

## TEMPORAL VARIATION OF PAHS IN SOILS FROM THE BIOBÍO REGION: CENTRAL SOUTHERN CHILE

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## ABSTRACT

In this short communication we describe the temporal variation of PAHs fingerprints and burden in surface soils from coastal and central valley sites in South Central Chile, with different anthropogenic influence. PAHs were extracted with accelerated solvent extraction and measured by HPLC with fluorescence detection. Levels of  $\Sigma$  15 PAHs were relatively low in both sites ranging between 190 to 3396 ng g<sup>-1</sup> TOC of soil. However, the fingerprints were different in both sites an increment in the total concentrations was observed ( $p < 0.001$ ) in summer compared to winter periods (May 2001 and January 2002). These results suggest a temporal change in the total burden of PAHs and that the sources are related to biomass and coal combustion.

**Keyword:** PAHs, Soil, Temporal variation, Pollution, Chile

## INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in the environment. The origins are mainly from incomplete combustion both from natural and anthropogenic sources [1]. Once PAHs are emitted into the atmosphere, they can be redistributed between the gas and particle phases, and are subsequently deposited to the terrestrial environment through dry or wet deposition.

Soils are a primary sink for contaminants due to their large capacity for retaining hydrophobic chemicals [2-4]. The accumulation of PAHs in soil is a result of an increment of the deposition over the degradation factors.

The increment or decrease of PAHs levels in soil results from differences between degradation and loss processes and inputs from natural or anthropogenic sources such as atmospheric deposition. Therefore, the temporal study of PAHs burden in soils could be an indicator of the pollution status of the soil compartment. In Chile only the studies of Barra et al [5] and Henríquez et al [6] described PAHs levels in soils samples.

The study focuses on the evaluation of temporal variation of 15 USEPA PAHs in forest soils of two sites with different anthropogenic influence and sources. These results are complementary to those described by Barra et al., [5].

## EXPERIMENTAL

## Sampling sites

Lleulleu site is located in coast zone with a low anthropogenic influence with land use mainly forestry and agriculture.

Cholguan site is located in the Central Valley zone with an industrial setting (sawmill and wood-panel production). The land use is mainly forestry.

## Sampling procedure

In both sampling sites soils were taken from the top 10 cm with a small metallic shovel. Two replicas of five points distributed on the corner of a square matrix of 100 x 100 m were considered for the soil sampling, in addition the central point of the square were also sampled. Samples were stored in aluminum foil and then covered in plastic hermetic bags until analysis.

## Analytical procedures

The extraction methodology was based in Quiroz et al., [7]. Soil samples were mixed with anhydrous sodium sulfate, and then extracted with Accelerated Solvent Extraction with acetone:cyclohexane (1:1) at 150°C, 14 MPa for 5 minutes (three times). Extracts were combined and concentrated to 5 ml.

For the analysis of PAHs compounds 2 ml of the above extracts were concentrated to 0.2 ml and then cleaned-up in a Florisil column (10 mm i.d., 3g Florisil). Quantitation was performed by HPLC with fluorescence detector

for PAHs

PAHs analysis was performed in 200  $\mu$ l of the above extracts, concentrated to dryness and resuspended in 200  $\mu$ l of acetonitrile, the homogenization was performed by sonication (5 min). In this case the analysis was performed with an HPLC HP1050 with fluorescence programmable detector using a chromatographic column LiChroCART 250-3, Lichrospher PAH (5  $\mu$ m) at 20°C temperature. Mobile phase was acetonitrile:water (50% V:V), increasing the acetonitrile proportion to 60% (0-3 min) and 100% (3-14 min). This proportion was maintained constant until 24 min.

## Quality control /Assurance

The PAH calibration mix (10mg of each compound per ml acetonitrile) was supplied by Supelco. HPLC grade water and acetonitrile were supplied by Baker.

Procedural blanks were performed with each set of samples to check for the presence of interfering peaks. Detection limits were determined by injecting decreasing concentrations of PAH standards. A signal-to-noise ratio of 3:1 was used as the criteria for the limit of detection. PAH detection limits were between 0.03 ng/g (benzo(k)fluoranthene) and 0.15 ng/g (indeno(1,2,3-cd)pyrene) and the detection limits of the other compounds were between 0.01 ng/g and 0.03 ng/g.

## Organic carbon determination

Total organic carbon (TOC) was determined according to the method of Gaudette et al. [8]. Ten milliliters of 1N K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution was added to 0.5 g of dry soil; then 20 ml of concentrated sulfuric acid was added and the mixture was gently shaken, and left to digest for 30 min. The solution was then diluted to 200 ml with distilled water, and 10ml of phosphoric acid and 0.2 g of NaF was added. Finally, the solution was cooled and titrated with anhydrous ferrous sulfate ammonium.

## Statistical analysis

Statistical analysis was performed using standardized data through a statistical software package (STATISTICA, Statsoft Inc., 1997). For comparison of median and principal component & classification analysis (PCCA), values lower of limit of detection (LOD) and limit of quantification (LOQ) were estimated by half of LOD and LOQ, respectively.

## RESULTS AND DISCUSSION

PAHs levels in each site are reported in table 1. Total PAHs for Lleulleu were 190 and 648 ng g<sup>-1</sup> TOC; and for Cholguan were 580 and 3396 ng g<sup>-1</sup> dw, respectively. In both sampling campaigns the levels were higher at the Cholguan site ( $p < 0.001$ ) (table 1). In Cholguan site the observed levels were related to an anthropogenic source, due to the presence of a wood pallet mill using boilers feed with wood residues. Lleulleu site corresponded to typical background levels [5].