



## Short communication

# First evidences of Amazonian wildlife feeding on petroleum-contaminated soils: A new exposure route to petrogenic compounds?



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## ARTICLE INFO

## Keywords:

Oil extraction

Geophagy

Indigenous health

Subsistence hunting

Amazon

## ABSTRACT

Videos recorded with infrared camera traps placed in petroleum contaminated areas of the Peruvian Amazon have shown that four wildlife species, the most important for indigenous peoples' diet (lowland tapir, paca, red-brocket deer and collared peccary), consume oil-contaminated soils and water. Further research is needed to clarify whether Amazonian wildlife's geophagy can be a route of exposure to petrogenic contamination for populations living in the vicinity of oil extraction areas and relying on subsistence hunting.

## 1. Main Text

The oil extraction industry can be very hazardous for the environment (Epstein and Selber, 2002). The main by-product of oil extraction industry is produced water. Worldwide, every day 300 million barrels (i.e. 48 million m<sup>3</sup>) of produced water are brought to the surface during oil and gas extraction operations (Long et al., 2013). Produced water can contain a number of potentially toxic agents, including radioactive isotopes, dispersed hydrocarbons (i.e. phenolic and polyaromatic molecules among others), and heavy metals (i.e. cadmium, chromium, lead and barium among others) (Fakhrul-Razi et al., 2009). The safe disposal of produced water is starting to create concern among environmental health researchers (Konkel, 2016). The use of sub-standard technologies for their disposal in low and middle income countries -LMICs- may add a further twist to this concern for public health (Jernelöv, 2010).

Oil and gas reserves overlap with 30% of the world's rainforests; and the Amazon is the tropical rainforest with the highest percentage (39.4%) of such overlap (own calculations based on Butt et al., 2013).

Hydrocarbon extraction activities in the Amazon region started in the 1930's (Orta Martínez et al., 2007) and, in 2008, they spread over 688,000 km<sup>2</sup> of the western Amazon, in Bolivia, Brazil, Colombia, Ecuador and Peru (Finer et al., 2008). Despite the intense decades-long oil extraction activity in tropical rainforests and the toxicological effects of some oil-related pollutants, there is a dearth of scientific data on the potential impacts that oil extraction may have on this environment and on the health of people living in the vicinities of oil extraction sites (O'Callaghan-Gordo et al., 2016).

In the Northern Peruvian Amazon, oil concessions 1AB/192<sup>1</sup> and 8<sup>2</sup> were leased in the late 1960s. These concessions are the most productive ones in Peru, with 39% of total national accumulated oil production (Orta Martínez et al., 2007). The area within these oil concessions is inhabited by more than 45,000 Achuar, Quechua, Kichwa, Kukama-Kukamilla and Urarina indigenous people. Between 1987 and 2013, several official documents issued by different Peruvian state agencies reported that concentrations of hydrocarbons, hexavalent chromium, lead, mercury, barium and chlorides in soils, river waters and sediments from these areas were above the Peruvian maximum permissible limits

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<sup>1</sup> First held by Occidental Petroleum Corporation -Oxy-, then transferred to Pluspetrol Corporation S.A. in 2001, and to Pacific Stratus Energy/Frontera Energy Corporation in 2015.

<sup>2</sup> Initially operated by PetroPeru, then transferred to Pluspetrol Corporation S.A. in 1996.

and that concentrations of cadmium and lead in fish were above acceptable limits for human consumption (Orta Martínez et al., 2007). In 2005, the Ministry of Health, found that 98.6% and 66.2% of Achuar children of 2–17 years of age exceeded the acceptable limits for cadmium and lead in blood, as well as 99.2% and 79.2% of adults (Orta Martínez et al., 2007). In 2013 and in 2014, the Peruvian government declared the environmental and health emergency, respectively, in the area (Ministerial Resolutions No 064–2013, 094–2013, 263–2013 and 370–2013, from the Ministry of the Environment and, Supreme Decree No 006–2014 from the Ministry of Health).

