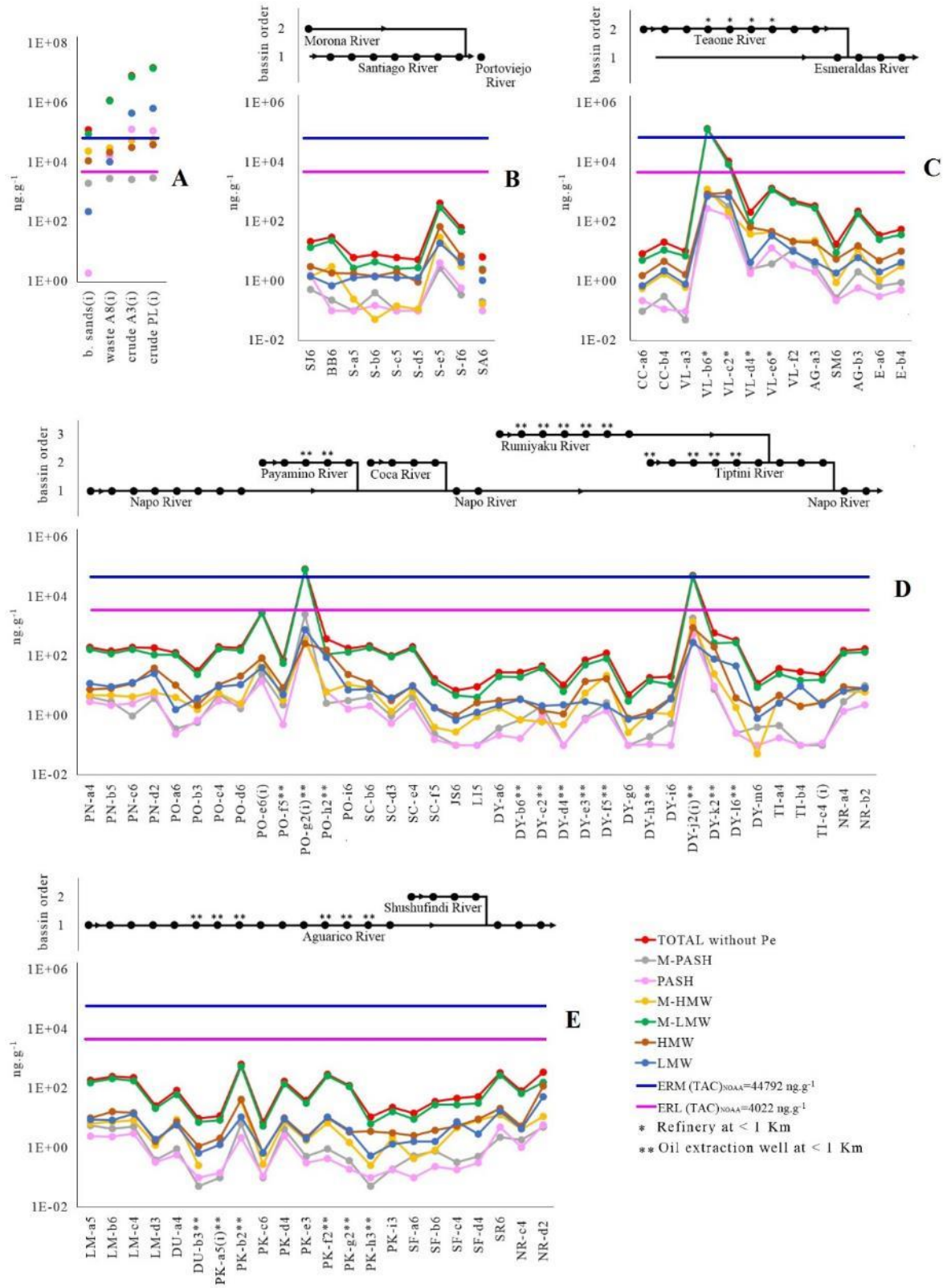


Figure 1-5. Distribution of PAHs concentrations (ng.g^{-1} dw; log scale) in sediments from upstream to downstream in the study basins. LMW=Low molecular weight, HMW=high molecular weight, PASH= Polycyclic aromatic sulfur heterocycles, M=methylated molecules, Perylene is excluded, ERL=effect range low; ERM= effet range median; PN=Puerto Napo, PO=Puerto Francisco de Orellana, SC=San sebastian del Coca, JS=Joya de los Sachas, LI=Limoncocha, DY=Dayuma, TI=Tiputini, NR=Nuevo Rocafuerte, A8=crude waste pit, A3=Crude Auca oilfield, PL= LM=Lumbaqui, DU=Dureno, PK=Pacayacu, SF=Shushufindi, SR=San Roque, SJ=San José, BB=Bomboiza, S=Santiago, CC=Carlos Concha, VL=Vuelta Larga, AG=5 de Agosto, SM=San Mateo, E=Esmeraldas, SA=Santa Ana. The number at the end of the site's code indicates the year of sampling (2:2012, 3:2013, 4:2014, 5:2015 and 6: 2016) and the lowercase letter indicates the location of the sampling points from upstream (a) to downstream (d) from a same parish, village or city.

3.3 Oil activities tracing (source tracing)

Trace sourcing was done by using different isomeric ratios and treated by a PCA and a HCA (**Figure 1-7** and **Figure 1-8**). The isomeric ratios are reported in the **Table SI-9**. The results show that in all the basins, dimethyl and three-methyl phenanthrenes; and methyl chrysene strongly influence the analysis.

In the **Pacific Coast**; the refinery effluents are similar to the ancient oil waste pits found in Auca08; showing that refining process results in a nature similar to ancient non-restored waste pools, and a fingerprint downstream similar to bituminous sands. In the Napo Basin, the Tiputini River from a black water river is totally independent from the others, showing the forest fingerprint (biogenic). Different associations were detected, most of the points show a

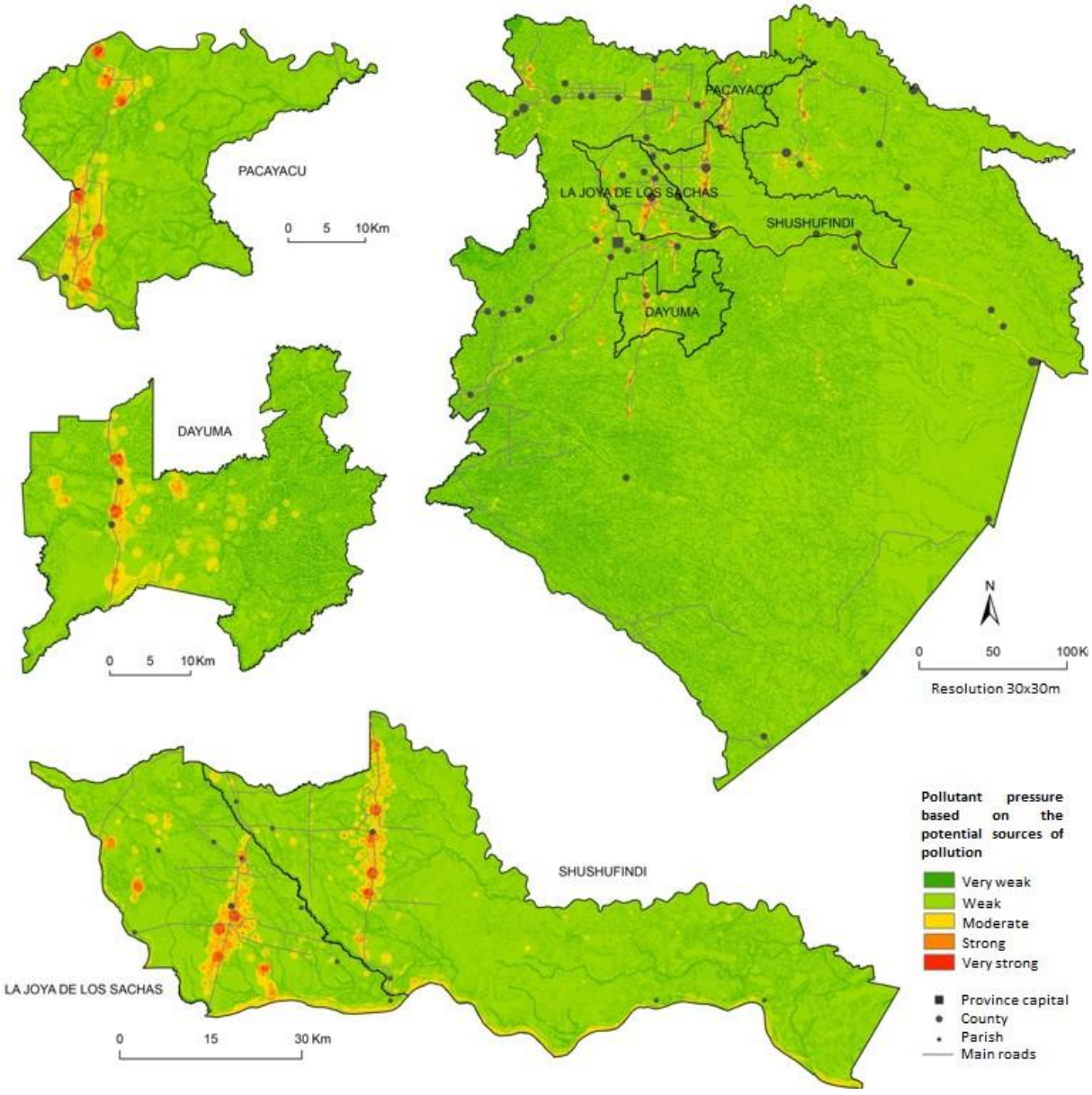


Figure 1-6. Oil pollution hazard map by runoff accumulation area (by Cadot.E ; MONOIL, 2017).

fingerprint similar to bituminous sands and oil waste soil, only one point (recent oil spill) is connected to pipeline crude sample, point for the main villages show a fingerprint similar to the oil waste soil and bituminous sands. In the Aguarico basin a similar distribution is observed, two main clusters, one tied to waste oil pit and another one to bituminous sands. Tracing sources allowed to manifest that ancient oil spills (oil waste) or the natural background of hydrocarbons (bituminous sands) are more related to the concentrations in sediment samples than fresh crude oil.

4. Conclusions

Low molecular weight-PAHs and its corresponding methylated molecules contribute with the highest proportion to the total aromatic charge in the dissolved and in the sedimentary phases.

Surface water samples do not show pollution related with PAHs; the international permissible levels are not exceeded in most of the study sites. In fact, only in the case of direct contact with fresh crude oil like in Auca 22 or the dumping of refining liquid byproducts like in the Teaone River, showed naphthalene, anthracene and pyrene in concentrations higher than the permissible levels.

Sedimentary charge is in compliance with the different water quality guidelines, with punctual pollution in sites close to active extraction or refining facilities.

The biogenic fingerprint is manifested since the concentrations of Perylene, in particular downstream of the Andes influence; it was manifested in a black-water river in the Tiputini Ecological Reserve. Perylene is presented in nearly all the samples, confirming that the amazon rainforest is a source of this molecule.

Since not important values were manifested downstream of punctual pollution, except in the closer samples (< 1km); we can affirm that oil production and refining processes are not important sources of contamination neither in the Pacific Coast nor in the Amazon Region. Because the results in the present study (dissolved phase) are similar to values found in cities with some industrial, agricultural and urban activities, we claim that even with only 5% of the Ecuadorian population living in the Amazon region, not only oil processes, but also urban activities altogether with local agriculture contribute to the presence of PAHs in the dissolved phase. On the other hand, in the Pacific Coast, the Esmeraldas Refinery represents the main source of surface water pollution, within 1 km from the effluents affecting the Teaone River, but not the Esmeraldas River, whose values remain similar upstream and downstream the

confluence with the Teaone River. It was confirmed by the hierarchical cluster analysis applied to the sedimentary phase, where most of the analyzed places are not directly influenced by fresh crude oil, but by ancient waste or similar to the geochemical background (bituminous sands). HCA showed different associations with the main populated sites and agricultural emplacements that need a deeper analysis in order to characterize these origins. Local efforts to improve environmental quality should be reflected in future studies about local pollution in Refining Ecuadorian zones.

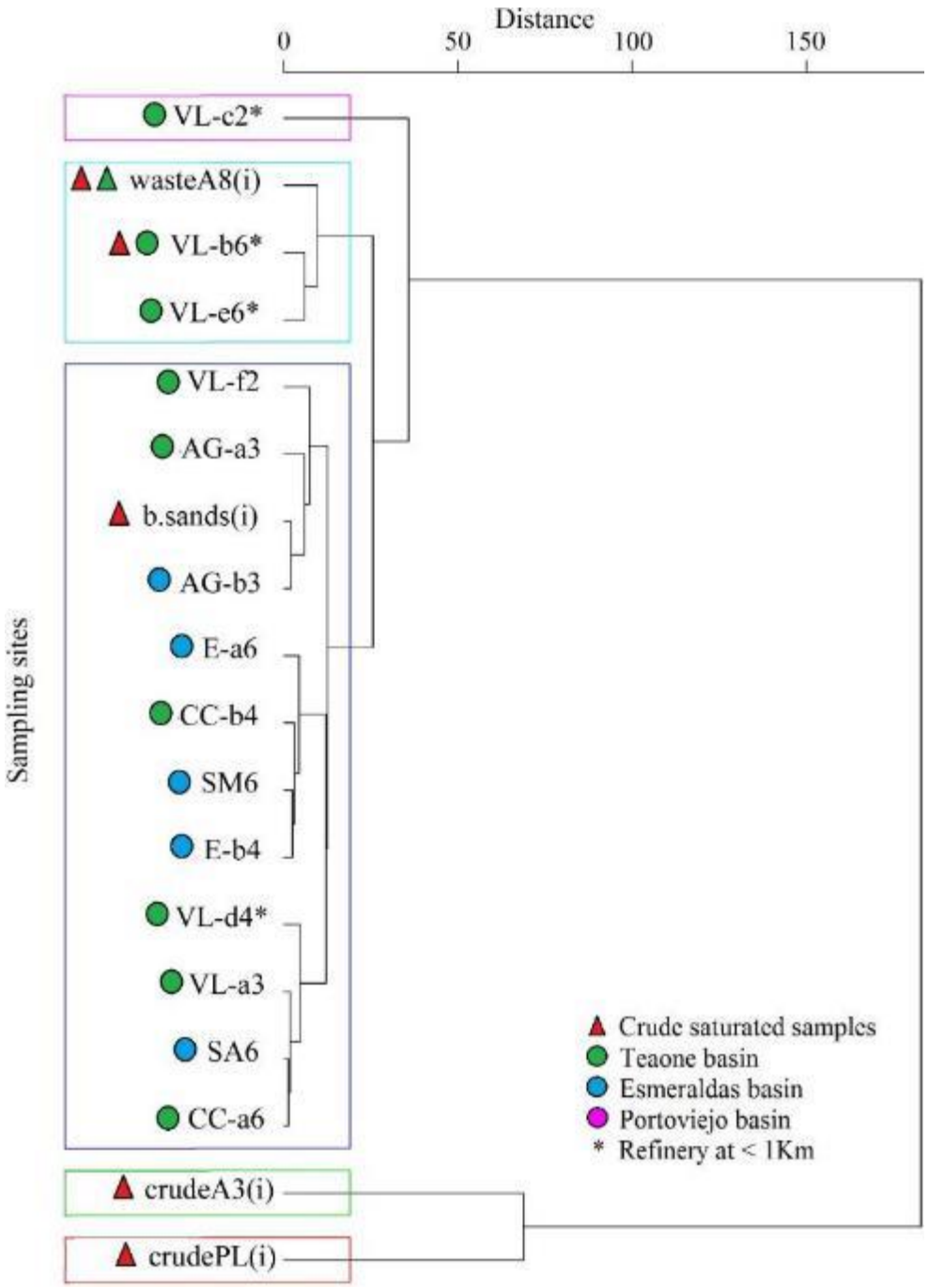


Figure 1-7. Hierarchical Cluster Analysis (HCA)-Complete-linkage method based on the isomeric ratios of aromatic charge in sediments (N and Pe excluded), Esmeraldas Basin.

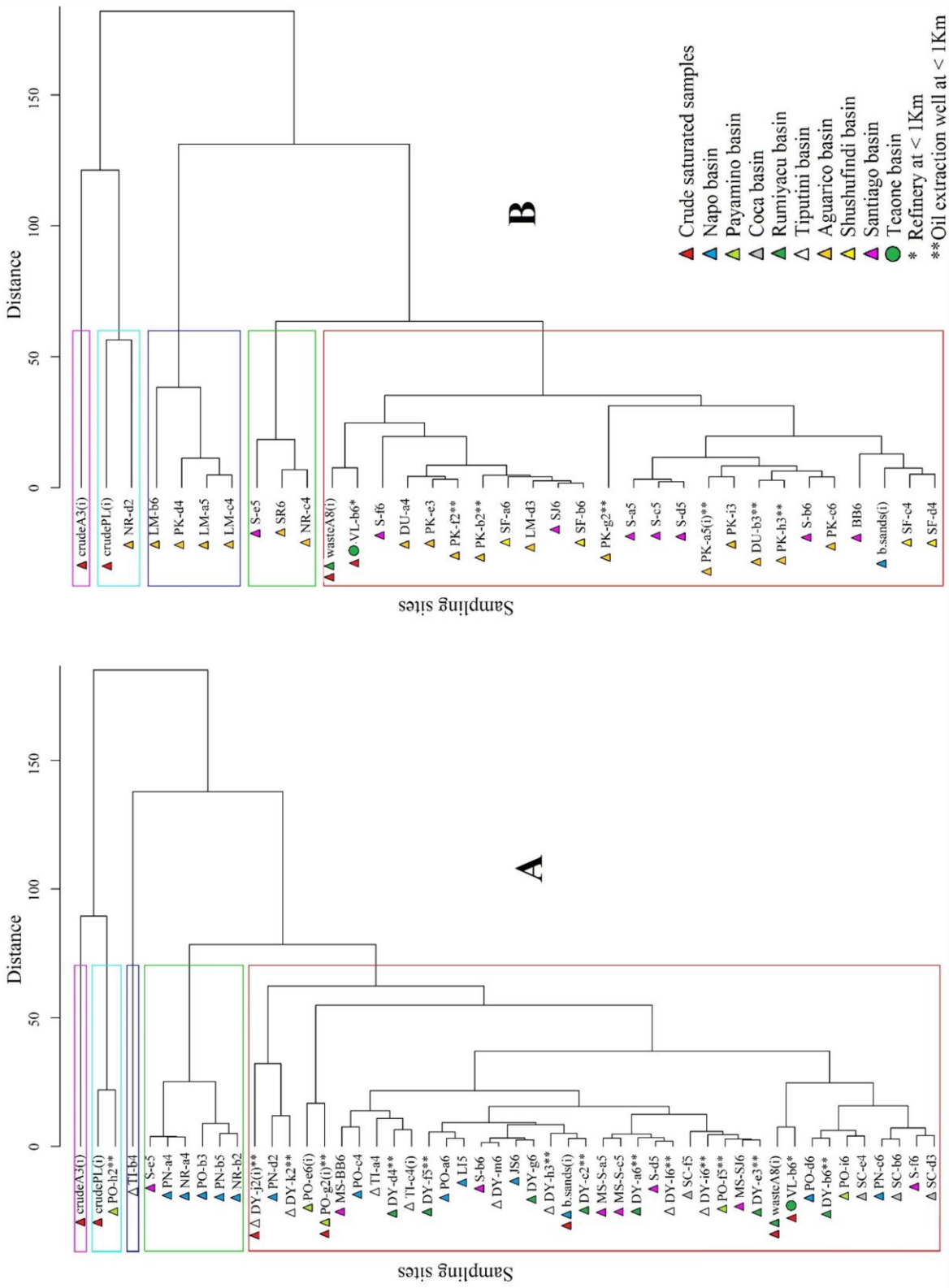


Figure 1-8. Hierarchical Cluster Analysis (HCA)-Complete-linkage method based on the isomeric ratios of aromatic charge in sediments (N and Pe excluded): A) Napo Basin, B) Aguarico Basin.

Quotients like mPELQ and mERMQ were accurate for determining the environmental risk since a scale is proposed. But a complete human hazard risk based in sediments concentrations could help to better understand the risk to local populations that are accustomed to swim and fish in the studied rivers.

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Supplementary Information 1

Table SI-1. List and proprieties of organic molecules analyzed in the present study

GROUP	MOLECULE	RING	SOLUBILITY (mg L^{-1})	MOLECULAR WEIGHT (g $mole^{-1}$)	IARC GROUP	ABBREVIATION
US-EPA PARENT PAHs	Naphthalene	2	31	128.17	2B	N
	Acenaphthylene	3	3.9	152.20	-	Ac
	Acenaphthene	3	3.8	154.21	3	Ace
	Fluorene	3	1.9	166.22	3	Fl
	Phenanthrene	3	1.1	178.23	3	Ph
	Anthracene	3	0.045	178.23	3	A
	Fluoranthene	4	0.26	202.26	3	Fa
	Pyrene	4	0.132	202.26	3	Py
	Benzo[*a*]anthracene	4	0.011	228.29	2B	BaA
	Chrysene*	4	0.0015	228.29	2B	Ch
	Benzo[*b*]fluoranthene**	5	0.0015	252.32	2B	BbjkF
	Benzo[*k*]fluoranthene**	5	0.0008	252.32	2B	BbjkF
	Benzo[*a*]pyrene	5	0.0038	252.32	1	BaP
	Indeno[1,2,3-*cd*]pyrene	6	0.062	276.34	2B	IP
	Dibenzo[*a,h*]anthracene***	5	0.0005	278.35	2A	DBA
	Benzo[*g,h,i*]perylene	6	0.00026	276.34	3	BPe
OTHER PARENT PAHs	Triphenylene*	4	0.0066	228.29	3	Ch
	Benzo[e]pyrene	5	0.0063	252.32	3	BeP
	Benzo[j]fluoranthene**	5	0.0025	252.32	2B	BbjkF
	Dibenzo[a,c]anthracene***	5	0.0016	278.35	3	DBA
	Perylene	5	0.0004	252.32	3	Pe
METHYL And THIO PAHs	1Methylnaphthalene	2	25	142.2	-	1MN
	2Methylnaphthalene	2	24.6	142.2	-	2MN
	ΣDimethylnaphthalene	2	2-11	156.2	-	∑DMN
	ΣTrimethylnaphthalene	2	1.7-2.0	170.3	-	∑TMN
	ΣTetramethylnaphthalene	2	-	184.3	-	∑TeMN
	2Methylanthracene	3	0.021	192.3	-	MA
	1Methylanthracene****	3	0.27	192.3	-	MPhMA
	[9+4]Methylphenanthrene****	3	-	192.3	-	MPhMA
	[4,5]Methylenephenanthrene****	3	1.1	190.2	-	MPhMA
	1Methylphenanthrene	3	0.3	192.3	3	1MPh
	2Methylphenanthrene	3	0.3	192.3	-	2MPh
	3Methylphenanthrene	3	-	192.3	3	3MPh
	ΣDimethylphenanthrene	3	-	206.2	3	∑DMPh
	ΣTrimethylphenanthrene	3	-	220.3	-	∑TMPh
	ΣMethylchrysene	4	0.062-0.065	242.3	2B#, 3	MCh
	ΣMethyldibenzothiophene	3	-	198.3	-	∑MDBT
	Dibenzothiophene	3	1.47	184.3	3	DBT
	2,1-Benzonaphtothiophene	4	-	234.32	3	BNT

Source:(Bojes and Pope, 2007; International Agency for Research on Cancer (IARC), 2018; National Center for Biotechnology Information (NCBI) and US National Library of Medicine (USNLM), 2018); IARC=International Agency for Research on Cancer; * Ch= Chrysene+Triphenylene=this two compounds are in the same analytical ensemble; Triphenylene is not in the US-EPA list **BbjkF= Benzo[*b,j,k*]fluoranthene=this three compounds are in the same analytical ensemble; Benzo[j]fluoranthene is not in the US-EPA list; ***DBA=dibenzo[a,h]anthracene+dibenzo[a,c]anthracene ; ****MPhMA =[9+4]methylphenanthrene+ [4,5]methylenephenanthrene +1methylanthracene, this three compounds belongs to the same analytical ensemble. # only for 5-MCh.

Table SI-2. National and international water quality guidelines in freshwater.

MOLECULE(S)	RAOHE[a]	USEPA[b]	CCME[b]	EU[b]	FR[b]
TSS[#]	1700	--	--	--	--
N	--	--	**1100**	2400	130000
Ace	--	--	**5800**	--	--
Fl	--	--	**3000**	--	--
Ph	--	--	**400**	--	--
A	--	--	**12**	400	100
Fa	--	--	**40**	1000	120
Py	--	--	**25**	--	--
BaA	--	--	**18**	--	--
BbjkF	--	--	--	30	**17**
BaP	--	--	**15**	100	270
IP	--	--	--	**2**	--
BPe	--	--	--	**2**	8,2
WQG USEPA	--	**31**	--	--	--
WQG EC	300	--	--	--	--

a At least 300 m downstream of the discharge point
b=freshwater (inland)
#=in $mg.L^{-1}$

Table SI-3. Spearman's correlation ($p<0.05$) for the main variables in sediments.

r(p<0.05)	hazard	clays	silts	sands	TC	OC	TN	TS	16PAH	LMW	HMW	TAC	MPAH
hazard	1.00												
clays	0.00	1.00											
silts	-0.07	0.36	1.00										
sands	0.10	-0.73	-0.85	1.00									
TC	0.02	0.22	0.44	-0.33	1.00								
OC	0.11	0.21	0.41	-0.31	0.94	1.00							
TN	-0.06	0.38	0.50	-0.46	0.96	0.90	1.00						
TS	-0.13	-0.14	0.32	-0.17	0.34	0.43	0.19	1.00					
$_{16}$PAH	0.16	0.03	0.33	-0.24	0.22	0.24	0.10	0.43	1.00				
LMW	0.12	-0.03	0.31	-0.21	0.21	0.25	0.05	0.44	0.95	1.00			
HMW	0.15	0.04	0.32	-0.23	0.24	0.26	0.14	0.40	0.96	0.84	1.00		
TAC	0.22	0.14	0.35	-0.31	0.18	0.21	0.03	0.26	0.86	0.79	0.84	1.00	
MPAH	0.17	-0.04	0.22	-0.13	0.17	0.18	-0.06	0.40	0.92	0.89	0.88	0.85	1.00

Table SI-4. Normality test (Shapiro-Wilk) applied to PAHs concentrations in bottom sediments.

VARIABLE	AMAZON		COAST		AMAZON*		COAST*	
	W	p-value	W	p-value	W	p-value	W	p-value
hazard	8.88E-01	1.91E-05	--	--	9.39E-01	7.81E-03	--	--
≤ 4 µm	9.01E-01	6.00E-05	8.94E-01	9.21E-02	9.58E-01	2.50E-02	9.50E-01	5.66E-01
4-63 µm	9.28E-01	7.85E-04	9.36E-01	3.73E-01	6.97E-01	1.84E-10	9.12E-01	1.71E-01
≤ 63 µm	9.37E-01	2.06E-03	9.66E-01	8.15E-01	7.31E-01	9.00E-10	9.41E-01	4.29E-01
> 63µm	9.37E-01	2.06E-03	9.66E-01	8.15E-01	9.70E-01	1.06E-01	9.67E-01	8.37E-01
TC (%)	7.39E-01	1.40E-09	9.00E-01	1.13E-01	9.64E-01	4.81E-02	9.09E-01	1.52E-01
OC (%)	6.87E-01	1.17E-10	9.17E-01	1.98E-01	9.46E-01	6.00E-03	9.68E-01	8.47E-01
N	4.31E-01	1.11E-14	5.11E-01	7.17E-06	9.74E-01	1.81E-01	8.40E-01	1.61E-02
Ac	1.50E-01	<2.2E-16	3.10E-01	2.64E-07	4.31E-01	1.13E-14	5.81E-01	2.77E-05
Ace	1.49E-01	<2.2E-16	3.62E-01	5.87E-07	6.85E-01	1.06E-10	7.18E-01	5.74E-04
Fl	1.44E-01	<2.2E-16	4.64E-01	3.12E-06	8.12E-01	8.11E-08	8.17E-01	8.17E-03
Ph	3.77E-01	2.37E-15	4.59E-01	2.88E-06	9.26E-01	6.67E-04	8.40E-01	1.61E-02
A	3.44E-01	1.66E-15	4.44E-01	2.22E-06	6.50E-01	3.61E-11	8.31E-01	1.23E-02
Fa	3.37E-01	7.94E-16	3.22E-01	3.19E-07	8.35E-01	3.76E-07	8.26E-01	1.06E-02
Py	3.53E-01	1.23E-15	4.66E-01	3.23E-06	9.22E-01	4.24E-04	9.06E-01	1.40E-01
BaA	2.98E-01	2.96E-16	4.37E-01	1.96E-06	8.99E-01	5.22E-05	9.48E-01	5.27E-01
Ch	1.75E-01	<2.2E-16	4.14E-01	1.34E-06	9.57E-01	2.02E-02	9.40E-01	4.19E-01
BbjkF	2.17E-01	<2.2E-16	5.08E-01	6.81E-06	9.69E-01	8.71E-02	9.36E-01	3.67E-01
BaP	5.03E-01	1.69E-13	4.22E-01	1.53E-06	9.64E-01	5.26E-02	9.55E-01	6.36E-01
IP	3.54E-01	1.28E-15	7.26E-01	6.90E-04	9.57E-01	2.17E-02	9.54E-01	6.23E-01
DBA	1.72E-01	<2.2E-16	4.61E-01	2.99E-06	8.39E-01	6.75E-07	9.71E-01	8.86E-01
BPe	3.77E-01	3.07E-15	5.71E-01	2.27E-05	9.74E-01	1.72E-01	9.66E-01	8.22E-01
$_{16}$PAH	2.92E-01	2.51E-16	4.69E-01	3.41E-06	9.18E-01	2.99E-04	8.70E-01	4.20E-02
BeP	2.38E-01	<2.2E-16	4.39E-01	2.04E-06	9.59E-01	2.79E-02	9.47E-01	5.20E-01
Pe	5.27E-01	2.35E-13	9.03E-01	1.25E-01	9.33E-01	1.38E-03	9.51E-01	5.82E-01
MCh	1.66E-01	<2.2E-16	3.95E-01	9.83E-07	9.61E-01	3.77E-02	9.57E-01	6.71E-01
BNT	1.54E-01	<2.2E-16	4.43E-01	2.20E-06	8.01E-01	4.14E-08	8.50E-01	2.20E-02
3MPh	1.71E-01	<2.2E-16	4.07E-01	1.20E-06	9.04E-01	8.11E-05	9.00E-01	1.12E-01
2MPh	1.74E-01	<2.2E-16	3.71E-01	6.77E-07	9.19E-01	3.38E-04	9.01E-01	1.16E-01
MA	1.91E-01	<2.2E-16	4.44E-01	2.23E-06	6.54E-01	3.41E-11	7.90E-01	3.79E-03
MPhMA	1.78E-01	<2.2E-16	3.89E-01	8.96E-07	9.18E-01	3.45E-04	9.21E-01	2.27E-01
1MPh	1.71E-01	<2.2E-16	3.95E-01	9.85E-07	9.00E-01	6.36E-05	9.01E-01	1.18E-01
∑DMPh	1.73E-01	<2.2E-16	3.90E-01	9.10E-07	9.06E-01	9.57E-05	9.70E-01	8.75E-01
∑TMPh	1.74E-01	<2.2E-16	3.88E-01	8.86E-07	9.13E-01	1.86E-04	9.67E-01	8.40E-01
2MN	1.74E-01	<2.2E-16	3.93E-01	9.55E-07	9.45E-01	4.86E-03	8.16E-01	7.98E-03
1MN	1.66E-01	<2.2E-16	3.87E-01	8.75E-07	9.34E-01	1.59E-03	7.91E-01	3.86E-03
∑DMN	1.50E-01	<2.2E-16	3.20E-01	3.09E-07	9.10E-01	1.43E-04	8.34E-01	1.34E-02
∑TMN	1.61E-01	<2.2E-16	3.17E-01	2.94E-07	8.90E-01	2.25E-05	8.85E-01	6.84E-02
∑TeMN	1.73E-01	<2.2E-16	3.18E-01	3.01E-07	8.56E-01	1.65E-06	8.97E-01	1.01E-01
DBT	1.82E-01	<2.2E-16	4.65E-01	3.21E-06	8.70E-01	4.54E-06	8.59E-01	2.95E-02
∑MDBT	1.70E-01	<2.2E-16	4.01E-01	1.09E-06	8.69E-01	4.40E-06	9.02E-01	1.20E-01

*****Logaritmic transformation

Table SI-5. Total aromatic charge (ng.g^{-1}), mean-SQG quotients and total-equivalent quantity (TEQ-BaP, ng.g^{-1}) in sediments from Napo, Aguarico and Esmeraldas basins.

