PAHs in coal cleaning rejects from Santa Catarina, Brazil

HPAs em rejeitados de beneficiamento de carvão de Santa Catarina, Brasil

J. Ribeiro1,2*, C. Neto2, M. Braga3, L. F.O. Silva3, D. Flores1,2

Abstract: The coal cleaning rejects (CCRs) from mining activities in Santa Catarina State, Brazil, were investigated aiming the identification and quantification of the 16 priority polycyclic aromatic hydrocarbons (PAHs). A total of 5 CCRs samples, essentially composed of a mixture of coaly and mineral matter, were selected for this study. The concentration of the environmental 16 priority PAHs was determined in the samples by gas chromatography coupled to mass spectrometry. The results indicate that 7 of the 16 priority PAHs were detected and the sum of PAHs concentration is within the values reported for the coal rank that corresponds to the coal in Santa Catarina. The native or petrogenic PAHs determined in the CCRs landfills may adversely impact soil, water, and plants and, consequently, affect the human health and biodiversity, depending mainly on the extent of exposure, concentrations and characteristics, and whether exposure occurs via inhalation, ingestion or skin contact.

Keywords: Coal mining, Coal cleaning rejects, Petrogenic PAHs, Environmental impacts.

1. Introduction

The southern region of Brazil, including Paraná, Santa Catarina and Rio Grande do Sul regions, has been known for its abundant and economically important coal deposits. The coal in Brazil has been used for thermoelectric power generation for nearly 80 years (Silva et al., 2010 and references therein). The coal from Santa Catarina provides around 2-5% of the energy production in the country (Oliveira et al., 2013) and it is classified as high volatile bituminous coal, with vitrinite reflectance ranging between 0.7% and 1.0% (Kalkreuth et al., 2004, 2006).

The coal mining activities in Santa Catarina State produces 3.5 million ton/year of rejected material that is disposed in landfills and, due to the environmental concerns related with soils and waters pollution, the region was already classified as an environmental endangered area by the Government (Silva et al., 2010 and references therein). A set of measures to reduce the environmental impact of coal mining and beneficiation activities have been applied; however, these measures have proven to be insufficient to prevent the damage caused by mining activity at Santa Catarina coal mines over the time. Leaching from coal cleaning rejects (CCRs) disposal may severely impact the soil, surface water and groundwater resources if no prevention/remediation measures will be applied (Silva et al., 2010). Consequently, the CCRs resulting from coal beneficiation is receiving great attention in some recent studies (Silva et al., 2009, 2010; Oliveira et al., 2013; Dias et al., 2014). Nevertheless, the study of polycyclic aromatic hydrocarbons (PAHs), which are known as a group of environmental organic pollutants that are harmful to environment and human health, was never addressed. The U.S. Environmental Protection Agency (US-EPA) has fixed 16 priority PAHs, which are the main focus in this research.

Natural sources of PAHs include coal seams and carbonaceous rocks, volcanic activity and forest fires, while anthropogenic sources include incomplete combustion of fossil fuels, industries, internal combustion and diesel engine exhausts, as well as aviation exhaust, cigarette smoking, among others (Achten & Hofmann,
The combustion of fossil fuels is considered as the major anthropogenic source of PAHs in the environment (pyrolytic source) while the natural source of PAHs is related to native PAHs in fossil fuels (petrogenic source). The petrogenic source of PAHs in the environment can also result from anthropogenic activities, such as coal mining or oil spills. A review on the natural occurrence of PAHs in coals supported that PAHs in coal, arising from chemical conversion of organic matter, can also be a source of contamination (Achten & Hofmann, 2009).

Considering the environmental concerns related with the disposal of CCRs from Santa Catarina mining activities and the increasing evidence of the ubiquitous presence of PAHs in environment and the health risk associated with their exposure, the main goal of this study is to contribute for the mitigation of the environmental legacy in Santa Catarina. It is expected to provide information that can assist the local entities for managing pollution and application of mitigation measures. Besides, this work reports the first data about PAHs in CCRs from Santa Catarina and the environmental problems associated with their disposal in the landfills. The results may be useful for prediction and optimization of coal cleaning technologies, considering both the efficiency and environmental issues. For that the specific objectives of this work includes: (i) identification and quantification of the 16 priority PAHs in coal cleaning rejects; (ii) identification of potential environmental impacts associated the CCRs disposal.

