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Impact of the Oil Extraction in Ecosystems in Ecuador: A Study of the Contamination with Polycyclic Aromatic Hydrocarbons (PAHs) in Fish Exposed to the Oil Exploitation Activities in Shushufindi, Sucumbíos, Ecuador

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Abstract: Fish are visible members of aquatic communities that are vulnerable to contamination with polycyclic aromatic hydrocarbons (PAHs). Fish can have complicated life cycles and behavior. They can be exposed to PAH-contaminated sediments and water by a variety of routes, including respiration; ingestion of food, sediment, and detritus; and dermal absorption. This investigation involves a preliminary assessment of the sixteen PAHs issued by the United Stations Environmental Protection Agency (U.S. EPA) that were identified in entrails and muscles of fish affected by the oil exploitation in Shushufindi, Sucumbios Province, Ecuador. The PAHs were extracted from the matrix, concentrated, purified by florisil column and analyzed using Gas Chromatography/Mass Spectrometry GC/MS. Three different sampling places were selected. Also, the collected fish were classified according their feeding behavior. Additionally, the contents of PAHs in the sediments to establish a relation between the contamination level in fishes and their feeding behavior were analyzed. This information and the knowledge about the food habits of the population in Shushufindi can show the possible contamination of the people from this zone.

Keywords: Polycyclic Aromatic Hydrocarbons, Fish, Oil Contamination, Hydrocarbon Contamination, Biomarkers

Introduction

PETROLEUM HAS A vast significance for modern society. On one hand, it represents energy, transport, the present quality of life and it is also connected with a lot of products that are used every day. On the other hand, oil has some negative sides. One of these is determined by the changes of the world economy and the economical crisis caused due to this market. The other dark side is shown through the environmental problems associated with the exploitation and use of oil. The presence of this unique product in the environment means also a lot of serious problems connected with contamination, decrease of the quality of water, soil and the life of many plants and animals. These effects can also affect, in the end, the life of human beings (San Sebastián, M. & Hurtig, A. K., 2004) who are connected to this environmental problem trough the air, water and the food chain. The

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contaminants will reach the population because of the fishing practice in the area that has been part of their culture for many years and has also been learned by the settlers. A constant and sustained exposure of humans to polycyclic aromatic hydrocarbons (PAHs) could lead to develop genotoxic diseases such as cancer (Vives *et al.* 2001).

Oil exploitation in Ecuador began in 1911 with the drilling of the first oil bearing well: Ancon 1 at Santa Elena Peninsula. But it was not untill 1972 that the oil activity started at large scale, in the jungle region (Dueñas, 2008). There are different oil companies working in Ecuador. One is the governmental company Petroecuador and some other international companies (Bustamante & Jarrín, 2005; Amazonía por la vida, 2007).

The main areas for the oil extraction activity in Ecuador are located in the jungle in the Amazon region, where 80% of the oil exploitation in Ecuador takes place. The principal places are: Lago Agrio, Shushufindi, Orellana, La Joya de los Sachas (Amazonía por la vida, 2007).

Oil production has represented for Ecuador the first income for the last 40 years. For the last 10 years, the oil exportation has been located between 43% and 66% of the total exports of the country (Guaranda, 2009).

Oil spills are continuously produced in the exploitation zones. This problem represents serious damage for plants, animals and the people in the region. The quality of water, soil and food is compromised in this contamination process (Guaranda, 2009).

The future development of the existing ecosystems is at risk, especially, due to the fact that the process is carried out on a very vulnerable sector of the planet.

Oil Activity in Shushufindi

Shushufindi belongs to the Sucumbios Province in Ecuador. The area of this canton is 2,485 km^2, with a population of 19,000 inhabitants and vegetation that corresponds to a tropical humid forest, with an average temperature of 28 °C.

Shushufindi has the following basic oil infrastructure:

Five storing stations (Shushufindi Centro, Norte, Sur, Suroeste and Aguarico)
A refinery
A gas processing plant
A gas pipeline
More than 100 pools of waste

The oil infrastructure is too big for the area in relation to the size of the city and the population (Amazonia por la vida, 2007).