BASIN	SITE	TAC (nonPe)	mERM-Q	mPEL_Q	TEQ-BaP	SUB-BASIN
	b.sands(i)	112594	2.7E-01	8.6E-01	2289	--
	wasteA8(i)	1158235	1.3E+00	4.6E+00	2476	--
	crudeA3(i)	7636490	7.6E+01	2.8E+02	3354	--
	crudePL(i)	13743430	1.3E+02	4.5E+02	4804	--
	SJ6	21	1.9E-04	6.5E-04	0.54	M.Santiago
	BB6	29	1.0E-04	3.7E-04	0.44	M.Santiago
	S-a5	6	1.5E-04	5.4E-04	0.36	M.Santiago
	S-b6	8	1.4E-04	5.5E-04	0.38	M.Santiago
	S-c5	6	1.5E-04	5.3E-04	0.40	M.Santiago
	S-d5	5	1.5E-04	5.3E-04	0.32	M.Santiago
	S-e5	410	2.6E-03	8.5E-03	8.50	M.Santiago
	S-f6	60	5.0E-04	1.7E-03	1.07	M.Santiago
	SA6	6	1.1E-04	4.2E-04	0.25	Portoviejo
	PN-a4	194	1.7E-03	5.9E-03	1.04	Napo
	PN-b5	146	1.4E-03	5.1E-03	1.17	Napo
	PN-c6	197	1.6E-03	5.8E-03	1.69	Napo
	PN-d2	190	2.9E-03	1.0E-02	1.44	Napo
	PO-a6	127	5.4E-04	1.7E-03	2.41	Napo
	PO-b3	32	3.9E-04	1.3E-03	0.96	Napo
	PO-c4	205	1.6E-03	6.0E-03	1.74	Napo
	PO-d6	189	1.5E-03	5.2E-03	3.07	Napo
	PO-e6(i)	3003	1.4E-02	4.8E-02	17.20	Payamino
NAPO	**PO-f5****	77	5.9E-04	2.0E-03	1.52	Payamino
	PO-g2(i)**	83473	2.7E-01	9.9E-01	21.43	Payamino
	PO-h2**	376	1.1E-02	3.7E-02	2.16	Payamino
	PO-i6	182	1.1E-03	3.5E-03	3.84	Payamino
	SC-b6	225	1.3E-03	4.4E-03	1.66	Coca
	SC-d3	101	9.1E-04	3.1E-03	0.98	Coca
	SC-e4	204	1.4E-03	4.9E-03	1.44	Coca
	SC-f5	17	2.1E-04	7.3E-04	0.40	Coca
	JS6	7	8.5E-05	3.1E-04	0.33	Napo
	LI5	9	1.5E-04	5.3E-04	0.59	Napo
	DY-a6**	28	2.2E-04	8.1E-04	0.44	Rumiyacu
	DY-b6**	28	3.6E-04	1.3E-03	1.13	Rumiyacu
	DY-c2**	47	3.9E-04	1.4E-03	0.96	Rumiyacu
	DY-d4**	10	1.8E-04	7.7E-04	0.05	Rumiyacu
	DY-e3**	73	5.1E-04	1.7E-03	1.86	Rumiyacu
	DY-f5**	126	6.7E-04	2.1E-03	3.55	Rumiyacu
	DY-g6	5	9.1E-05	3.3E-04	0.32	Rumiyacu
	DY-h3**	18	1.5E-04	5.0E-04	0.94	Tiputini
	DY-i6**	20	3.4E-04	1.3E-03	1.31	Tiputini
	DY-j2(i)**	52243	8.3E-02	2.9E-01	128.16	Tiputini
	DY-k2**	596	1.2E-02	4.0E-02	8.01	Tiputini
	DY-l6**	335	1.1E-02	4.0E-02	0.70	Tiputini
	DY-m6	12	1.3E-04	4.4E-04	0.79	Tiputini
	TI-a4	37	2.8E-04	1.1E-03	1.03	Tiputini
	TI-b4	29	5.8E-04	2.0E-03	0.99	Tiputini
	TI-c4(i)	24	2.1E-04	7.9E-04	1.03	Tiputini
	NR-a4	153	1.4E-03	4.1E-03	7.55	Napo
	NR-b2	170	1.2E-03	4.2E-03	1.10	Napo
	LM-a5	189	1.3E-03	4.6E-03	1.24	Aguarico
	LM-b6	253	1.6E-03	5.4E-03	2.38	Aguarico
	LM-c4	227	1.8E-03	6.5E-03	2.58	Aguarico
	LM-d3	26	3.1E-04	1.0E-03	0.95	Aguarico
AGUARICO	**DU-a4**	87	5.2E-04	2.0E-03	1.23	Aguarico
	DU-b3**	10	1.2E-04	3.7E-04	0.94	Aguarico
	PK-a5(i)**	12	1.4E-04	5.1E-04	0.38	Aguarico
	PK-b2**	639	7.9E-03	2.7E-02	6.89	Aguarico
	PK-c6	7	9.2E-05	3.5E-04	0.11	Aguarico

Table SI-5. Total aromatic charge (ng.g-1), mean-SQG quotients and total-equivalent quantity (TEQ-BaP, ng.g-1) in sediments from Napo, Aguarico and Esmeraldas basins. (continued)

BASIN	SITE	TAC #	mERM-Q	mPEL_Q	TEQ-BaP	SUB-BASIN
	PK-d4	173	1.3E-03	4.5E-03	1.13	Aguarico
	PK-e3	39	3.5E-04	1.1E-03	0.95	Aguarico
	PK-f2**	291	8.2E-03	2.8E-02	1.93	Aguarico
AGUARICO	**PK-g2****	124	3.2E-03	1.1E-02	1.05	Aguarico
	PK-h3**	11	2.0E-04	5.1E-04	2.86	Aguarico
	PK-i3	23	2.2E-04	7.2E-04	1.08	Aguarico
	SF-a6	15	1.5E-04	5.5E-04	0.23	Shushufindi
	SF-b6	36	1.9E-04	6.6E-04	0.69	Shushufindi
	SF-c4	46	5.7E-04	2.3E-03	2.00	Shushufindi
	SF-d4	53	3.5E-04	1.2E-03	1.62	Shushufindi
	SR6	336	2.4E-03	8.3E-03	3.07	Aguarico
	NR-c4	83	5.8E-04	2.0E-03	1.02	Aguarico
	NR-d2	349	6.5E-03	2.2E-02	2.21	Aguarico
	CC-a6	8	9.8E-05	3.5E-04	0.37	Teaone
	CC-b4	21	2.7E-04	9.5E-04	1.37	Teaone
	VL-a3	11	1.5E-04	4.8E-04	0.95	Teaone
	VL-b6*	136627	1.3E-01	4.5E-01	136.25	Teaone
	VL-c2*	11266	8.7E-02	3.1E-01	33.89	Teaone
ESMERALDAS	**VL-d4***	208	1.5E-03	4.7E-03	12.83	Teaone
	VL-e6*	1335	7.6E-03	2.7E-02	7.00	Teaone
	VL-f2	515	3.7E-03	1.3E-02	3.30	Teaone
	AG-a3	349	1.0E-03	3.5E-03	4.24	Teaone
	SM6	18	2.5E-04	8.6E-04	0.85	Esmeraldas
	AG-b3	228	9.7E-04	3.2E-03	3.57	Esmeraldas
	E-a6	35	2.8E-04	9.6E-04	0.82	Esmeraldas
	E-b4	57	4.9E-04	1.7E-03	1.64	Esmeraldas

Perylene non included

Table SI-6. Toxicological reference values (TRV) for sediments in $ng.g^{-1}$, TEF is dimensionless.

MOLECULE	Swartz ,1999				NOAA/CCME				NOAA		TOXICITY EQUIVALENT FACTOR		
					freshwater		seawater				(Montuori, 2016 ; EPA, 1993,2019)	(Keshavarzi, 2015 Nisbet,1992 Collins,1998)	(CCME,2010)
	TEL	PEL	ERL	ERM	TEL	PEL	TEL	PEL	ERL	ERM			
Ace	10	90	20	500	6.71	88.9	6.71	88.9		500	--	0.001	--
Ac	10	130	40	640	5.87	128	5.87	128	44	640	--	0.001	--
A	50	240	90	1100	46.9	245	46.9	245	85	1100	--	0.01	--
F	20	140	20	540	21.2	144	21.2	144	19	540	--	0.001	--
N	30	390	160	2100	34.6	391	34.6	391	160	2100	--	0.001	--
Ph	90	540	240	1500	41.9	515	86.7	544	240	1500	--	0.001	--
LMW-PAH	210	1530	570	6380	157.2	1423	312	1442	552	3160	--	--	--
BaA	70	690	260	1600	31.7	385	74.8	693	261	1600	0.1	0.1	0.1
BbF	70	710	320	1880	--	--	--	--	--	--	0.1	0.1	0.1
BkF	60	610	280	1620	--	--	--	--	--	--	*0.01*	*0.1*	*0.1*
BaP	90	760	430	1600	31.9	782	88.8	763	430	1600	**1**	**1**	**1**
DBA	--	--	--	--	6.22	135	6.22	135	63	260	1	5*	1.000
Ch	110	850	380	2800	57.1	682	108	846	384	2800	*0.001*	*0.01*	*0.01*
Fa	110	1490	600	5100	111	2355	113	1494	600	5100	--	0.001	--
Py	150	1400	660	2600	53	875	153	1398	665	2600	--	0.001	--
IP	--	--	--	--	--	--	--	--	--	--	0.1	0.1	0.1
HMW-PAHs	660	6510	2930	17200	290.92	5214	655	6676	1700	9600	--	--	--
TAC	870	8040	3500	23580	448.10	6637	1684	16770	4022	44792	--	--	--
BPe	--	--	--	--	--	--	--	--	--	--	--	0.01	0.01
2MN	--	--	--	--	20.2	201	20.2	201	70	670	--	0.001	--

*Only for diluted water

NOAA, 2008; CCME, 2010

Table SI-7. Ranges of dissolved organic carbon (mg.L^{-1}), total suspended solids (mg.L^{-1}), and dissolved PAHS (ng.L^{-1}) in surface water from different basins 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).

VARIABLE	NEAR							SEAR	NEPC		SEPC	ALL	LD	LQ	RECOVERY
	Napo	Payamino	Coca	Rumiyacu	Tiputini	Aguarico	Shushufindi	Santiago	Teaone	Esmeraldas	Portoviejo	>LQ#			%
DOC	0.7-49.8	1.6-28.4	0.8-35.7	1.9-218	2.9-130.7	1.1-110.2	1.1-4.9	1-100.4	2.3-12.8	1.8-2.6	2.5*	100%	0.2	0.5	105
TSS	5-167	5-21	4-128	5-47	14-94	2-1378	9-19	1-292	5-126	14-175	137*	--	--	--	--
N	3.0-27.5	3.0-8.6	3.0-16.6	3.0-8.8	3.0-1830.3	3.0-29.3	3.0-9.4	<3.0	3.0-21.9	3.0-8.2	<3.0*	40%	0.5	3.0	98
Ac	0.7-1.4	<0.67	0.7-1.9	<0.67	1.5-99.1	0.67-1.79	0.67-1.32	<0.67	0.67-1.65	<0.67	<0.67*	13%	0.2	0.7	98
Ace	0.6-3.2	0.6-4.6	0.6-1.3	0.6-5.9	0.6-128.9	0.6-11.3	0.6-0.9	<0.6	0.6-7.5	0.6-2.0	<0.6*	27%	0.2	0.6	103
Fl	0.4-26.3	0.4-9.7	0.4-6.5	0.4-9.1	0.4-212.0	0.4-34.8	0.4-0.7	0.4-1.4	0.4-4.0	0.7-2.1	<0.4*	56%	0.1	0.4	106
Ph	0.4-4.7	1.2-3.5	0.4-4.7	0.4-7.3	0.4-141.5	0.4-6.1	0.7-1.7	0.4-4	1.2-7.2(i)	1.5-2.5	<0.4*	87%	0.2	0.5	106
A	0.4-0.63	<0.4	<0.4	0.4-0.6	0.4-13.37	0.4-0.63	<0.4	<0.4	0.4-0.9(i)	<0.4	<0.4*	8%	0.1	0.4	105
Fa	0.3-2.1	0.3-0.9	0.3-0.6	0.3-2.6	0.3-5.0	0.3-1.5	0.3-0.7	<0.3	0.3-0.9	0.3-1	<0.3*	39%	0.1	0.3	102
Py	0.3-1.6	0.3-0.9	0.3-0.9	0.3-5.1	0.3-6.8	0.3-3.3	0.3-0.7	0.3-0.6	0.3-78.6	0.3-2.4	<0.3*	47%	0.1	0.3	102
BaA	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40*	0%	0.1	0.4	103
Ch	<0.39	<0.39	<0.39	0.39-2.13	0.39-2.78	0.39-4.8	<0.39	<0.39	0.39-8.46	<0.39	0.27*	10%	0.1	0.4	101
BbjkF	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	0%	0.3	1.0	104
BaP	<1.0	nd	<1.0	<1.0	nd	<1.0	nd	<1.0	<1.0	nd	nd	0%	0.3	1.0	97
IP	<1.0	nd	nd	<1.0	nd	nd	nd	nd	nd	nd	nd	0%	0.3	1.0	103
DBA	<1.0	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0%	0.3	1.0	102
BPe	<1.0	nd	<1.0	<1.0	nd	<1.0	nd	<1.0	<1.0	nd	nd	0%	0.3	1.0	100
$_{16}$PAH	6-37	7-28	5-28	4-33	4-2437	4-66	6-13	6-10	6-102	10-15	6*	--	--	--	--
US$_{WQG}$	2-6	3-3.5	1.4-6.5	0.6-7.3	0.3-240.6	0.3-7.8	1.6-3.1	1.6-5	1.8-10.9	2-3.9	2.3*	--	--	--	--
EC$_{WQG}$	0.2-3.2	0.9-0.9	0.2-1.7	0.2-2.6	0.2-5.0	0.2-1.7	0.2-0.9	0.9-2.4	0.2-3.1	0.7-1	1.0*	--	--	--	--
BeP	<1.0	<1.0	nd	<1.0	<1.0	<1.0	nd	<1.0	1.0-2.5	nd	<1.0*	1%	0.3	1.0	99
Pe	<1.0	<1.0	<1.0	<1.0	1.0-1.8	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0*	1%	0.3	1.0	98
MCh	<0.52	<0.52	<0.52	0.67-1.73	0.52-8.31	0.52-7.83	<0.52	<0.52	1.6-6.89	3.63-3.63	<0.52*	10%	0.2	0.5	101
3MPh	0.3-1.8	0.4-1.5	0.3-1.1	0.3-2.7	0.3-131.4	0.3-6.2	0.3-0.7	0.3-4.8	0.5-9.7(i)	0.9-1.5	<0.3*	69%	0.1	0.3	106
2MPh	0.3-2.3	0.41-1.7	0.3-1.4	0.3-3.2	0.3-57.9	0.3-3.4	0.3-0.9	0.3-5.0	0.37-10.3(i)	0.59-1.7	<0.3*	71%	0.1	0.3	106
MA	0.3-1.3	0.3-1	<0.3	0.3-5.1	0.3-0.5	0.3-1.6	<0.3	0.3-0.5	0.3-2(i)	0.3-0.3	<0.3*	17%	0.1	0.3	106
MPhMA	0.3-2.2	0.5-1.6	0.3-1.3	0.3-3.2	0.3-132.9	0.3-8.0	0.3-0.9	0.3-3.7	0.3-11.4(i)	1.1-1.9	<0.3*	69%	0.1	0.3	106
1MPh	0.3-2	0.4-1.4	0.3-1.3	0.3-2.5	0.3-274.5	0.3-7.6	0.3-0.6	0.3-2.7	0.3-8.6(i)	0.5-1.4	<0.3*	63%	0.1	0.3	106
mMPh	0.6-8	1.6-6.2	0.6-5	0.6-10.5	0.6-596.7	0.6-25.2	0.6-3.1	0.6-16.1	1.6-39.9(i)	3.2-6.5	0.6*	--	--	--	--
∑DMPh	3.0-11.5	3.0-21.1	3.0-5	3.0-23.8	3.0-728.8	3.0-69.2	3.0-5.2	3.0-19.3	3.0-75.8	3.0-11.6	<3.0*	33%	1.0	3.0	106

Table SI-7. Ranges of dissolved organic carbon (mg.L^{-1}), total suspended solids (mg.L^{-1}), and dissolved PAHS (ng.L^{-1}) in surface water from different basins 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). (continued)

VARIABLE	NEAR							SEAR	NEPC		SEPC	ALL	LD	LQ	RECOVERY
	Napo	Payamino	Coca	Rumiyacu	Tiputini	Aguarico	Shushufindi	Santiago	Teaone	Esmeraldas	Portoviejo	>LQ#			%
∑TMPh	3.0-10.4	3.0-10.7	<3.0	3.0-16.7	3.0-272.7	3.0-74.5	3.0-5.9	3.0-9.3	3.0-46.1	3.0-8.7	<3.0*	23%	1.0	3.0	106
2MN	2-14	6-12	1-16	4-11	1-4500	1-46	3-14	2-12	4-66	9-33	10*	97%	0.4	1.3	98
1MN	1-9	4-7	1-10	1-18	1-7416	1-43	2-12	1-9	3-65	6-22	5*	87%	0.4	1.1	98
∑DMN	10-106	23-70	7-120	18-194	17-1084	14-191	14-74	8-48	51-326	59-120	43*	100%	1.6	5.0	98
∑TMN	7-114	36-95	7-166	18-268	12.7-84044	13-328	18-103	3-64	38-537	100-133	25.4*	99%	1.6	5.0	98
∑TeMN	8-57	39-60	9-68	6-292	6-29089	8-532	10-85	3-72	16-1021	50-100	30*	99%	1.6	5.0	98
nMN	30-287	112-214	25-378	48-784	47-126133	38-912	52-269	17-181	129-1690	244-385	113*	--	--	--	--
BNT	<0.4	<0.4	<0.4	0.4-0.5	<0.4	0.4-1.1	<0.4	<0.4	0.4-2.5	<0.4	<0.4*	3%	0.1	0.4	101
DBT	0.4-0.7	<0.4	0.4-0.8	0.4-3	0.4-465.3	0.4-2.6	<0.4	0.4-1.1	0.4-3.7	0.4-0.7	<0.4*	30%	0.1	0.4	--
∑MDBT	1.0-5.4	1.0-3.5	<1.0	1.0-13.5	1.0-1083.8	1.0-24.5	<1.0	1.0-6.5	1.0-23.4	1.0-4.8	<1.0*	14%	0.3	1.0	--
TAC	47-325	131-281	37-421	57-869	58-131726	47-1134	66-292	31-244	142-1803	285-425	129*	--	--	--	--
nMN/TAC	0.6-0.9	0.76-0.89	0.7-0.9	0.75-0.90	0.8-0.96	0.66-0.94	0.78-0.92	0.54-0.91	0.82-0.94	0.85-0.93	0.88*	--	--	--	--
$_{16}$PAH/TAC	0.1-0.2	0.03-0.10	0.1-0.2	0.02-0.11	0.02-0.13	0.02-0.19	0.03-0.10	0.04-0.22	0.03-0.07	0.03-0.05	0.05*	--	--	--	--

NEAR=North Ecuadorian Amazon Region; SEAR= South Ecuadorian Amazon Region; NEPC= North Ecuadorian Pacific Coast; SEPC= South Ecuadorian Pacific Coast; DOC=dissolved organic carbon ; TSS=total suspended solids; N=naphthalene; Ac=acenaphthylene; Ace=acenaphthene; Fl=Fluorene; Ph=phenanthrene; A=anthracene; Fa=Fluoranthene; Py=pyrene; BaA=benzo[a]anthracene; Ch= chrysene + triphenylene; BbjkF=benzo[bjk]fluoranthene; BaP=benzo[a]pyrene; IP=indeno[1,2,3-cd]pyrene; DBA=dibenzo[ah]anthracene; BPe=benzo[ghi]perylene; $_{16}$PAH=∑US-EPA PAHs; US$_{WQG}$=B[bjk]Fa+B[ghi]Pe+IP; EC$_{WQG}$ =Fa+B[bjk]Fa+B[a]P+B[ghi]Pe+IP;BeP=benzo[e]Pyrene; Pe= perylene; MCh=methylchrysene; 3MPh=3Methylphenanthrene; 2MPh=2methylphenanthrene; MA=2methylanthracene; MPhMA=[9+4]methylphenanthrene+1methylanthracene+ 4,5methylenephenanthrene; 1MPh=1methylphenanthrene; mMPh=∑mono-methyl phenanthrenes ; ∑DMPh=∑dimethylphenanthrene; ∑TMPh=∑trimethylphenanthrene; 2MN=2methylnaphthalene; 1MN=1methyl-naphthalene; ∑DMN=∑dimethylnaphthalene; ∑TMN=∑trimethylnaphthalene; ∑TeMN=∑tetramethylnaphthalene; nMN= ∑methylnaphthalenes; BNT=2,1benzonaphtothiophene; DBT=dibenzothiophene; ∑MDBT=∑methyldibenzothiophene; TAC=total aromatic charge; *= single value (n=1); nd=non detected (<LD); --=non measured data; (i)=interference; #= percentage of analyzed samples (all sites) over the quantification limit(LQ).

Detected molecules with an average concentration between LD and LQ are reported as <LQ.

Table SI-8. Ranges of pollution hazard, grain size (%) and average concentration (ng.g^{-1}dw) of PAHS in sediments from different basins 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).

VARIABLE	NEAR							SEAR	NEPC		SEPC	ALL	LD	LQ	REC
	Napo	Payamino	Coca	Rumiyacu	Tiputini	Aguarico	Shushufindi	Santiago	Teaone	Esmeraldas	Portoviejo	>LQ#			%
hazard	0-2.21	1.62-3.29	1.63-2	1.74-3.41	1.5-3.75	1.53-3.34	2.11-3.74	0-0	0-0	0-0	0*	--	--	--	--
≤ 4 µm	6-31	7-21	2-11	12-17	9-30	2-38	8-22	11-42	9-19	10-13	12*	--	--	--	101
4-63 µm	35-68	38-62	15-62	38-61	30-63	7-73	44-54	44-55	33-68	41-62	44*	--	--	--	101
≤ 63 µm	51-89	46-78	17-72	50-78	39-89	9-91	53-74	55-91	42-85	54-75	57*	--	--	--	101
> 63µm	11-49	22-54	28-83	22-50	11-61	9-91	26-47	9-45	15-58	25-46	43*	--	--	--	101
TC (%)	0.3-2.6	0.6-10.1	0.1-10.0	0.4-2.5	0.4-3.9	0.1-4.9	1.6-3.4	0.1-2.7	0.8-3.0	0.9-2.2	0.8*	--	0.0	0.1	98
OC (%)	0.2-2.3	0.4-10.1	0.1-1.0	0.1-2.1	0.2-2.8	0.1-4.9	1.2-3.1	0.1-2.1	0.5-2.9	0.8-1.2	0.5*	--	0.0	0.1	98
N	1.2-6.3	1.2-26.5	1.2-3.5	1.2-1.8	1.2-54.6	1.2-8.7	1.2-6.1	1.2-2.6	1.2-111.9	1.2-1.5	<1.2*	73%	0.3	1.2	79
Ac	0.1-0.5	0.1-70.3	<0.1	<0.1	0.1-18.1	0.1-3.3	<0.1	<0.1	0.1-14.3	0.1-0.3	<0.1*	27%	0.0	0.1	74
Ace	0.1-1.4	0.1-130.9	0.1-0.2	0.1-0.1	0.1-18.3	0.1-2.5	0.1-0.2	0.1-0.2	0.1-73.0	0.1-0.2	<0.1*	58%	0.0	0.1	76
Fl	0.2-2.2	0.3-412.4	0.2-0.6	0.2-0.3	0.2-81.9	0.2-4.9	<0.2	0.2-0.63	0.2-105.1	0.2-1.0	<0.2*	80%	0.0	0.2	96
Ph	0.7-15.3	3.0-122.4	0.8-5.2	0.7-1.4	0.7-112.9	0.7-33.7	0.8-1.1	0.7-14.8	0.7-497.6	0.9-3.2	<0.7*	79%	0.2	0.7	111
A	0.1-1.1	0.16-3.1	0.1-0.2	0.1-0.1	0.1-3.5	0.1-2.7	0.1-0.1	0.1-0.2	0.1-53.5	0.1-0.5	<0.1*	51%	0.0	0.1	87
LMW	1-26	5-759	2-10	1-4	1-286	1-52	2-8	1-19	1-720	2-6	1*	--	--	--	--
Fa	0.2-17.4	1.4-83.3	0.2-1.0	0.2-1.4	0.2-89.8	0.2-57.6	0.2-1.1	0.2-2.2	0.2-462.1	0.6-1.8	0.2*	93%	0.0	0.2	96
Py	0.2-13.9	1.1-64.9	0.3-1.7	0.1-2.5	0.2-67.4	0.2-42.1	0.2-1.3	0.2-6.3	0.2-371.5	0.9-3.4	<0.2*	90%	0.1	0.2	86
BaA	0.1-2.8	0.1-11.9	0.1-0.6	0.1-0.8	0.1-22.5	0.1-2.3	0.1-0.4	0.1-1.9	0.1-76.7	0.2-1.0	<0.1*	84%	0.0	0.1	94
Ch	0.2-2.8	0.8-123.6	0.2-3.1	0.1-3.9	0.2-448.1	0.1-10.6	0.3-1.1	0.1-16.2	0.3-280.4	0.7-2.3	0.2*	95%	0.0	0.1	81
BbjkF	0.3-1.9	1.4-13.8	0.3-1.3	0.3-1.9	0.3-76.3	0.3-3.5	0.5-1.7	0.3-7.9	0.3-52.9	0.7-1.4	<0.3*	86%	0.1	0.3	99
BaP	0.2-1.4	0.6-6.5	0.2-0.6	0.2-0.8	0.2-1.4	0.2-2.1	0.2-0.6	0.2-1.7	0.2-58.3	0.3-1.1	<0.2*	75%	0.1	0.2	88
IP	0.2-8.2	0.4-2.1	0.2-0.7	0.2-1.0	0.2-10.8	0.2-1.1	0.4-0.9	0.2-0.7	0.2-6.0	0.4-1.2	<0.2*	75%	0.1	0.2	80
DBA	0.2-1.4	0.2-2.4	0.2-0.2	0.2-0.5	0.2-22.1	0.2-0.9	0.2-0.3	0.2-1.1	0.2-11.9	0.2-0.4	<0.2*	52%	0.1	0.2	76
BPe	0.2-3.1	0.2-7.8	0.2-1.9	0.2-3.2	0.2-31.0	0.2-7.3	0.5-1.1	0.2-8.5	0.2-32.6	0.6-1.9	1.2*	90%	0.1	0.2	84
16PAH	2-63	13-1005	3.4-18	1.5-15	2-1042	1-166	4-13	2-65	2-1677	7-20	3*	--	--	--	--
BeP	0.2-1.6	0.7-27.8	0.2-2.4	0.2-3.8	0.2-130.5	0.2-13.0	0.24-0.9	0.2-19.1	0.2-108.1	0.4-1.5	<0.2*	89%	0.1	0.2	89
HMW[##]	1-39	9-264	2-13	1-17	2-887	1-117	3-9	1-66	2-981	5-16	2*	--			
Pe	3.1-435.0	71.8-488.0	9.3-37.9	1.5-76.2	0.2-126.1	0.5-555.5	59.1-122.9	0.2-37.9	5.8-86.9	13.6-57.0	2.7*	98%	0.1	0.2	88
MCh	0.3-6.3	3.3-343.7	0.4-8.3	0.3-21.5	0.3-1419.7	0.3-38.6	0.4-8.5	0.3-29.0	0.6-1271	0.9-12.0	<0.3*	95%	0.1	0.3	81
3MPh	0.1-3.0	1.1-879.8	0.2-3.1	0.1-1.0	0.1-423.4	0.1-6.7	0.2-0.4	0.1-6.7	0.1-822.4	0.3-1.4	<0.1*	89%	0.0	0.1	111
2MPh	0.1-4.4	1.5-1028.8	0.3-3.6	0.1-1.2	0.1-532.2	0.1-10.5	0.2-0.6	0.1-8.1	0.1-1122.3	0.4-1.8	<0.1*	91%	0.0	0.1	111
MA	0.1-1.0	0.1-65.6	0.1-0.3	0.1-0.2	0.1-48.3	0.1-1.4	<0.1	0.1-0.3	0.1-95.4	0.1-0.3	<0.1*	51%	0.0	0.1	111
MPhMA	0.1-5.6	2.1-1327.2	0.4-5.5	0.1-1.8	0.1-786.6	0.1-10.9	0.2-0.8	0.1-13.3	0.1-770.5	0.3-1.9	<0.1*	93%	0.0	0.1	111
1MPh	0.1-4.2	2.1-1527.4	0.4-5.2	0.1-1.6	0.1-790.6	0.1-7.4	0.3-1.1	0.1-11.1	0.1-643.7	0.2-1.5	<0.1*	91%	0.0	0.1	111
∑DMPh	1-25	13-8701	2-30	1-20	1-8220	1-58	1-6	1-53	1-7740	2-48	<1*	89%	0.3	1.0	111

Table SI-8. Ranges of pollution hazard, grain size (%) and average concentration (ng.g^{-1} dw) of PAHS in sediments from different basins 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).(continued)

	NEAR							SEAR	NEPC		SEPC	ALL	LD	LQ	REC
VARIABLE	Napo	Payamino	Coca	Rumiyacu	Tiputini	Aguarico	Shushufindi	Santiago	Teaone	Esmeraldas	Portoviejo	>LQ[#]			%
∑TMPh	1-25	9-7785	2-31	1-24	1-10850	1-125	1-6	1-38	1-7512	3-66	<1*	88%	0.3	1.0	111
2MN	0.3-7.5	1.0-1283.7	0.5-5.9	0.3-2.0	0.3-254.6	0.3-65.1	0.3-0.7	0.3-4.0	0.3-578.5	0.3-0.9	<0.3*	78%	0.1	0.3	79
1MN	0.3-6.5	0.7-1240.9	0.4-5.2	0.3-1.8	0.3-223.3	0.3-55.5	0.3-0.7	0.3-7.3	0.3-470.2	0.3-0.5	<0.3*	75%	0.1	0.3	79
∑DMN	1-29	6-13802	2-26	1-6	2-3640	1-117	1-4	1-37	1-27134	1-7	<1*	79%	0.3	1.1	79
∑TMN	1-44	11-25854	3-52	1-10	1-10491	1-69	2-6	1-64	1-50908	1-25	<1*	84%	0.3	1.1	79
∑TeMN	1-30	5-15749	2-25	1-14	3-10975	1-56	3-11	1-47	1-34446	2-37	<1*	88%	0.3	1.1	79
MPAH	5-177	60-79587	13-199	3-103	9-48655	6-577	10-40	3-319	6-133514	10-203	3*	--			
BNT	0.1-0.9	0.1-66.4	0.1-0.9	0.1-1.1	0.1-231.8	0.1-2.3	0.1-0.2	0.1-2.3	0.1-79.8	0.1-0.3	<0.1*	67%	0.0	0.1	81
DBT	0.1-4.3	0.4-321.7	0.1-1.3	0.1-0.9	0.1-297.3	0.1-4.0	0.1-0.1	0.1-1.8	0.1-202.6	0.1-0.6	<0.1*	78%	0.0	0.1	
PASH	0.1-5.1	0.5-388.1	0.2-2.1	0.1-1.5	0.1-529.2	0.1-5.9	0.1-0.3	0.1-4.1	0.1-282.3	0.2-0.6	0.1*				
∑MDBT	0.2-10.1	2.3-2474.9	0.2-4.2	0.2-2.7	0.2-1886.1	0.2-6.5	0.3-0.8	0.2-2.7	0.2-1245.3	0.27-2.08	0.2*	81%	0.1	0.2	
TAC	40-442	149-83767	26-263	21-165	19-52267	8-641	112-144	5-413	50-136667	32-243	9*	--	0.3	1.0	111
T AC##	7-205	77-83473	17-225	5-126	12-52243	7-639	15-53	5-410	8-136625	18-228	6*	--	0.1	0.3	79
Pe/TAC	0.02-0.98	0.00-0.73	0.09-0.35	0.03-0.86	0.00-0.80	0.00-0.98	0.53-0.89	0.01-0.64	0.00-0.87	0.06-0.62	0.30*	--	0.1	0.3	79

NEAR=North Ecuadorian Amazon Region; SEAR= South Ecuadorian Amazon Region; NEPC= North Ecuadorian Pacific Coast; SEPC= South Ecuadorian Pacific Coast; TC=total carbon ; OC=organic carbon; N=naphthalene; Ac=acenaphthylene; Ace=acenaphthene; Fl=Fluorene; Ph=phenanthrene; A=anthracene; LMW=low molecular weight; Fa=Fluoranthene; Py=pyrene; BaA=benzo[a]anthracene; Ch= chrysene + triphenylene; BbjkF=benzo[bjk]fluoranthene; BaP=benzo[a]pyrene; IP=indeno[1,2,3-cd]pyrene; DBA=dibenzo[ah]anthracene; BPe=benzo[ghi]perylene; 16PAH=∑US-EPA-PAHs; HMW=high molecular weight; Pe= perylene; MCh=methylchrysene; 3MPh=3Methylphenanthrene; 2MPh=2methylphenanthrene; MA=2methylanthracene; MPhMA=[9+4]methylphenanthrene+ 1methylanthracene+ 4,5methylenephenanthrene; 1MPh=1methylphenanthrene; mMPhe=∑mono-methyl phenanthrenes ; ∑DMPh=∑dimethylphenanthrene; ∑TMPh=∑trimethylphenanthrene; 2MN=2methylnaphthalene; 1MN=1methyl- naphthalene; ∑DMN=∑dimethylnaphthalene; ∑TMN=∑trimethylnaphthalene; ∑TeMN=∑tetramethylnaphthalene; MPAH= total methyl-aromatic charge; BNT=2,1benzonaphtothiophene; DBT=dibenzothiophene; ∑MDBT=∑methyldibenzothiophene; TAC=total aromatic charge; ; ##=Pe excluded; *= single value (n=1); --=non measured data; #= percentage of analyzed samples (all sites) over the quantification limit(LQ).

Detected molecules with an average concentration between LD and LQ are reported as <LQ.

Table SI-9. Isomeric ratios since PAH concentration in sediments.