2. Materials and methods

A total of 5 coal cleaning reject samples from four mining areas of Santa Catarina (Fig. 1) were selected for this study: Treviso (CR 4, CR 48), Laura Müller area (CR 39), Urusanga (CR 59), and Criciúma (CR 57). The CCRs are essentially composed of a mixture of coaly and mineral matter, characterized by the occurrence of sulphide minerals and leachable hazardous elements (Silva et al., 2010).

The concentration of the environmental 16 priority PAHs was determined in the samples by gas chromatography coupled to mass spectrometry (GC-MS). For the GC-MS analysis, PAHs were removed from samples by Soxhlet extraction using dichloromethane as solvent. The extracts were separated into saturated, aromatic and polar fractions with a chromatographic column. The aromatic hydrocarbon fractions were then analyzed using an Agilent gas chromatograph 6890N equipped with a 7683B auto sampler and coupled to a mass spectrometer detector 5975B system. The analyses were performed with a DB – 5 column (50 m x 0.25 mm i.d) coated with a 0.25 µm stationary phase film. The experimental conditions were as follows: the carrier gas was He at 1.2 mL min⁻¹, in constant flow mode; the injector temperature was 290°C; the gas chromatographer oven temperature program was: 40°C (3 min) to 300°C at 8°C min⁻¹, held for 15 min. The mass spectrometer was operated in the electron impact ionization mode at 70 eV. Samples were analyzed in the selective ion monitoring (SIM) mode and the quantification was done by preparing five calibration standard solutions of a standard mixture containing the 16 priority PAHs. Blanks, duplicate samples and internal standard addition were employed for analytical assurance and deuterated pyrene (D10 – pyrene) was used as internal standard. The identification of compounds was accomplished by comparing the retention time of the samples to that of PAHs standards under the same conditions and the corresponding mass spectra. The relative response factors of the calibration standard solutions were used to calculate the concentrations of the 16 priority PAHs in the studied samples.

![Fig. 1. Geographical setting of Santa Catarina coal mining area.](image)

3. Results and discussion

The individual and total concentrations of the priority PAHs in CCRs from Santa Catarina are presented in table 1, together with the relative percentages of low molecular weight (LMW) PAHs and high molecular weight (HMW) PAHs. The results demonstrated that 7 of the 16 priority PAHs were detected, namely, phenanthrene, fluoranthene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[ghi]perylene, and dibenzo[ah]anthracene. The most abundant PAHs in the samples are benzo[k]fluoranthene, ranging between 3.8 ng g⁻¹ and 204.9 ng g⁻¹, phenanthrene ranging between 17.0 ng g⁻¹ and 116.6 ng g⁻¹, and benzo[a]anthracene with concentrations between 24.5 ng g⁻¹ and 156.9 ng g⁻¹, followed by minor proportions of dibenzo[ah]anthracene, benzo[b]fluoranthene, and fluoranthene. Usually, PAHs from petrogenic origin have higher amounts of naphthalene and phenanthrene (Schwarzbauer, 2006), which is in accordance with the great amounts of phenanthrene found in these samples (Table 1). The absence of naphthalene could be attributed to its volatilization during the extraction procedures.
The sum of the priority PAHs ranges between 8.5 ng g\(^{-1}\) and 610.4 ng g\(^{-1}\), with a mean value of 241.9 ng g\(^{-1}\). The highest value is reported for sample CR 39 (from Laura Muller mining region) and the lowest for sample CR 59 (from Urusanga mining region). Maximum concentrations of the 16 priority PAHs in coal were established for high volatile bituminous coals: 35 to 11,000 ng g\(^{-1}\) (Stout & Emsbo-Mattingly, 2008). The sum of priority PAHs in the studied samples, which result from high volatile bituminous coal, are within the values reported in the literature, except sample CR 59.