Shushufindi suffers the effects of oil activity which includes pollution, health problems in the population, and also violence associated with the economical situation in the region connected to the oil activities (Amazonia por la vida, 2007).

The environment of this region is affected by oil activity and among the most important contaminants are PAHs.

Polycyclic Aromatic Hydrocarbons (PAHs)

PAHs are hydrocarbons derived from benzene. They present two or more benzene rings fused together. They have low solubility in water and high solubility in organic solvents and therefore high lipophilicity. PAHs are considered persistent and some of them are toxic and carcinogenic (Rakoff & Rose, 1994; Vollhardt & Schore, 2007; Ortiz, 2002).

There are two sources of PAHs: petrogenic and pyrogenic. PAHs are present as natural components of petroleum and these PAHs are called petrogenic. Pyrogenic PAHs are formed when carbon-containing materials are burnt incompletely. Elevated indoors concentrations of PAHs are typically due to the burning of wood, coal and tobacco smoking (Pointet & Milliet, 1999). Forest fires can be identified as natural sources of PAHs and burning of solid wastes, industrial processes and electrical generators can be mentioned as anthropogenic sources (Peña *et al.*, 2003; Phillips *et al.*, 2000).

Some PAHs have carcinogenic and mutagenic properties. The most notorious and common carcinogenic PAH is benzo[α]pyrene (BaP), which contains five fused benzene rings. The $LogK_{ow}$ value for this PAH is 6.3, that corresponds to a high rate of bioaccumulation in the food chain (Baird & Cann, 2005).

Due to their properties, PAHs can bioaccumulate in the fatty tissues of some marine organisms and have been linked to the production of liver lesions and tumors in some fish. They also remain in the sediments and soils and this is another way to reach the fish (Mastandrea *et al.*, 2005).

United States EPA establishes sixteen PAHs as priority pollutants: Acenaphthene, Acenaphthylene, Anthracene, Benzo (a) Anthracene, Benzo (a) Pyrene, Benzo (b) Fluoranthene, Benzo (g,h,i) Perylene, Benzo (k) Fluoranthene, Chrysene, Dibenz (a,h) Anthracene, Fluoranthene, Fluorene, Indeno (1,2,3-cd) Pyrene, Naphthalene, Phenanthrene and Pyrene (U.S. EPA, 1988). These compounds were analyzed and quantified in this study.

Methodology

Selection of the Places for the Sampling

This research work was carried out in Shushufindi, Sucumbíos, Ecuador (figure 1).

Figure 1: Location of Shushufindi in Ecuador

(Source: Microsoft Encarta, 2007)
Three places were selected to collect fish samples as well as soil samples.

Fishing Techniques

Different fishing techniques with hooks and nets (e.g. trammels and trawls) were necessary to collect the fish samples according to the selected place.
The collected fish were divided into two main groups, according to the habitat: 'Pelagic' fish and 'Benthic' fish. 'Pelagic' fish live in the water column. 'Benthic' fish is a kind of fish that feeds from the bottom of the water bodies.

Soil Sampling

The soil samples were collected from the same points as for the fish using an auger.

PAHs Extraction from Fish Samples

The samples were dissected to obtain the entrails or the muscles, according to the analysis to be performed. The isolated parts were homogenized. The extraction of PAHs was carried out in a Bood tube connected to a reflux tube with dichloromethane and after concentration in a Rota vapor. Samples of 50 g were used for the process. The concentrated extract was cleaned up in a column packed with florisil. The obtained sample was again concentrated to secure 1 or 2 mL of an extract that could be analyzed by GC/MS (U.S. EPA, 2000).

Soil Samples Preparation and Extraction

The soil samples were dried at atmospheric conditions in Quito (20°C and 540 mmHg), grinded, quartered, sifted and weighed. Finally, the samples were stored in flasks protected from the light with aluminum foil.

The samples were mixed with dichloromethane and sodium sulfate. The resulted mixture was extracted during 26 h in a Soxhlet equipment. The subsequent procedure was similar as the one followed for the fish samples with the concentration, cleaning up and second concentration steps before the injection of the samples to a GC/MS (U.S. EPA, 1996).