MAIN-BASIN	SUB-BASIN	CODE	$\frac{Ph}{A}$	$\frac{Fa}{Py}$	$\frac{Fa}{Fa+Py}$	$\frac{A}{A(A+Ph)}$	$\frac{BaA}{BaA+Ch}$	$\frac{BaA}{Ch}$	$\frac{BbjkF}{BbjkF+BeP}$	$\frac{BaP}{BaP+BeP}$	$\frac{BaP}{BeP}$	$\frac{IP}{IP+BPe}$	$\frac{Py}{BaP}$	$\frac{MPh}{Ph}$	$\frac{23MPh}{19MPh}$	$\frac{MCh}{Ch}$
--	Napo	b. sands	6.67	0.31	0.24	0.13	0.10	0.11	0.45	0.21	0.26	0.00	1.69	0.60	1.00	5.67
--	Rumiyacu	wasteA8	19.40	0.70	0.41	0.05	0.07	0.08	0.45	0.12	0.14	0.16	3.00	12.06	0.68	2.59
--	Tiputini	crudeA3	94.31	0.51	0.34	0.01	0.06	0.07	0.32	0.05	0.05	0.00	158.6	3.28	0.77	2.76
--	Napo	CrudePL	37.98	0.51	0.34	0.03	0.07	0.07	0.32	0.07	0.08	0.00	119.2	3.04	0.63	2.48
MORONA SANTIAGO	Morona	SJ6	19.11	0.88	0.47	0.05	0.14	0.17	0.68	0.28	0.39	0.31	2.45	1.39	0.75	1.87
	Santiago	BB6	5.00	0.48	0.32	0.17	0.32	0.48	0.70	0.49	0.98	0.35	3.17	8.15	1.17	15.77
	Santiago	S-a5	10.00	0.39	0.28	0.09	0.16	0.20	0.80	0.32	0.48	0.32	9.34	0.40	1.00	0.94
	Santiago	S-b6	5.00	1.24	0.55	0.17	0.16	0.19	0.75	0.31	0.45	0.45	1.69	1.41	1.14	0.19
	Santiago	S-c5	10.00	0.27	0.21	0.09	0.50	1.00	0.58	0.72	2.54	0.20	8.26	0.40	1.00	2.90
	Santiago	S-d5	10.00	0.38	0.28	0.09	0.50	1.00	0.50	0.50	1.00	0.41	6.89	0.48	0.94	2.25
	Santiago	S-e5	66.50	0.35	0.26	0.01	0.11	0.12	0.29	0.08	0.09	0.07	3.69	2.64	0.61	1.79
	Santiago	S-f6	35.65	0.60	0.38	0.03	0.10	0.11	0.59	0.20	0.24	0.22	3.63	1.68	1.06	1.80
PORTOVIEJO	Portoviejo	SA6	5.00	1.04	0.51	0.17	0.25	0.34	0.65	0.49	0.94	0.08	1.63	1.05	0.96	1.05
ESMERALDAS	Teaone	CC-a6	5.00	1.28	0.56	0.17	0.14	0.17	0.74	0.43	0.75	0.35	2.53	0.98	0.74	1.94
	Teaone	CC-b4	10.00	0.92	0.48	0.09	0.34	0.51	0.63	0.58	1.36	0.53	1.48	2.31	0.73	2.91
	Teaone	VL-a3	4.67	0.53	0.35	0.18	0.32	0.47	0.50	0.50	1.00	0.50	1.93	0.86	1.00	2.54
	Teaone	VL-b6*	22.29	0.11	0.10	0.04	0.21	0.27	0.33	0.35	0.54	0.16	3.67	6.75	1.38	4.53
	Teaone	VL-c2*	7.37	1.24	0.55	0.12	0.28	0.40	0.58	0.42	0.73	0.39	31.35	1.79	1.37	3.85
	Teaone	VL-d4*	1.64	0.45	0.31	0.38	0.12	0.13	0.25	0.20	0.25	0.17	1.13	2.98	0.86	3.22
	Teaone	VL-e6*	17.90	0.25	0.20	0.05	0.19	0.24	0.37	0.24	0.31	0.29	4.86	6.62	0.99	3.25
	Teaone	VL-f2	9.66	0.16	0.14	0.09	0.20	0.26	0.41	0.25	0.34	0.41	7.07	2.67	0.88	4.15
	Teaone	AG-a3	3.87	0.19	0.16	0.21	0.31	0.44	0.36	0.42	0.71	0.37	2.93	3.43	0.78	4.77
	Esmeraldas	SM6	11.25	0.82	0.45	0.08	0.27	0.36	0.66	0.43	0.75	0.36	3.04	1.27	1.19	1.40
	Esmeraldas	AG-b3	6.95	0.54	0.35	0.13	0.30	0.44	0.38	0.43	0.75	0.40	2.93	2.03	0.96	5.30
	Esmeraldas	E-a6	13.39	0.62	0.38	0.07	0.26	0.35	0.61	0.37	0.58	0.38	3.56	2.73	1.19	1.56
	Esmeraldas	E-b4	10.97	0.62	0.38	0.08	0.37	0.59	0.62	0.41	0.69	0.36	4.23	1.94	1.58	3.09
NAPO	Napo	PN-a4	66.80	0.49	0.33	0.01	0.08	0.09	0.28	0.10	0.11	0.12	6.86	2.30	0.51	1.86
	Napo	PN-b5	45.73	0.38	0.27	0.02	0.12	0.13	0.49	0.18	0.22	0.14	7.34	2.03	0.64	1.95
	Napo	PN-c6	31.18	0.60	0.38	0.03	0.19	0.24	0.39	0.23	0.29	0.07	3.34	2.17	0.68	1.81
	Napo	PN-d2	14.45	1.25	0.56	0.06	0.22	0.28	0.42	0.19	0.24	0.22	37.54	1.00	0.93	2.22
	Napo	PO-a6	12.12	0.78	0.44	0.08	0.37	0.60	0.63	0.55	1.21	0.34	0.67	3.11	0.63	3.20
	Napo	PO-b3	43.89	0.44	0.30	0.02	0.18	0.22	0.36	0.36	0.56	0.36	1.55	0.61	0.69	2.68
	Napo	PO-c4	7.74	0.49	0.33	0.11	0.86	6.31	0.44	0.26	0.36	0.28	3.45	9.33	0.67	12.75
	Napo	PO-d6	22.58	0.56	0.36	0.04	0.23	0.29	0.55	0.31	0.45	0.77	3.23	2.34	0.73	1.00
	Payamino	PO-e6	3.23	5.64	0.85	0.24	0.21	0.26	0.27	0.19	0.23	0.10	0.18	32.41	0.67	3.33
	Payamino	PO-f5**	19.10	0.83	0.45	0.05	0.28	0.40	0.65	0.56	1.28	0.85	2.08	2.25	0.63	3.88

Table SI-9. Isomeric ratios since PAH concentration in sediments. (continued)

MAIN-BASIN	SUB-BASIN	CODE	Ph / A	Fa / Py	Fa / Fa + Py	A / A(A + Ph)	BaA / BaA + Ch	BaA / Ch	BbjkF / BbjkF + BeP	BaP / BaP + BeP	BaP / BeP	IP / IP + BPe	Py / BaP	MPh / Ph	23MPh / 19MPh	MCh / Ch
	Payamino	PO-g2**	1.03	2.98	0.75	0.49	0.09	0.10	0.42	0.14	0.16	0.21	6.63	38.92	0.67	2.78
	Payamino	PO-h2**	18.78	1.28	0.56	0.05	0.31	0.44	0.73	0.34	0.52	0.43	111.12	0.36	1.90	2.38
	Payamino	PO-i6	28.34	0.59	0.37	0.03	0.20	0.26	0.36	0.21	0.27	0.08	1.78	2.93	0.59	2.61
	Coca	SC-b6	32.98	0.57	0.36	0.03	0.16	0.19	0.34	0.19	0.24	0.13	2.38	3.37	0.63	2.65
	Coca	SC-d3	37.93	0.46	0.31	0.03	0.25	0.33	0.20	0.20	0.26	0.28	2.14	1.39	0.62	1.66
	Coca	SC-e4	25.59	0.56	0.36	0.04	0.17	0.21	0.42	0.23	0.29	0.42	4.04	2.55	0.63	2.80
	Coca	SC-f5	15.02	0.40	0.29	0.06	0.19	0.23	0.59	0.39	0.64	0.28	5.30	1.74	0.70	1.70
	Napo	JS6	5.00	1.52	0.60	0.17	0.23	0.30	0.54	0.27	0.37	0.21	1.00	1.78	0.60	1.64
	Napo	LI5	10.00	0.61	0.38	0.09	0.28	0.40	0.60	0.47	0.88	0.37	1.63	1.23	0.56	3.07
NAPO	Rumiyacu	DY-a6**	8.30	0.75	0.43	0.11	0.10	0.11	0.41	0.10	0.11	0.25	6.37	1.80	0.78	2.95
	Rumiyacu	DY-b6**	23.93	1.00	0.50	0.04	0.35	0.55	0.76	0.51	1.03	0.46	1.72	1.16	0.75	2.67
	Rumiyacu	DY-c2**	5.28	0.82	0.45	0.16	0.29	0.41	0.57	0.66	1.90	0.50	0.45	0.86	0.81	4.88
	Rumiyacu	DY-d4**	10.00	0.60	0.38	0.09	0.42	0.73	0.63	0.23	0.30	0.50	5.56	0.52	0.84	7.21
	Rumiyacu	DY-e3**	17.32	0.55	0.35	0.05	0.25	0.34	0.44	0.33	0.49	0.30	3.27	1.96	0.74	2.39
	Rumiyacu	DY-f5**	9.48	0.39	0.28	0.10	0.09	0.10	0.33	0.16	0.19	0.17	2.14	5.16	0.64	5.55
	Rumiyacu	DY-g6	5.00	0.78	0.44	0.17	0.38	0.60	0.57	0.39	0.63	0.27	2.46	1.13	0.92	3.13
	Tiputini	DY-h3**	7.31	0.87	0.46	0.12	0.28	0.39	0.50	0.50	1.00	0.50	0.53	0.88	0.60	7.18
	Tiputini	DY-i6**	15.42	1.04	0.51	0.06	0.23	0.30	0.68	0.37	0.60	0.26	2.09	0.71	1.01	4.24
	Tiputini	DY-j2(i)**	6.91	1.65	0.62	0.13	0.05	0.05	0.37	0.01	0.01	0.26	40.15	22.43	0.61	3.17
	Tiputini	DY-k2**	15.47	1.32	0.57	0.06	0.08	0.09	0.23	0.10	0.11	0.26	49.34	0.43	1.77	1.89
	Tiputini	DY-l6**	9.26	0.58	0.37	0.10	0.05	0.06	0.23	0.08	0.08	0.18	6.01	0.75	1.06	2.07
	Tiputini	DY-m6	5.00	0.96	0.49	0.17	0.32	0.47	0.82	0.40	0.67	0.41	2.80	1.50	0.93	0.33
	Tiputini	TI-a4	4.42	1.35	0.57	0.18	0.30	0.43	0.87	0.12	0.14	0.49	7.10	2.22	0.78	16.21
	Tiputini	TI-b4	131.35	0.60	0.38	0.01	0.40	0.68	0.78	0.50	1.00	0.46	1.67	0.08	1.24	13.66
	Tiputini	TI-c4	9.83	0.60	0.38	0.09	0.35	0.54	0.73	0.36	0.56	0.52	1.67	0.91	0.72	12.35
	Napo	NR-a4	68.80	0.49	0.33	0.01	0.15	0.18	0.37	0.19	0.24	0.16	4.37	2.63	0.60	3.45
	Napo	NR-b2	50.31	0.44	0.31	0.02	0.20	0.24	0.37	0.10	0.11	0.09	7.43	1.33	0.64	2.95
	Aguarico	LM-a5	96.87	0.42	0.30	0.01	0.13	0.15	0.29	0.17	0.21	0.09	3.14	3.27	0.70	2.76
	Aguarico	LM-b6	135.13	0.68	0.40	0.01	0.04	0.05	0.43	0.07	0.08	0.16	3.69	2.41	0.90	1.14
	Aguarico	LM-c4	101.56	0.69	0.41	0.01	0.09	0.10	0.45	0.14	0.17	0.24	2.86	2.63	0.82	2.01
AGUARICO	Aguarico	LM-d3	19.93	0.47	0.32	0.05	0.13	0.14	0.50	0.50	1.00	0.50	0.78	1.28	1.26	2.56
	Aguarico	DU-a4	23.27	0.60	0.38	0.04	0.09	0.10	0.39	0.12	0.13	0.28	0.95	3.16	0.73	5.42
	Aguarico	DU-b3**	5.25	1.00	0.50	0.16	0.40	0.66	0.50	0.50	1.00	0.50	0.33	0.76	1.00	3.29
	Aguarico	PK-a5**	10.00	0.42	0.30	0.09	0.10	0.11	0.38	0.18	0.22	0.15	3.92	2.38	0.67	0.80
	Aguarico	PK-b2**	16.55	0.34	0.25	0.06	0.18	0.22	0.11	0.11	0.12	0.13	1.81	1.91	0.53	3.65

Table SI-9. Isomeric ratios since PAH concentration in sediments. (continued)

MAIN-BASIN	SUB-BASIN	CODE	$\frac{Ph}{A}$	$\frac{Fa}{Py}$	$\frac{Fa}{Fa+Py}$	$\frac{A}{A(A+Ph)}$	$\frac{BaA}{BaA+Ch}$	$\frac{BaA}{Ch}$	$\frac{BbjkF}{BbjkF+BeP}$	$\frac{BaP}{BaP+BeP}$	$\frac{BaP}{BeP}$	$\frac{IP}{IP+BPe}$	$\frac{Py}{BaP}$	$\frac{MPh}{Ph}$	$\frac{23MPh}{19MPh}$	$\frac{MCh}{Ch}$
	Aguarico	**PK-c6**	5.00	1.26	0.56	0.17	0.19	0.23	0.43	0.29	0.42	0.18	1.24	3.83	0.99	1.29
	Aguarico	**PK-d4**	107.08	0.51	0.34	0.01	0.04	0.04	0.41	0.07	0.07	0.10	7.76	2.86	0.77	2.21
	Aguarico	**PK-e3**	24.31	0.40	0.29	0.04	0.10	0.11	0.30	0.30	0.43	0.50	1.10	1.46	1.04	2.19
	Aguarico	**PK-f2****	22.03	0.62	0.38	0.04	0.17	0.20	0.33	0.10	0.12	0.19	2.19	0.93	0.81	3.00
	Aguarico	**PK-g2****	14.61	1.15	0.54	0.06	0.62	1.66	0.43	0.15	0.17	0.34	1.22	0.84	0.72	29.86
AGUARICO	**Aguarico**	**PK-h3****	5.38	1.00	0.50	0.16	0.50	1.00	0.18	0.75	3.07	0.50	0.02	0.95	0.77	5.00
	Aguarico	**PK-i3**	10.93	0.67	0.40	0.08	0.18	0.22	0.31	0.31	0.45	0.25	1.28	1.14	0.91	3.58
	Shushufindi	**SF-a6**	16.55	1.11	0.53	0.06	0.24	0.32	0.69	0.33	0.50	0.40	1.82	1.11	0.75	1.62
	Shushufindi	**SF-b6**	19.17	0.93	0.48	0.05	0.23	0.30	0.64	0.32	0.47	0.35	1.58	2.42	0.70	1.38
	Shushufindi	**SF-c4**	7.99	1.06	0.52	0.11	0.43	0.74	0.79	0.44	0.80	0.56	1.75	1.82	0.72	11.51
	Shushufindi	**SF-d4**	11.15	0.83	0.45	0.08	0.27	0.37	0.65	0.38	0.60	0.42	2.31	2.59	0.48	7.68
	Aguarico	**SR6**	55.07	0.33	0.25	0.02	0.08	0.09	0.36	0.14	0.16	0.13	3.17	3.11	0.85	1.61
	Aguarico	**NR-c4**	48.32	0.35	0.26	0.02	0.04	0.04	0.40	0.12	0.14	0.18	4.18	3.16	0.98	2.32
	Aguarico	**NR-d2**	12.48	1.37	0.58	0.07	0.18	0.21	0.51	0.15	0.18	0.28	69.31	0.88	1.39	1.82

*Close to crude oil extraction wells (1km)
**Close to crude oil refinery (1km)

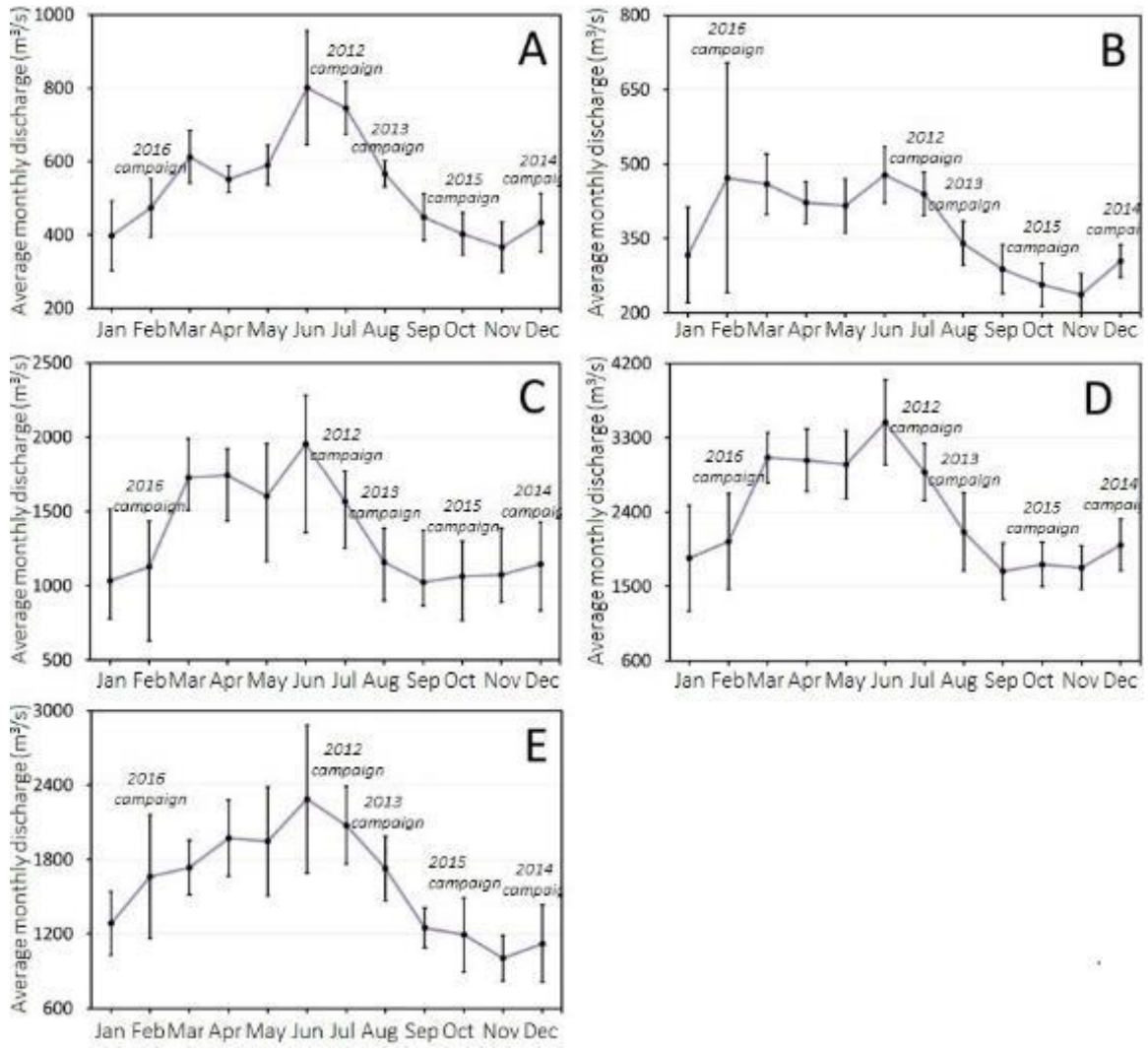


Figure SI-1. Interannual (2012-2016) average monthly discharge from five HyBAm stations: A) Aguarico_Nueva Loja, B) Coca_San Sebastian, C) Napo_Francisco de Orellana, D)Napo_Rocafuerte and E) Santiago_Batallon.

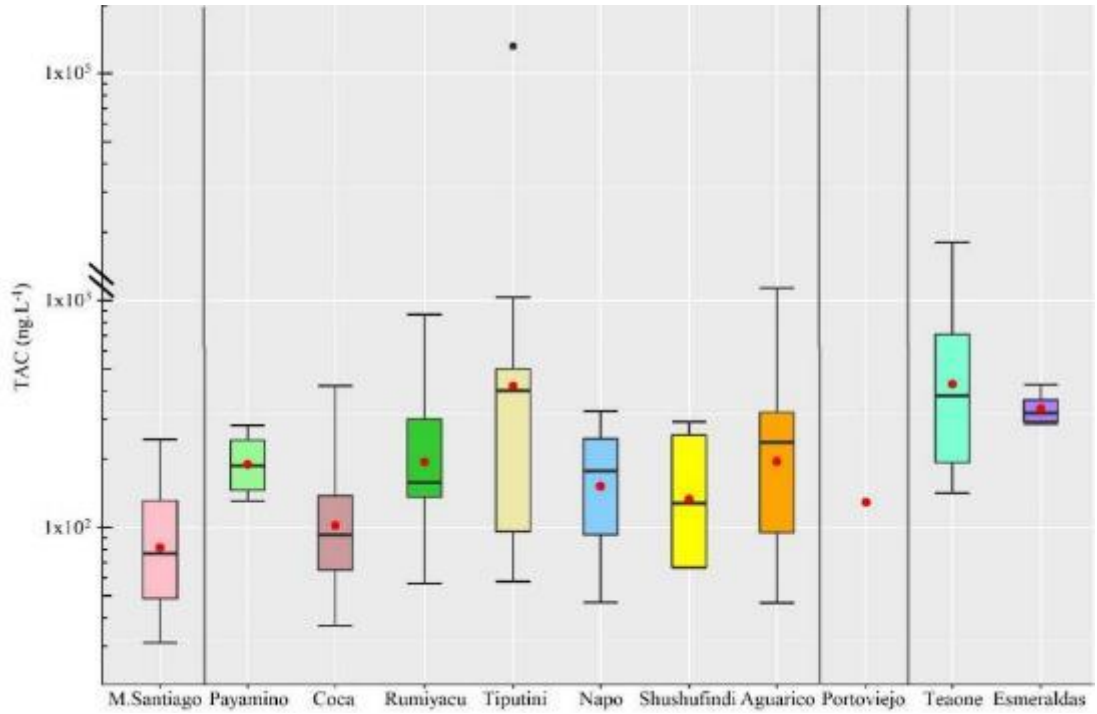


Figure SI-2. Dissolved-total aromatic charge (ng.L^{-1}) in the studied sub-basins.

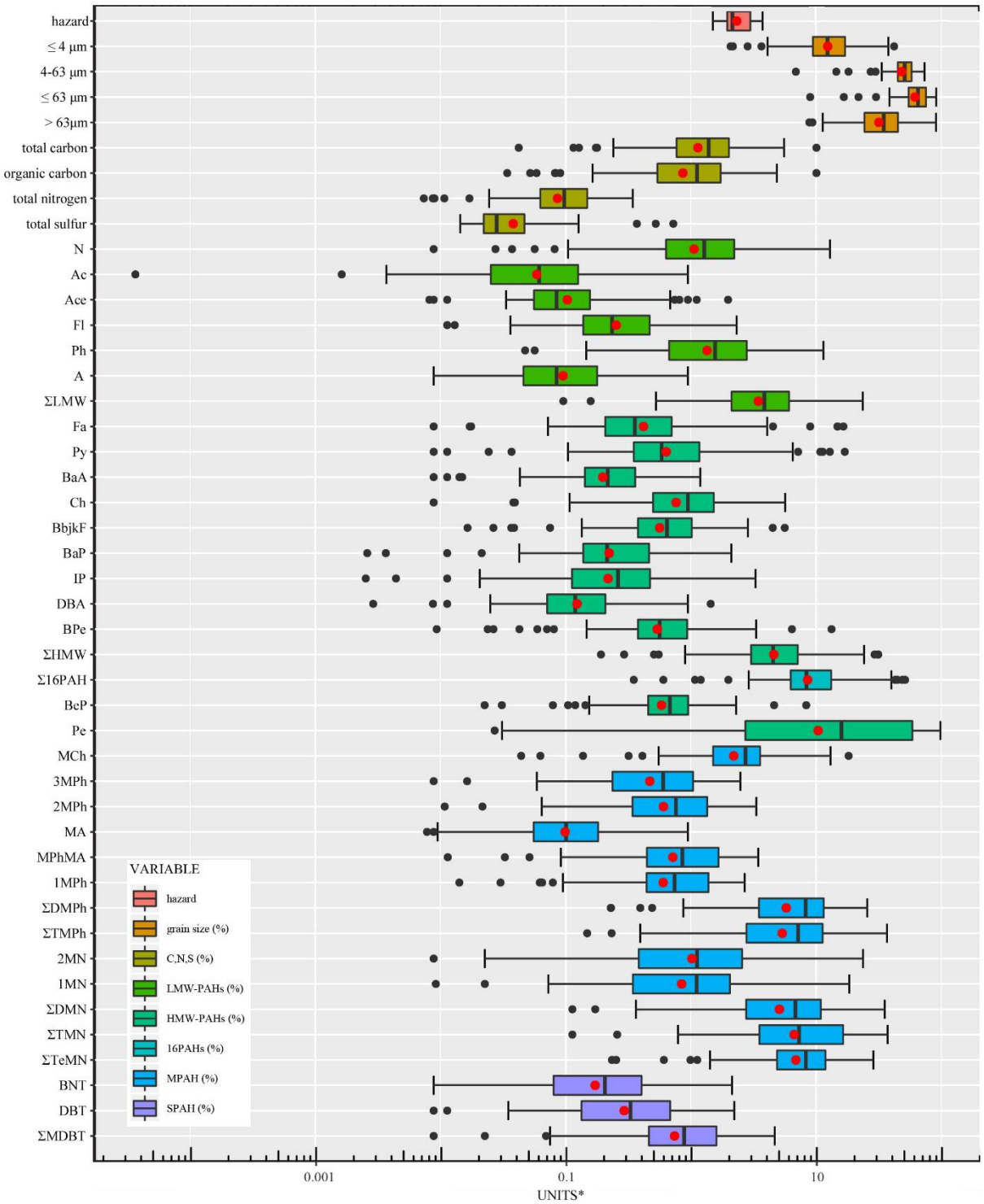


Figure SI-3. Hazard risk, grain size; carbon, nitrogen and sulfur and relative abundance of PAHs in sediments (%); *All the units are expressed in %, except the pollution hazard (dimensionless).

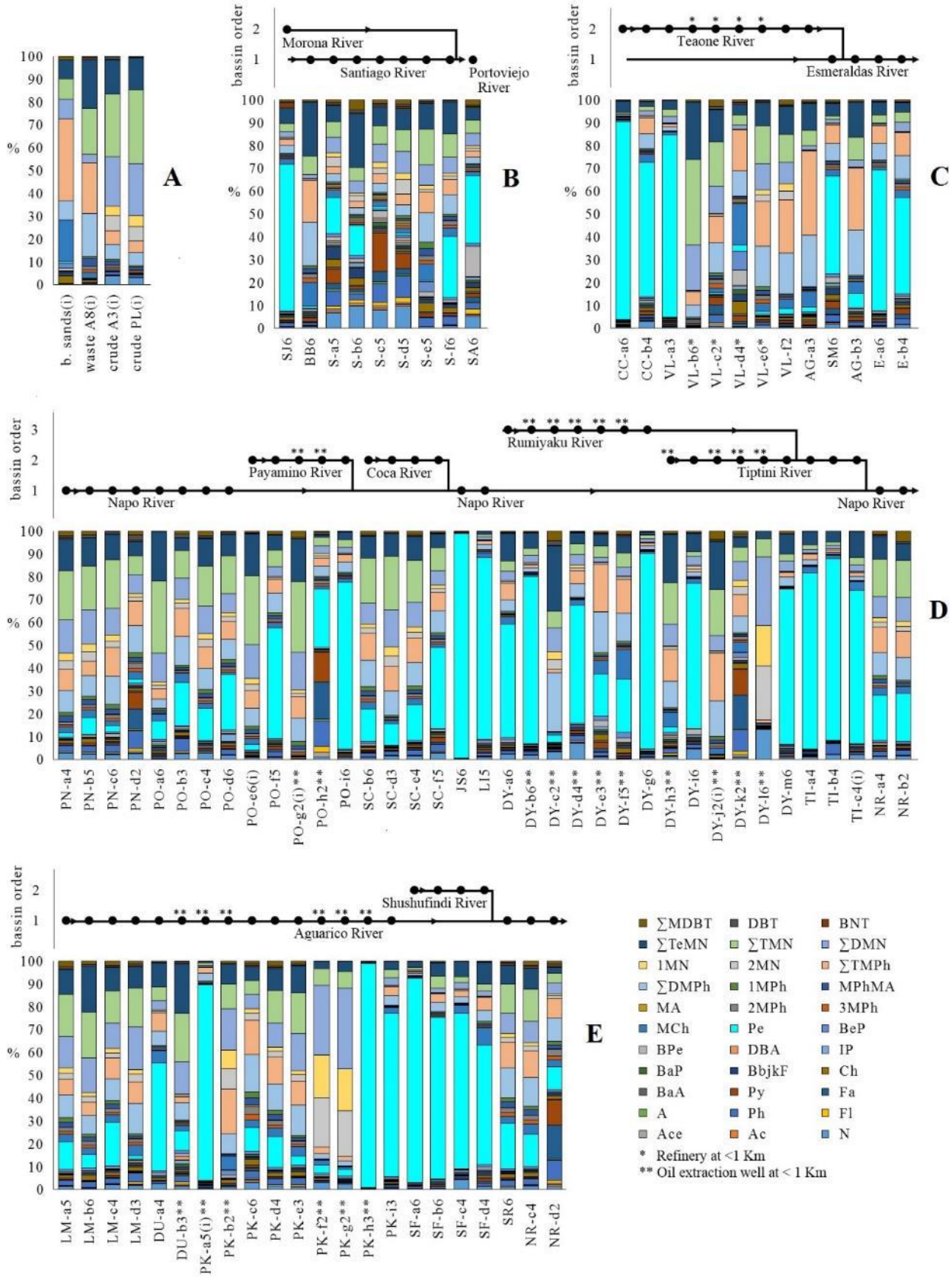


Figure SI-4. PAH distributions in sediments (naphthalene and perylene included); A) Crude oil and oil saturated samples; B) Control sites; C) Esmeraldas Basin; D) Napo Basin; E) Aguarico Basin.

CHAPTER 2. Oil pollution hazards and health quality of drinking waters in Ecuador

Forewords

"Nosotros no queremos plata, no queremos dinero, lo que queremos es tener dos cosas señores: agua queremos porque en la zona no hay como coger agua. Está contaminada. Por más que las autoridades locales quieran darnos agua no lo pueden, todo está contaminado, inclusive el aire. Queremos agua y justicia, nada más." -José Shingre, campesino ecuatoriano en la audiencia de la ONU, 2013

"We do not want money, we don't want cash, we only want two things, Sirs: we want water, because it is not possible to take water in the area. It is contaminated. Even if the local authorities want to give us water, they cannot, everything is contaminated, even the air. We want water and justice, nothing else." -José Shingre, Ecuadorian farmer at the parliamentary hearing at the United Nations, 2013

Insufficient and not-safe drinking water are the main causes of 842,000 deaths and billions of diarrheal-disease cases per year around the world, with children under-five being the most affected population (Kayser et al., 2015). Quantity and quality need to be considered at the moment of determining the adequacy of drinking water supply (Martínez et al., 2018). Access to safe water in Ecuador emphasizes the conflicts between environment and law in which local water governance has been developed. It constitutes an interesting case of study, and throughout the present chapter, these two aspects (water quality and its access as well as governance) are considered.

Although the high number of Ecuadorian water sources, safe water is not guaranteed for local populations (**Figure VII, A and B**). In Ecuador, the access to improved water sources (piped or not) increased from 74% in 1990 to 97 % in 2015; but, focalized in urban zones where 85% of the population uses water considered "free from any contamination" while in rural areas 46 % still uses water sources of doubtful quality (Kayser et al., 2015; WHO and UNICEF, 2017). Until the 2010 census **Figure VII**, **C and D**), the Andean region has been the only one with water system coverage above the national average, followed by the Coastal Region. Finally, the Amazon Region presents the lowest percentage of dwelling places with access to system water (IGM, 2013; Kayser et al., 2015). Only recently (2014-2018) the Amazon Region has improved its systems of water supply (75% of coverage), approaching the Coastal Region (82%), but still far from the 97% in the Andean Region (Fernández et al., 2018)

The inter-regional evolution in water-access gap in Ecuador is explained by the progress in water governance and other time-line events associated with oil production and agrarian

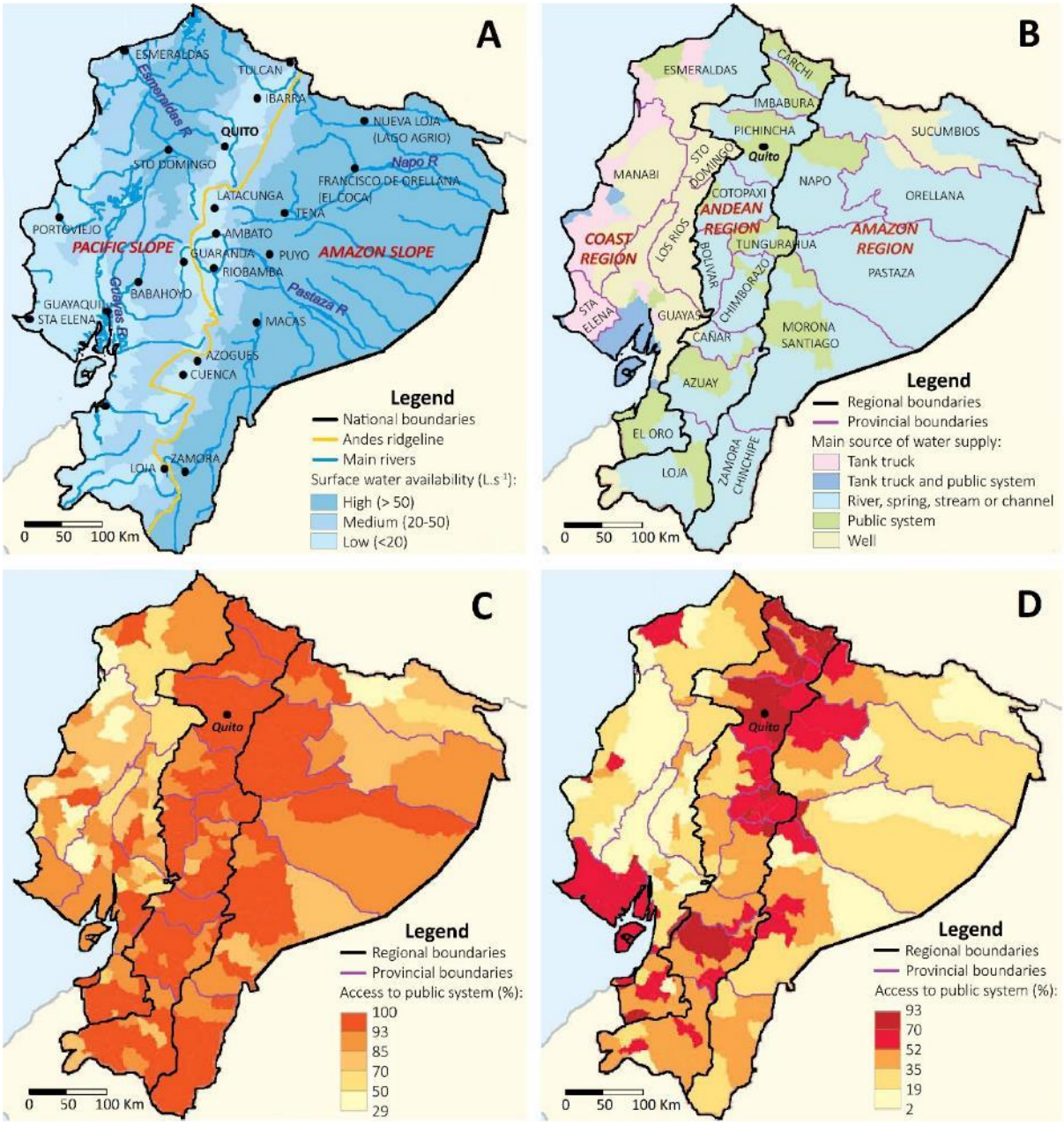


Figure VII. Water access in Ecuador: A. Available surface water flow. B. Main sources of drinking water supply. C. Percentage of urban homes with access to public water system. D. Percentage of rural homes with access to public water system. (modified from IGM, 2010)

reforms (Gondard and Mazurek, 2001; Wasserstrom and Southgate, 2013). Among these events, the social conflicts in the Amazon Region due to the Texaco trial (1993-2018) remain important, together with the implementation of national water quality guidelines (WQG) and the engagements of municipalities in water management and sanitation due to the constitutional reform (2008-2018) and PRAS missions (Fernández and Buitrón Cisneros, 2012; Kayser et al., 2015; Pinto et al., 2012).

The first document on water governance appeared in 1972 (Gobierno del Ecuador, 1972) with prioritization of irrigation water over drinking water, in raison of agrarian reforms (Martínez

et al., 2018). But Ecuadorian WQGs appeared late: the first one, the norm INEN 1108, was accepted as compulsory drinking water quality guidelines in 1984 (Gobierno del Ecuador, 2005). In 2003, a second group of WQGs was set up in the "Texto Unificado de Legislación Secundaria del Ministerio del Ambiente"(MAE, 2003); this updated version (MAE, 2015) is used as the current directive for environmental control. Both regulations are based on the WQGs given by the World Health Organization (Pinto et al., 2012). But, as similar regulatory frames in developing countries, Ecuadorian drinking water directives need to be improved towards more accurate risk-based management to better assure water safety (Martínez et al., 2018).

Although, 25 years have passed since Texaco left Ecuador and drinking water and health programs have been enhanced but the risk related to oil activities for human health is still present in local communities. Since 1973, people have struggled with the presence of crude oil residuals floating on water, roads covered by crude, oil waste pits (some of them are still present in their farms) and formation-water discharged in the nature. They have also faced cancer or other diseases, developing a local perception of the risk and declaring the effects of oil contamination in national and international courts during a long trial (1993-2018). Throughout this lawsuit, environmental damages were determined in about US$ 27 billons (BBC Press, 2018; Buccina et al., 2013).

Ecuadorians living closer to oil industrial zones are considered exposed to hazards (physical, chemical and biological) by consuming not safe water to drink, bath, wash clothes and cook (**Figure VIII**); it enables the entry of contaminants by ingestion or dermal contact and absorption. Metal(oid)s and hydrocarbons presented in byproducts from crude oil extraction or refining processes are suspected to reach surface waters and groundwaters affecting the sources of water supply and increasing the risk of acute and chronic diseases.

No health studies describing risks linked to oil pollution have been published from 1973 to 1993. The first epidemiological study on cancer incidence from 1989-1998 showed a cancer rate in the NEAR higher than in other places (IESC, 2004; San Sebastian, 2001; San Sebastián and Córdoba, 1999). But, further studies have not found correlation between oil activities and human health risks (Kelsh et al., 2009; Moolgavkar et al., 2014). This contradiction triggers the question of the human risk related with water uses, not only in the Amazon Region, but also in other areas influenced by oil industries.

However, local populations have linked abortions, cancer, skin problems, respiratory problems, digestive problems, etc. to oil pollution. Although many of these diseases are tied

to chemicals present in crude oil as Cd (itai-itai and cancer), Hg (Minamata desease), Pb (lead poisoning), As (arsenicosis and cancer) or B (a) Pyreno (cancer), the published studies are related with ecological activism and do not show any causal relationship between oil pollution and the identified pathologies (Bissardon et al., 2013b) In addition, the 2010 census in Ecuador shows that health problems are linked to lack of sanitation structures. In fact, the Amazon region presents the lowest access to public health services, sewage system and wastewater treatment; altogether with the highest rate of acute diarrheal diseases and respiratory infections (IGM, 2013), questioning the origin and nature of suspected hazards.



