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Distribution, contents and health risk assessment of metal(loid)s in small-scale farms in the Ecuadorian Amazon: An insight into impacts of oil activities

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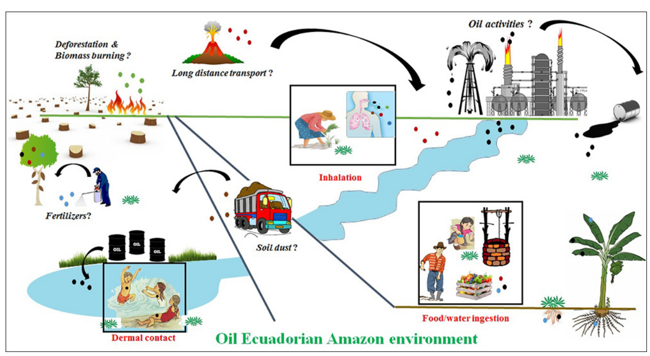
HIGHLIGHTS

- High levels of Ba, Cd, Cr and Mo were found in soils, crops, water and air (PM_{10}).
- Ba and Mo can be considered as proxies for effects of oil activities.
- Metal(loid)s risk indexes classify the population exposure as moderate to elevate.
- Inhalation and water ingestion accounted for 90% of the total cancer risk in children.
- Health risk assessment should also integrate social variables such as risk perception.

GRAPHICAL ABSTRACT



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ABSTRACT

In the last 50 years, oil extraction activities in the Northeast Amazonian Region (NAR) of Ecuador impacted ecosystems and may still affect the local population health. To our knowledge, no previous studies have determined the concentrations of metal(loid)s in the oil Ecuadorian Amazon environment. A total of 15 small farms, located in the Orellana and Sucumbíos provinces, were sampled in order to determine the concentrations of As, Ba, Co, Cu, Cd, Cr, Mn, Mo, Ni, Pb, V and Zn in soils, crops, drinking water and air (PM_{10}). Among non-essential metal(loid)s, Ba concentrations in soils exceeded the Ecuadorian limits of 200 mg kg^{-1} in 53% of the sampling sites. In crops, Cd concentrations in cacao and Pb in manioc exceeded the FAO/WHO recommendations. In drinking water and PM_{10}, regulated metal(loid)s did not exceed the international thresholds. Nevertheless metals such as Ba and Mo showed the highest annual mean concentrations in PM_{10} in both sampling sites. Natural (bedrock, volcanic ashes) and anthropogenic (oil activities, agrochemical products) sources could explain the high content of some meta(loid)s in the environment. According to the hazard quotient and cancer risk indexes, crops and water ingestion represent 71% and 88% of the exposure pathways for non-carcinogenic elements in adults and children respectively while inhalation is the main exposure pathways for carcinogenic elements for the whole population. Both indexes were 2 to 13 times higher than the US EPA recommended values. However, estimates of exposure pathways should be considered taking into account the risk perception of residents: they

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may be overestimated for people who are able to change their dietary and/or agricultural practices to limit their exposure, or underestimated in the case of persons who are socio-economically vulnerable and who cannot leave the impacted areas.

1. Introduction

Crude oil, despite being a non-renewable energy source, is a key strategic resource for the development of countries (E et al., 2017) especially in Latin America where the economy and government's budget are mainly based on the exploitation of raw materials (Arsel et al., 2016). In South America, Ecuador has the 3rd largest oil reserves as well as being ranked as the 4th largest oil producing country (equivalent to 549 thousand barrels per day), according to the Organization of the Petroleum Exporting Countries (OPEC, 2016). Most of the extractive activities have been developed in the Northeast Amazonian region (NAR), known as the "Oriente", for >50 years (Lessmann et al., 2016).

The Amazon basin also houses millions of hectares of tropical rainforest and near to 500,000 inhabitants including eight groups of indigenous people (30% of the total regional population) and rural population from Ecuador's coastal and highland regions (Lu et al., 2010; San Sebastián and Hurtig, 2004). Concerns have been raised over the environmental issues, specifically impacting on the Amazon biodiversity (Arellano et al., 2017) from burning large volumes of gas and whether reserves and conventional oil production have the capacity to meet the growing demands (Owen et al., 2010). For example, the clearing of lowlands forests for agricultural crops and by the opening of roads due to oil extraction and forest exploitation (Mosandl et al., 2008) has decreased prime Amazonian forest by approximately 44% (Welford and Yarbrough, 2015).

Crude oil is essentially formed by a complex mixture of hydrocarbons, sulfur, nitrogen, oxygen, organo-metallic compounds of Ni, V, and others trace metals (Speight and Özüm, 2002; Zhuang et al., 2016). Inorganic salts such as magnesium chloride ($MgCl_2$), sodium chloride (NaCl) and other mineral compounds are also present naturally, in formation waters (Moquet et al., 2014), or added as a part of chemicals injected during drilling and production operations (i.e. weighting agents like Barite, $BaSO_4$), as reported by Oskarsson (2015) and Speight and Özüm (2002). Outdated practices and technologies used during oil production in Ecuador, initiated by Texaco-Chevron, have released into the environment an estimated of 19.3 billion gallons of oil and left between 800 and 1000 unlined earthen waste pits (Buccina et al., 2013).