PAHs Analysis

A standard stock solution of 16 PAHs (defined by EPA as priority pollutants) was prepared. The concentration of this stock solution was 20 ppm for each PAH and the chromatographic system was a GC/MS Clarus 500 equipped with a column ZB-5 ms, 30m ′ 0,25mm; 0,25μm film thickness. The injection volume was 1 mL, with He as carrier gas. The temperature of the injector was 270 °C, transfer line temperature was 280 °C and ion source temperature 200 °C.

PAHs Identification

The PAHs identification and quantification was possible through comparison of retention times and mass spectrum of the identified peaks and the standard solution. Standard curves were built for every PAH.

The quantification of PAHs in fish was done only in the samples at the most contaminated point. On the other points, the analysis was only qualitative. In the soil samples the analysis was qualitative.

Results

Location of Selected Places for the Sampling

The selected places were named according to the position of the sampling place with respect to the Industrial Complex Shushufindi.

The selected places with their location details are described in the following tables:

Table 1: Location of North Station Small Affluent of River Eno s /n

	Location	Direction
Latitude	0°9'7"	S
Longitude	76°38'48"	W
Altitude	256 m asl	

Table 2: Location of Lake of Petroindustrial

	Location	Direction
Latitude	0°12'9"	S
Longitude	76°39'10"	W
Altitude	250 m asl	

Table 3: Location of South Station River " La Sur "

Point 1		
	Location	**Direction**
Latitude	0°14'47"	S
Longitude	76°38'54"	W
Altitude	244 m asl	
Point 2		
	Location	**Direction**
Latitude	0°15'7"	S
Longitude	76°39'5"	W
Altitude	259 m asl	

Collected Fish

The collected fish at the different sampling places were described in the following tables:

Table 4: Fish Collected at North Station

Scientific Name	Common Name	Type According Habitat
Aequidens tetramerus	Vieja	Pelagic fish
Crenicichla johanna	Chuti	Pelagic fish
Leporinus friderici	Sardina	Pelagic fish
Astyanax maximus	Sardina	Pelagic fish
Hoplios molaborieus	Guanchiche	Benthic fish
Ancistrus algoe	Carachama	Benthic fish
Rineloricaria lanceolata	Carachama	Benthic fish
Pimelodella grisea	Barbuda	Benthic fish
Squamata emorginatus	Carachama	Benthic fish
Pterigopliehtg gibbieeps	Carachama	Benthic fish

Table 5: Fish Collected at Lake of Petroindustrial

Scientific Name	Common Name	Type According Habitat
Aequidens tetramerus	Vieja	Pelagic fish
Hoplios molaborieus	Guanchiche	Benthic fish

Table 6: Fish Collected at South Station

Scientific Name	Common Name	Type According Habitat
Aequidens tetramerus	Vieja	Pelagic fish
Crenicichla lucius	Chuti	Pelagic fish
Squamata emorginatus	Carachama	Benthic fish
Pterygoplichthys punctatus	Carachama	Benthic fish
Ancistrus occidentalis	Carachama	Benthic fish
Pterigoplichthys stibario	Carachama	Benthic fish
Rineloricaria lanceolata	Carachama	Benthic fish

Quantification of PAHs in Fish Samples

In figure 2, the results of the analysis of PAHs in entrails of *Aequidens tetramerus* collected from Lake of Petroindustrial are shown. Seven PAHs were found at concentrations detailed in figure 2.

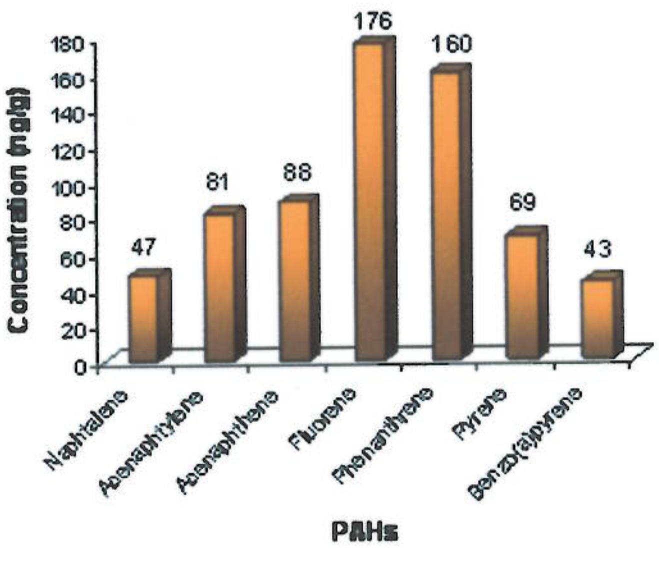

Figure 2: Average Concentration of PAHs (ng/g) in Entrails of *Aequidens Tetramerus* Samples from Lake of Petroindustrial