Figure VIII. Domestic water sources in Ecuador: A. Treated piped water network. B. Rainfall water collected in plastic tank. C. Spring water. D. Artesian private well. E. Deep public well. (Photo Credits : MONOIL®, 2016).

Thus, to define if human populations in oil-industrial zones are impacted by water consumption, five field campaigns were conducted and domestic waters (**Figure VIII**) were sampled from different sources (rainfall, river, spring, stream, system and well) in 18 Amazonian parishes and in 7 coastal parishes. We used different methods combining chemistry and spectroscopy (ICP-MS, ICP-OES, AFS and GC-MS) to define the concentrations of major anions (Ca, K, Mg, Na, and Si), 20 metallic elements and 38 organic compounds (PAHs and BTEX). We focalized our analyses and discussion on chemicals directly related with oil pollution (Ba, Mn, Ni, V and PAHs) and those that are known to involve risk for humans (As, Cd, Cr, Ni, Pb, PAHs and BTEX).

We also used the available WQGs (local and international) to define water quality and to determine the potential risks incurred by local populations. Drinking-water showing accepted WQGs is supposed not to present any significant risk for human health, as a result of individual substances concentrations (WHO, 2018). Although the water quality assessment based on WQGs is the most used method worldwide, it does not allow to really determine the risk related with a cocktail of chemicals. Some chemicals are harmless individually and/or at low doses, but can be harmful when they interact.

Amiard (2017) defines synergy, antagonism, inhibition and potentiation as the main ways in which chemicals can interact. The effect of each of these interactions in an organism is known as "the cocktail effect" and cannot be evaluated by the individual toxicity thresholds (WQGs). Then, we apply the Health Risk Assessment (HRA) developed by the US EPA (2004, 2003) to consider two mixtures of dissolved components (ETMs and PAHs), the local characteristics of the population (weight, daily ingestion, age and time of exposure) and the different exposure routes.

Thus, in the article below, we analyse water quality by comparing it with different WQGs. As water is defined as the main pathway of pollutants, we determine the main routes of exposure (dermal contact or ingestion), define the population potentially impacted (adults or children), the hazard of concern (chemical, microbiological and/or socio-economical) and the provenance of health hazards (industrial or public discharge).

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

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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.

Abstract

The unregulated oil exploitation in the Northern Ecuadorian Amazon Region (NEAR), mainly from 1964 to the 90's, led to toxic compounds largely released into the 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. The concentrations of major ions, trace elements, PAHs (polycyclic aromatic hydrocarbons) and BTEX (benzene, toluene, ethylbenzene, xylenes) were analyzed in different water sources to evaluate the impacts of oil extraction and refining. Samples were 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 Hazard Index was caused by arsenic concentrations. The hazard 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.

Keywords: Oil activities, domestic waters, hydrocarbons, metal(loid)s, demineralized waters, social risk perception.

GRAPHICAL ABSTRACT

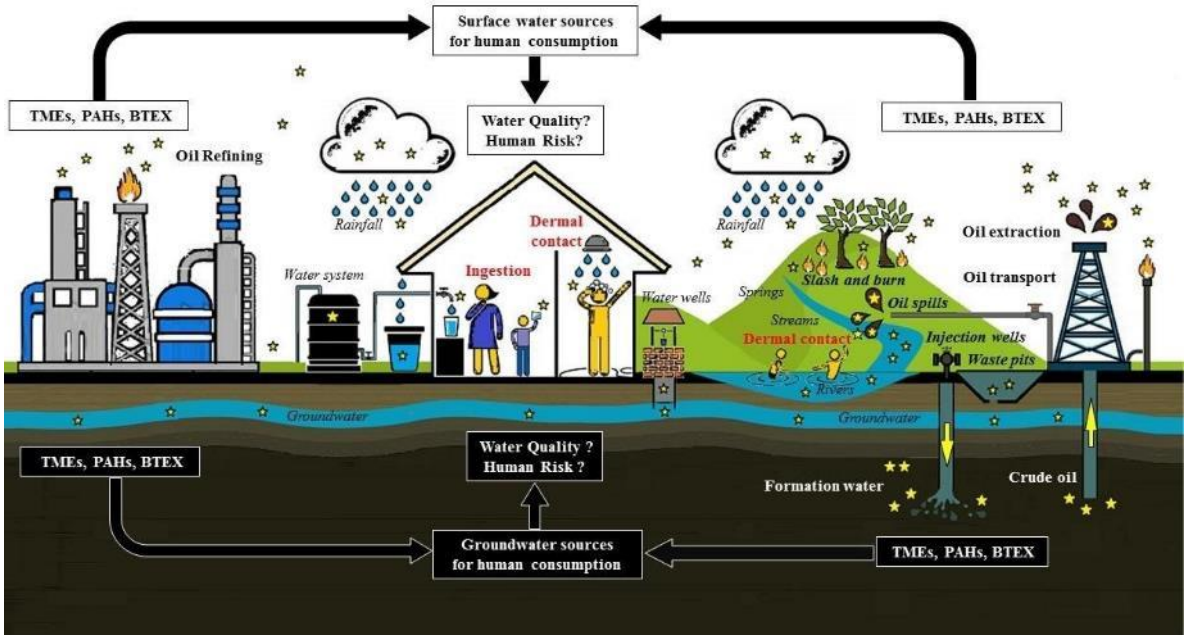


Figure 2-0. Human risk-drinking water (Grafical abstract)

1. Introduction

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 accidents occurring throughout the history of oil production demonstrates the devastating effects and the risks involved for exposed populations (Amiard, 2017; Levy and Nassetta, 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 2017 (BCE, 2010; Calderon et al., 2016; MCE, 2017). On the other hand, Ecuadorian oil industry is characterized by a long-term history of social and environmental conflicts (Fontaine, 2007).

The oil industry exerted with inadequate environmental standards is strongly suspected of polluting surface and ground waters, particularly in Orellana and Sucumbíos provinces where 80% of total oil spills and 97% of waste pits were recorded (Bustamante and Jarrín, 2005; MAE, 2015). During 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, since the 2000's the Ecuadorian legislation prohibited these practices, binding oil companies to redirect these waters into ancient oil wells. Nevertheless, local inhabitants testified that illegal polluting discharges are still released punctually and 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 genotoxic and carcinogenic effects (IARC, 2010). Twelve PAHs and BTEX have been classified as probable or suspected carcinogens in humans but only benzo(a)pyrene (BaP) and benzene are confirmed as carcinogenic (ATSDR, 2007; IARC, 2018; Tremblay et al., 2000). Despite their high toxicity, volatility and solubility in water, BTEX are not commonly studied; noting that they are responsible for acute and chronic effects including eyes and throat irritation, headaches, tachycardia, leukemia, affections to nervous system, cancer and death (Leusch and Bartkow, 2010; Mitra and Roy, 2011; Neghab et al., 2015). Previous epidemiological studies reported numerous chronic effects including psychological disorders, endocrine and reproductive affections and cases of cancers (Hurtig and San Sebastián, 2002; Levy and Nassetta, 2011; Ramirez et al., 2017; UDAPT-Clinica Ambiental-CSS, 2017; Webb et al., 2018). Genotoxic analyses on individuals from the NEAR showed that the exposition to hydrocarbons has caused DNA damage and increased the risk of developing cancer (Paz-y-Miño et al., 2008).

Although hydrocarbons constitute the main fraction (75%) of crude oil, petroleum is a complex mixture of elements, such as sulfur, major cations, anions, trace metal(oid)s (TME) and organic molecules. Major elements (potassium (K), magnesium (Mg), sodium (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 formation waters, while barium (Ba), cobalt (Co), arsenic (As) and lead (Pb) salts are added during the extraction, transportation or storage (Abdel-Raouf, 2012; Amiard, 2017; Speight, 2002). Though certain metallic elements are essential for biological functions, most of them could be highly toxic, even at low concentrations, and can cause hazardous effects due to their tendency to bio-accumulate (Jørgensen and Fath, 2010). In 2017, IARC listed cadmium (Cd), As, Cr and Ni as probed carcinogenic elements for humans (lungs, prostate, bladder, kidney, liver and stomach cancers); they can also affect nervous, immune and reproductive systems and can induce 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 (Amiard,

2017; Boehler et al., 2017; US EPA, 2000).

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.

In Ecuador, access to a water supply network has increased in recent years but the percentages of the supplied population are very heterogenous over the territory; in the studied cantons, it varies from 26,6% in Aguarico, to 33,7% in Shushufindi, 41,6% in Joya 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 washing clothes) is still a high-risk factor of exposition to toxic pollutants either by dermal contact or ingestion. In Esmeraldas city, along the Pacific coast, where refining activities take place, the water distribution system reaches most of the households but is unreliable supply and safety wise. Therefore, Amazonian and Esmeraldas inhabitants rely on different water sources such as rivers, springs, streams, rainwater, or private wells; sources that are not always safe (IGM, 2013). 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 not only reach the groundwater, as well as superficial waters (Webb et al., 2018; Wernersson, 2004), 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

2.1 Study area

Two oil areas were selected for this study (**Figure 2-1**). The first area is located in the Northern Ecuadorian Amazon Region (NEAR) between 76°30'20"-77°12'00"W and 00°05'01"N-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 (EP Petroecuador, 2013). 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.

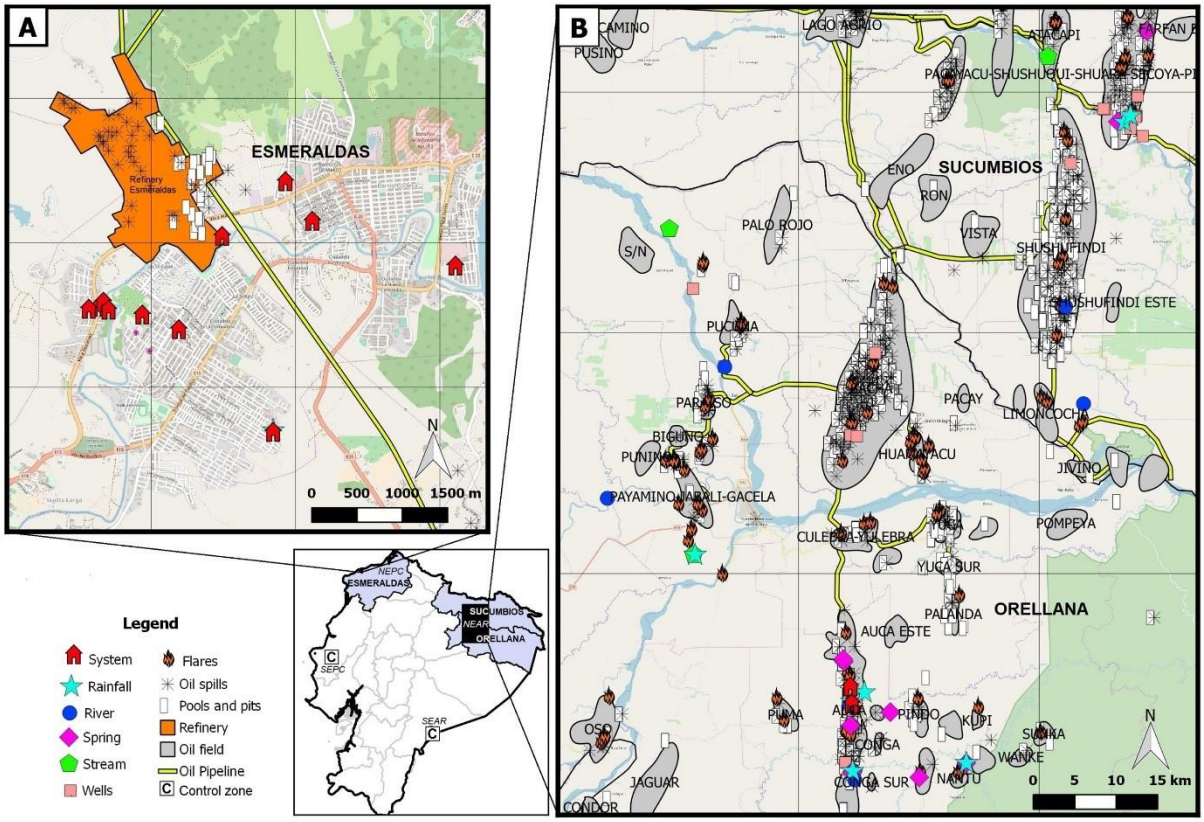


Figure 2-1. Hazards description (flares, oil spills, pools and pits, refinery, oil fields and pipelines) and sampling points of drinking waters (from various sources: rainfall, river, spring, stream, well) in four study areas: A) Northern Ecuadorian Pacific Coast (NEPC), B) Northern Ecuadorian Amazon Region (NEAR) and C) in two control zones (Southern Ecuadorian Amazon Region (SEAR) and Southern Ecuadorian Pacific Coast (SEPC)).

2.2 Water sample collection

From 2012 to 2016, 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 (**Table C-2**).

Water sampling was performed according to the US EPA method (US EPA, 1996) in Teflon bottles, using ultra-clean procedures. River waters were filtered (0.45 µm porosity) in the field on Teflon and cellulose acetate pre-cleaned 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 bottles (SPME 10 mL) previously calcined at 550°C 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 (TM) 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 EPA, 2002) using oxidation-reduction with BrCl and $SnCl_2$, 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 SII-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

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

An Agilent Technologies 7890A/5975C GC/MS (Palo Alto, CA, USA) was used for the analysis of BTEX. A MPS2XL autosampler (Gerstel®) was used to hold the 65 µm PDMS/DVB SPME fibre (Supelco) during extraction and injection. After the addition of perdeuterated surrogate standards, the fibre was immersed into the 10 mL water sample with agitation (250 rpm) at 40 °C during 30 min. After extraction, the fibre was thermally desorbed for 3 min into the liner of the GC injector port at 220 °C in pulsed splitless mode (25 psi, 1.5 min). Helium (6.0) was used as the carrier gas at a flow rate of 2 mL.min− . Analytes were separated on a DB-624 column (30 m × 0.32 mm, 1.8 µm film thickness; Agilent Technologies, J&W Scientific).

The column oven program was as follows: 0 °C (5 min) (liquid nitrogen) to 150 °C (1 min) at 5 °C·min−1 and then to 260 °C (8 min) at 30 °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 260, 230 and 150 °C, respectively. Parent and alkylated PAHs were analyzed using an Agilent Technologies 7890A/5973 GC/MS (Palo Alto, CA, USA) (Kanan et al., 2012). A GC Sampler 120 (Agilent Technologies) was used to hold the 100 µm PDMS SPME fibre fibre (Supelco) during extraction and injection. After the addition of perdeuterated surrogate standards, the fibre was immersed into the 8 mL water sample with agitation (250 rpm) at 40 °C during 60 min. After extraction, the fibre was thermally desorbed for 3 min into the 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 × 0.25 mm, 0.25 µm 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.

PAHs and BTEX were quantified by their perdeuterated surrogate standards using their molecular ions (SIM mode). Analyzed compounds (and acronyms) and their limits of quantification (LQs) are listed in **Table SII-2** and **Table SII-1**, respectively. A fibre blank was measured before each water sample by exposing the SPME fibre in an empty vial under the same conditions as the samples. A blank sample (reagents and surrogate standards) and a

control sample (blank sample spiked with model compounds) were performed for each batch of experiments in order to check the background contamination 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, respectively) and remained between 100 and 105% (CV b 10%) for parent and alkylated PAHs and 89–98% (CV b 10%) for BTEX. Limits of quantification (LQs) were determined from a 10 signal to noise ratio (SNR) observed in low-spiked samples, except for compounds present in blanks. For these latter compounds, LQs were determined using blank levels, assuming at least a factor three between the analyte mass in the sample and that found in the blank. LQs are in the range 0.3–5.0 $ng \cdot L^{-1}$ for parent and alkylated PAHs, and 2–9 $ng \cdot L^{-1}$ for BTEX, except for benzene (100 $ng \cdot L^{-1}$).

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™ Petrifilm™ 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

Sociological methods "Risk culture" refers to the oil contamination risks awareness, behaviors 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., 2016). 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 data was collected during various field surveys between 2014 and 2016. Were realized 160 qualitative interviews, according various levels of exposure, living next to possible sources of

[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.

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.).

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; Choudhury et al., 2000) 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 Environmental Protection Agency (US EPA), 2015c, 2015d).

Mathematical equations of the Probabilistic Risk Assessment (as published by Barraza et al., 2018) allow us to evaluate the Hazard Index (HI) and the Total Cancer Risk (TCR), which are defined as the addition of individual quotients of non-carcinogenic (HQ) and carcinogenic (CR) elements respectively, obtained from the average daily dose (ADD), the lifetime average daily dose (LADD) and the references doses (RfD) (US Environmental Protection Agency (US EPA), 2015d, 2015c). For drinking water, we supposed a daily consumption rate of 3 L and 1.5 L for adults and children, respectively and an annual exposure frequency of 350 days per year, assuming that people moved 15 days every year in the Amazonian 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).

2.6 Statistical analysis

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 (**Figure SII-1**), 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.

3. Results

3.1 Physico-chemical parameters

Physico-chemical parameters of drinking waters (**Table 2-1**) were compared with the different water quality guidelines (WQGs) reported in the Supplementary Information (**Table SII-3**).

In the drinking water sources of the Amazonian 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 (min: 6.5; max: 8.5). 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 $\mu S.cm^{-1}$; average: 122±204 $\mu S.cm^{-1}$) showed that all the samples were lower than the maximum recommended value (1100 $\mu S.cm^{-1}$), except in a deep well (26 m) in Pacayacu (NEAR). Only 19% of the samples were in line with the WQG used in France (200-1100 $\mu S.cm^{-1}$): most of the water samples (78%) showed conductivity lower than 200 $\mu S.cm^{-1}$, and can be considered as demineralized waters. In the Amazon Region, rainwaters showed the lowest conductivity in both, the oil (11.9±12.9 $\mu S.cm^{-1}$) and control area (5.21 $\mu S.cm^{-1}$).

Only the deep wells (272.2±348.5 $\mu S.cm^{-1}$) and system waters (224.3±152.2 $\mu S.cm^{-1}$) in the NEAR, and river surface water (237.7±139.2 $\mu S.cm^{-1}$) in the SEAR showed conductivity higher than the recommended value (200 $\mu S.cm^{-1}$). However, in Esmeraldas, the tap water conductivity never reached the minimum WQG (200 $\mu S.cm^{-1}$).

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 250-500 $mg.L^{-1}$ set by WHO. Only water from deep wells and the distribution system met the minimum recommended value.

3.2 Major and TME concentrations

The analyzed anions (**Table 2-1**) 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' concentrations (for example Ca and Mg) were lower than the minimum 2005 WHO guidelines (**Figure 2-2**).

Regarding Al concentrations (**Figure 2-3**), 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, these concentrations exceeded regularly 200 $\mu g.L^{-1}$, 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; Quesada et al., 2011).

Manganese concentrations in drinking water sources ranged between 0 and 2373 $\mu g.L^{-1}$, and averaged 72 $\mu g.L^{-1}$; 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 $\mu g.L^{-1}$), and a fortiori France and Canada (50 $\mu g.L^{-1}$), while in rivers, springs and water systems, they were acceptable (**Figure 2-3**).

The Zn concentrations in samples collected from rainwater tanks were significantly higher than other sources (**Figure 2-3**). 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 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.

Regarding Ba distribution, rainwater presents the lowest concentrations (2 to 30 $\mu g.L^{-1}$).

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±5.44 $\mu g.L^{-1}$) 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±0.097 $\mu g.L^{-1}$) higher than in the other sources, but lower than the recommended values.

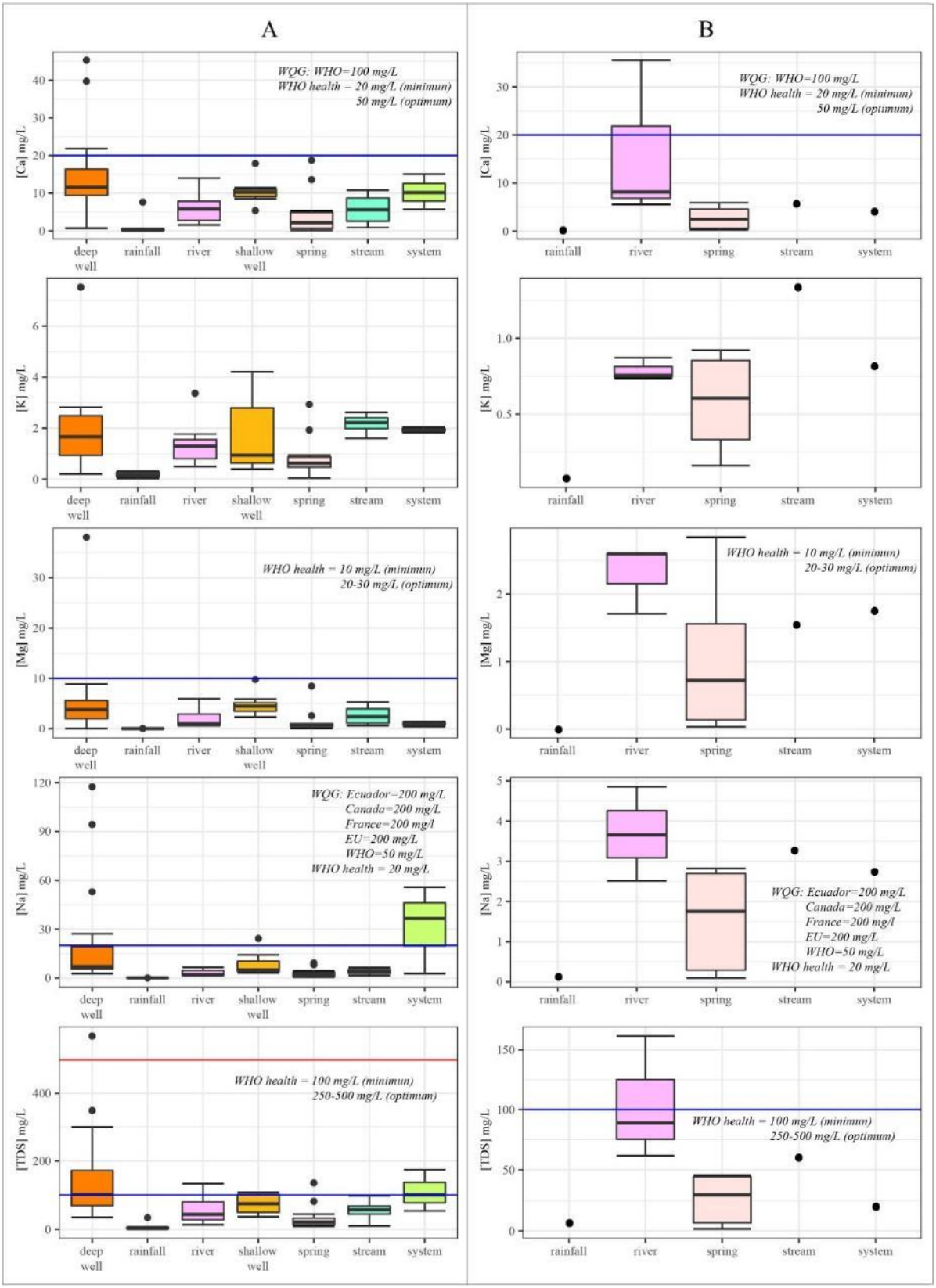


Figure 2-2. Major element concentrations in drinking water sampled during the 2012-2016 period, in (A) the Northern Ecuadorian Amazon Region (NEAR) and in (B) the control zone in the Southern Ecuadorian Amazon Region (SEAR); the red and blue lines report maximum a nd minimum values recommended by the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

Table 2-1. Local metrics[#,##,b,c], inorganic major elements [b] and metal(oid)s average concentrations[d,e] (±Standard Deviation) 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).

PARAMETER	NEAR							SEAR					NEPC		SEPC	
	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*
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]	25.3±83.5	0.19±0.11	0.96±0.83	10.7±11.3	0.92±1.39	0.55±0.43	36.6±33.0	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±2.7	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*	21.0±6.1	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]	15.3±12.2	1.28±2.81	6.1±4.34	10.6±3.8	4.53±5.8	5.71±4.52	10.3±4.7	0.06*	16.4±16.6	2.71±2.45	5.53*	3.94*	0.56*	12.0±7.8	21.19*	104.13*
K[b]	1.99±1.73	0.18±0.11	1.41±0.96	1.78±1.5	0.86±0.81	2.17±0.43	1.9±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	4.8±2.5	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]	24.1±35.9	0.12±0.05	3.25±2.08	8.75±7.81	3.09±2.86	4.07±2.07	31.7±26.9	<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]	18.6±8.2	0.44±0.72	13.8±11.3	11.9±3.9	11.5±7.6	19.8±12.1	7.46±3.87	0.02*	8.45±4.53	6.19±4.66	10.69*	9.44*	0.10*	13.7±0.6	15.64*	39.73*
SiO_2[b]	39.9±17.5	0.95±1.54	29.6±24.1	25.4±8.2	24.5±16.3	42.4±26.0	15.96±8.29	0.04*	18.07±9.7	13.23±9.98	22.87*	20.2*	0.21*	29.4±1.2	33.45*	85.01*
Hardness**	0.63±0.62	0.03±0.07	0.24±0.19	0.45±0.1	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*	--	--	--	--	--
Al[e]	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	5.8±10.7	10.7±32.8	4.15±3.96	29.5±50.7	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	0.8±0.7	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*

Table 2-1. Local metrics[#,##,b,c], inorganic major elements [b] and metal(oid)s average concentrations[d,e] (±Standard Deviation) 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). (continued)

PARAMETER	NEAR							SEAR					NEPC		SEPC	
	deep well	rainfall	river	shallow well	spring	stream	system	rainfall	river	spring	stream	system	rainfall	system	system	shallow well
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±635	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	8.7±13.3	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	3317*	3.5±1.2	8.5±11	0.2*	4*	999.3*	144.7±338	14.3*	25.5*
As[e]	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]	207±197	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]	0.04±0.05	0.02±0.01	0.02±0.02	0.08±0.08	0.04±0.04	0.04±0.06	0.02±0.01	0.036*	0.09±0.15	0.04±0.08	0.003*	0.001*	0.02*	1.38±4.71	0.006*	0.071*
Sb[e]	0.02±0.03	0.09±0.1	0.01±0.01	0.03±0.03	<0.011	0.02±0.02	0.06±0.03	0.23*	0.03±0.03	0.02±0.01	0.033*	<0.011*	0.163*	0.28±0.31	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]	0.51±0.64	1.17±1.99	0.084±0.15	1.6±2.8	0.247±0.293	0.129±0.117	0.95±0.85	0.151*	0.25±0.10	0.81±1.02	0.003*	0.090*	0.146*	0.45±0.68	0.768*	0.451*
U[e]	0.07±0.12	0.004±0.009	0.03±0.02	0.02±0.02	0.068±0.077	0.069±0.089	0.40±0.64	0.001*	0.04±0.07	0.008±0.004	0.009*	0.004*	0.001*	0.05±0.09	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} ; e= µg.L^{-1}.

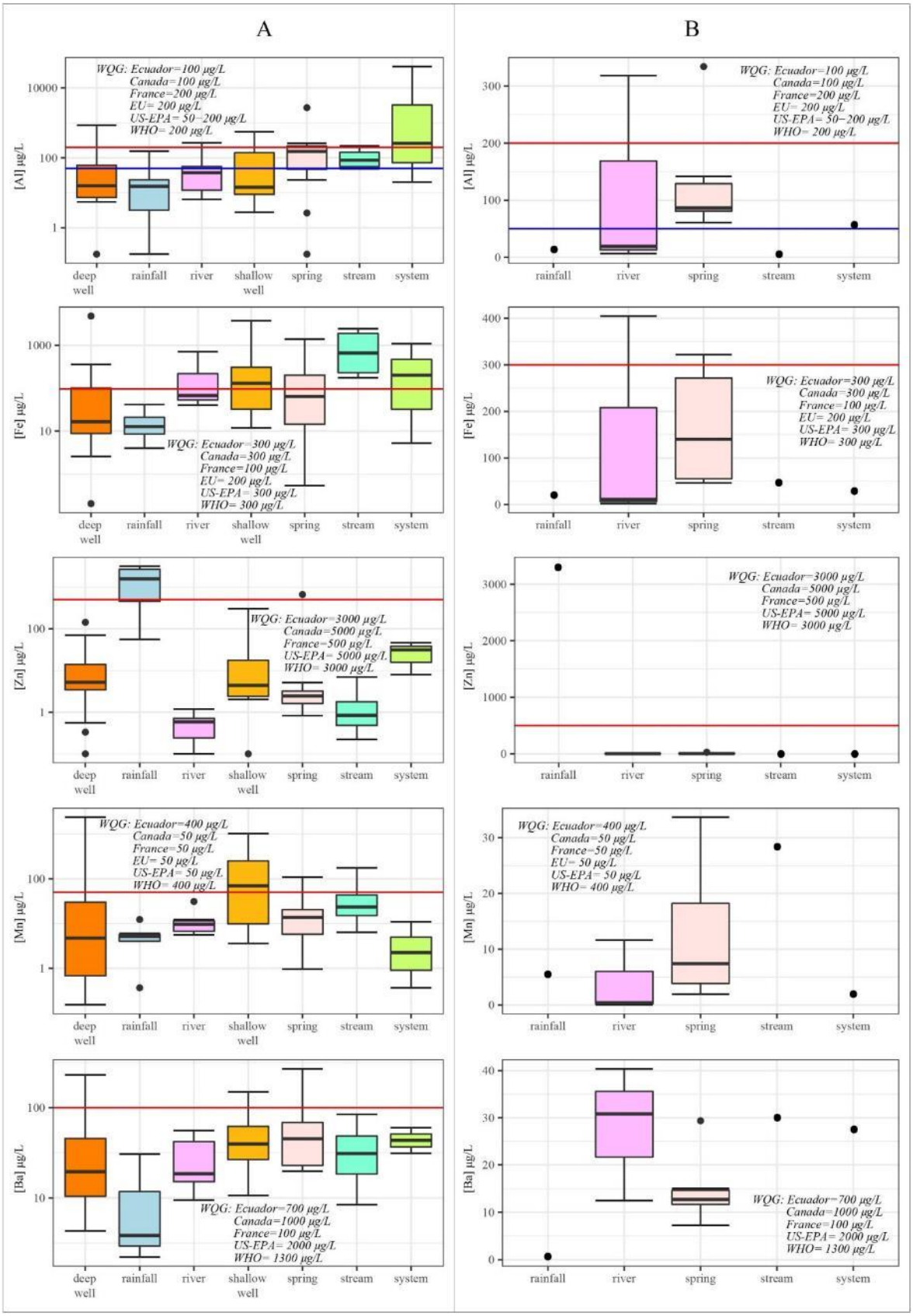


Figure 2-3. Al, Fe, Mn, Zn and Ba concentrations in drinking water sampled during the 2012-2016 period, in (A) the Northern Ecuadorian Amazon Region (NEAR) and in (B) the control zone in the Southern Ecuadorian Amazon Region (SEAR). The red and blue lines report maximum and minimum values recommended by the World Health Organization for drinking water (2005), respectively; international quality guidelines (WQG) are reported.

3.3 PAHs concentrations

All aromatic organic compounds (PAHs and BTEX) concentrations measured in the analyzed drinking waters (**Table SII-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 2-2**), the ingestion hazard index (HIing) showed a contribution of 99 to 100% to the non-carcinogenic total hazard index (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 values of HI ranged from $3.4x10^{-02}$ to 2.6 and from $1.4x10^{-04}$ to $2.0x10^{-02}$ for ingestion and dermal routes, respectively. From the sites that shows HQ values > 1 (**Table SII-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 of the country; this elevated HI (1.8) is mainly explained by the Cd content (HQ=1.5).

For children, no contribution of dermal exposure was found in the total hazard index. The ingestion route in the THI ranged from $7.5x10^{-02}$ to 5.5. From all the samples, 9 (11%) were higher than the reference value (US EPA, 2015). The highest THI values were found in deep wells waters of the NEAR, two in Pacayacu (HI =1.6 and 0.61 due to Mn concentrations), and two in Dayuma (HI=1.32 and 1.38 explained by As concentrations), in a private well and in the stadium, respectively. Individually, hazard quotients >1 in rainwater were found in the whole Amazon region, being Zn the element that contributed to most of the total hazard index (HQ of Zn=1.01 and 1.06, in the NEAR and SEAR respectively).

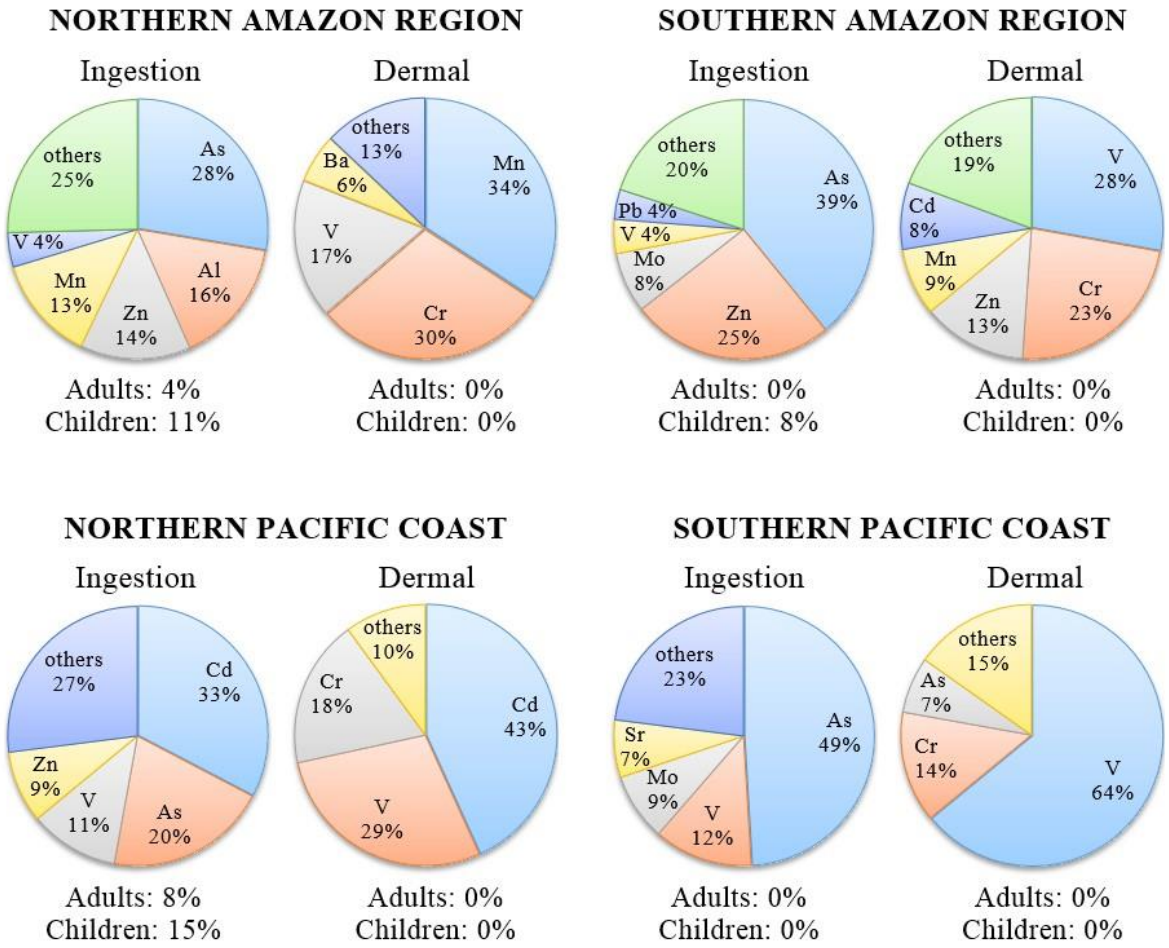


Figure 2-4. Distribution of ingestion and dermal contact Hazard Index (HI) for the Amazon and Pacific Ecuadorian regions, followed by the percentage of samples that overcome the Total HI reference value (US EPA, 2015) in children and adults.