Despite the evidence that the population living in the area is exposed to high levels of contamination, no studies have been conducted to identify the exposure routes to these contaminants. Consumption of wild animals from the area has been suggested as a potential source of exposure by the local indigenous populations, which have repeatedly reported that many wildlife species ingest soil and water in places affected by the dumping of produced waters and oil. Intentional geophagy (i.e. deliberate ingestion of soil) in nutrient-poor ecosystems such as the Amazon, is a widespread behavior frequently observed in herbivores and omnivorous wildlife (Dudley et al., 2012). Geophagy is an important route for contaminant exposure in industrial areas, posing a risk to animal's health (Beyer and Fries, 2002). Thus, the soil-animal pathway to humans is important in many risk assessments (Beyer and Fries, 2002). The aim of the current study was to investigate whether wildlife species, through geophagy, are ingesting petroleum pollutants at the 1AB/192 oil block with camera trapping field observations.

## 2. Intentional ingestion of petroleum-contaminated soils

We selected two study sites within the 1AB/192 oil block (Department of Loreto, Province of Loreto) where, according to the local population, game species gathered to ingest soil. These sites were considered locally as hunting hotspots. Infrared camera traps (Bushnell 8MP Trophy Cam HD) were placed in both sites in May 2013. In site 1 (18 M 336588 9701714), a camera trap was placed overlooking a swamp located just below the overflow pipe of an uncovered sump tank. Sump tanks are designed to contain oil and produced water overflowing from a well due to unexpected increases in pressure. However, in the study area oil and produced water are rarely recovered from these tanks, and uncovered tanks often overflow with the regular heavy tropical rainfalls (Orta Martínez et al., 2007). In site 2 (18 M

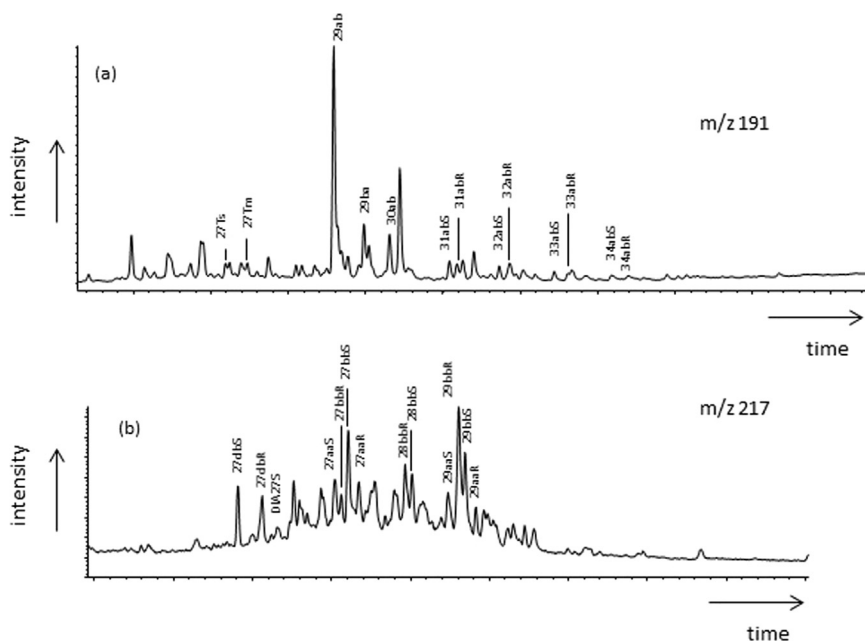
**Table 1**

Compound identities and  $m/z$  of the ion used to identify the hopanes and steranes in the soil sample, displayed in Fig. 1.

