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Persistence of Polycyclic Aromatic Hydrocarbons in the Soil of a Burned Area for Agricultural Purposes in Brazil

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Vegetation burning is still a common and widely used practice in Brazil and many other Third World countries as a tool for soil preparation before agriculture and even to agricultural frontier expansion (Crutzen & Andreae, 1990). Major effects of this practice are soil humidity reduction, increased soil erosion, nutrient loss and organic matter destruction, whose extension depends on vegetation and soil involved (Cardoso et al., 2003). As a long-term consequence, soils get poorer and the need of using fertilizers and soil correctives prior to cultivation increases agricultural costs. Vegetation burning is also responsible for the emission of large amounts of atmospheric pollutants such as CO_2 and particulate matter which are related to the global warming effect (Scholes et al., 1996) and several gases (CH_4, NO_x, CO) (Lacaux et al., 1996; Scholes et al., 1996) considered atmospheric precursors of Ozone (Parrish & Fehsenfeld, 2000). Besides there is emission of many classes of organic pollutants including polycyclic aromatic hydrocarbons (PAHs) (IPCS, 1998; Vo Dinh, 1998) which are of concern since many of them and several PAH mixtures exhibit mutagenic and/or pro-carcinogenic properties (Boffetta et al. 1997; IPCS, 1998; Pereira Netto et al. 2000). PAH formation and emission occur independently of the burned vegetation. In Brazil, PAHs were found in total suspended particulate (TSP) in the Amazonian Forest during forest burning (Vasconcellos et al., 1998) and over sugarcane plantations during foliage burning (Azevedo et al., 2003; Santos et al., 2003). PAHs were also identified in sugarcane ashes after foliage burning (Zamperlini et al., 1997; 2000).

However there are few data about PAHs in Brazilian soils (Wilcke et al., 1999) and there are no data on PAHs in soils after vegetation burning. There is concern about PAHs in soils since they are relatively persistent and stable in that medium and because through physicochemical processes they may be transferred into the other compartments. For example, PAHs from soil can be resuspended leading to human exposure through inhalation. Moreover, direct human exposure to PAHs present in soils, ashes and dusts after vegetation burning is possible during manipulation of agricultural soils. This paper aims to present some quantitative results on PAH in agricultural soils from a small agricultural area localized in a non-polluted rural region of São Pedro da Serra, a very small village which belongs to Nova Friburgo municipality, RJ, Brazil. Major interest of our work derives from the fact that the studied area may be considered an example of many

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Correspondence to: A. D. Pereira Netto other widespread cultivation areas that are submitted to similar processes.

MATERIALS AND METHODS

A standard solution containing all 16 EPA target PAHs at concentrations of 0.2 mg/mL (AccuStandard, USA) and solid PAHs from Aldrich Chemical Co. (USA) or AccuStandard were employed. Perdeuterated PAHs (naphthalene-D8, phenanthrene-D10, pyrene-D10, chrysene-D12, benzo[a]pyrene-D12 and perylene-D12) from Isotech (USA) or Cambridge Isotope Laboratories (USA) were used as internal standards. Hexane and toluene (both Omnisolv - Residue Analysis - E M Science, USA) and dichloromethane (Absolv – Tedia, RJ, Brazil) were employed. SPE SiO_2 cartridges (6 mL; 1000 mg) and a SPE Vacuum Manifold from Waters Corporation (USA) were used to clean up sample extracts.

Pooled surface soil samples were collected in October 10th, 2002 (1 week after vegetation burning) and in January 12th, 2003 (3 months after burning). Samples were collected with a metallic tool and kept in amber flasks in freezer prior to analysis. Part of each sample was homogenized, air dried as previously described (Sisinno et al., 2003) and ~ 5 g of the fraction $< 1\ mm^2$ were precisely weighted and submitted to ultrasonic extraction as previously described for soil (Sisinno et al., 2003) and total suspended particulate (TSP) or street dust (SD) (Pereira Netto et al., 2001, 2002a,b). An ash sample collected in October 10th, 2002 was also processed and analyzed in the same way. Concentrated extracts were submitted to clean up on SiO_2 SPE cartridges (6 mL; 1000 mg) previously activated with DCM. The PAH rich fraction was eluted with DCM (10% v/v) in hexane, evaporated under N_2 flow and kept in 2-mL vials, in refrigerator, until analysis.