Finally, in the system water from Dayuma (NEAR), we found one point with a high concentration of Al in Auca 09 field corresponding to THI equal to 3.9. In the NEPC, the highest risk explained by Cd (HI=3.13) and As (HI=0.38) concentrations were found in Esmeraldas, in the potable water pumping station and in a particular house, 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 dermal-HI, 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 49% of the total ingestion HI (**Figure 2-4**), while As concentrations never exceeded 3 $\mu g \cdot L^{-1}$. In the Total Hazard Index (THI) calculated for carcinogenic elements (As, Cd, Cr and Ni), arsenic contributes with 51% to 100% in 65 points (78% of the total sampling points). In Esmeraldas, Cd contributes with 56% to 94% of the THI in 4 system water samples.

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 A-1**). High concentrations of V (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 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. 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 (Armijos et al., 2013) 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 most of the WQGs except French-WQG (100 $\mu g \cdot L^{-1}$). 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.

Table 2-2. 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	**HI*ing***	$3.2x10^{-1}$	$2.9x10^{-1}$	$8.3x10^{-2}$	$2.3x10^{-1}$	$1.1x10^{-1}$	$1.7x10^{-1}$	$9.3x10^{-1}$	$5.3x10^{-1}$	$1.9x10^{-1}$	$1.0x10^{-1}$	$1.1x10^{-1}$	$1.5x10^{-1}$	$3.6x10^{-1}$	$3.5x10^{-1}$	$4.5x10^{-1}$	$2.7x10^{-1}$
	HI*der*	$2.2x10^{-3}$	$8.0x10^{-4}$	$7.2x10^{-4}$	$1.7x10^{-3}$	$9.8x10^{-4}$	$1.1x10^{-3}$	$3.8x10^{-3}$	$1.2x10^{-3}$	$8.0x10^{-4}$	$4.8x10^{-4}$	$3.9x10^{-4}$	$4.1x10^{-4}$	$5.1x10^{-3}$	$3.1x10^{-3}$	$2.1x10^{-3}$	$1.2x10^{-3}$
	THI	$3.2x10^{-1}$	$2.9x10^{-1}$	$8.4x10^{-2}$	$2.3x10^{-1}$	$1.1x10^{-1}$	$1.7x10^{-1}$	$9.3x10^{-1}$	$5.3x10^{-1}$	$1.9x10^{-1}$	$1.0x10^{-1}$	$1.1x10^{-1}$	$1.5x10^{-1}$	$3.6x10^{-1}$	$3.5x10^{-1}$	$4.5x10^{-1}$	$2.7x10^{-1}$
	> 1	7%	0%	0%	0%	0%	0%	33%	0%	0%	0%	0%	0%	0%	8%	0%	0%
	CR*ing*	$2.5x10^{-5}$	$9.5x10^{-7}$	$6.3x10^{-6}$	$1.2x10^{-5}$	$4.8x10^{-6}$	$1.8x10^{-5}$	$3.4x10^{-5}$	$2.4x10^{-7}$	$1.7x10^{-5}$	$9.7x10^{-6}$	$1.4x10^{-5}$	$2.4x10^{-5}$	$1.3x10^{-6}$	$1.5x10^{-5}$	$3.9x10^{-5}$	$2.9x10^{-5}$
	CR*der*	$6.5x10^{-9}$	$2.5x10^{-10}$	$1.7x10^{-9}$	$3.1x10^{-9}$	$1.3x10^{-9}$	$4.7x10^{-9}$	$9.0x10^{-9}$	$6.2x10^{-11}$	$4.6x10^{-9}$	$2.6x10^{-9}$	$3.8x10^{-9}$	$6.4x10^{-9}$	$3.4x10^{-10}$	$3.8x10^{-9}$	$1.0x10^{-8}$	$7.7x10^{-9}$
	TCR	$2.5x10^{-5}$	$9.5x10^{-7}$	$6.3x10^{-6}$	$1.2x10^{-5}$	$4.8x10^{-6}$	$1.8x10^{-5}$	$3.4x10^{-5}$	$2.4x10^{-7}$	$1.7x10^{-5}$	$9.7x10^{-6}$	$1.4x10^{-5}$	$2.4x10^{-5}$	$1.3x10^{-6}$	$1.5x10^{-5}$	$3.9x10^{-5}$	$2.9x10^{-5}$
	$>10^{-4}$	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%
CHILDREN	**HI*ing***	$6.9x10^{-1}$	$6.2x10^{-1}$	$1.8x10^{-1}$	$5.0x10^{-1}$	$2.4x10^{-1}$	$3.7x10^{-1}$	$2.0x10^{-0}$	$1.1\ x10^{-0}$	$4.2x10^{-1}$	$2.2x10^{-1}$	$2.3x10^{-1}$	$3.3x10^{-1}$	$7.8x10^{-1}$	$7.5x10^{-1}$	$9.8x10^{-1}$	$5.8x10^{-1}$
	HI*der*	$3.8x10^{-4}$	$1.4x10^{-4}$	$1.3x10^{-4}$	$2.9x10^{-4}$	$1.7x10^{-4}$	$1.9x10^{-4}$	$6.5x10^{-4}$	$2.0x10^{-4}$	$1.4x10^{-4}$	$8.3x10^{-5}$	$6.8x10^{-5}$	$7.2x10^{-5}$	$8.8x10^{-4}$	$5.4x10^{-4}$	$3.7x10^{-4}$	$2.1x10^{-4}$
	THI	$6.9x10^{-1}$	$6.2x10^{-1}$	$1.8x10^{-1}$	$5.0x10^{-1}$	$2.4x10^{-1}$	$3.6x10^{-1}$	$2.0x10^{-0}$	$1.1x10^{-0}$	$4.2x10^{-1}$	$2.2x10^{-1}$	$2.3x10^{-1}$	$3.3x10^{-1}$	$7.8x10^{-1}$	$7.5x10^{-1}$	$9.8x10^{-1}$	$5.8x10^{-1}$
	> 1	27%	14%	0%	0%	0%	0%	33%	100%	0%	0%	0%	0%	0%	17%	0%	0%
	CR*ing*	$1.1x10^{-5}$	$4.1x10^{-7}$	$2.7x10^{-6}$	$5.1x10^{-6}$	$2.1x10^{-6}$	$7.7x10^{-6}$	$1.5x10^{-5}$	$1.0x10^{-7}$	$7.5x10^{-6}$	$4.2x10^{-6}$	$6.2x10^{-6}$	$1.1x10^{-5}$	$5.5x10^{-7}$	$6.3x10^{-6}$	$1.7x10^{-5}$	$1.3x10^{-5}$
	CR*der*	$2.8x10^{-9}$	$1.1x10^{-10}$	$7.2x10^{-10}$	$1.3x10^{-9}$	$5.5x10^{-10}$	$2.0x10^{-9}$	$3.9x10^{-9}$	$2.7x10^{-11}$	$2.0x10^{-9}$	$1.1x10^{-9}$	$1.6x10^{-9}$	$2.8x10^{-9}$	$1.5x10^{-10}$	$1.7x10^{-9}$	$4.4x10^{-9}$	$3.4x10^{-9}$
	TCR	$1.1x10^{-5}$	$4.1x10^{-7}$	$2.7x10^{-6}$	$5.1x10^{-6}$	$2.1x10^{-6}$	$7.7x10^{-6}$	$1.5x10^{-5}$	$1.0x10^{-7}$	$7.5x10^{-6}$	$4.2x10^{-6}$	$6.2x10^{-6}$	$1.1x10^{-5}$	$5.5x10^{-7}$	$6.3x10^{-6}$	$1.7x10^{-5}$	$1.3x10^{-5}$
	$>10^{-4}$	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; HI*ing*=hazard index for ingestion exposition; Hi*der*= hazard index for dermal exposition; THI=total hazard index.

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 $\mu g.L^{-1}$ 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 (Brunet, 2006). 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 (Baird et al., 2007) 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 toxicity or cancer risk from chronic exposure to individual alkylated PAHs 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**).

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.

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 distribution pipes and modify the taste. Acidic pH is a characteristic of rainwaters which feed spring and shallow groundwater in the Amazon basin 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 that should be in demineralized water. After evaluating the available health, organoleptic and other information, they 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 (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, 2011).

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 could not provide all essential elements in sufficient quantities to 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) 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 2-2**, **Table SII-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's 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. Regarding the inorganic compounds**,** from 34 parameters considered in the 2006, only 18 were proposed in 2014. Even the maximum permissible limits became less restrictive, like for example the Mn threshold values that 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) higher than in the 2006 version. For BTEX molecules, benzene and

xylene remained unchanged, while toluene MPV became more permissive, from 0.17 $ng.L^{-1}$ in 2006 to 0.7 $ng.L^{-1}$ in actual versions, and ethylbenzene regulation disappeared in the last text. 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.

The second Ecuadorian regulation, TULSMA, is applicable to natural water sources for human consumption prior to any treatment. In its last version (November 2015), this regulation eliminated in its classification, the type of waters that only required disinfection and only considered treated-clean waters and raw water that needed a physical treatment. The latest version of TULSMA presented a lower number of parameters than the former text. The MPV of some elements, such as Cd, increased from 0.003 $mg.L^{-1}$ in February, 2015 to 0.02 $mg.L^{-1}$ in November, 2015. Concentrations of PAHs and BTEX in drinking water sources are not regulated. Fecal coliforms for water requiring conventional treatment, the current version (November, 2015) set up a lower concentration (1000 NMP.100 ml^{-1}) than the previous ones (2000 NMP/100 ml) but it still remains very high.

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

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. 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

4.4.1. Perceived environment and perceived exposure to health risks

In the Amazon basin, traditionally, indigenous and mestizo use water sources close to their



Figure 2-5. The 20 most cited words in Spanish by local people living in Dayuma and Pacayacu villages. (©NVivo simulation.)

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 (**Figure 2-5**), 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 et al., 2017)): *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 takes 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.

4.4.2. 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 (Langumier, 2006; 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 Kichwa 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 mountain (Béguet, 2015) . Furthermore, in indigenous groups, environmental pollution is unequally perceived. We observed in Shuar and Kichwa 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 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.

4.4.3. Chronic and historical distrust of oil companies.

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 health of inhabitants, 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. 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 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 since almost five decades. Local people living in areas affected by oil activities 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.

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Supplementary Information 2

Table SII-1. Detection and quantification limits and recovery percentage in water analysis.

GROUP	ANALYTE	DL	QL	RECOVERY	ANALYTE	LD	LQ	RECOVERY
MAJOR ELEMENTS [a]	Ca	0.006	0.019	107%	Chlorides	0.003	0.009	98%
	K	0.018	0.061	104%	Sulfates	0.003	0.009	101%
	Mg	0.003	0.011	105%	Nitrates	0.002	0.006	106%
	Na	0.057	0.189	105%	Bicarbonates	0.188	0.626	104%
	Si	0.001	0.003	107%	Fluorides	0.005	0.015	--
TRACE ELEMENTS [b]	Hg[c]	0.023	0.078	92%	Zn	0.066	0.218	103%
	Al	0.120	0.401	101%	As	0.005	0.016	92%
	Ti	0.007	0.024	90%	Se	0.017	0.058	101%
	V	0.018	0.061	100%	Sr	0.007	0.023	99%
	Cr	0.004	0.013	100%	Mo	0.007	0.022	91%
	Mn	0.003	0.009	97%	Cd	0.000	0.001	105%
	Fe	0.158	0.528	97%	Sb	0.003	0.010	93%
	Co	0.001	0.003	101%	Ba	0.002	0.008	99%
	Ni	0.010	0.033	99%	Pb	0.001	0.004	85%
	Cu	0.014	0.045	104%	U	0.000	0.001	93%
PAHS and BTEX[c]	N	0.5	3.0	98%	3MPh	0.1	0.3	106%
	Ac	0.2	0.7	98%	2MPh	0.1	0.3	106%
	Ace	0.2	0.6	103%	MA	0.1	0.3	106%
	Fl	0.1	0.4	106%	MPhMA	0.1	0.3	106%
	Ph	0.2	0.5	106%	1MPh	0.1	0.3	106%
	A	0.1	0.4	105%	∑DMPh	1.0	3.0	106%
	Fa	0.1	0.3	102%	∑TMPh	1.0	3.0	106%
	Py	0.1	0.3	102%	2MN	0.4	1.3	98%
	BaA	0.1	0.4	103%	1MN	0.4	1.1	98%
	Ch	0.1	0.4	101%	∑DMN	1.6	5.0	98%
	BbjkF	0.3	1.0	104%	∑TMN	1.6	5.0	98%
	BaP	0.3	1.0	97%	∑TeMN	1.6	5.0	98%
	IPy	0.3	1.0	103%	DBT	0.1	0.4	--
	DBA	0.3	1.0	102%	∑MDBT	0.3	1.0	--
	BPe	0.3	1.0	100%	Benzene	50	150	--
	BePy	0.3	1.0	99%	Toluene	5.7	17.0	--
	Pe	0.3	1.0	98%	Ethylbenzene	0.7	2.0	--
	MCh	0.2	0.5	101%	pm-xylene	1.5	4.5	--
	BNT	0.1	0.4	101%	o-xylene	0.7	2.0	--

a=mg.L^{-1}; b=µg.L^{-1}; c=ng.L^{-1}; N=naphthalene; Ac=acenaphthylene; Ace=acenaphthene; Fl=Fluorene; Ph=phenanthrene; A=anthracene; Fa=Fluoranthene; Py=pyrene; BaA=benzo[a]anthracene; Ch= chrysene+triphenylene; BbjkF=benzo[bjk]fluoranthene; BaP=benzo[a]pyrene; IPy=indeno[1,2,3-cd]pyrene; DBA=dibenzo[ah]anthracene; BPe=benzo[ghi]perylene; BePy=benzo[e]Pyrene; Pe=perylene; MCh=methylchrysene; BNT=2,1benzonaphtothiophene; 3MPh=3Methylphenanthrene; 2MPh=2methylphenanthrene; MA=2methylanthracene; MPhMA=[9+4]methylphenanthrene+ 1methylanthracene+ 4,5methylenephenanthrene; 1MPh=1methylphenanthrene; ∑DMPh=∑dimethylphenanthrene; ∑TMPh=∑trimethylphenanthrene; 2MN=2methylnaphthalene; 1MN=1methyl-naphthalene; ∑DMN=∑dimethylnaphthalene; ∑TMN=∑trimethylnaphthalene; ∑TeMN=∑tetramethylnaphthalene; DBT=dibenzothiophene; ∑MDBT=∑methyldibenzothiophene; ∑MN= Σmethylnaphthalenes; -- = non certified

Table SII-2. List and proprieties of PAHs and BTEX analyzed in the present study.

GROUP	MOLECULE	RINGS	SOLUBILITY (mg L^{-1})	MOLECULAR WEIGHT (g $mole^{-1}$)	IARC GROUP	ABBREVIATION
US-EPA PARENT PAHs	Naphthalene	2	31	128.17	2B	N
	Acenaphthene	3	16.1	152.20	3	Ace
	Acenaphthylene	3	3.8	154.21	-	Ac
	Anthracene	3	1.9	166.22	3	A
	Phenanthrene	3	1.1	178.23	3	Ph
	Fluoranthene	4	0.26	202.26	3	Fa
	Chrysene	4	0.132	202.26	2B	Ch
	Benzo[*ghi*]perylene	6	0.062	276.34	3	BPe
	Fluorene	3	0.045	178.23	3	Fl
	Pyrene	4	0.011	228.29	3	Py
	Benzo[*b*]fluoranthene*	5	0.0038	252.32	2B	
	Benzo[j]fluoranthene*	5	0.0025	252.32	2B	BbjkF
	Benzo[*k*]fluoranthene*	5	0.0015	252.32	2B	
	Benz[*a*]anthracene	4	0.0015	228.29	2B	BaA
	Benzo[*a*]pyrene	5	0.0008	252.32	1	BaP
	Indeno[1,2,3-*cd*]pyrene	6	0.0005	278.35	2B	IP
	Dibenzo[*a*,*h*]anthracene	6	0.00026	276.34	2A	DBA
OTHER PARENT PAHs	Benzo[e]pyrene	5	0.0063	252.32	3	BeP
	Perylene	5	0.0004	252.09	3	Pe
	2,1-Benzonaphtothiophene	3	-	234.32	3	BNT
METHYL PAHs	2Methylnaphthalene	2	24.6	142.2	-	2MN
	1Methylnaphthalene	2	25	142.2	-	1MN
	Dibenzothiophene	2	1.47	184.3	3	DBT
	ΣMethylchrysene	4	-	242.3	3	MCh
	3Methylphenanthrene	3	-	192.3	3	3MPh
	2Methylphenanthrene	3	-	192.3	-	2MPh
	2Methylanthracene	3	-	192.3	-	MA
	9+4Methylphenanthrene**	3	-	192.3	-	
	[4,5]Methylenephenanthrene**	3	-	192.3		MPhMA
	1Methylanthracene**	3	-	190.3		
	1Methylphenanthrene	3	-	192.3	3	1MPh
	ΣDimethylphenanthrene	3	-	206.2	3	∑DMPh
	ΣTrimethylphenanthrene	3	-	220.3	-	∑TMPh
	ΣDimethylnaphthalene	2	-	156.2	-	∑DMN
	ΣTrimethylnaphthalene	2	-	170.3	-	∑TMN
	ΣTetramethylnaphthalene	2	-	184.3	-	∑TeMN
	ΣMethyldibenzothiophene	2	-	198.3	-	∑MDBT
	ΣMethilnaphthalenes	2	-	142.2-184.3	-	∑MN
BTEX	Benzene	1	1790	78.1	1	Benzene
	Toluene	1	526	92.1	3	Toluene
	Ethylbenzene	1	169	106.2	2B	EB
	[p+m]-xylene	1	162	106.2	-	pm-xyl
	o-xylene	1	178	106.2	-	o-xyl
	∑xylenes	1	-	106.2	3	∑xyl

Source:(Bojes and Pope, 2007; NCBI and USNLM, 2018);
* BbjkF=Benzo[*bjk*]fluoranthene=this three compounds belongs to the same analytical ensemble, they are reported as one, Benzo[j]fluoranthene is not in the US-EPA list; ** MPhMA =9+4Methylphenanthrene+ [4,5]Methylenephenanthrene +1Methylanthracene, this three compounds belongs to the same analytical ensemble, they are reported as a unique one.

Table SII-3. Water quality guidelines (WQG) and minimum health requirement for treated and natural water intended for human consumption.

PARAMETER	Ministry of the Environment-Ecuador[a]	Ministry of the Environment-Ecuador[b]	Ministry of the Environment-Ecuador[c]	Health Canada[a]	Ministry of Solidarity and Health-France[a]	Ministry of Solidarity and Health-France[b]	Ministry of Solidarity and Health-France[c]	The Council of the European Union[a]	US-EPA[a]	WHO[a]	WHO[m]	WHO[s]
CE (µS cm^{-1})	–	–	–	–	200 – 1100[R]	–	1100	<2500[h]	–	–	–	–
pH	6.5-8.5[d]	6.0-9.0	6.0-9.0[g]	7.0-10.5	6.5-9.0	–	6.5-8.5[R]	6.5-9.5[h]	6.5-8.5[i]	6.5-8.5[j]	–	–
F (mg L^{-1})	<1.5	<1.5	<1.4[f]	<1.5	<1.5	–	0.7-1.0[R]	<1.5	<4.0	<1.5	–	0.5-1.0
Cl (mg L^{-1})	<250[d]	–	–	<250[AO]	< 250	< 250	<200[R]	<250[h]	<250[i]	<250[j]	–	–
$SO_4^{=}$ (mg L^{-1})	<200[d]	<500	<250[g]	< 500[AO]	< 250	< 250	< 150[R]	< 250[h]	<250[i]	<500[j]	–	–
NO_3^- (mg L^{-1})	<50	<50	<50[g]	<45	<50	<50 or <100	<25	<50	<10[R]	<50	–	–
$HCO3^-$(mg L^{-1})	–	–	–	–	–	–	–	–	–	–	30	–
Ca (mg L^{-1})	–	–	–	–	–	–	–	–	–	<100[j,R]	20	40-80 (50)
Mg (mg L^{-1})	–	–	–	–	–	–	–	–	–	–	10	20-30
TDS (mg L^{-1})	–	–	–	–	–	–	–	–	–	–	100	250-500
Na (mg L^{-1})	< 200[d,R]	< 200[f]	< 200[f]	< 200[AO,R]	< 200[R]	< 200[R]	–	< 200[h,R]	–	<200[j,R]	20	–
As_µg/L	<10[R]	<100	<10[g,R]	<10[R]	<10[R]	<100	<10[R]	<10[R]	<10[R]	<10[R]	–	–
Cd (µg L^{-1})	<3	<20	<3[g]	<5	<5	<5	<1[R]	<5	<5	<3	–	–
Cr (µg L^{-1})	<50[R]	–	–	<50[R]	<50[R]	<50[R]	<50[R]	<50[R]	<100	<50[R]	–	–
Ni (µg L^{-1})	<70	–	<25[f]	–	<20[R]	–	–	<20[R]	–	<70	–	–
Pb (µg L^{-1})	<10[R]	<10[R]	<10[g]	<10[R]	<10[R]	<50	<10[R]	<10[R]	<15	<10[R]	–	–
Al (µg L^{-1})	<250[d]	<200[g,R]	<100[g]	<100	<200[R]	–	–	< 200[h]	50 - 200[i]	<200[j,R]	–	–
V (µg L^{-1})	<100[d,R]	–	–	–	–	–	–	<140	–	–	–	–
Mn (µg L^{-1})	<400[e]	<100[f]	<100[f]	<50[R]	<50[R]	–	<50[R]	<50[h,R]	<50[i,R]	<400[j]	–	–
Fe (µg L^{-1})	<300[d]	<1000	<300[g]	<300	<200	–	<100[R]	< 200[h]	<300[i]	300[j]	–	–
Co (µg L^{-1})	<200[d,R]	–	–	–	–	–	–	–	–	–	–	–
Cu (µg L^{-1})	<2000	<2000	<2000[g]	<1000	<1000	–	<20[R]	<2000	<1300	<2000	–	–
Zn (µg L^{-1})	<3000[d]	<5000[g]	<5000[g]	<5000	–	<5000	<500[R]	–	<5000[i]	<3000[j]	–	–
Se (µg L^{-1})	<40	<10[R]	<10[g,R]	<50	<10[R]	<10[R]	<10[R]	<10[R]	<50	<40	–	–
Mo (µg L^{-1})	–	–	–	–	–	–	–	–	–	<70[j,R]	–	–
Sb (µg L^{-1})	<20	–	–	<6	<5[R]	–	–	<5[R]	<6	<20	–	–
Ba (µg L^{-1})	<700	<1000	<700[g]	<1000	<700	<100[R]	<100[R]	–	<2000	<1300	–	–
Hg (µg L^{-1})	<6	<6	<6[g]	<1	<1	<1	<0.5[R]	<1	<2	<6	–	–
U (µg L^{-1})	–	–	–	<20[R]	–	–	–	–	<30	<30	–	–
Fa (µg L^{-1})	–	–	–	–	–	<1**	<0.2**	–	–	<4[j,R]	–	–
B[bk]Fa (µg L^{-1})	–	–	–	–	<0.1*	<1**	<0.2**	<0.1*	–	–	–	–
B[a]P (µg L^{-1})	<0.7	<0.01[f,R]	<0.01[f,R]	<0.04	<0.01[R]	<1**	<0.2**	<0.01[R]	<0.2	<0.7	–	–
IP (µg L^{-1})	<0.03[d,R]	–	–	–	<0.1*	<1**	<0.2**	<0.1*	–	–	–	–
B[ghi]Pe (µg L^{-1})	<0.03[d,R]	–	–	–	<0.1*	<1**	<0.2**	<0.1*	–	–	–	–

Table SII-3. Water quality guidelines (WQG) and minimum health requirement for treated and natural water intended for human consumption. (continued)

PARAMETER	Ministry of the Environment-Ecuador[a]	Ministry of the Environment-Ecuador[b]	Ministry of the Environment-Ecuador[c]	Health Canada[a]	Ministry of Solidarity and Health-France[a]	Ministry of Solidarity and Health-France[b]	Ministry of Solidarity and Health-France[c]	The Council of the European Union[a]	US-EPA[a]	WHO[a]	WHO[m]	WHO[s]
Benzene (µg L^{-1})	<10	<10[f]	–	<5	<1[R]	–	–	<1[R]	<5	<10	–	–
Toluene (µg L^{-1})	<700	<1000[f]	–	<60[R]	–	–	–	–	<1000	<700	–	–
Ethylbenzene (µg L^{-1})	<200d	<700[f]	–	<140[R]	–	–	–	–	<700	<300	–	–
Xylenes (µg L^{-1})	<500	<10000[f]	–	<90	–	–	–	–	<10000	<500	–	–
E. Coli[k]	<1 CFU	1000 MPN	20 MPN[g]	0 CFU	0 CFU	20000 CFU	20 CFU	0 CFU	<2.5%[l]	0 CFU	–	–
Total coliforms[k]	<1 CFU [d]	2000 MPN[g]	200 MPN[g]	0 CFU	0 CFU	–	50 CFU	0 CFU	<2.5%[l]	0 CFU	–	–

US-EPA=US Environmental Protection Agency; WHO=World Health Organization; a= treated-clean water sources; b= raw water that needs treatment; c= raw water that needs simple physical treatment and/or disinfection; AO=aesthetic observation (taste or smell); d= INEN-2006; e= INEN-2011; f=TULSMA-2003; g=TULSMA-Feb 2015; h= Indicator parameters; i= Non-enforceable guidelines cosmetic effects; j= non established guideline; k=counted in 100 ml volume; l= If <40 samples/month. maximun one sample (2.5%) can be positive; m=minimum health requirement; s=optimal health requierement; *B[bk]Fa+B[ghi]Pe+IP; **Fa+B[bk]Fa+B[a]P+B[ghi]Pe+IP; Fa=fluoranthene; B[bk]Fa=benzo[bk]fluoranthene; B[a]P=benzo[a]pyrene; IP=indeno[1,2,3-cd]pyrene; B[ghi]Pe CFU=colony forming units; MPN=most probable number; R=value considered in the present study.

Table SII-4. Average (± Standard Deviation) PAHs and BTEX concentrations (ng.L^{-1}) and coliforms (CFU.100 mL^{-1}) in different sources of domestic water collected in the Northern and Southern Ecuadorian Amazon Region (NEAR and SEAR, respectively) and in the Northern and in the Northern and Southern Ecuadorian Pacific Coast (NEPC and SEPC, respectively).

	NEAR							SEAR					NEPC		SEPC	
PARAMETER	**deep well**	**rainfall**	**river**	**shallow well**	**spring**	**stream**	**system**	**rainfall**	**river**	**spring**	**stream**	**system**	**rainfall**	**system**	**system**	**shallow well**
N	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	5.6*	<5.0	<5.0	<5.0*	<5.0*	8.2*	<5.0	<5.0*	<5.0*
AC	<0.9	0.9±0.7	<0.9	<0.9	1.7±2.1	<0.9	nd	3.1*	<0.9	<0.9	<0.9*	nd*	1.5*	1.6±3.1	<0.9*	nd*
ACE	<0.9	<0.9	<0.9	<0.9	<0.9	0.9±0.8	<0.9	<0.9*	<0.9	<0.9	<0.9*	<0.9*	1.2*	<0.9	<0.9*	<0.9*
Fl	1±2.4	0.6±0.4	<0.6	<0.6	3.4±10	12.6±24.7	<0.6	0.8*	0.8±0.5	<0.6	<0.6*	<0.6*	3.5*	0.9±1.4	<0.6*	<0.6*
Ph	1±1.1	2.6±1.9	0.8±0.6	1±0.6	1.6±2.7	2.7±4	1.4±0.7	5.8*	1.8±1.9	0.6±0.3	<0.6*	<0.6*	8.6*	4.7±9.8	<0.6*	<0.6*
A	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	0.8*	<0.6	<0.6	<0.6*	nd*	<0.6*	0.7±1.3	<0.6*	<0.6*
Fa	<0.4	0.7±0.5	<0.4	<0.4	0.6±0.6	<0.4	0.5±0.3	2*	<0.4	<0.4	<0.4*	<0.4*	1*	1.7±3.6	0.4*	<0.4*
Py	0.4±0.3	0.7±0.7	<0.4	<0.4	0.6±0.7	0.6±0.8	0.5±0.3	1.7*	0.4±0.2	0.4±0.3	<0.4*	<0.4*	1.2*	2.2±4.8	<0.4*	<0.4*
BaA	0.8±1.2	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5*	<0.5	<0.5	<0.5*	nd*	<0.5*	<0.5	<0.5*	nd*
Ch	<0.5	<0.5	<0.5	<0.5	<0.5	0.9±1.3	<0.5	<0.5*	<0.5	<0.5	<0.5*	nd*	<0.5*	<0.5	<0.5*	<0.5*
BbjkF	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5*	<1.5	<1.5	<1.5*	nd*	<1.5*	<1.5	<1.5*	<1.5*
BaPy	<1.5	<1.5	<1.5	nd	<1.5	<1.5	nd	<1.5*	nd	<1.5	nd*	nd*	<1.5*	<1.5	<1.5*	<1.5*
IPy	<1.5	<1.5	<1.5	nd	nd	nd	nd	nd*	nd	nd	nd*	nd*	<1.5*	nd	nd*	nd*
DBA	nd	nd	<1.5	<1.5	<1.5	nd	nd	nd*	nd	nd	nd*	nd*	nd*	nd	nd*	nd*
BPe	<1.5	<1.5	<1.5	nd	nd	nd	nd	<1.5*	nd	<1.5	nd*	nd*	<1.5*	<1.5	<1.5*	nd*
∑16PAHs	8.8±10.2	11.4±4.5	7±3	6±1.3	10.9±15.3	23.4±35.1	6.7±0.9	23*	7.7±2.5	6.4±1.1	6.0*	4.7*	29.1*	17.7±27.8	7.7*	6*
∑Norm1	0.8±0.2	0.8±1	0.4±0.8	0.3±0.4	0.1±0.3	0.2±0.4	0.2±0.4	1.5*	0.7±0	0.7±0.5	0.7*	0.7*	2.2±*	0.8±0.4	1.5*	0.7*
∑Norm2	0.9±0.6	1.7±1.4	0.8±1.1	0.6±0.3	0.8±0.7	0.7±0.7	0.7±0.2	4.2*	0.9±0	1.2±0.8	0.9*	0.9*	4±*	3±3.3	2.6*	1.7*
BePy	nd	<1.5	nd	nd	nd	nd	nd	<1.5*	nd	nd	nd*	nd*	<1.5*	<1.5	<1.5*	<1.5*
Pe	<1.5	nd	<1.5	nd	nd	<1.5	nd	<1.5*	nd	nd	<1.5*	nd*	<1.5*	<1.5	<1.5*	nd*
MCh	<0.6	<0.6	<0.6	nd	<0.6	nd	<0.6	<0.6*	<0.6	<0.6	nd*	nd*	<0.6*	<0.6	nd*	nd*
BNT	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	nd	<0.5*	<0.5	<0.5	<0.5*	<0.5*	<0.5*	<0.5	nd*	<0.5*
3MPh	0.3±0.3	0.8±1.2	0.3±0.2	0.3±0.2	0.4±0.5	0.8±1.3	1.1±1.6	0.8*	1.9±2.5	<0.3.1	<0.3*	<0.3*	1*	1.8±3.9	<0.3*	<0.3*
2MPh	0.3±0.2	1.1±1.5	0.3±0.2	0.3±0.2	0.6±0.9	1±1.8	1.1±1.1	0.7*	2±2.6	<0.3.1	<0.3*	<0.3*	1.2*	2.4±5.6	<0.3*	<0.3*
MA	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3*	0.3±0.2	<0.3	<0.3*	<0.3*	--	0.3±0.2	<0.3*	<0.3*
MPh-MA	0.3±0.2	1±1.8	0.3±0.3	0.3±0.1	0.4±0.7	1.4±2.4	0.7±0.9	0.7*	1.6±1.8	<0.3.1	<0.3*	<0.3*	1.2*	2.8±5.6	<0.3*	<0.3*

Table SII-4. Average (± Standard Deviation) PAHs and BTEX concentrations (ng.L^{-1}) and coliforms (CFU.100 mL^{-1}) in different sources of domestic water collected in the Northern and Southern Ecuadorian Amazon Region (NEAR and SEAR, respectively) and in the Northern and in the Northern and Southern Ecuadorian Pacific Coast (NEPC and SEPC, respectively). (continued)

PARAMETER	NEAR							SEAR					NEPC		SEPC	
	deep well	rainfall	river	shallow well	spring	stream	system	rainfall	river	spring	stream	system	rainfall	system	system	shallow well
1MPh	<0.3.1	1.2±2.4	0.3±0.2	<0.3.1	0.4±0.6	1.3±2.3	0.4±0.3	0.6*	1.2±1.3	<0.3	<0.3*	<0.3*	1.6*	2.7±5.6	<0.3*	<0.3*
∑DMPh	<5.0.9	5.1±7.3	<5.0	<5.0	<5.0	10.5±16	4.4±3.2	<5.0*	8.1±9.7	<5.0	<5.0*	<5.0*	<5.0*	14.9±31.4	<5.0*	<5.0*
∑TMPh	<5.0	3.8±3.5	<5.0	<5.0	<5.0	14.9±17.5	<5.0	<5.0*	<5.0	<5.0	<5.0*	nd*	<5.0*	255±795.2	<5.0*	nd*
2MN	12±33.9	6.1±6	5.8±4.5	3.7±3.2	3.6±3.7	5.6±7.2	5.3±4.1	7.2*	5.3±3.4	<2.0	6.1*	<2.0*	13.7*	5.6±5.4	5.5*	2.8*
1MN	9.4±29.8	4.2±4.7	3.4±4	1.6±1.2	2.2±2.7	4.9±8.3	3.2±3.4	4.1*	3±1.9	<1.5	3.6*	<1.5*	7.7*	3.6±4.9	2.1*	<1.5*
∑DMN	57±153	37.6±28	28±22	23±12	24±19	49±77	35±10	17*	28±15	9±2	24*	6.3*	44.4*	25±35	12.5*	7.0*
∑TMN	45±124	44±38.	33±27	25±17	29±36	106±190	36±32	12*	38±27	6±3	20*	5.8*	49.8*	340±85	9.1*	<5.0*
∑TeMN	19.5±39.1	20±15	20±15	13.6±4	18±19	75±134	26±13	12*	36±32	6±3	15*	5.3*	40.3*	41±79	7.1*	<5.0*
DBT	<0.6	<0.6	<0.6	<0.6	<0.6	1±1.4	<0.6	<0.6*	0.7±0.4	<0.6	<0.6*	<0.6*	0.7*	0.7±1.1	<0.6*	<0.6*
∑MDBT	<2.5	<2.5	<2.5	<2.5	<2.5	3.8±5	<2.5	<2.5*	3±3	<2.5	<2.5*	<2.5*	<2.5*	4.4±6.3	<2.5*	<2.5*
∑MN	135±370	112±83	92±71	67±35	77±80	240±416	106±49	52*	110±73	23±7	69*	19*	156*	114±208	36*	16*
Benzene	<100	<100	<100	<100	<100	<100	<100	<100 *	--	<100	<100*	<100*	<100*	224±242	825*	334*
Toluene	1182±2040	19±15	20±4	<9	47±50	15±11	70	59 *	--	40±14	81*	61*	54*	45±52	36*	25*
Ethylbenzene	32±16	77±96	16±8	13±8	89±105	17±2	44 *	19 *	--	14±1	40*	19*	160*	144±200	175*	109*
pm-xylene	31±22	72±77	23±4	30±17	79±89	17±3	61*	36 *	--	19±3	53*	41*	163*	108±146	122*	121*
o-xylene	6±8	11±11	5±0	10±5	11±9	5±1	17 *	14 *	--	6±2	12*	20*	31*	22±22	18*	22*
∑xylenes	38±30	83±87	28±4	40±22	90±98	22±4	78 *	50 *	--	24±4	65*	61*	194*	177±177	140*	143*
E. Coli	19±20	--	5*	--	0	--	0	--	--	--	--	--	--	--	--	--
Total coliforms	347±350	--	530	--	328±441	--	29	--	--	--	--	--	--	--	--	--

NEAR=North Ecuadorian Amazon Region; SEAR= South Ecuadorian Amazon Region; NEPC= North Ecuadorian Pacific Coast ;SEPC= South Ecuadorian Pacific Coast; * single value (n=1); N=naphthalene; AC=acenaphthylene; ACE=acenaphthene; Fl=Fluorene; Ph=phenanthrene; A=anthracene; Fa=Fluoranthene; Py=pyrene; BaA=benzo[a]anthracene; Ch=chrysene+triphenylene; BbjkF=benzo[bjk]fluoranthene; BaPy=benzo[a]pyrene; IPy=indeno[1,2,3-cd]pyrene; DBA=dibenzo[ah]anthracene; BPe=benzo[ghi]perylene; BePy=benzo[e]Pyrene; Pe=perylene; MCh=methylchrysene;BNT=2,1benzonaphtothiophene; 3MPh=3Methylphenanthrene; 2MPh=2methylphenanthrene;MA=2methylanthracene; MPhMA=[9+4]methylphenanthrene+ 1methylanthracene+ 4,5methylenephenanthrene; 1MPh=1methylphenanthrene; ∑DMPh=∑dimethylphenanthrene; ∑TMPh=∑trimethylphenanthrene; 2MN=2methylnaphthalene; 1MN=1methyl- naphthalene; ∑DMN=∑dimethylnaphthalene; ∑TMN=∑trimethylnaphthalene; ∑TeMN=∑tetramethylnaphthalene; DBT=dibenzothiophene; ∑MDBT=∑methyldibenzothiophene; ∑MN= Σmethylnaphthalenes; ∑Norm1=B[bjk]Fa+B[ghi]Pe+IP; ∑Norm2=Fa+B[bjk]Fa+B[a]P+B[ghi]Pe+IP.