In a previous study, the percentage recovery of PAHs in fish samples was found to be between 70.8 and 89.8% which are acceptable values according to international standards (AESAN, 2002) and (AOAC, 2002).
The results of this study were similar to the values reported by COIRCO, 2006 from the Colorado river (Mendoza, Argentina) representative of an oil exploitation zone, and the study developed by Pointet & Milliet, 1999 in the natural reserve of Camargue (France) which is an ecosystem exposed to the atmospheric discharges from an established petrochemical industry.
The other analyses were qualitative. PAHs were identified on the other sampling places in muscle tissues of the examined fish.
The results are summarized in table 7.

Table 7: Qualitative Results of PAHs Contamination in Fish Samples from the Shushufindi Region

Location	Type of Fish	Fish part Analyzed	PAH	Number of Samples
Lake of Petroindustrial	Benthic fish	Muscles	Anthracene	4
North Station	Pelagic fish	Muscles	Anthracene	2
South Station	Pelagic fish	Muscles	Anthracene	1
South Station	Benthic fish	Muscles	Anthracene	1

These results showed that PAHs were found in the muscles of many fish. This is an important finding because the accumulation of PAHs in this part of the fish can become a problem for the population in Shushufindi. Franco *et al.*, 2003 reported a reference value for maximum content of PAHs in fish used as food (4 ng/g FW).
The qualitative results in soil samples are summarized in table 8.

Table 8: Qualitative Results of PAHs Contamination in Soil Samples from the Shushufindi Region

Location	PAH	Number of Samples
Lake of Petroindustrial	Anthracene	1
Lake of Petroindustrial	Phenanthrene	1
North Station	Benzo(k)fluoranthene	1
South Station	Benzo(b)fluoranthene	1

The PAHs in this case were not the same as in fish, except for the place named Lake of Petroindustrial.
The time and process of contamination in every fish is unknown. The metabolism of PAHs in fish is complex and therefore, a direct correlation between the soil contamination and the PAH residues found in fish entrails and muscle was not observed. In the liver, PAHs are transformed into other substances usually oxidized. The probability to find PAHs contamin-

ation in pelagic and benthic fish is the same because the ways of contamination are equally important (HCPEC, 2010).

Behavior of the Population

In this research work a group of ten questions to be answered by the population was prepared and fifty people were interviewed. The main results of this questionnaire are as follows:

1. The population fishes and consumes the species from the lakes and rivers in Shushufindi. They consider that these fish are better than the fish brought from the Coastal area, fresher, easier to get and less expensive.
2. Fishing can be done all throughout the year but the people prefer fishing during summer when the water level is lower.
3. The population knows that the fish abundance and the diversity have decreased during the last years but they think this problem is connected to bad fishing practices and not to the oil exploitation activities.

Conclusions

1. This study confirmed the presence of PAHs in entrails and muscles of fish collected from water bodies affected by the oil activity in Shushufindi, .
2. The concentration of PAHs in entrails of *Aequidens tetramerus* was determined in amounts between 43 and 176 ng/g.
3. The most common PAH was anthracene.
4. The presence of PAHs in fish muscles is a finding that must be considered as a concern because the population might be getting contaminated through fish consumption.
5. This work showed that the ecosystem in Shushufindi is not sustainable under oil activity conditions as in we have now also the population in danger.
6. If we want to maintain the jungle as an important ecosystem, it is necessary to change a lot of techniques, methods and responsibilities.

Future Work

1. It is necessary to quantify the PAHs identified in some fish and soil samples.
2. It is necessary to do a study to analyze the health problems of the population connected to fish contamination.

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