Extracts and standards were analyzed by HRGC-MS in a gas chromatograph 6890 (Agilent, USA) interfaced to a mass selective detector 5973N (Agilent). A DB5-ms column (30 m; 0.25 μm; 0.25 mm; J&W, CA, USA) was used in previously optimized chromatographic conditions. Oven temperatures were: 80°C during 0.5 min, heated to 120°C at 20°C/min, kept at this temperature for 2 min and increased to 290°C at 4°C/min, with 15 min final hold. Transfer line was kept at 260°C and injector was kept at 300°C. All injections were done in splitless mode by automatic sampler. Extracts and standards were analyzed in full scan mode and/or by selected ion monitoring (SIM). Ionization was performed by electron impact at 70eV. Mass spectra were recorded between 50 and 350 u.m.a.. Molecular ions (Tuominem et al. 1986) were used to draw reconstructed chromatograms and in SIM mode. PAHs were identified by combining data from SIM and comparison of retention times of true compounds. Quantitative analysis was performed in the SIM mode. Perdeuterated PAHs were used as internal standards and calibration was performed by external standards.

RESULTS AND DISCUSSION

In soil samples, 21 PAHs were identified, including the 16 EPA priority PAHs together with 2-methylphenanthrene, benzo[b]fluorene, benzo[e]pyrene, perylene and coronene. The identification of benzo[a]anthracene, benzo[a]pyrene and of dibenzo[a,c]anthracene classified by IARC as probably carcinogenic (2A) and of benzo[b]fluoranthene, benzo[k]fluoranthene and indene[1,23-cd]pyrene classified as possibly carcinogenic (2B) in soil samples indicate the toxicity potential of those samples and the risks associated to human exposition.

However, many PAHs identified in this work were previously described by Zamperlini et al. (1997; 2000) in sugar cane ashes. When comparing our data with those previously obtained for TSP collected over sugar cane cultivation areas during foliage burning (Azevedo et al., 2003; Santos et al., 2003) and in the Amazonian Forest (Vasconcellos et al., 1998) it is shown that besides deposition, part of the PAHs get dispersed in the atmosphere representing another way of human exposure even far from the emission point. The potential for contamination of the environment can be shown by the presence in soils and ashes of phenanthrene, pyrene and fluoranthene which are considered responsible for most of sediment toxicity (Boxall & Maltby, 1997).

PAH concentrations between below the detection limit (~ 1 ng/g) and 40.5 ng/g were found in soil (Table 1). Naphthalene, acenaphtylene and phenanthrene predominated in the sample collected just after vegetation burning while naphthalene and phenanthrene predominated in the sample collected 3 months after vegetation burning. Total PAH concentration (ΣPAHs) accounted for 174.4 ng/g in October 10th, 2002 and 89.2 ng/g in the sample taken in January 12th, 2003. However the found levels were lower than those previously reported in polluted soils from urban areas (Sptizer and Kuwatzuka, 1993

PAHs with molecular weights ≤ 228 u.m.a. predominated in soil samples. They corresponded to ~ 88 % of total PAH concentration (ΣPAHs) in the sample collected in October and for ~ 83 % of ΣPAHs in the sample collected in January. PAHs with molecular weights ≤ 228 u.m.a. predominated also in the ash sample with levels varying from below the detection limit (~ 1 ng/g) to 1435 ng/g (naphthalene). Heavier PAHs were found only in trace amounts in this sample.

Total carcinogenic PAHs (ΣCARC) in soils corresponded to ~ 10% of ΣPAHs which is lower than the value previously found in TSP and SD samples (Pereira Netto et al., 2001, 2002a,b; 2003).