Detected molecules with an average concentration between LD and LQ are reported as <LQ.

Data lower than the DL are reported as nd=non detected. --: not measured.

Table SII-5. Individual hazard quotient (HQ) for ingestion pathway in the Ecuadorian amazon region.

POPULATION	PARAMETER	NEAR							SEAR				
		deep well	rainfall	river	shallow well	spring	stream	system	rainfall	river	spring	stream	system
ADULTS	As	$1.28x10^{-1}$	$4.94x10^{-3}$	$3.26x10^{-2}$	$6.08x10^{-2}$	$2.50x10^{-2}$	$9.20x10^{-2}$	$1.75x10^{-1}$	$1.22x10^{-3}$	$8.93x10^{-2}$	$5.03x10^{-2}$	$7.37x10^{-2}$	$1.25x10^{-1}$
	Cd	$3.17x10^{-3}$	$1.98x10^{-3}$	$1.72x10^{-3}$	$7.52x10^{-3}$	$3.69x10^{-3}$	$3.52x10^{-3}$	$1.29x10^{-3}$	$3.20x10^{-3}$	$7.89x10^{-3}$	$3.42x10^{-3}$	$2.84x10^{-4}$	$9.40x10^{-5}$
	Cr	$9.10x10^{-3}$	$3.35x10^{-3}$	$3.79x10^{-3}$	$2.04x10^{-3}$	$9.07x10^{-3}$	$3.12x10^{-3}$	$5.42x10^{-2}$	$7.35x10^{-4}$	$4.67x10^{-3}$	$2.72x10^{-3}$	$9.42x10^{-4}$	$1.67x10^{-3}$
	Ni	$1.26x10^{-3}$	$5.70x10^{-4}$	$4.08x10^{-4}$	$8.40x10^{-4}$	$1.71x10^{-3}$	$1.19x10^{-3}$	$1.82x10^{-3}$	$1.74x10^{-3}$	$5.70x10^{-4}$	$5.49x10^{-4}$	$4.53x10^{-4}$	$3.88x10^{-4}$
	Hg	$3.13x10^{-4}$	$2.76x10^{-4}$	$2.46x10^{-4}$	$1.22x10^{-4}$	$3.90x10^{-4}$	$2.23x10^{-4}$	$1.18x10^{-3}$	–	–	–	$2.28x10^{-4}$	–
	Al	$4.87x10^{-3}$	$1.43x10^{-3}$	$2.85x10^{-3}$	$5.57x10^{-3}$	$1.51x10^{-2}$	$4.99x10^{-3}$	$6.06x10^{-1}$	$6.01x10^{-4}$	$5.08x10^{-3}$	$5.82x10^{-3}$	$2.40x10^{-4}$	$2.44x10^{-3}$
	V	$1.13x10^{-2}$	$2.21x10^{-3}$	$1.50x10^{-2}$	$5.31x10^{-3}$	$7.95x10^{-3}$	$1.97x10^{-2}$	$3.08x10^{-2}$	$3.84x10^{-4}$	$1.30x10^{-2}$	$5.70x10^{-3}$	$3.09x10^{-3}$	$7.11x10^{-3}$
	Mn	$7.28x10^{-2}$	$1.68x10^{-3}$	$3.75x10^{-3}$	$7.33x10^{-2}$	$6.91x10^{-3}$	$1.81x10^{-2}$	$1.43x10^{-3}$	$1.69x10^{-3}$	$1.27x10^{-3}$	$3.95x10^{-3}$	$8.93x10^{-3}$	$5.80x10^{-4}$
	Co	$5.11x10^{-4}$	$9.26x10^{-5}$	$2.41x10^{-4}$	$1.33x10^{-3}$	$7.15x10^{-4}$	$8.38x10^{-4}$	$2.01x10^{-4}$	$7.43x10^{-5}$	$1.95x10^{-4}$	$2.88x10^{-4}$	$4.14x10^{-4}$	$6.86x10^{-5}$
	Cu	$8.59x10^{-3}$	$1.69x10^{-3}$	$4.01x10^{-4}$	$9.82x10^{-3}$	$1.19x10^{-3}$	$7.83x10^{-4}$	$7.55x10^{-3}$	$6.70x10^{-4}$	$2.83x10^{-3}$	$9.58x10^{-3}$	$5.69x10^{-4}$	$2.22x10^{-3}$
	Zn	$3.00x10^{-3}$	$2.40x10^{-1}$	$7.98x10^{-5}$	$7.36x10^{-3}$	$8.48x10^{-3}$	$3.30x10^{-4}$	$4.20x10^{-3}$	$4.89x10^{-1}$	$5.19x10^{-4}$	$1.26x10^{-3}$	$2.97x10^{-5}$	$5.91x10^{-4}$
	Se	$1.47x10^{-2}$	$2.39x10^{-3}$	$3.20x10^{-3}$	$1.09x10^{-2}$	$3.88x10^{-3}$	$2.69x10^{-3}$	$1.86x10^{-3}$	$2.57x10^{-4}$	$7.11x10^{-4}$	$2.57x10^{-4}$	$5.92x10^{-4}$	$2.57x10^{-4}$
	Sr	$1.52x10^{-2}$	$2.84x10^{-4}$	$5.23x10^{-3}$	$9.26x10^{-3}$	$5.43x10^{-3}$	$5.57x10^{-3}$	$4.99x10^{-3}$	$2.49x10^{-5}$	$4.17x10^{-3}$	$1.79x10^{-3}$	$4.33x10^{-3}$	$1.95x10^{-3}$
	Mo	$2.29x10^{-2}$	$2.54x10^{-4}$	$4.83x10^{-3}$	$5.79x10^{-4}$	$6.17x10^{-4}$	$1.71x10^{-3}$	$2.87x10^{-3}$	$1.15x10^{-4}$	$4.87x10^{-2}$	$2.14x10^{-4}$	$1.10x10^{-3}$	$1.15x10^{-4}$
	Sb	$2.61x10^{-3}$	$9.64x10^{-3}$	$1.48x10^{-3}$	$3.05x10^{-3}$	$1.22x10^{-3}$	$2.59x10^{-3}$	$6.05x10^{-3}$	$2.54x10^{-2}$	$3.13x10^{-3}$	$1.83x10^{-3}$	$3.62x10^{-3}$	$8.70x10^{-4}$
	Ba	$1.21x10^{-2}$	$2.09x10^{-3}$	$6.27x10^{-3}$	$1.20x10^{-2}$	$1.39x10^{-2}$	$8.69x10^{-3}$	$9.93x10^{-3}$	$1.20x10^{-4}$	$6.17x10^{-3}$	$3.27x10^{-3}$	$6.60x10^{-3}$	$6.08x10^{-3}$
	Pb	$6.43x10^{-3}$	$1.48x10^{-2}$	$1.06x10^{-3}$	$1.94x10^{-2}$	$3.13x10^{-3}$	$1.63x10^{-3}$	$1.20x10^{-2}$	$1.90x10^{-3}$	$3.12x10^{-3}$	$1.02x10^{-2}$	$4.23x10^{-5}$	$1.14x10^{-3}$
	U	$1.04x10^{-3}$	$6.54x10^{-5}$	$3.98x10^{-4}$	$3.26x10^{-4}$	$1.01x10^{-3}$	$1.02x10^{-3}$	$5.83x10^{-3}$	$1.59x10^{-5}$	$6.13x10^{-4}$	$1.16x10^{-4}$	$1.34x10^{-4}$	$5.26x10^{-5}$
	HI	***$3.17x10^{-1}$***	***$2.88x10^{-1}$***	***$8.34x10^{-2}$***	***$2.29x10^{-1}$***	***$1.09x10^{-1}$***	***$1.69x10^{-1}$***	***$9.27x10^{-1}$***	***$5.27x10^{-1}$***	***$1.92x10^{-1}$***	***$1.01x10^{-1}$***	***$1.05x10^{-1}$***	***$1.51x10^{-1}$***
CHILDREN	As	$2.77x10^{-1}$	$1.07x10^{-2}$	$7.06x10^{-2}$	$1.32x10^{-1}$	$5.43x10^{-2}$	$1.99x10^{-1}$	$3.80x10^{-1}$	$2.64x10^{-3}$	$1.93x10^{-1}$	$1.09x10^{-1}$	$1.60x10^{-1}$	$2.72x10^{-1}$
	Cd	$6.86x10^{-3}$	$4.28x10^{-3}$	$3.72x10^{-3}$	$1.63x10^{-2}$	$7.99x10^{-3}$	$7.62x10^{-3}$	$2.80x10^{-3}$	$6.94x10^{-3}$	$1.71x10^{-2}$	$7.40x10^{-3}$	$6.15x10^{-4}$	$2.04x10^{-4}$
	Cr	$1.97x10^{-2}$	$7.26x10^{-3}$	$8.21x10^{-3}$	$4.42x10^{-3}$	$1.97x10^{-2}$	$6.77x10^{-3}$	$1.17x10^{-1}$	$1.59x10^{-3}$	$1.01x10^{-2}$	$5.88x10^{-3}$	$2.04x10^{-3}$	$3.62x10^{-3}$
	Ni	$2.72x10^{-3}$	$1.24x10^{-3}$	$8.84x10^{-4}$	$1.82x10^{-3}$	$3.70x10^{-3}$	$2.59x10^{-3}$	$3.94x10^{-3}$	$3.76x10^{-3}$	$1.24x10^{-3}$	$1.19x10^{-3}$	$9.81x10^{-4}$	$8.41x10^{-4}$
	Hg	$6.79x10^{-4}$	$5.97x10^{-4}$	$5.32x10^{-4}$	$2.64x10^{-4}$	$8.44x10^{-4}$	$4.83x10^{-4}$	$2.55x10^{-3}$	–	–	–	$4.95x10^{-4}$	–

Table SII-5. Individual hazard quotient (HQ) for ingestion pathway in the Ecuadorian amazon region. (continued)

POPULATION	PARAMETER	NEAR							SEAR				
		deep well	rainfall	river	shallow well	spring	stream	system	rainfall	river	spring	stream	system
CHILDREN	Al	$1.06x10^{-2}$	$3.09x10^{-3}$	$6.17x10^{-3}$	$1.21x10^{-2}$	$3.26x10^{-2}$	$1.08x10^{-2}$	1.31x10+00	$1.30x10^{-3}$	$1.10x10^{-2}$	$1.26x10^{-2}$	$5.20x10^{-4}$	$5.28x10^{-3}$
	V	$2.45x10^{-2}$	$4.79x10^{-3}$	$3.24x10^{-2}$	$1.15x10^{-2}$	$1.72x10^{-2}$	$4.26x10^{-2}$	$6.67x10^{-2}$	$8.32x10^{-4}$	$2.82x10^{-2}$	$1.24x10^{-2}$	$6.69x10^{-3}$	$1.54x10^{-2}$
	Mn	$1.58x10^{-1}$	$3.65x10^{-3}$	$8.13x10^{-3}$	$1.59x10^{-1}$	$1.50x10^{-2}$	$3.92x10^{-2}$	$3.09x10^{-3}$	$3.66x10^{-3}$	$2.76x10^{-3}$	$8.55x10^{-3}$	$1.94x10^{-2}$	$1.26x10^{-3}$
	Co	$1.11x10^{-3}$	$2.01x10^{-4}$	$5.21x10^{-4}$	$2.88x10^{-3}$	$1.55x10^{-3}$	$1.81x10^{-3}$	$4.35x10^{-4}$	$1.61x10^{-4}$	$4.23x10^{-4}$	$6.24x10^{-4}$	$8.96x10^{-4}$	$1.49x10^{-4}$
	Cu	$1.86x10^{-2}$	$3.65x10^{-3}$	$8.68x10^{-4}$	$2.13x10^{-2}$	$2.57x10^{-3}$	$1.70x10^{-3}$	$1.64x10^{-2}$	$1.45x10^{-3}$	$6.14x10^{-3}$	$2.08x10^{-2}$	$1.23x10^{-3}$	$4.81x10^{-3}$
	Zn	$6.50x10^{-3}$	$5.21x10^{-1}$	$1.73x10^{-4}$	$1.60x10^{-2}$	$1.84x10^{-2}$	$7.15x10^{-4}$	$9.10x10^{-3}$	1.06x10+00	$1.12x10^{-3}$	$2.72x10^{-3}$	$6.44x10^{-5}$	$1.28x10^{-3}$
	Se	$3.18x10^{-2}$	$5.17x10^{-3}$	$6.93x10^{-3}$	$2.36x10^{-2}$	$8.40x10^{-3}$	$5.82x10^{-3}$	$4.03x10^{-3}$	$5.57x10^{-4}$	$1.54x10^{-3}$	$5.57x10^{-4}$	$1.28x10^{-3}$	$5.57x10^{-4}$
	Sr	$3.30x10^{-2}$	$6.14x10^{-4}$	$1.13x10^{-2}$	$2.01x10^{-2}$	$1.18x10^{-2}$	$1.21x10^{-2}$	$1.08x10^{-2}$	$5.39x10^{-5}$	$9.03x10^{-3}$	$3.87x10^{-3}$	$9.38x10^{-3}$	$4.21x10^{-3}$
	Mo	$4.96x10^{-2}$	$5.51x10^{-4}$	$1.05x10^{-2}$	$1.25x10^{-3}$	$1.34x10^{-3}$	$3.70x10^{-3}$	$6.23x10^{-3}$	$2.49x10^{-4}$	$1.06x10^{-1}$	$4.63x10^{-4}$	$2.39x10^{-3}$	$2.49x10^{-4}$
	Sb	$5.66x10^{-3}$	$2.09x10^{-2}$	$3.22x10^{-3}$	$6.62x10^{-3}$	$2.64x10^{-3}$	$5.61x10^{-3}$	$1.31x10^{-2}$	$5.51x10^{-2}$	$6.77x10^{-3}$	$3.96x10^{-3}$	$7.85x10^{-3}$	$1.89x10^{-3}$
	Ba	$2.62x10^{-2}$	$4.53x10^{-3}$	$1.36x10^{-2}$	$2.60x10^{-2}$	$3.01x10^{-2}$	$1.88x10^{-2}$	$2.15x10^{-2}$	$2.61x10^{-4}$	$1.34x10^{-2}$	$7.08x10^{-3}$	$1.43x10^{-2}$	$1.32x10^{-2}$
	Pb	$1.39x10^{-2}$	$3.20x10^{-2}$	$2.30x10^{-3}$	$4.21x10^{-2}$	$6.77x10^{-3}$	$3.53x10^{-3}$	$2.60x10^{-2}$	$4.12x10^{-3}$	$6.75x10^{-3}$	$2.21x10^{-2}$	$9.16x10^{-5}$	$2.47x10^{-3}$
	U	$2.26x10^{-3}$	$1.42x10^{-4}$	$8.62x10^{-4}$	$7.06x10^{-4}$	$2.19x10^{-3}$	$2.22x10^{-3}$	$1.26x10^{-2}$	$3.44x10^{-5}$	$1.33x10^{-3}$	$2.52x10^{-4}$	$2.90x10^{-4}$	$1.14x10^{-4}$
	HI	***$6.88x10^{-1}$***	***$6.24x10^{-1}$***	***$1.81x10^{-1}$***	***$4.97x10^{-1}$***	***$2.37x10^{-1}$***	***$3.65x10^{-1}$***	***$2.01x10^{0}$***	***$1.14x10^{0}$***	***$4.16x10^{-1}$***	***$2.19x10^{-1}$***	***$2.28x10^{-1}$***	***$3.27x10^{-1}$***

NEAR=North Ecuadorian Amazon Region; SEAR= South Ecuadorian Amazon Region.

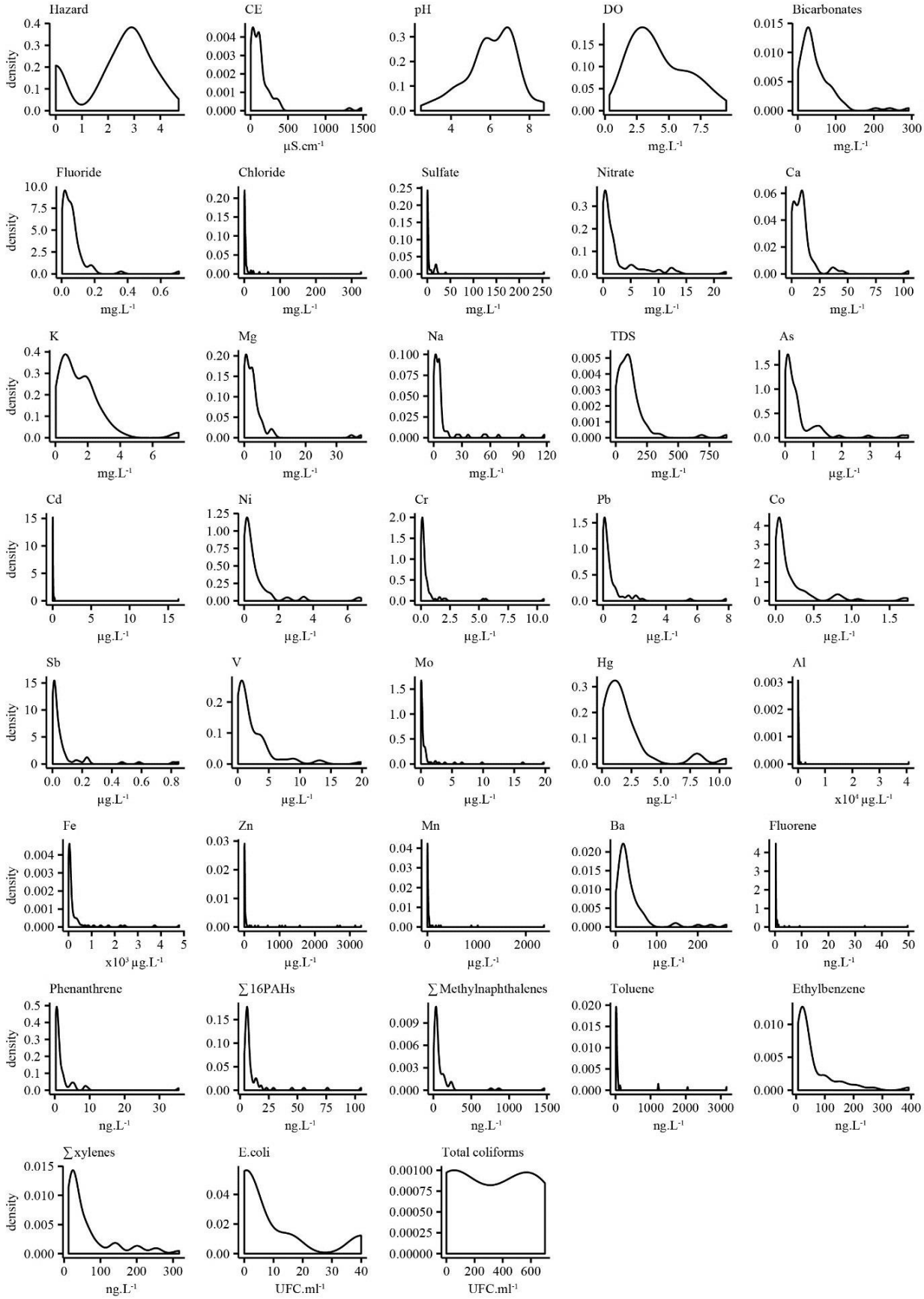


Figure SII-1. Kernel Density Plots for pollution hazard and the different variables in domestic water.

CONCLUSIONS, RECOMMANDATIONS ET PERSPECTIVES (FR)

Conclusion Générale

L'économie équatorienne est historiquement liée aux cours des différentes matières premières exportées, au premier rang desquelles figure le pétrole qui représente la moitié de la valeur des exportations. C'est aujourd'hui 45% du budget général de l'Etat, majoritairement alloué au remboursement de la dette. L'écrasante majorité des réserves de pétrole se trouve en Amazonie, dans les provinces de Sucumbíos et d'Orellana. La production nationale de pétrole représentait en janvier 2012, 15,6 millions de barils dont près de 72% reviennent à l'entreprise publique Petroecuador. Avec ses géo-ressources, la région amazonienne représente à elle seule la plus grande part des revenus du pays. Si elle occupe 45% de la surface territoriale du pays, elle ne compte que 5% de la population équatorienne dont 71% vivant en situation de pauvreté, contre 45% au niveau national (INEC, 2010).

Or, du fait des activités pétrolières intenses d'extraction ou de raffinage, actuelles et passées en Equateur, l'environnement des régions amazoniennes d'une part et de la côte Pacifique d'autre part a souvent été impacté par des contaminations.

En effet, depuis plus de 40 ans, la contamination environnementale due à l'industrie du pétrole est ponctuelle, accidentelle ou continue, et distribuée sur une grande partie de l'Amazonie équatorienne, principalement dans la partie nord. Les principales sources de contamination sont les rejets d'hydrocarbures liquides et d'eaux de formation dans les sols, les eaux de surface et souterraines ainsi que les rejets gazeux dans l'atmosphère. Les effets sur l'environnement dépendent des différentes phases d'exploration et d'exploitation, depuis les études sismiques, les perforations, la production, mais aussi le transport jusqu'au raffinage. Le procédé d'exploitation pétrolière génère des déchets (boues et liquides) hautement toxiques qui peuvent être stockés de manière temporaire dans des fosses, étanches ou non, pour être ensuite brûlés ou réinjectés dans des zones perforées en sous-sol ou directement rejetées vers les sols et eaux de surface. En particulier, le processus de production génère des « eaux de formation » qui combinent des quantités élevées de sels, de métaux lourds et du pétrole « en émulsion ». A cette « contamination routinière » (Maldonado et Narvaez, 2005) s'ajoutent les fuites liées aux ruptures de canalisations ou aux dysfonctionnements de puits d'exploitation. Ces accidents restent malheureusement fréquents, et encore difficiles à maitriser.

Cependant, l'impact réel de ces activités pétrolières sur la qualité des eaux de surface et des

sédiments associés a longtemps été supposé mais peu d'études ont effectivement évalué ces effets, et les conséquences induites sur la santé des populations, dans un pays où les difficultés sociales et sanitaires restent importantes. En effet, les déchets du pétrole contiennent principalement des métaux et métalloïdes co-émis avec des HAPs, et tout aussi toxiques pour l'Homme et l'envir onnement. Etant donné qu'ils peuvent être facilement transférés dans les eaux, leur quantification dans les principaux cours d'eau et les eaux de consommation semble essentielle.

Ainsi, les deux principaux objectifs de notre étude étaient :

1. Évaluer les **niveaux de contamination en HAPs** -comme principaux polluants de l'activité pétrolières – et leur **distribution dans les principaux bassins versants Amazoniens et de la côte Pacifique au Nord** (régions NEPC et NEAR impactées par les activités pétrolières) et au Sud du pays (SEAR et SEPC, répertoriées comme zone contrôle), afin de déterminer la qualité environnementale des eaux (phase dissoute et particulaire, mais aussi sédiments) des rivières situées en zone d'exploitation pétrolière et de raffinage mais aussi les risques impliqués pour la santé humaine,
2. Estimer **la qualité sanitaire** (liée au potentiel cocktail de métaux, métalloïdes et HAPs) **des eaux de consommation, en comparaison aux normes de potabilité** en vigueur dans le monde, dans un pays où l'accès à la ressource en eau reste très inégalitaire.

L'idée étant toujours de comparer nos zones *a priori* impactées par les activités extractives ou de raffinage à des zones jugées comme « témoins », car exemptes d'activités pétrolières.

A cela s'ajoutaient des sous-objectifs d'identification des sources des contaminants organiques et métalliques dans les eaux de consommation et de traçage du devenir des HAPs dans les eaux de surface. Nous avions également pour objectif de comparer les résultats obtenus avec les normes nationales et internationales de protection de l'environnement mais aussi de calculer des indices de risque sanitaire pour les éléments cancérigènes et non cancérigènes mesurés dans les eaux de consommation. Enfin, comme ce projet s'inscrit dans une démarche sociale d'amélioration et de développement dans un pays largement impacté, il nous tenait à cœur de pouvoir proposer des recommandations pour réduire le risque d'exposition des populations locales.

Plusieurs méthodes analytiques biogéochimiques, impliquant des analyses de molécules organiques comme de métaux lourds, ainsi qu'une approche sociologique, ont été combinées dans le cadre du programme de recherche interdisciplinaire ANR MONOIL dans lequel s'inscrit pleinement cette thèse. Au total 160 échantillons d'eau et 90 de sédiments ont été analysés,

dont 60% utilisés par les populations locales dans leurs activités quotidiennes. L'échantillonnage a été réalisé sur plusieurs années consécutives (2012-2016, dont 3 campagnes de terrain réalisées au cours de cette thèse), en saison sèche et saison humide, depuis le piémont andin jusqu'à la frontière péruvienne, et le long du bassin de la rivière Teaone jusqu'à l'embouchure de la rivière Esmeraldas dans l'océan Pacifique. Un contrôle de la qualité chimique a également été réalisé dans la partie sud du bassin, sur des tributaires non affectés par des activités extractives (minières ou pétrolières).

Les principaux résultats de cette recherche concernent alors la distribution des HAPs dans les eaux de surface et les sédiments, mais aussi la qualité sanitaire des eaux de consommation dans les zones impactées par les activités pétrolières.

- ***Pour les teneurs en HAPs dans les eaux de surface et les sédiments :***

Comme des valeurs non importantes se sont manifestées en aval de la pollution ponctuelle, sauf dans les échantillons les plus proches (< 1 km), on peut affirmer que les processus de production et de raffinage du pétrole ne sont pas des sources importantes de contamination ni sur la côte Pacifique ni dans la région Amazonienne. Étant donné que les résultats de la présente étude (phase dissoute) sont similaires aux valeurs observées dans les villes ayant certaines activités industrielles, agricoles et urbaines, nous affirmons que même avec seulement 5% de la population équatorienne vivant dans la région amazonienne, non seulement les processus pétroliers, mais aussi les activités urbaines et l'agriculture locale contribuent à la présence des HAP dans la phase dissoute. D'autre part, sur la côte Pacifique, la raffinerie d'Esmeraldas représente la principale source de pollution des eaux de surface, à moins de 1 km des effluents affectant la rivière Teaone, mais pas la rivière Esmeraldas, dont les valeurs restent similaires en amont et en aval du confluent avec la rivière Teaone. Cela a été confirmé par l'analyse hiérarchique des grappes appliquée à la phase sédimentaire, où la plupart des lieux analysés ne sont pas directement influencés par le pétrole brut frais, mais par des déchets anciens ou similaires au fond géochimique (sable bitumineux). HCA a montré différentes associations avec les principaux sites peuplés et les sites agricoles qui nécessitent une analyse plus approfondie afin de caractériser ces origines. Les efforts locaux visant à améliorer la qualité de l'environnement devraient se refléter dans les futures études sur la pollution locale dans les zones de raffinage équatoriennes.

Des quotients comme mPELQ et mERMQ étaient précis pour déterminer le risque environnemental, puisqu'une échelle est proposée. Mais un risque complet de danger pour l'homme basé sur les concentrations de sédiments pourrait aider à mieux comprendre le

risque pour les populations locales qui sont habituées à nager et à pêcher dans les rivières étudiées.

- ***Pour la qualité sanitaire des eaux de consommation :***

Aucune pollution par les hydrocarbures pétroliers les plus courants n'a été constatée dans les échantillons d'eau de consommation de notre étude. La principale préoccupation en lien avec les activités pétrolières et mise en évidence dans certaines sources d'eau potable est le toluène, ainsi que des concentrations totales élevées en méthylnaphtalène mesurées dans plusieurs puits profonds de la communauté de San Carlos (situés à proximité des camps pétroliers gérés par la société Rio Napo), sans toutefois dépasser les directives nationales et internationales.

Dans l'ensemble de la région amazonienne et le long de la côte du Pacifique, les approvisionnements en eau étudiés présentaient de très faibles niveaux de minéralisation, jusqu'à 10 à 100 fois inférieures aux concentrations minimales recommandées par l'OMS (OMS, 2006), à quelques exceptions près dans les puits profonds. Si des concentrations élevées en certains éléments majeurs peuvent affecter la santé humaine, les eaux acides et/ou faiblement minéralisées sont également à surveiller pour garantir la santé des habitants. Un pH acide peut accélérer la lixiviation des métaux toxiques et d'autres éléments toxiques présents dans les réseaux de distribution de l'eau et aussi en modifier le goût. En outre, le manque de minéraux peut avoir des effets néfastes directs sur la santé. Un autre problème lié à l'utilisation domestique régulière d'eau peu minéralisée est la perte de minéraux essentiels contenus dans les aliments pendant la cuisson, principalement le magnésium et la calcium et, dans une moindre mesure, les microéléments essentiels (Cu, Mn et Co). Un régime alimentaire peu diversifié du fait de conditions de vie précaires et de l'utilisation domestique d'eau déminéralisée ne pourrait alors pas fournir tous les éléments essentiels en quantité suffisante aux populations locales.

Par ailleurs, bien que les eaux investiguées restent conformes aux restrictions en lien avec leur consommation, notre étude a mis en évidence des limitations dans les normes en vigueur et leur évolution dans le temps. En effet, nous avons montré qu'au cours de la dernière décennie, la réglementation équatorienne (via INEN et TULSMA) a non seulement réduit le nombre de paramètres de contrôle, mais a également proposé des valeurs moins restrictives sans tenir compte des recommandations internationales. Les réglementations internationales, reposant sur des études épidémiologiques et d'évaluation des risques, apparaissent donc comme des références plus adéquates pour la qualité de l'eau à des fins de consommation. Néanmoins,

les seuils établis ne tiennent pas compte des effets « cocktail » de polluants, ni de l'exposition chronique et des effets éventuels à plus long terme.

Finalement, cette étude a montré que les conditions de vie précaires pourraient avoir plus de répercussions sur la santé que l'exposition à une eau impactée par les activités pétrolières environnantes, en Amazonie Equatorienne. Par ailleurs, la perception du risque prend ici tout son sens… les populations se tournent vers certains réseaux d'approvisionnements pour éviter des eaux qu'ils jugent *a priori* contaminées, sans aucune certitude scientifique…

Jusqu'à présent, en l'absence d'une reconnaissance satisfaisante des impacts historiques des activités pétrolières en Equateur, les habitants de l'Amazonie cristallisent leurs problèmes sur les entreprises pétrolières en ignorant ainsi d'autres sources de contamination et d'impacts sanitaires possibles, telles que les pratiques agricoles ou le manque de traitement de l'eau.

Enfin, les principaux résultats de cette thèse ont déjà été largement communiqués auprès de populations locales, notamment via les colloques de restitution du programme MONOIL réalisés à Quito mais aussi dans les différentes provinces où ont eu lieu les échantillonnages d'eaux (surface et consommation) et sédiments. Notre objectif était un transfert des données acquises vers les populations, sous des formes vulgarisées et percutantes, dans le simple objectif d'éveiller la connaissance des habitants et de leur éviter de faire certains choix par dépit ou simple ignorance des enjeux sanitaires et environnementaux.

Recommandations et perspectives

D'un point de vue environnemental, la distribution des polluants proposée dans le Chapitre 1 ne considère que les molécules organiques HAPs. Malheureusement, par manque de temps, les résultats des composés métalliques dans les eaux de surface et les sédiments des zones d'étude n'ont pas pu être intégrés dans ce travail de thèse, mais les données en cours de traitement sont prometteuses. Les résultats montrent notamment des contaminations de ces eaux en métaux lourds très localisées et sur de petits tronçons : au pied de plates-formes pétrolières qui fuient ou de piscines non remédiées ou en voie de remédiation. Si l'on se réfère aux normes nationales et internationales de potabilité, ces points de contamination n'affectent pas la qualité des rivières à l'échelle du bassin versant. Cependant, de fortes teneurs en sodium, chlorures (et HAP comme évoqué précédemment) ont été mesurées dans les eaux de certains puits profonds (> 8 m), mettant en évidence un mélange d'eaux souterraines naturelles avec des rejets d'eaux de formation, caractérisées par de fortes

teneurs en sels et en hydrocarbures.

D'un point de vue sanitaire, l'étude des eaux de consommation dans le pays a montré que la principale recommandation à apporter à la population est de saler l'eau utilisée pour la cuisine, afin de garantir des apports satisfaisants en sels minéraux essentiels au bon développement des personnes. Avant la consommation, il semble primordial également de désinfecter ou de faire bouillir toutes les sources d'eau de la région amazonienne avant de les utiliser. Au niveau national, les politiques publiques devraient s'attaquer à ce problème en étendant les systèmes d'approvisionnement en eau potable et de traitement des eaux usées des zones rurales aux communautés vivant dans des régions reculées de la région amazonienne.

En termes de risques potentiellement associés à la présence, même en faible quantité de métaux lourds et métalloïdes dans les eaux de surface et les sédiments, une première évaluation quantitative des risques sanitaires sera proposée dans une étude à venir.

Par ailleurs, il est important de noter que la législation en termes d'éléments contaminants propose des valeurs seuils de risque par élément (organique ou inorganique) sans prendre en compte les risques sanitaires liés à l'effet cumulé de ces contaminants. Il serait alors judicieux de pouvoir en tenir compte par la suite afin d'évaluer les impacts potentiels combinés de ces composés sur la santé humaine.

Par la suite, nous envisageons aussi de réaliser une évaluation sanitaire des risques encourus par les populations en intégrant tous les facteurs de risques mais aussi en prenant en compte l'ensemble des voies d'exposition (inhalation, ingestion et contact cutané), ce qui suggère un état des lieux très détaillé des régimes alimentaires, des habitudes de vie, des expositions selon le genre, l'âge, l'origine et les prédispositions sociales, etc.