Polycyclic Aromatic Hydrocarbons (PAHs), Volatile Organic Compounds (VOCs), metals and metalloids are the main contaminants generated by oil production or refining activities (Baltrenas et al., 2011; Sarma et al., 2016). The intentional or accidental release of such contaminants have resulted in a long-term pollution of air, soil, plants, rivers, streams and groundwater (Finer et al., 2008).

Some metals such as Co, Cr (III), Cu, Mn, Mo and Zn (Cobbina et al., 2015) are considered as essential compounds for humans at low concentrations because they are usually involved in metabolic functions. However, an excess may lead to adverse health effects (Crichton, 2016). Other elements like As, Ba, Cd, Pb and Sb are toxic and have no beneficial effects. Nickel and V seem to have biological functions in plants and some animals, but their importance in humans is yet to be shown (Kabata-Pendias and Szteke, 2015). According to the International Agency for Research on Cancer (IARC), As, Cd, Cr hexavalent compounds and Ni are classified as carcinogenic, whereas Co, Pb and Sb trioxide are considered as possibly carcinogenic (Mulware, 2013). Diseases such as skin and lung lesions, bladder, hepatic or renal cancers, damage of the central and peripheral nervous systems and adverse effects on fetuses and infants have been described in populations exposed to these toxic metals (Masto et al., 2017; Nordberg and Nordberg, 2016).

The three main exposure pathways to contaminants are: water and crops ingestion, inhalation of particulate matter (PM) and dermal contact (Huang et al., 2016; Swartjes and Cornelis, 2011).

As a general pattern, once the contaminant is transferred from a mobile phase (i.e. pore water soil) into a contact medium (i.e. fruits), it enters the body through an intake pathway; one part can be carried by the blood stream to target organs, and finally the remaining part is excreted. For dermal contact, direct intake can pass through the skin (e.g. shower with contaminated water) (Elert et al., 2011). The consumption of vegetables and fruits is one of the main exposure routes to metal(loid)s (McLaughlin et al., 2011) especially for people who do not frequently eat marine or freshwater fish. Contaminant concentrations in the edible parts of crops are the result of their capacity to uptake (by roots or leaves), transport, accumulate and even degrade bioavailable metal species (Elert et al., 2011). Atmospheric particulate matter (PM), depending on their diameter and emission sources, also carry an important source of metal(loid)s that can be absorbed into the lung tissues while breathing (Jena and Singh, 2017; Mousavian et al., 2017). While dermal contact usually accounts for a small percentage within the whole risk assessment evaluation (WHO, 2014), this pathway is relevant under certain conditions, especially for young children in the NAR, where swimming and bathing in contaminated waters or playing outside are common activities. Soil ingestion is also considered as a significant exposure pathway towards children due to specific age-related activities such as the hand-to-mouth behavior (Tepanosyan et al., 2017).

As recommended by the Agency for Toxic Substances and Disease Registry (ATSDR, 2005), the evaluation of these exposure pathways must consider past, current, and future exposure conditions.

The potential or proven impact of oil activities on the environment and on human health is still poorly documented in Ecuador. A few studies suggest the presence of cancer, birth defects, miscarriages, and other diseases in the local population (Maddela et al., 2016; San Sebastián et al., 2002). San Sebastián et al. (2001) previously showed that women living close to oil wells and platforms in the Orellana Province, in Sachas and Shushufindi villages (NAR), regularly suffered from fungal skin infections, nose, eye and throat irritations, fatigue, headaches, earaches, diarrhea or gastritis. These results were based on the correlation between water samples collected in the main rivers of the area, with levels of Total Petroleum Hydrocarbons (TPH) above Ecuadorian thresholds, and epidemiological studies.

In Ecuador, the environmental policy which characterizes a populations' vulnerability to oil contamination is based on the distance of the source (i.e. oil pools, spills or pits), the residence time in the contaminated area, the density of oil infrastructures and the potential impacts of oil activities in the water resources (MAE-PRAS, 2010). In accordance with these policies, a large national program dedicated to repair social and environmental impacts was established in the NAR. In the absence of remediation, families were moved into social housing and kept away from contaminated sources (Becerra et al., 2016).

However, there is a lack of information regarding metal(loid)s co-emitted with PAHs in the other environmental compartments: the soil-crop continuum and the air (PM), as well as their harmful effects on NAR population. Most of the families living in the "Oriente" region consume a large amount of the products they cultivate in their own small-scale farms, usually located in the proximity of oil facilities. At each facility, over 16.3 million liters of liquid wastes are generated