Abbreviation	Name	$m/z$
27Ts (Ts)	18 $\alpha$ (H)-22,29,30-trisnorhopane	191
27Tm	17 $\alpha$ (H)-22,29,30-trisnorhopane	191
29ab	17 $\alpha$ (H),21 $\beta$ (H)-30-norhopane	191
29ba	17 $\beta$ (H),21 $\alpha$ (H)-30-normoretane (normoretane)	191
30ab	17 $\alpha$ (H),21 $\beta$ (H)-30-hopane	191
31abS	22S-17 $\alpha$ (H),21 $\beta$ (H)-30-homohopane	191
31abR	22R-17 $\alpha$ (H),21 $\beta$ (H)-30-homohopane	191
32abS	22S-17 $\alpha$ (H),21 $\beta$ (H)-30-bishomohopane	191
32abR	22R-17 $\alpha$ (H),21 $\beta$ (H)-30-bishomohopane	191
33abS	22S-17 $\alpha$ (H),21 $\beta$ (H)-30-trishomohopane	191
33abR	22R-17 $\alpha$ (H),21 $\beta$ (H)-30-trishomohopane	191
34abS	22S-17 $\alpha$ (H),21 $\beta$ (H)-30-tetrakishomohopane	191
34abR	22R-17 $\alpha$ (H),21 $\beta$ (H)-30-tetrakishomohopane	191
27dbS	13 $\beta$ (H),17 $\alpha$ (H),20S-cholestane (diasterane)	217
27dbR	13 $\beta$ (H),17 $\alpha$ (H),20R-cholestane (diasterane)	217
DIA27S	13 $\alpha$ (H),17 $\beta$ (H)-20S-cholestane (diasterane)	217
27aaS	5 $\alpha$ (H),14 $\alpha$ (H),17 $\alpha$ (H)-20S-cholestane	217
27bbR	5 $\alpha$ (H),14 $\beta$ (H),17 $\beta$ (H),20R-cholestane	217
27bbS	5 $\alpha$ (H),14 $\beta$ (H),17 $\beta$ (H),20S-cholestane	218
27aaR	5 $\alpha$ (H),14 $\alpha$ (H),17 $\alpha$ (H),20R-cholestane	218
28bbR	24-Methyl-5 $\alpha$ (H),14 $\beta$ (H),17 $\beta$ (H),20R-cholestane	218
28bbS	24-Methyl-5 $\alpha$ (H),14 $\beta$ (H),17 $\beta$ (H),20S-cholestane	218
29aaS	24-Ethyl-5 $\alpha$ (H),14 $\alpha$ (H),17 $\alpha$ (H),20S-cholestane	217
29bbR	24-Ethyl-5 $\alpha$ (H),14 $\beta$ (H),17 $\beta$ (H),20R-cholestane	218
29bbS	24-Ethyl-5 $\alpha$ (H),14 $\beta$ (H),17 $\beta$ (H),20S-cholestane	218
29aaR	24-Ethyl-5 $\alpha$ (H),14 $\alpha$ (H),17 $\alpha$ (H),20R-cholestane	217

350590 9679070), a camera trap was located next to an abandoned oil well. This well was drilled in 1970 and sealed in 1982. However, when the study was conducted, an unidentified fluid leaked from the well.

Soil from both sites were analyzed to assess the presence of petrogenic pollutants, using petroleum biomarkers (i.e. steranes and hopanes) as proxy indicators (Rosell-Melé et al., 2010). We took three soil samples in each site between 0 and 20 cm depth and a 10 × 10 cm section (after removing overlaying leaf litter) separated by several meters. We homogenized and pooled the three soil samples before the analysis. Approximately five grams of dry soil were extracted with 10 mL of trace analysis grade n-hexane–acetone (1:1, v/v) (Merck, Darmstadt, Germany) in the ultrasonic bath for 15 min. The extraction process was repeated three times. The identification of biomarkers was



**Fig. 1.** Mass fragmentograms obtained by gas chromatography-mass spectrometry to investigate the presence of hopanes (a) and steranes (b) in the soil organic extract. Peak identities are provided in Table 1.

carried out in an Agilent 7890 A gas chromatograph (GC) coupled to an Agilent 5975 C mass spectrometer (MS). The MS was used in both scan mode and single ion mass mode at a time, monitoring  $m/z = 71$  for the *n*-alkanes,  $m/z = 191$  for the hopanes and  $m/z = 217$ – $218$  for the steranes.