Il est également conseillé aux habitants de sélectionner leurs voies d'approvisionnement en eau de consommation, lorsqu'ils en ont la possibilité. Les populations locales vivant dans des zones touchées par les activités pétrolières subissent encore la prise en compte insuffisante des impacts historiques de l'exploitation pétrolière par l'État équatorien, ce qui confirme que les informations peuvent être considérées comme une sorte de pouvoir qui devrait être partagé. Un travail sociétal conséquent est ici à développer afin que la perception du risque, parfois erronée, ne conduise pas à des mises en danger supplémentaire, par manque de confiance dans les entreprises pétrolières et leurs agissements. Cette donnée concernant la perception du risque a fait l'objet d'étude approfondies, notamment via le volet sociétal du programme MONOIL, et dont la confrontation avec nos données a permis de mieux

comprendre les habitudes et modes de vie, souvent à l'origine d'une exposition inconsciente et finalement plus forte.

Cette perception du risque et les interactions avec les sciences sociales au cours de cette thèse ont mis en évidence l'intérêt majeur de l'interdisciplinarité dans ce type de préoccupation environnementale et sanitaire, et ses atouts pour ouvrir un nouveau champ des possibles dans le traitement et la mise en commun des données scientifiques sur une même zone d'étude.

Enfin, le cas de l'Equateur, largement étudié dans cette thèse mais aussi à travers tout le programme MONOIL, pourra être transposé à des pays voisins ou des sociétés similaires, subissant les mêmes dommages historiques des activités extractives, pétrolières ou minières, et partageant les mêmes espoirs de remédiation.

CONCLUSIONS, RECOMMENDATIONS AND PERSPECTIVES (EN)

General Conclusion

Ecuadorian economy is historically linked to the incomes of various exported raw materials, with oil being the most important, accounting for half of the exported products. Today, oil economy represents 45% of the general budget of Ecuador, whereas most of which is allocated to debt payment. The majority of oil reserves are located in the Amazon Region, and more precisely in the Sucumbíos and Orellana provinces. In January 2012, national oil production represented 15.6 million barrels, nearly 72% corresponding the state-owned Petroecuador. With its geo-resources, the Amazon region alone accounts for the largest share of the country's income. Even if Amazon region occupies 45% of the country's territorial area, it accounts for only 5% of the Ecuadorian population (of which 71% are living in poverty, compared to 45% at the national level, INEC, 2010). Due to current and past intense-oil activities (extraction and refining) in Ecuador, the environment of the Amazon regions on the one hand and the Pacific coast on the other has often been affected by contamination.

Actually, for over 40 years, environmental contamination caused by oil industry has been punctual, accidental or continuous, and distributed over a large part of the Ecuadorian Amazon, mainly in the northern part of the country. The main sources of contamination are the discharges of liquid hydrocarbons and formation water into soils, surface and groundwaters; as well as gaseous discharges into the atmosphere. The environmental effects are related to the different phases of exploration and exploitation of petroleum; from seismic exploration, perforation, production, to transport and refining. The oil industry process generates highly toxic waste (sludge and liquids) that can be temporarily stored in pits, sealed or not, and then burned or re-injected into perforated areas underground or directly discharged into soil and surface water. In particular, extraction process generates "formation waters" that contain high quantities of salts, heavy metals and oil in "emulsion". In addition to this daily contamination (Maldonado and Narvaez, 2005), there are leaks related to pipe breaks or malfunctions in operating wells. Unfortunately, these accidents are still frequent and difficult to control.

Even though the real impact of these oil activities on the quality of surface waters and sediments has long been assumed, few studies have really assessed these impacts and their consequences on local human populations, in a country where social and health difficulties remain significant. Oil waste mainly contains metals and metalloids co-emitted with PAHs, also

toxic for humans and the environment. Since these contaminants can be easily transferred to water, their quantification in major rivers and drinking waters seems essential.

Thus, the two main objectives of our study were:

1. To assess the **contamination level of PAHs** as the main pollutants of oil activity, and their **distribution in the main rivers from the Amazon and Pacific** coast in the North (NEPC and NEAR regions affected by oil activities) and in the South of the country (SEAR and SEPC, listed as control areas), in order to determine the environmental quality of water (dissolved phase, but also sediments) in rivers located in extraction and refining areas, but also the risks involved for human health;
2. To assess **the health quality** (related to the potential cocktail of metals, metalloids and PAHs) **of drinking waters, by comparison with guidelines currently used worldwide,** in a country where access to water resources remains highly inequitable.

The main purpose of this manuscript was then to compare our areas supposed to be impacted by extraction or refining activities with areas considered as "control", as they are free of oil activities.

In addition, some specific objectives were proposed for identifying the sources of organic and metallic contaminants in drinking water and for tracing the fate of PAHs in surface water. We also aimed to compare the results obtained with national and international environmental protection standards and to calculate health risk indices for carcinogenic and non-carcinogenic elements measured in drinking water. Finally, as this project is included in a larger program (ANR MONOIL) with a strong social dimension of improvement and development in a country widely impacted, we have also planned to propose recommendations to reduce the risk of exposure of local populations.

Several biogeochemical methods, involving analyses of organic molecules and heavy metals, as well as a sociological approach, have been combined within the framework of the interdisciplinary research program ANR MONOIL, in which this thesis is fully integrated. A total of 160 water samples and 90 sediment samples were analyzed, 60% of water samples belongs to sources widely used by local populations in their daily activities. Sampling was carried out over several consecutive years (2012-2016, including 3 field campaigns), in both the dry and wet seasons, from the Andean foothills to the Peruvian border; and along the Teaone River to the mouth of the Esmeraldas River in the Pacific Coast. A chemical monitoring of the environmental quality was also performed in the southern part of the basin, on areas not affected by (mining or oil) extractive activities.

The main results of this research focused on the distribution of PAHs in surface waters and sediments, but also on the health quality of drinking water in areas impacted by oil activities.

- ***For PAH contents in surface waters and sediments:***

Since not important values were manifested downstream of punctual pollution, except in the closer samples (< 1km); we can affirm that oil production and refining processes are not important sources of contamination neither in the Pacific Coast nor in the Amazon Region. Since results in the present study (dissolved phase) are similar to values found in cities with some industrial, agricultural and urban activities, we claim that even with only 5% of the Ecuadorian population living in the Amazon region, not only oil processes, but also urban activities altogether with local agriculture contribute to the presence of PAHs in the dissolved phase. On the other hand, in the Pacific Coast, the Esmeraldas Refinery represents the main source of surface water pollution, within 1 km from the effluents affecting the Teaone River, but not the Esmeraldas River, whose values remain similar upstream and downstream the confluence with the Teaone River. It was confirmed by the hierarchical cluster analysis applied to the sedimentary phase, where most of the analyzed places are not directly influenced by fresh crude oil, but by ancient waste or similar to the geochemical background (bituminous sands). HCA showed different associations with the main populated sites and agricultural emplacements that need an deeper analysis in order to characterize these origins. Local efforts to improve environmental quality should be reflected in future studies about local pollution in Refining Ecuadorian zones.

Quotients like mPELQ and mERMQ were accurate for determining the environmental risk, since a scale is proposed. But a complete human hazard risk based in sediments concentrations could help to better understand the risk to local populations that are accustomed swim and fish in the studied rivers.

- ***For drinking water quality:***

No pollution by the most common hydrocarbons was found in the drinking water samples collected for this study. The main concern related to oil activities and identified in some drinking water sources is toluene, as well as high total methylnaphthalene concentrations measured in several deep wells in the San Carlos community (located near the oil camps managed by Rio Napo), but not exceeding national and international guidelines.

Across the Amazon region and along the Pacific coast, the water supplies studied had very low levels of mineralization, about 10 to 100 times below the minimum concentrations recommended by WHO (WHO, 2006), with a few exceptions in deep wells. Not only high

concentrations of some major elements can affect human health; acid and/or low mineralized waters should also be monitored to ensure the health of residents, as well. An acidic pH can for example accelerate the leaching of toxic metals and other toxic elements from water distribution systems changing their taste. In addition, lack of minerals can have direct detrimental effects on human health. Another problem related to the regular domestic use of low mineralized water is the loss of essential minerals contained in food during cooking, mainly magnesium and calcium and, to a lesser extent, essential microelements (Cu, Mn and Co). A poorly diversified diet due to precarious living conditions and the domestic use of demineralized water would then not be able to provide all the essential elements in sufficient quantities to local populations.

Moreover, although the waters investigated remain in compliance with the regulatory restrictions related to their consumption, our study highlighted limitations in the current standards and their evolution over time. Indeed, we have shown that over the last decade, Ecuadorian regulations (INEN and TULSMA) have not only reduced the number of control parameters, but have also proposed less restrictive values without taking into account international recommendations. International regulations based on epidemiological and risk assessment studies appear to be more appropriate references for controlling the quality of water for human consumption; nevertheless, these thresholds do not take into account the "cocktail effect" of pollutants, the chronic exposure and the potential long-term effects. Finally, this study showed that precarious living conditions could have more impact on health than exposure to water impacted by surrounding oil activities in Ecuador. Moreover, the perception of risk takes here a high importance... people often avoid some water supply networks as they consider them as contaminated *a priori*, without any scientific demonstration...

So far, in the absence of a satisfactory recognition of the historical impacts of oil activities in Ecuador, Amazon people are crystallizing their problems on oil companies, thus in this way, they ignore other sources of contamination and possible health impacts, such as agricultural practices or lack of water treatment.

Finally, the main results of this thesis have already been widely communicated to local populations, in particular through the restitution conference of the MONOIL program held in Quito but also in the various provinces where surface and drinking water as well as sediment samplings took place. Our objective was to transfer the acquired data to the local populations, in popularized and powerful forms, with the simple objective of awakening the knowledge of

the inhabitants and avoiding them to make some choices out of spite or for lack of information about the health and environmental issues.

Recommendations and perspectives

From an environmental point of view, the distribution of pollutants proposed in Chapter 1 only considers organic PAH molecules. Unfortunately, due to time constraints, the results of metallic compounds in surface waters and sediments in the studied areas could not be integrated into this thesis work, but the data being processed are promising. The results show in particular a contamination of these waters with very localized heavy metals and on small sections: at the foot of leaking oil platforms or pools that are not remedied or are being remedied. According to national and international drinking water standards, these contamination points do not affect the quality of rivers at the scale of the catchment area. However, high levels of sodium, chlorides (and PAHs as mentioned above) have been measured in the waters from some deep wells (> 8 m), showing a mixture of natural groundwater with formation water discharges, characterized by high salt and hydrocarbon contents.

From a health point of view, the study of drinking water in this country has shown that the main recommendation to be made to the population is to salt the water used for cooking, in order to guarantee supplies of mineral salts essential for the proper development of people. Before consumption, it also seems essential to disinfect or boil water whatever the sources in the Amazon region before using them. At the national level, public policies should address this problem by extending rural drinking water supply and wastewater treatment systems to communities in remote areas of the Amazon region.

In terms of risks potentially associated to the presence, even in small quantities, of heavy metals and metalloids in surface waters and sediments, a first quantitative assessment of health risks will be proposed in a future study.

In addition, it is important to note that legislation in terms of contaminants proposes threshold risk values per element (organic or inorganic) without taking into account the health risks associated with the cumulative effect of these contaminants. It would then be appropriate to be able to take them into account later in order to assess the combined potential impacts of these compounds on human health.

Subsequently, we also propose to carry out a health assessment of the risks incurred by

populations by integrating all risk factors but also by taking into account all exposure routes (inhalation, ingestion and dermal contact), which suggests a very detailed inventory of diets, lifestyle habits, exposures by gender, age, origin and social predispositions, etc.

Residents are also advised to select their drinking-water supply sources, where they have the opportunity to do so. Local populations living in areas affected by oil activities still suffer from insufficient attention of the historical impacts of oil exploitation by the Ecuadorian State, which confirms that information can be considered as a kind of power that should be shared. A substantial amount of societal work needs to be developed here so that the sometimes erroneous perception of risk does not lead to additional threats, due to a lack of confidence in oil companies and their actions. This data on risk perception has been the subject of in-depth studies, particularly via the societal component of the MONOIL program, whose comparison with our data has made it possible to better understand habits and lifestyles, often at the origin of unconscious and ultimately higher exposure. This perception of risk and the interactions with the social sciences during this manuscript highlighted the major interest of “interdisciplinarity” in this kind of environmental and health research, and its advantages in opening up a new field of possibilities in the processing and sharing of scientific data in the same study area.

Finally, the case of Ecuador, which is widely studied in this thesis but also throughout the MONOIL program, could be transposed to neighboring countries or similar social groups suffering the same historical damage from oil extraction or mining activities, and sharing the same hopes of remediation.

LIMITATIONS

1- One of the main difficulties found during the development of this project was the impossibility to find a non-anthropized zone. Areas considered as reference (geochemical background) showed concentrations similar to the anthropized areas.

2-The distance between the different sampling points generates the problem of homogenization in the specialization of the sites, since the points considered in this study are extremely distant from each other (some kilometers) with important different characteristics (Andean foothills and amazon lowland).

3-Sediments are considered as excellent tracers of historic pollution, but scraping the 2 centimeters of the first sedimentary layer is not enough to characterize the contaminating history of oil activities. In addition to not knowing the dynamics of pollutant degradation, the sedimentation velocity cannot be defined (hydrological dynamics of each sampling site).

4-The relative abundance of PAHs in sediments is considered non-variable with time in samples from the same source. So, ancient samples polluted by petrol can present different PAHs distribution than recently polluted sites, causing a misinterpretation of the PAH-distribution patterns.

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ANNEX A: Composition of Ecuadorian crude oil

Table A-1. Trace elements (μg.g^{-1}) and PAHs (ng.g^{-1}) concentrations (average±SD) in Ecuadorian Amazon crude oil and natural bituminous sandstone.

PARAMETER	NATIONAL PIPELINE	AUCA 03 OIL WELL	AUCA 08 WASTE POOL	BITUMINOUS SANDSTONES
Hg	<1	<1	<1	<1
Al	<0.025	<0.025	3.48/2.42*	2.03±0.14
Ti	<1	<1	108±5	240±17
V	158.1±0.3	278±11	305±36	25±2
Cr	<5	<5	<5	<5/12*
Mn	<1	<1	34±4	2.7/1.7*
Fe	<20	57±8	1.55±0.08	2.37±0.02
Co	0.45±0.01	0.77±0.05	1.82±0.04	0.5±0.1
Ni	58±2	87±4	99±11	24±2
Cu	<1	<1	4.1±0.6	2.36±0.5
Zn	<5	<5	13.7±0.2	<5
As	<0.1	<0.1	0.33±0.01	2.4±0.3
Mo	<0.5	0.6/1.9*	0.93±0.02	1.5±0.3
Cd	<0.1	<0.1	<0.1	<0.1
Ba	<0.1	7±1	133±5	16.0±0.7
Pb	<0.2	<0.2	3.0±0.5	30/59*
U	<0.1	<0.1	0.14±0.01	0.23±0.02
N	391159	274832	22	<20
Ac	<2.30	<2.30	<2.30	81
Ace	12778	9336	841	<2
Fl	35872	25799	1783	101
Ph	146635	98999	6496	<20
A	3861	1050	335	<3
BaA	1567	1209	836	427
Ch	21563	17642	10482	3760
BbjkF	2747	2386	2615	1810
BaP	460	<0.35	445	582
IPy	<0.35	<0.35	328	<0.35
DBA	443	332	303	286
BPe	2476	2167	1752	1330
BePy	5854	4984	3213	2205
Pe	<0.35	<0.35	<0.35	852
MCh	53487	48686	27179	21310
BNT	15256	14730	7172	<0.35
3MPh	84939	64407	14700	<3
2MPh	87773	77322	17085	<3
MA	4483	1236	715	<3
MPhMA	161054	122653	36321	<3
1MPh	112516	60351	10267	<3
∑DMPh	758012	475565	205049	9329
∑TMPh	688377	430727	241733	41451

Table A.1. Trace elements (μg.g^{-1}) and PAHs (ng.g^{-1}) concentrations (average±SD) in Ecuadorian Amazon crude oil and natural bituminous sandstone. (continued)

PARAMETER	NATIONAL PIPELINE	AUCA 03 OIL WELL	AUCA 08 WASTE POOL	BITUMINOUS SANDSTONES
2MN	830311	474908	725	55
1MN	650847	308722	836	70
∑DMN	3068374	1579610	41148	9653
∑TMN	4381888	2007652	218295	10514
∑TeMN	1854331	1097326	235404	9595
DBT	88143	103169	7846	<3
∑MDBT	2747	2386	2615	1810
∑MN	391159	274832	22	<20

* heterogeneous sample; N=naphthalene; Ac=acenaphthylene; Ace=acenaphthene; Fl= fluorene; Ph=phenanthrene; A=anthracene; BaA=benzo[a]anthracene; Ch= chrysene+triphenylene; BbjkF=benzo[bjk]fluoranthene; BaP=benzo[a]pyrene; IPy=indeno[1,2,3-cd]pyrene; DBA=dibenzo[ah]anthracene; BPe= benzo[ghi]perylene; BePy=benzo[e]Pyrene; Pe=perylene; MCh=methylchrysene; BNT= 2,1benzonaphtothiophene; 3MPh=3Methylphenanthrene; 2MPh=2methylphenanthrene; MA=2methylanthracene; MPhMA=[9+4]methylphenanthrene+ 1methylanthracene+ 4,5 methylenephenanthrene; 1MPh=1methylphenanthrene; ∑DMPh= ∑dimethylphenanthrene; ∑TMPh=∑trimethylphenanthrene; 2MN=2methylnaphthalene; 1MN=1methylnaphthalene; ∑DMN=∑dimethylnaphthalene; ∑TMN= ∑trimethylnaphthalene; ∑TeMN=∑tetramethylnaphthalene; DBT=dibenzothiophene; ∑MDBT=∑methyldibenzothiophene; ∑MN= Σmethylnaphthalenes; i=interference.

ANNEX B: Article published in *Science of the Total Environment*

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

ANNEX B

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

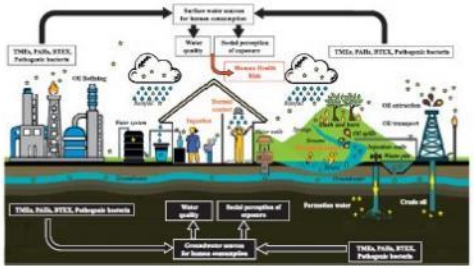
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HIGHLIGHTS

- 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.

GRAPHICAL ABSTRACT



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ABSTRACT

The unregulated oil exploitation in the Northern Ecuadorian Amazon Region (NEAR), mainly from 1964 to the 90's, led to toxic compounds largely released into the 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. The concentrations of major ions, trace elements, PAHs (polycyclic aromatic hydrocarbons) and BTEX (benzene, toluene, ethylbenzene, xylenes) were analyzed in different water sources to evaluate the impacts of oil extraction and refining. Samples were 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 aluminum. 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

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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.

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1. Introduction

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 accidents occurring throughout the history of oil production demonstrates the devastating effects and the risks involved for exposed populations (Amiard, 2017; Levy and Nassetta, 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 2017 (Banco Central del Ecuador (BCE), 2010; Calderón et al., 2016; MCE, 2017). On the other hand, Ecuadorian oil industry is characterized by a long-term history of social and environmental conflicts (Fontaine, 2007).

The oil industry exerted with inadequate environmental standards is strongly suspected of polluting surface and ground waters, particularly in Orellana and Sucumbíos provinces where 80% of total oil spills and 97% of waste pits were recorded (MAE, 2015). During 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, since the 2000's the Ecuadorian legislation prohibited these practices, binding oil companies to redirect these waters into ancient oil wells (Decree 1215, 2001). Nevertheless, local inhabitants testified that illegal polluting discharges are still released punctually and 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 genotoxic and carcinogenic effects (IARC, 2010). Twelve PAHs and BTEX have been classified as probable or suspected carcinogens in humans but only benzo(a)pyrene (BaP) and benzene are confirmed as carcinogenic (ATSDR, 2007; IARC, 2018). Despite their high toxicity, volatility and solubility in water, BTEX are not commonly studied; noting that they are responsible for acute and chronic effects including eyes and throat irritation, headaches, tachycardia, leukemia, affections to nervous system, cancer and death (Leusch and Bartkow, 2010; Mitra and Roy, 2011; Neghab et al., 2015). Previous epidemiological studies reported numerous chronic effects including psychological disorders, endocrine and reproductive affections and cases of cancers (Hurtig and San Sebastián, 2002; Levy and Nassetta, 2011; Ramirez et al., 2017; Clínica Ambiental, 2017; Webb et al., 2018). Genotoxic analyses on individuals from the NEAR showed that the exposure to hydrocarbons has caused DNA damage and increased the risk of developing cancer (Paz-y-Miño et al., 2008).

Although hydrocarbons constitute the main fraction (75%) of crude oil, petroleum is a complex mixture of elements, such as sulfur, major cations, anions, trace metal(oid)s (TME) and organic molecules. Major elements (potassium (K), magnesium (Mg), sodium (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 formation waters, while barium (Ba), cobalt (Co), arsenic (As) and lead (Pb) salts are added during the extraction, transportation or storage (Amiard, 2017). Though certain metallic elements are essential for biological functions, most of them could be highly toxic, even at low concentrations, and can cause hazardous effects due to their tendency to bioaccumulate (Jørgensen and Fath, 2010). In 2017, IARC listed cadmium (Cd), As, Cr and Ni as probed carcinogenic elements for humans (lungs, prostate, bladder, kidney, liver and stomach cancers); they can also affect nervous, immune and reproductive systems and can induce 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.

In Ecuador, access to a water supply network has increased in recent years but the percentages of the supplied population are very heterogenous over the territory; in the studied cantons, it varies from 26,6% in Aguarico, to 33,7% in Shushufindi, 41,6% in Joya 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 washing clothes) is still a high-risk factor of exposure to toxic pollutants either by dermal contact or ingestion. In Esmeraldas city, along the Pacific coast, where refining activities take place, the water distribution system reaches most of the households but is unreliable supply and safety wise. Therefore, Amazonian and Esmeraldas inhabitants rely on different water sources such as rivers, springs, streams, rainwater, or private wells; sources that are 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?

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2. Materials and methods

2.1. Study area

Two oil areas were selected for this study (Fig. 1). The first area is located in the Northern Ecuadorian Amazon Region (NEAR) between 76°30′20″–77°12′00″W and 00°05′01″N-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 pre-cleaned 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 7500 CE). Total Hg analysis were performed according to the US EPA Methods 1631 (US Environmental Protection Agency (US EPA), 2002) using

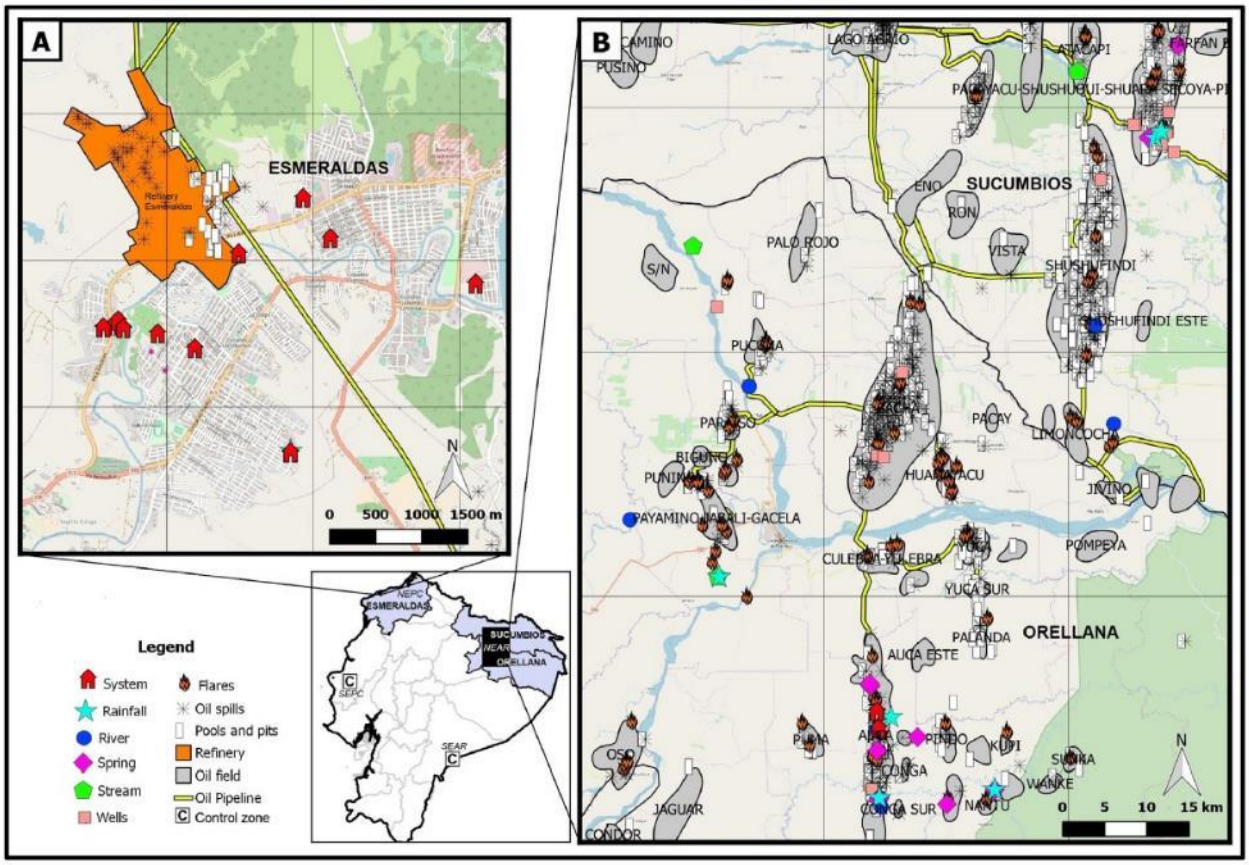


Fig. 1. Hazards description (flares, oil spills, pools and pits, refinery, oil fields and pipelines) and sampling points of drinking waters (from various sources: rainfall, river, spring, stream, well) in four study areas: A) Northern Ecuadorian Pacific Coast (NEPC), B) Northern Ecuadorian Amazon Region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

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oxidation-reduction with BrCl and $SnCl_2$, 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

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).

An Agilent Technologies 7890A/5975C GC/MS (Palo Alto, CA, USA) was used for the analysis of BTEX. A MPS2XL autosampler (Gerstel®) was used to hold the 65 μm PDMS/DVB SPME fibre (Supelco) during extraction and injection. After the addition of perdeuterated surrogate standards, the fibre was immersed into the 10 mL water sample with agitation (250 rpm) at 40 °C during 30 min. After extraction, the fibre was thermally desorbed for 3 min into the liner of the GC injector port at 220 °C in pulsed splitless mode (25 psi, 1.5 min). Helium (6.0) was used as the carrier gas at a flow rate of 2 $mL{\cdot}min^{-1}$. Analytes were separated on a DB-624 column (30 m × 0.32 mm, 1.8 μm film thickness; Agilent Technologies, J&W Scientific). The column oven program was as follows: 0 °C (5 min) (liquid nitrogen) to 150 °C (1 min) at 5 $°C{\cdot}min^{-1}$ and then to 260 °C (8 min) at 30 $°C{\cdot}min^{-1}$. The MSD was operated with electron impact ionization (70 eV) in selected ion monitoring (SIM) mode. The transfer line, source and quadrupole temperatures were 260, 230 and 150 °C, respectively. Parent and alkylated PAHs were analyzed using an Agilent Technologies 7890A/5973 GC/MS (Palo Alto, CA, USA) (Kanan et al., 2012). A GC Sampler 120 (Agilent Technologies) was used to hold the 100 μm PDMS SPME fibre fibre (Supelco) during extraction and injection. After the addition of perdeuterated surrogate standards, the fibre was immersed into the 8 mL water sample with agitation (250 rpm) at 40 °C during 60 min. After extraction, the fibre was thermally desorbed for 3 min into the 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 $mL{\cdot}min^{-1}$. Analytes were separated on a HP-5MS-UI column (30 m × 0.25 mm, 0.25 μm 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 $°C{\cdot}min^{-1}$. 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.

PAHs and BTEX were quantified by their perdeuterated surrogate standards using their molecular ions (SIM mode). Analyzed compounds (and acronyms) and their limits of quantification (LQs) are listed in Table SI_2 and Table SI_4, respectively. A fibre blank was measured before each water sample by exposing the SPME fibre in an empty vial under the same conditions as the samples. A blank sample (reagents and surrogate standards) and a control sample (blank sample spiked with model compounds) were performed for each batch of experiments in order to check the background contamination and the analytical performance. Whole-method accuracy was determined on spiked water samples (at 10 $ng{\cdot}L^{-1}$ in Milli-Q water and 50 $ng{\cdot}L^{-1}$ in Vittel water for PAHs and BTEX, respectively) and remained between 100 and 105% (CV < 10%) for parent and alkylated PAHs 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 compounds present in blanks. For these latter compounds, LQs were determined using blank levels, assuming at least a factor three between the analyte mass in the sample and that found in the blank. LQs are in the range 0.3–5.0 $ng{\cdot}L^{-1}$ for parent and alkylated PAHs, and 2–9 $ng{\cdot}L^{-1}$ for BTEX, except for benzene (100 $ng{\cdot}L^{-1}$).

2.3.3. Microbiological analysis

Water samples were collected in sterile flasks, refrigerated and analyzed within 12 h of collection. One mL of raw sample was plated onto selective 3 M™ Petrifilm™ 6404/6414/6444 plates (3 M 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 and 250 colonies of total coliforms per plate.

2.4. Sociological methods

"Risk culture" refers to the oil contamination risks awareness, behaviors 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 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.).

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, 2015b).

Mathematical equations of the Probabilistic Risk Assessment (as published by Barraza et al., 2018) allow us to evaluate the Hazard Index (HI) and the Total Cancer Risk (TCR), which are defined as the addition of individual quotients of non-carcinogenic (HQ) and carcinogenic (CR) elements respectively, obtained from the average daily dose (ADD), the lifetime average daily dose (LADD) and the references doses (RfD) (US Environmental Protection Agency (US EPA), 2015a, 2015b). For drinking water, we supposed a daily consumption rate of 3 L and 1.5 L for adults and children, respectively and an annual exposure frequency of 350 days per year, assuming that people moved

[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.

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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).

2.6. Statistical analysis

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.

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), 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 $\mu S \cdot cm^{-1}$; average: 122 ± 204 $\mu S \cdot cm^{-1}$) showed that all the samples were lower than the maximum recommended value (1100 $\mu S \cdot cm^{-1}$), except in a deep well (26 m) in Pacayacu (NEAR). Only 19% of the samples were in line with the WQG used in France (200–1100 $\mu S \cdot cm^{-1}$): most of the water samples (78%) showed conductivity lower than 200 $\mu S \cdot cm^{-1}$, and can be considered as demineralized waters. In the Amazon Region, rainwaters showed the lowest conductivity in both, the oil (11.9 ± 12.9 $\mu S \cdot cm^{-1}$) and control area (5.21 $\mu S \cdot cm^{-1}$). Only the deep wells (272.2 ± 348.5 $\mu S \cdot cm^{-1}$) and system waters (224.3 ± 152.2 $\mu S \cdot cm^{-1}$) in the NEAR, and river surface water (237.7 ± 139.2 $\mu S \cdot cm^{-1}$) in the SEAR showed conductivity higher than the recommended value (200 $\mu S \cdot cm^{-1}$). However, in Esmeraldas, the tap water conductivity never reached the minimum WQG (200 $\mu S \cdot cm^{-1}$).

Concerning the total dissolved salts (TDS) content of the samples, it was found to be very low falling below the minimum concentration of 100 $mg \cdot L^{-1}$ and the optimal range of 250–500 $mg \cdot L^{-1}$ set by WHO. Only water from deep wells and the distribution system met the minimum recommended value.

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 $mg \cdot L^{-1}$ recommended by WHO (2005) for dental health. Similarly, most of the major cations' concentrations (for example Ca and Mg) were lower than the minimum 2005 WHO 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 $\mu g \cdot L^{-1}$, 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 $\mu g \cdot L^{-1}$, and averaged 72 $\mu g \cdot L^{-1}$; 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 $\mu g \cdot L^{-1}$), and *a fortiori* France and Canada (50 $\mu g \cdot L^{-1}$), 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 μg/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 ± 5.44 $\mu g \cdot L^{-1}$) and the maximum value (10.57 $\mu g \cdot L^{-1}$), 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 ± 0.097 $\mu g \cdot L^{-1}$) 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 $ng \cdot L^{-1}$) 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 $ng \cdot L^{-1}$) close to the WQG (1000 $ng \cdot L^{-1}$), 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 $CFU \cdot 100\ mL^{-1}$, 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

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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).

Parameter	NEAR							SEAR					NEPC		SEPC	
	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*
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]	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*
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*	–	–	–	–	–
Al[e]	110 ± 230	32 ± 55	64 ± 93	126 ± 202	340 ± 755	113 ± 79	13,693 ± 23,475	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*
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*
As[e]	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*

ANNEX B

Table 1 (*continued*)

Parameter	NEAR							SEAR					NEPC		SEPC	
	Deep well	Rainfall	River	Shallow well	Spring	Stream	System	Rainfall	River	Spring	Stream	System	Rainfall	System	System	Shallow well
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); ## = °C; *single value (n = 1); **Ca + Mg (mmol·L^{-1}); [a] = µS·cm^{-1}; [b] = mg·L^{-1}; [c] = %saturation; [d] = ng·L^{-1}; e = µg·L^{-1}.

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 (HIing) showed a contribution of 99 to 100% to the non-carcinogenic total health risk (THI). Compared to the reference value (US EPA, 2015a, 2015b), 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 of the country; this elevated HI (1.8) is mainly explained by the Cd content (HQ = 1.5).

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 higher than the reference value (US EPA, 2015a, 2015b). The highest THI values were found in deep wells waters of the NEAR, two in Pacayacu (HI = 1.6 and 0.61 due to Mn concentrations), and two in Dayuma (HI = 1.32 and 1.38 explained by As concentrations), in a private well and in the stadium, respectively. Individually, hazard quotients >1 in rainwater were found in the whole Amazon region, being Zn the element that contributed to most of the total hazard index (HQ of Zn = 1.01 and 1.06, in the NEAR and SEAR respectively). Finally, in the system water from Dayuma (NEAR), we found one point with a high concentration of Al in Auca 09 field corresponding to THI equal to 3.9. In the NEPC, the highest risk explained by Cd (HI = 3.13) and As (HI = 0.38) concentrations were found in Esmeraldas, in the potable water pumping station and in a particular house, 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 dermal-HI, 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.