The persistence of individual PAHs varied from 100% (acenaphthene) to 18.2% (acenaphthylene) with a mean of 57.7% (Table 1). Except for acenaphthene and naphthalene, PAHs of highest molecular weights showed the largest persistences in soil. This fact may be related to their low water solubilities and to their low vapor pressures, which possibly reduce transport by runoff and atmospheric gas phase dispersion. It is shown also that ~51% of the initial ΣPAHs remains in the soil 3 months after vegetation burning. In this way, our results indicate that even during summer, which in the studied area corresponds to a rainy and hot season, PAHs remain in the soil where they cause environmental contamination and may lead to human exposure.

Table 1. PAHs levels (ng/g) found in soil and ash samples.

	PAH concentration in sample (ng/g)			
Date	Soil 10/10/2002	Soil 12/01/2003	Persistency[1] (%)	Ashes 10/10/2002
Naphthalene	40.5	34.7	85.5	1435
Acenaphthylene	21.1	3.84	18.2	633
Acenaphthene	3.06	3.10	101.4	127
Fluorene	12.1	4.22	34.8	333
Phenanthrene	30.2	9.79	32.4	591
Anthracene	4.70	2.13	45.3	116
2-Methilphenanthrene	4.97	3.19	64.3	117
Fluorantene	13.9	5.39	38.9	152
Pyrene	11.2	3.52	31.4	117
Benzo[b]fluorene	2.53	0.59	23.5	34.4
Benzo[a]anthracene	3.95	1.55	39.3	64.0
Chrysene+Triphenylene[2]	4.98	2.13	42.7	71.0
Benzo[b]fluoranthene	4.36	2.23	51.3	tr
Benzo[k]fluoranthene	2.59	2.10	80.9	tr
Benzo[e]pyrene	3.21	2.25	70.0	tr
Benzo[a]pyrene	3.05	2.07	67.8	tr
Perylene	1.86	1.74	93.7	tr
Indene[1,2,3-cd]pyrene	2.16	1.48	68.6	tr
Dibenzoanthracenes[3]	Tr	nd	---	tr
Benzo[ghi]perylene	2.20	1.71	77.6	tr
Coronene	1.71	1.49	86.8	tr
Total PAHs (ΣPAHs)CARC	174.4	89.2		3791
Total of carcinogenic PAHs[4]	16.1	9.43		
% of carcinogenic PAHs	9.23	10.57		
Mean value			57.7	

(1) % of each PAH 3 months after vegetation burning
(2) not separated in the GC conditions
(3) isomeric dibenzo[ah]anthracene and dibenzo[ac] anthracene are coeluted
tr = trace amounts (bellow detection limit) nd = not detected

Good linear correlation (R = 0.856) were found among PAH levels in both dates indicating that the values found 3 months after vegetation burning depend on the initial levels of those substances in the soil. Good correlations (R > 0,900) between the levels of PAHs with molecular weights ≤ 228 u.m.a. in soil and in ashes were also observed. For the sample collected in October 10th, 2002), a correlation coefficient of 0.936 was found suggesting that vegetation burning effectively contributes to the PAH levels found in soil. The correlation between PAH levels in soil of January 12th, 2003 and in ashes collected in October 10th, 2002 was also high (R = 0.929). This fact may be related to the transport of PAHs from ashes to soil by rains, since in January there were no visible intact ashes in the sampling area.

Our data show that vegetation burning leads to soil contamination with PAHs since atmospheric deposition of those substances has relatively lower importance in the studied area (rural site). Due to their physicochemical properties, a considerable part (~ 58 %) of the total initial PAH concentration remains in soil 3 months after vegetation burning. As this practice is frequent in many areas (once a year) those results indicate that soil may be reloaded every year for PAHs.

Our results suggest also that this agricultural practice may represent a risk for environmental contamination and human exposure since PAHs may be dispersed in the atmosphere over large areas and they may be carried into water bodies contaminating biota and sediments

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