Steranes and hopanes were present in the soils analyzed (Fig. 1, Table 1). Hopanes having the  $17\alpha(H),21\beta(H)$ - stereochemistry predominate, which indicates a substantial contribution from petroleum. No  $\beta\beta$ -isomers were detected, and thus we can exclude significant inputs of hopanes from modern living organisms. The steranes in petroleum are derived from sterols, and can be expected to occur as the C27, C28 and C29 homologous series in different proportions (Rosell-Melé et al., 2010). They have a number of isomeric forms with different stereochemistries at positions 5, 14, 17, 20 and 24. These are in fact the type of distribution found in the samples, which further confirms the occurrence of petrogenic inputs to the soils investigated.

The camera traps were set, in both sites, on video mode to record during one minute every time they were triggered. After recording a video, camera traps remained deactivated for one minute before being able to be triggered again. Cameras were operative for 115 h in site 1, and 243 h in site 2. Videos were analyzed to identify species and visit frequency. Consecutive videos of the same species were considered to represent different visits (or individuals) to the sites only when there was at least a 30-min interval between captures (following Bowkett et al., 2007), unless different individuals were clearly identifiable by unique markings or gender.

Supplementary material related to this article can be found online at <http://dx.doi.org/10.1016/j.envres.2017.10.009>.

We obtained 74 videos, corresponding to 47 different visits (1.6 visits per day and site). Four species of wild mammals were observed visiting the sites. The most frequently observed species were the lowland tapir (*Tapirus terrestris*, 78.7%; Fig. 2), followed by the paca (*Cuniculus paca*, 12.8%), red-brocket deer (*Mazama americana*, 6.4%) and collared peccary (*Peccary tajacu*, 2.1%). Consumption (i.e. apprehending, licking, chewing and swallowing) of contaminated soils and water was observed for the four species in 61.7% of the visits ( $n = 29$ ,

1.0 visit per day and site). Recordings from site 1 clearly show those four species ingesting soil and water from the drainage channel of the sump tank, and recordings from site 2 show tapirs licking the abandoned oil well and ingesting fluids leaking from it (Fig. 2 and Video 1/ Supplementary material).

### 3. Geophagy: a new exposure route to petrogenic compounds?

Our results draw attention to ingestion of soil and water in oil-contaminated areas in tropical rainforests as a potential source of exposure to petrogenic compounds for wildlife and human communities that rely on subsistence hunting. First, although soil ingestion varies among species, large amounts of soil (up to ~30% of ingesta) are ingested by vertebrate species visiting mineral licks (Beyer and Fries, 2002). Second, there is extensive scientific literature on bioaccumulation of petrogenic contaminants that occur in produced water (Neff, 2002) and laboratory studies have demonstrated both the bioavailability and the toxicity of environmental contaminants in soil and sediment ingested by wildlife (Beyer and Fries, 2002). Third, subsistence hunting of the four species recorded in this study play an important role in the diet of rural Amazonian human populations and account for a high percentage of daily protein intake. Several studies conducted in the Northern Peruvian Amazon, concluded that the four recorded species represent 47.1–67.4% of hunted biomass by native communities (Bodmer and Lozano, 2001). Fourth, the portion of the hunting grounds affected could be quite high taking into account the large home ranges of these species and the fact that some of these species show long-distance travel (i.e. 10 km) outside of their home-range to visit a mineral lick (Tobler, 2008).