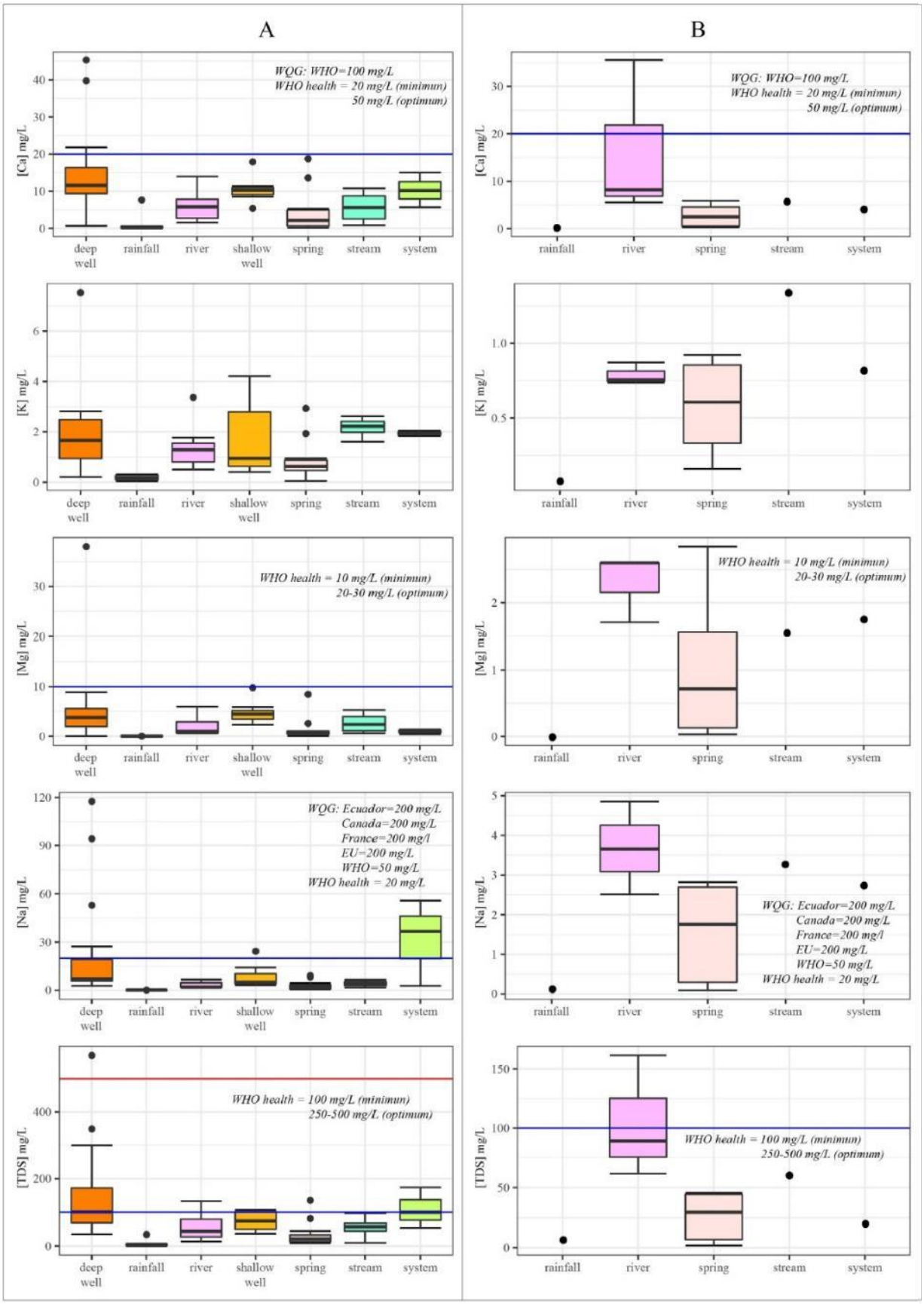
It is interesting to notice that, the hazard quotient of arsenic represents between 20% and 49% of the total ingestion HI (Fig. 4), while As concentrations never exceeded 3 µg·L^{-1}. In the Total Cancer Risk (TCR) calculated for carcinogenic elements (As, Cd, Cr and Ni), arsenic contributes with 51%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

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 ± 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 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

ANNEX B


A
B
[Ca] mg/L
WQG: WHO=100 mg/L
WHO health = 20 mg/L (minimun)
50 mg/L (optimum)
[K] mg/L
[Mg] mg/L
WHO health = 10 mg/L (minimun)
20-30 mg/L (optimum)
[Na] mg/L
WQG: Ecuador=200 mg/L
Canada=200 mg/L
France=200 mg/l
EU=200 mg/L
WHO=50 mg/L
WHO health = 20 mg/L
[TDS] mg/L
WHO health = 100 mg/L (minimun)
250-500 mg/L (optimum)
deep well
rainfall
river
shallow well
spring
stream
system

ANNEX B

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 trimethylnaphthalenes 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).

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.

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 $mg \cdot L^{-1}$, respectively, and an optimum range of 20–30 and 40–80 $mg \cdot L^{-1}$, respectively. For total water hardness, the sum of Ca and Mg should be 2 to 4 $mmol \cdot L^{-1}$ (Kozisek, 2005). In rainwater, the most important drinking water source for Amazonian communities, the Mg and Ca average concentrations were <0.01 and 1.28 $mg \cdot L^{-1}$, respectively. Average concentration of Na in rainwater was 0.12 $mg \cdot L^{-1}$, 2000 less than the minimum recommended value (WHO, 2011).

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) 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's 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.

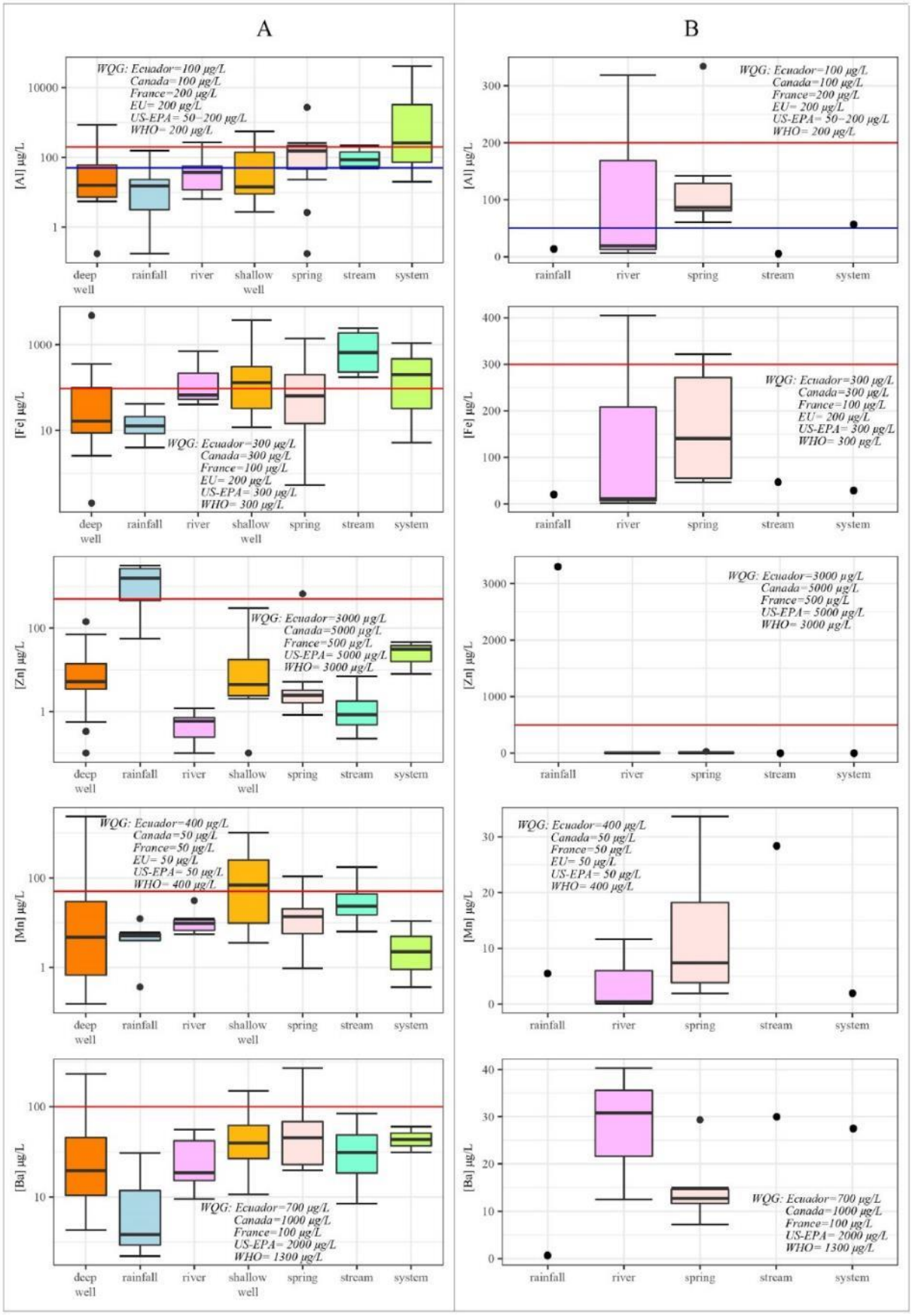
4.3.1. Legal limits

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 $mg \cdot L^{-1}$ in 2006 to 0.4 $mg \cdot L^{-1}$ 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) 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 $NMP \cdot 100\ mL^{-1}$ in 2006 to 1.1 $NMP \cdot 100\ mL^{-1}$ currently, and eliminating total coliforms guidelines.

The second Ecuadorian regulation, TULSMA, is applicable to natural water sources for human consumption prior to any treatment. In its

Fig. 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. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

ANNEX B


A
B
[Al] µg/L
WQG: Ecuador=100 µg/L
Canada=100 µg/L
France=200 µg/L
EU= 200 µg/L
US-EPA= 50–200 µg/L
WHO= 200 µg/L
[Fe] µg/L
WQG: Ecuador=300 µg/L
Canada=300 µg/L
France=100 µg/L
EU= 200 µg/L
US-EPA= 300 µg/L
WHO= 300 µg/L
[Zn] µg/L
WQG: Ecuador=3000 µg/L
Canada=5000 µg/L
France=500 µg/L
US-EPA= 5000 µg/L
WHO= 3000 µg/L
[Mn] µg/L
WQG: Ecuador=400 µg/L
Canada=50 µg/L
France=50 µg/L
EU= 50 µg/L
US-EPA= 50 µg/L
WHO= 400 µg/L
[Ba] µg/L
WQG: Ecuador=700 µg/L
Canada=1000 µg/L
France=100 µg/L
US-EPA= 2000 µg/L
WHO= 1300 µg/L
deep well
rainfall
river
shallow well
spring
stream
system

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last version (November 2015), this regulation only considered treated-clean waters and raw water that needed a physical treatment and presented a lower number of parameters than the former text. The MPV of some elements, such as Cd, increased from 0.003 $mg \cdot L^{-1}$ in February 2015 to 0.02 $mg \cdot L^{-1}$ in November 2015. Concentrations of PAHs and BTEX in drinking water sources are not regulated. The current version for fecal coliforms set up a lower concentration (1000 $NMP \cdot 100\ mL^{-1}$) than the previous ones (2000 NMP/100 mL) but it still remains very high.

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

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

4.4.1. 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 et al., 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.

4.4.2. 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 (Weis 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 emotion were evaluated in order to understand why people resist to change their practices to face supposed polluted water sources.

4.4.2.1. 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.

4.4.2.2. Cultural ideals and practices. Change to prevent sanitary risk depends first on social perceptions of the risks, and secondly on a cultura

Fig. 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. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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Table 2
Health Index for ingestion and dermal exposure pathways (HI*ing* and HI*der*), Total Hazard Index (THI), Cancer Risk for ingestion and dermal exposure pathways (CR*ing* and CR*der*), 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	HI*ing*	3.17×10^{-1}	2.88×10^{-1}	8.34×10^{-2}	2.29×10^{-1}	1.09×10^{-1}	1.69×10^{-1}	9.27×10^{-1}	5.27×10^{-1}	1.92×10^{-1}	1.01×10^{-1}	1.05×10^{-1}	1.51×10^{-1}	3.58×10^{-1}	3.45×10^{-1}	4.52×10^{-1}	2.67×10^{-1}
	HI*der*	2.16×10^{-3}	8.03×10^{-4}	7.23×10^{-4}	1.69×10^{-3}	9.79×10^{-4}	1.12×10^{-3}	3.77×10^{-3}	1.15×10^{-3}	8.05×10^{-4}	4.77×10^{-4}	3.94×10^{-4}	4.14×10^{-4}	5.06×10^{-3}	3.13×10^{-3}	2.13×10^{-3}	1.21×10^{-3}
	THI	3.20×10^{-1}	2.89×10^{-1}	8.41×10^{-2}	2.31×10^{-1}	1.10×10^{-1}	1.70×10^{-1}	9.30×10^{-1}	5.29×10^{-1}	1.93×10^{-1}	1.02×10^{-1}	1.06×10^{-1}	1.51×10^{-1}	3.63×10^{-1}	3.48×10^{-1}	4.54×10^{-1}	2.68×10^{-1}
	>1	7%	0%	0%	0%	0%	0%	33%	0%	0%	0%	0%	0%	0%	8%	0%	0%
	CR*ing*	2.46×10^{-5}	9.53×10^{-7}	6.28×10^{-6}	1.17×10^{-5}	4.83×10^{-6}	1.77×10^{-5}	3.38×10^{-5}	2.35×10^{-7}	1.72×10^{-5}	9.71×10^{-6}	1.42×10^{-5}	2.42×10^{-5}	1.27×10^{-6}	1.45×10^{-5}	3.87×10^{-5}	2.93×10^{-5}
	CR*der*	6.52×10^{-9}	2.52×10^{-10}	1.66×10^{-9}	3.10×10^{-9}	1.33×10^{-9}	4.70×10^{-9}	8.95×10^{-9}	6.22×10^{-11}	4.56×10^{-9}	2.57×10^{-9}	3.76×10^{-9}	6.40×10^{-9}	3.35×10^{-10}	3.84×10^{-9}	1.02×10^{-8}	7.75×10^{-9}
	TCR	2.46×10^{-5}	9.53×10^{-7}	6.28×10^{-6}	1.17×10^{-5}	4.83×10^{-6}	1.77×10^{-5}	3.38×10^{-5}	2.35×10^{-7}	1.72×10^{-5}	9.71×10^{-6}	1.42×10^{-5}	2.42×10^{-5}	1.27×10^{-6}	1.45×10^{-5}	3.87×10^{-5}	2.93×10^{-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%
Children	HI*ing*	6.88×10^{-1}	6.24×10^{-1}	1.81×10^{-1}	4.97×10^{-1}	2.37×10^{-1}	3.65×10^{-1}	2.01×10^{-0}	1.14×10^{-0}	4.16×10^{-1}	2.19×10^{-1}	2.28×10^{-1}	3.27×10^{-1}	7.75×10^{-1}	7.47×10^{-1}	9.79×10^{-1}	5.78×10^{-1}
	HI*der*	3.75×10^{-4}	1.39×10^{-4}	1.25×10^{-4}	2.93×10^{-4}	1.70×10^{-4}	1.94×10^{-4}	6.53×10^{-4}	1.99×10^{-4}	1.40×10^{-4}	8.27×10^{-5}	6.82×10^{-5}	7.18×10^{-5}	8.78×10^{-4}	5.42×10^{-4}	3.69×10^{-4}	2.10×10^{-4}
	THI	6.88×10^{-1}	6.24×10^{-1}	1.81×10^{-1}	4.97×10^{-1}	2.37×10^{-1}	3.65×10^{-1}	2.01×10^{-0}	1.14×10^{-0}	4.16×10^{-1}	2.20×10^{-1}	2.28×10^{-1}	3.27×10^{-1}	7.76×10^{-1}	7.48×10^{-1}	9.79×10^{-1}	5.78×10^{-1}
	> 1	27%	14%	0%	0%	0%	0%	33%	100%	0%	0%	0%	0%	0%	17%	0%	0%
	CR*ing*	1.07×10^{-5}	4.13×10^{-7}	2.72×10^{-6}	5.08×10^{-6}	2.09×10^{-6}	7.69×10^{-6}	1.47×10^{-5}	1.02×10^{-7}	7.46×10^{-6}	4.21×10^{-6}	6.16×10^{-6}	1.05×10^{-5}	5.49×10^{-7}	6.28×10^{-6}	1.68×10^{-5}	1.27×10^{-5}
	CR*der*	2.82×10^{-9}	1.09×10^{-10}	7.19×10^{-10}	1.34×10^{-9}	5.53×10^{-10}	2.03×10^{-9}	3.87×10^{-9}	2.69×10^{-11}	1.97×10^{-9}	1.11×10^{-9}	1.63×10^{-9}	2.77×10^{-9}	1.45×10^{-10}	1.66×10^{-9}	4.42×10^{-9}	3.35×10^{-9}
	TCR	1.07×10^{-5}	4.13×10^{-7}	2.72×10^{-6}	5.08×10^{-6}	2.09×10^{-6}	7.69×10^{-6}	1.47×10^{-5}	1.02×10^{-7}	7.46×10^{-6}	4.21×10^{-6}	6.16×10^{-6}	1.05×10^{-5}	5.49×10^{-7}	6.28×10^{-6}	1.68×10^{-5}	1.27×10^{-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; HI*ing* = hazard index for ingestion exposition; HI*der* = hazard index for dermal exposition; THI = total hazard index.

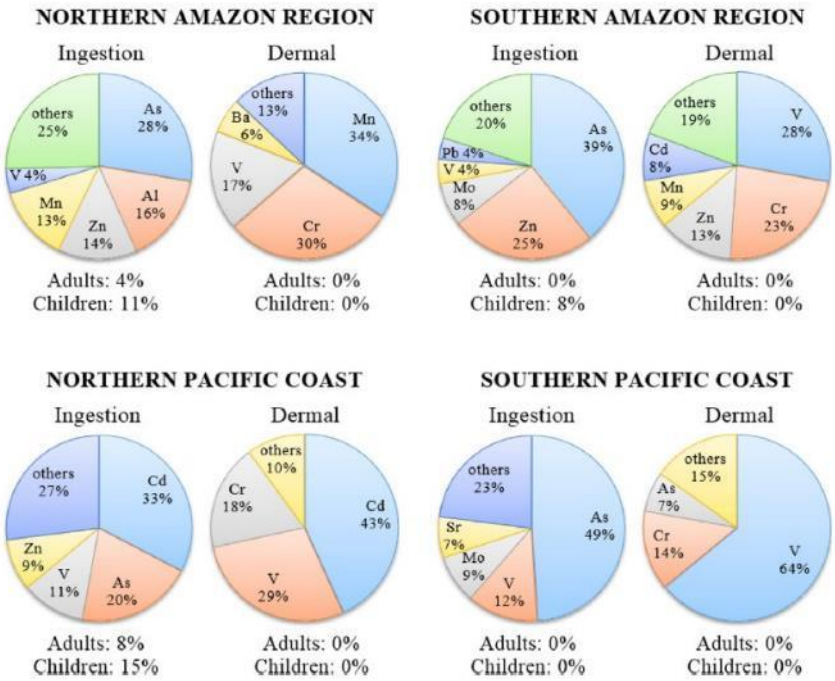


Fig. 4. Distribution of ingestion and dermal contact Hazard Index (HI) for the Amazon and Pacific Ecuadorian regions, followed by the percentage of samples that overcome the Total HI reference value (United States Environmental Protection Agency (US EPA), 2015a, 2015b) in children and adults.

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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 towards 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).

4.4.2.3. 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 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.

4.4.3. Chronic and historical distrust of oil companies

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.



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

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 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.

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Appendix A. Supplementary data

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ANNEX C: Coordinates of sampling points

Table C-1. Localization (UTM coordinates) of surface water sampling points (Chapter 1).

BASIN	SUB-BASIN	CODE	PARISHES	UTM COORDINATES	WATER	SEDIMENT
	Napo	b. sand	Pto. Misahualli	18 M 194628 9921851	✓	✓
	Napo	PN-a4	Pto. Napo	18M 188685 9884404	✓	✓
	Napo	PN-b5	Pto. Napo	18M 188685 9884404	✓	✓
	Napo	PN-c6	Pto. Napo	18M 188625 9884480	✓	✓
	Napo	PN-d2	Pto. Misahualli	18M 200126 9884189	✓	✓
	Napo	PO-a6'	Pto. Fco. de Orellana	18M 271659 9943790	✓	**X**
	Napo	PO-a6	Pto. Fco. de Orellana	18M 271819 9943587	✓	✓
	Napo	PO-b3	Pto. Fco. de Orellana	18M 276524 9945544	✓	✓
	Napo	PO-c4	Pto. Fco. de Orellana	18M 276520 9945556	✓	✓
	Payamino	PO-d6	Pto. Fco. de Orellana	18M 276443 9945371	✓	✓
	Payamino	PO-e6	Pto. Fco. de Orellana	18M 261244 9950543	✓	✓
	Payamino	PO-f5**	Pto. Fco. de Orellana	18M 269232 9955379	✓	✓
	Payamino	PO-g2**	Pto. Fco. de Orellana	18M 270389 9954665	**X**	✓
	Payamino	PO-h2**	Pto. Fco. de Orellana	18M 270562 9955067	✓	✓
	Payamino	PO-i6	Pto. Fco. de Orellana	18M 276701 9950922	✓	✓
	Coca	SC-a6	San Sebastian del Coca	18M 268710 9982811	✓	**X**
	Coca	SC-b6	San Sebastian del Coca	18M 267272 9982580	✓	✓
	Coca	SC-c6	San Sebastian del Coca	18M 275397 9966278	✓	**X**
	Coca	SC-d3	San Sebastian del Coca	18M 276655 9962158	✓	✓
	Coca	SC-d'6	San Sebastian del Coca	18M 276679 9962184	✓	**X**
	Coca	SC-e4	San Sebastian del Coca	18M 276655 9962158	✓	✓
NAPO	Coca	SC-f5	San Sebastian del Coca	18M 279648 9963505	✓	✓
(NEAR)	Napo	PO-j2	Pto. Fco. de Orellana	18M 287234 9948808	✓	**X**
	Napo	JS6	Joya de los Sachas	18M 293465 9958342	✓	✓
	Napo	LI5	Limoncocha	18M 318689 9961878	✓	✓
	Rumiyacu	waste A8	Dayuma	18M 291093 9928465	✓	✓
	Rumiyacu	DY-a6**	Dayuma	18M 292198 9927298	✓	✓
	Rumiyacu	DY-b6**	Dayuma	18M 290458 9925971	✓	✓
	Rumiyacu	DY-b3**	Dayuma	18M 290458 9925971	✓	**X**
	Rumiyacu	DY-c2**	Dayuma	18M 291054 9926304	✓	✓
	Rumiyacu	DY-d4**	Dayuma	18M 291034 9926303	✓	✓
	Rumiyacu	DY-e3**	Dayuma	18M 291064 9926301	✓	✓
	Rumiyacu	DY-f5**	Dayuma	18M 291520 9923055	✓	✓
	Rumiyacu	DY-g6	Dayuma	18M 295243 9925497	✓	✓
	Tiputini	DY-h3**	Dayuma	18M 291087 9916886	✓	✓
	Tiputini	DY-i6**	Dayuma	18M 289918 9918913	✓	✓
	Tiputini	DY-j2**	Dayuma	18M 290977 9917803	**X**	✓
	Tiputini	DY-j4**	Dayuma	18M 290978 9917805	✓	**X**
	Tiputini	DY-k2**	Dayuma	18M 290906 9917788	✓	✓
	Tiputini	DY-l6**	Dayuma	18M 290802 9917724	✓	✓
	Tiputini	DY-m6	Dayuma	18M 299005 9917233	✓	✓
	Tiputini	TI-a4	Tiputini	18M 336619 9932675	✓	✓
	Tiputini	TI-b4	Tiputini	18M 369683 9929565	✓	✓
	Tiputini	TI-c4	Tiputini	18M 438642 9908793	✓	✓
	Napo	NR-a4	Nuevo Rocafuerte	18M 454177 9899407	✓	✓
	Napo	NR-b2	Nuevo Rocafuerte	18M 454645 9899031	✓	✓

Table C-1. Localization (UTM coordinates) of surface-water sampling points (Chapter 1) .(continued)

BASIN	SUB-BASIN	CODE	PARISHES	UTM COORDINATES	WATER	SEDIMENT
	Aguarico	LM-a5	Lumbaqui	18N 233592 3169	✓	✓
	Aguarico	LM-b6	Lumbaqui	18N 243266 5986	✓	✓
	Aguarico	LM-c4	Lumbaqui	18N 243266 5986	✓	✓
	Aguarico	LM-d3	Lumbaqui	18N 243387 5825	✓	✓
	Aguarico	DU-a4	Dureno	18N 313064 5723	✓	✓
	Aguarico	DU-b3**	Dureno	18N 314380 3433	✓	✓
	Aguarico	DU-c3**	Dureno	18N 314380 3433	✓	**X**
AGUARICO	Aguarico	PK_a4**	Pacayacu	18N 326418 6748	✓	**X**
(NEAR)	Aguarico	PK-a5**	Pacayacu	18N 325469 141	✓	✓
	Aguarico	PK-b2**	Pacayacu	18M 323625 9998301	✓	✓
	Aguarico	PK-c6	Pacayacu	18M 320944 9997146	✓	✓
	Aguarico	PK-d4	Pacayacu	18M 320987 9997151	✓	✓
	Aguarico	PK-e3	Pacayacu	18M 320967 9997141	✓	✓
	Aguarico	PK-f2**	Pacayacu	18M 323427 9994136	✓	✓
	Aguarico	PK-g2**	Pacayacu	18M 327601 9997831	✓	✓
	Aguarico	PK-h3**	Pacayacu	18M 325818 9994400	✓	✓
	Aguarico	PK-i3	Pacayacu	18M 327116 9993763	✓	✓
	Shushufindi	SF-a6	Shushufindi	18M 312277 9979792	✓	✓
	Shushufindi	SF-b6	Shushufindi	18M 316303 9986562	✓	✓
	Shushufindi	SF-c4	Shushufindi	18M 316522 9973520	✓	✓
	Shushufindi	SF-d4	Shushufindi	18M 315038 9979506	✓	✓
	Aguarico	SR6	San Roque	18M 347130 9967006	✓	✓
	Aguarico	NR-c4	Nuevo Rocafuerte	18M 474080 9896603	✓	✓
	Aguarico	NR-d2	Nuevo Rocafuerte	18M 474267 9896576	✓	✓
	M.Santiago	SJ6	San José de Morona	18M 199581 9680317	✓	✓
	M.Santiago	BB6	Bomboiza	17M769754 9611197	✓	✓
	M.Santiago	S-a5	Santiago	17M829941 9663837	✓	✓
M.SANTIAGO	M.Santiago	S-b6	Santiago	17M829941 9663837	✓	✓
(SEAR)	M.Santiago	S-b6'	Santiago	17M 832422 9662617	✓	**X**
	M.Santiago	S-c5	Santiago	18M 167464 9663947	✓	✓
	M.Santiago	S-d5	Santiago	18M 168127 9664373	✓	✓
	M.Santiago	S-e5	Santiago	18M 177656 9668659	✓	✓
	M.Santiago	S-f6	Santiago	18M 181321 9670666	✓	✓
	Teaone	CC-a6	Carlos Concha	17N 645312 78233	✓	✓
	Teaone	CC-b4	Carlos Concha	17N 645665 78232	✓	✓
ESMERALDAS	Teaone	VL-a3	Vuelta Larga	17N 644715 99347	✓	✓
(NEPC)	Teaone	VL-b4*	Vuelta Larga	17N 646183 102590	✓	**X**
	Teaone	VL-b6*	Vuelta Larga	17N 646440 102360	✓	✓
	Teaone	VL-c2*	Vuelta Larga	17N 646459 102350	**X**	✓
	Teaone	VL-d4*	Vuelta Larga	17N 646489 102370	✓	✓
	Teaone	VL-e6*	Vuelta Larga	17N 646489 102370	✓	✓
	Teaone	VL-f2	Vuelta Larga	17N 647300 102237	**X**	✓
	Teaone	AG-a3	5 de Agosto	17N 647302 102241	✓	✓
	Esmeraldas	SM6	San Mateo	17N 653546 92500	✓	✓
	Esmeraldas	AG-b3	5 de Agosto	17N 649225 102340	✓	✓
	Esmeraldas	E-a6	Esmeraldas	17N 651667 105863	✓	✓
	Esmeraldas	E-b4	Esmeraldas	17N 651729 106065	✓	✓
PORTOVIEJO (SEPC)	Portoviejo	SA6	Sta Ana	17M 574450 9868014	✓	✓

✓ = sample collected and analyzed ; **X** = non sample collected ; NEAR= Northern Ecuadorian Amazon Region; NEPC= Northern Ecuadorian Pacific Coast ; SEAR= Southern Ecuadorian Amazon Region ; SEPC= Southern Ecuadorian Pacific Coast.

Table C-2. Localization (UTM) coordinates of drinking-water sampling points (Chapter 2).

STUDY AREA	SOURCE	CODE	PARISHES	UTM COORDINATES
	deep well	M12-17	Pacayacu	18M 325220 9998734
	deep well	M13-02	Pacayacu	18M 321263 9997172
	deep well	M13-04	Pacayacu	18M 324943 9996358
	deep well	M14-15	Pacayacu	18N 326344 6528
	deep well	M14-21	Pacayacu	18M 324345 9996378
	deep well	M16-07	Dayuma	18M 290875 9926921
	deep well	M16-13	Dayuma	18M 289988 9918939
	deep well	M16-21	Dayuma	18M 291280 9926372
	deep well	M16-26	San Sebastian del Coca	18M 275333 9966352
	deep well	M16-28	San Sebastian del Coca	18M 271576 9975651
	deep well	M16-33	Shushufindi	18M 317150 9990663
	deep well	M16-39	Joya de los Sachas	18M 293549 9967979
	deep well	M16-40	Joya de los Sachas	18M 290576 9958107
	deep well	M16-41	Joya de los Sachas	18M 291345 9957984
	deep well	M16-43	Pacayacu	18M 321072 9997195
	rainfall	M12-15	Pacayacu	18M 323603 9995592
	rainfall	M13-13	Dayuma	18M 289959 9912027
	rainfall	M14-05	Dayuma	18M 290749 9926167
	rainfall	M14-23	Pacayacu	18M 324345 9996378
	rainfall	M16-09	Dayuma	18M 292270 9927287
	rainfall	M16-15	Dayuma	18M 290854 9917918
	rainfall	M16-19	Dayuma	18M 304564 9918887
	rainfall	M16-23	Puerto Fco. de Orellana	18M 271822 9943776
NEAR	river	M13-14	Dayuma	18M 291087 9916886
	river	M13-16	Dayuma	18M 290458 9925971
	river	M14-20	Shushufindi	18M 316522 9973520
	river	M15-02	Limoncocha	18M 318689 9961878
	river	M16-04	Dayuma	18M 290458 9925971
	river	M16-22	Puerto Fco. de Orellana	18M 261244 9950543
	river	M16-27	San Sebastian del Coca	18M 275397 9966278
	shallow well	M12-14	Pacayacu	18M 323603 9995592
	shallow well	M13-03	Pacayacu	18M 325073 9996386
	shallow well	M13-07	Pacayacu	18M 325834 9993929
	shallow well	M13-08	Pacayacu	18M 324372 9994867
	shallow well	M14-22	Pacayacu	18M 324345 9996378
	shallow well	M16-36	Pacayacu	18M 324955 9996238
	shallow well	M16-37	Pacayacu	18M 323541 9995623
	spring	M12-11	Dayuma	18M 290853 9917917
	spring	M13-01	Pacayacu	18M 322806 9995660
	spring	M13-17	Dayuma	18M 289790 9931001
	spring	M13-18	Dayuma	18M 289720 9931296
	spring	M13-18F	Dayuma	18M 289720 9931296
	spring	M14-12	Dayuma	18M 290854 9917918
	spring	M14-14	Pacayacu	18N 326344 6528
	spring	M16-02	Dayuma	18M 295397 9924949
	spring	M16-05	Dayuma	18M 290605 9923356
	spring	M16-14	Dayuma	18M 290802 9917724
	spring	M16-17	Dayuma	18M 298886 9917180
	spring	M16-20	Dayuma	18M 304564 9918887
	stream	M12-12	Dayuma	18M 290906 9917788
	stream	M13-09	Dureno	18N 314380 3433
	stream	M16-25	Puerto Fco. de Orellana	18M 271659 9943790
	stream	M16-29	San Sebastian del Coca	18M 268710 9982811

Table C- 2. Localization (UTM) coordinates of drinking-water sampling points (Chapter 2). (continued)

STUDY AREA	SOURCE	CODE	PARISHES	UTM COORDINATES
	system	M14-04	Dayuma	18M 290749 9926167
NEAR	system	M16-06	Dayuma	18M 290749 9926167
	system	M16-11	Dayuma	18M 290576 9928171
	spring	M15-08C	Santiago	18M 168127 9664373
	rainfall	M16-53	Santiago	18M 172629 9666674
	river	M15-09C	Santiago	17M 829941 9663837
	river	M15-10C	Santiago	18M 177656 9668659
	river	M15-11C	Santiago	18M 167464 9663947
SEAR	spring	M16-47	Bomboiza	17M 769851 9610949
	spring	M16-48	Bomboiza	17M 769851 9610949
	spring	M16-52	Santiago	17M 832422 9662617
	spring	M16-54	Santiago	18M 172629 9666674
	spring	M16-56	Santiago	18M 172253 9665191
	stream	M16-46	Bomboiza	17M 769754 9611197
	system	M16-55	Santiago	17M 832361 9662423
	system	M16-59	Vuelta Larga	17N 646394 102410
	system	M14-29	Vuelta Larga	17N 645029 101631
	rainfall	M16-67	Vuelta Larga	17N 646959 100260
	system	M16-61	Vuelta Larga	17N 645029 101631
	system	M16-64	Vuelta Larga	17N 645083 101687
NEPC	system	M16-65	Vuelta Larga	17N 645139 101601
	system	M16-66	Vuelta Larga	17N 644921 101610
	system	M16-68	Vuelta Larga	17N 646959 100260
	system	M16-69	Vuelta Larga	17N 645512 101547
	system	M16-70	5 de Agosto	17N 647094 103010
	system	M16-71	5 de Agosto	17N 647392 102576
	system	M16-72	5 de Agosto	17N 648973 102086
	system	M16-73	Vuelta Larga	17N 645916 101387
SEPC	shallow well	M16-77	Sta Ana	17M 574193 9864533
	system	M16-76	Sta Ana	17M 572397 9865618

NEAR= Northern Ecuadorian Amazon Region; NEPC= Northern Ecuadorian Pacific Coast ; SEAR= Southern Ecuadorian Amazon Region ; SEPC= Southern Ecuadorian Pacific Coast.

"When the moment comes to choose between economic growth and ecological stability, politicians, CEOs and voters almost always prefer growth. In the twenty-first century, we shall have to do better if we are to avoid catastrophe"

-**Yuval Noah Harari, 2016**

LOPEZ MEDINA Fausto

TITLE: Environmental impacts of current and past oil activities on water quality in Ecuador

ABSTRACT:

Spills and discharges of solid and liquid residues caused by the oil industry in Ecuador have resulted in the presence of pollutants with a high content of hydrocarbons (PAHs and BTEX) and metal elements (salts), which are known for their acute and/or chronic toxicity.
This study aims to assess the quality of the aquatic environment in three watersheds (Esmeraldas, Napo and Aguarico) in the extraction and refining zones in order to determine the level of environmental and human risk from different water sources.
The sources analyzed are in compliance with environmental guidelines and are defined as "non-toxic". Pollution from oil activities is punctual. Urbanization and agriculture are also visualized as stress factors for water bodies. Human risk is mainly related to low water mineralization and in some cases to the presence of inorganic elements (Mn, As, Al and Zn).

KEYWORDS:

Ecuador; oil activities; water quality; polycyclic aromatic hydrocarbons, metal(loid)s; health risk.

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TITRE : Impacts environnementaux des activités pétrolières actuelles et passées sur la qualité des eaux en Equateur

DIRECTRICES DE THESE : Laurence MAURICE, Eva SCHRECK,

ET DATE DE SOUTENANCE : Toulouse, le 10 juillet 2019.

RESUME :

Les déversements et le rejet de résidus solides et liquides causés par l'industrie pétrolière en Équateur ont entraîné la présence de déchets à forte teneur en hydrocarbures (HAP et BTEX) et en éléments métalliques (sels), qui sont reconnus pour leur toxicité aiguë et/ou chronique. Cette étude vise à évaluer la qualité du milieu aquatique dans trois bassins versants (Esmeraldas, Napo et Aguarico) sur les zones d'extraction et de raffinage afin de déterminer le niveau de risque environnemental et humain à partir de différentes sources d'eau.
Les sources analysées sont conformes aux indicateurs environnementaux et définis comme "non toxiques". La pollution due aux activités pétrolières est ponctuelle. L'urbanisation et l'agriculture sont aussi visualisées comme facteurs de stress des masses d'eau. Le risque humain est lié principalement à la faible minéralisation de l'eau et dans certains cas à la présence d'éléments inorganiques (Mn, As, Al et Zn).

MOTS-CLES : Equateur; Activités pétrolières; Qualité des eaux, hydrocarbures aromatiques polycycliques, Métaux; Risque sanitaire.

DISCIPLINE ADMINISTRATIVE : SURFACES ET INTERFACES CONTINENTALES, HYDROLOGIE

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