On the basis of the number of aromatic rings, PAHs are classified as LMW PAHs containing 2 to 3 rings and HMW PAHs with 4 to 6 rings. The sum of the relative percentages of LMW PAHs and HMW PAHs of CCRs were calculated and the results are shown in table 1. The results demonstrate the predominance of HMW PAHs (62.9% - 100%) comparatively with the LMW PAHs (0.0% - 37.1%). Differences in the structure and size of individual PAHs result in substantial variability in the physical and chemical properties of these compounds and, consequently, their behavior and fate in the environment.

Table 1. Concentration of the 16 priority PAHs in the studied samples, their sum in each sample and relative percentages of LMW PAHs and HMW PAHs.

<table>
<thead>
<tr>
<th>16 priority PAHs (ng g(^{-1}))</th>
<th>Aromatic rings</th>
<th>Molecular weight</th>
<th>CR8</th>
<th>CR39</th>
<th>CR48</th>
<th>CR57</th>
<th>CR59</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Acenaphthylene</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Acenaphthyrene</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fluorene</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
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<td>-</td>
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<tr>
<td>Fluoranthene</td>
<td>4</td>
<td>-</td>
<td>14.6</td>
<td>14.6</td>
<td>5.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pyrene</td>
<td>3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>-</td>
</tr>
<tr>
<td>Benzo[a]anthracene</td>
<td>4</td>
<td>-</td>
<td>51.0</td>
<td>156.9</td>
<td>58.8</td>
<td>24.5</td>
<td>-</td>
</tr>
<tr>
<td>Chrysene</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>-</td>
</tr>
<tr>
<td>Benzo[ghi]fluoranthene</td>
<td>4</td>
<td>-</td>
<td>21.3</td>
<td>58.8</td>
<td>26.6</td>
<td>9.3</td>
<td>1.6</td>
</tr>
<tr>
<td>Benzo[k]fluoranthene</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Benzo[a]pyrene</td>
<td>5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Indeno[123-cd]pyrene</td>
<td>5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>-</td>
</tr>
<tr>
<td>Dibenz[a]anthracene</td>
<td>6</td>
<td>-</td>
<td>42.6</td>
<td>58.7</td>
<td>21.0</td>
<td>11.8</td>
<td>3.1</td>
</tr>
<tr>
<td>Benzo[b]pyrene</td>
<td>5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

1 16 priority PAHs \(\text{ng g}^{-1}\)

% LMW PAHs | 25.3 | 19.1 | 37.1 | 17.0 | 0.0  

% HMW PAHs | 74.7 | 80.9 | 62.9 | 83.0 | 100  

The transport, deposition and chemical transformation of the PAHs depends on their form of occurrence (Ravindra et al., 2008). The PAHs bounded to the particulate matter may be leachate and therefore transported and incorporated in a variety of other environmental media such as soils, surface and ground waters, in proximate or distal areas and consequently affecting human health and ecosystems. Furthermore, HMW PAHs exhibit a high resistance to biodegradation (Berkowitz et al., 2008). Therefore, the concentrations of PAHs in CCRs landfills may adversely impact soil, water, and plants and, consequently, affect the human health and biodiversity, depending mainly on the extent of exposure, concentrations and characteristics, and whether exposure occurs via inhalation, ingestion or skin contact. If safe exposure limits of PAHs to humans are exceeded they become toxic or poisonous leading to a wide range of human health problems and diseases.

4. Conclusions

The assessment of the PAHs concentration in CCRs from Santa Catarina was the main goal of this work. The focus of this study on PAHs is justified by their negative impact in the environment, biodiversity and effects on human health.

The results demonstrated that 7 of the 16 priority PAHs were detected; the most abundant PAHs in the samples are benzo[k]fluoranthene, phenanthrene, and benzo[a]anthracene, followed by minor proportions of dibenzo[ah]anthracene, benzo[h]fluoranthene, and fluoranthene. The sum of priority PAHs in the studied samples, are generally within the values reported in the literature for high volatile bituminous coals. It was also noticed the predominance of HMW PAHs comparatively with the LMW PAHs.

The concentrations of native or petrogenic PAHs in the CCRs landfills may adversely impact soil, water, and plants and, consequently, affect the human health and biodiversity, depending mainly on the extent of exposure, concentrations and characteristics, and whether exposure occurs via inhalation, ingestion or skin contact.

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