There are several non-mutually exclusive hypotheses for explaining mineral lick visitation and geophagy (e.g. detoxification of alkaloids and other toxins). Evidence suggests that vertebrates visit mineral licks for sodium supplementation, given the low concentration of this element in plant tissues consumed by these taxa in a salt-deprived regions such as the western Amazon (Dudley et al., 2012). Since produced waters of block 1AB/192 have a very high salinity up to 193,000 mg/L (Yusta-García et al., 2017), it seems plausible that these animals approach produced water damped soils to ingest them. Around 1 million barrels/day of produced water have been directly released on soils and rivers in the study area, between the beginning of oil extraction and 2010, when re-injection of produced water back to the oil reservoir was implemented in the area (Orta Martínez et al., 2007). This discharge has led to an increase of 12% and 20–30% in sodium and chloride concentrations in the Amazon river (Óbidos, Pará), thousands of kilometers downstream in Brazil (Yusta-García et al., 2017). The dumping of produced water on the environment has been a common practice in oil operations in tropical countries, where the oil industry uses sub-standard technology not in accordance with the state-of-the-art employed in its home countries (Jernelöv, 2010). Moreover, worldwide, leakage from abandoned oil wells it is an unresolved problem, as at least 4 million onshore hydrocarbon wells are abandoned all over the world and high proportion of seals placed in wells may be faulty (Davies et al., 2014). In the Peruvian Amazon, 335 out of 628 drilled oil wells are now abandoned (Orta Martínez et al., 2007).

The health effect that the ingestion of oil-polluted soil by Amazonian frugivorous and herbivores may have on wildlife and human population has not yet been studied. It could potentially result in bioaccumulation and biomagnification of hydrocarbons and heavy metals, and could be hazardous for the conservation of top predators in the tropical rainforests and, more worrisome, for the health of local indigenous peoples that rely on subsistence hunting. The unprecedented images of wildlife ingesting oil-polluted soil in the Peruvian Amazon reported here, illustrate that there are still substantial gaps in our basic understanding of the environmental and health impacts generated by oil extraction activities. As worldwide rainforests are facing a steep increase in hydrocarbon-related activity and



Fig. 2. Pictures taken in 1AB/192 oil block in the Peruvian Amazon of (A) lowland tapirs (*Tapirus terrestris*) licking from an abandoned oil well in site 2, and (B) oil-coated faeces of lowland tapir (*Tapirus terrestris*).

petrogenic contaminants on the ground become more frequent and widespread in these remote and intact areas, geophagy may emerge as an increasingly important route for contaminant exposure. It is urgently needed to assess this potential new route of exposure for both wildlife and human populations, and study the health risks of wildlife consumption for the local populations that live in the vicinity of oil extraction areas and rely on subsistence hunting.

### Acknowledgments

We appreciate the participation of local indigenous communities and the indigenous federations of the Pastaza and Corrientes River basins (FEDIQUEP and FECONACO, respectively). We also appreciate the financial support of the Fundació Autònoma Solidària, IDEAWILD, Earthwatch Institute and Rufford Foundation (13621-1). Orta-Martínez benefited from the financial support of the Marie Curie Actions (REA agreement N° 289374 - ENTITLE), the ‘Conflict and Cooperation over Natural Resources in Developing Countries’ program of The Netherlands Organisation for Scientific Research (NWO) - [www.iss.nl/nebe-](http://www.iss.nl/nebe-) and the ‘International Initiative for Impact Evaluation’ (3ie).

### Funding

This work was supported by the *Fundació Autònoma Solidària* (FSXXX-18, 2013), the Rufford Foundation (13621-1, 2013), the *Direcció General de Recerca de la Generalitat de Catalunya* (FI-DGR 2014–2017), the Marie Curie Actions (REA agreement 289374 - ENTITLE), the ‘Conflict and Cooperation over Natural Resources in Developing Countries’ programme of The Netherlands Organisation for Scientific Research -NWO (NEBE, 2014) and, the ‘International Initiative for Impact Evaluation’ – 3ie (TW8R2.1006 and TW8R2.1021, 2015). ISGlobal is a member of the CERCA Programme, *Generalitat de Catalunya*.

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