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Presence of Polycyclic Aromatic Hydrocarbons (PAHs) in Apple in Rural Terrains from Mexico City

Rutilio Ortiz Salinas · Gilberto Díaz González · Beatriz Schettino Bermudez · Rey Gutiérrez Tolentino · Salvador Vega y León

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Abstract This paper describes PAH concentrations in apple crops that are growing in rural terrains in Mexico City. The concentrations of individual PAHs showed great variability, there being low and high molecular weight compounds in dry (high molecular weight for Tlahuac 7.06 μg/g and Milpa Alta 3.96 μg/g) and wet months (high molecular weight for Tlahuac 11.25 μg/g and Milpa Alta 12.05 μg/g). Some PAHs indicators and cross plot ratios Ant/(Ant + Phe) and Flu/(Flu + Pyr) define fossil fuels and vegetation combustion as the source of contamination over the cuticle of the apples. It is likely that deposition (dry and wet) is the principal source o f contamination over the apple surface. This study reveals the presence of PAHs in apples due to the high air contamination of Mexico City.

Keywords Contamination · Deposition · PAHs

Polycyclic aromatic hydrocarbons (PAHs) are products of the incomplete combustion of organic material; other sources are incineration, fossil fuel combustion and industrial activities. In general, human activities contribute high concentrations of these organic compounds in comparison to natural sources such as volcanic eruptions, diagenesis and natural forest fires (Kipopoulou et al. 1999; Cai et al. 2007). Some PAHs are carcinogenic and/or mutagenic; therefore, they may pose a human health threat (IARC 2000). Several studies have showed the presence of these compounds on food due to contamination of water, soil and air by processes of adsorption, deposition and bioaccumulation, mainly (Martens et al. 1997; Chung et al. 2008).

For some vegetables and fruits, PAHs are found on surfaces as a result of the atmospheric deposition of particle bound compounds and the retention of vapor phase PAHs on the waxy leaf cuticle (Kipopoulou et al. 1999; Jánská et al. 2006). In reports related to contamination of vegetables, these organic contaminants of low molecular weight (2–3 aromatic ring) are found in higher abundance because their vapor pressure, water solubility and bioavailability are greater than heavier PAHs which preferentially are associated with particulate matter (Jánská et al. 2006).

Mexico City's government has encouraged sustainable agricultural activities in rural areas and considers that agricultural land should be protected from further urban growth in order to support the recharge of the aquifer under the city as well as for growing important crops such as maize, flowers, vegetables and fruit trees (GDF 2003; Grupo Produce 2006). The government of the Federal District (the central part of the metropolitan area of Mexico City) has encouraged the growing of commercial crops (vegetables, flowers, cactus stems and fruits trees) in relatively rural terrains as an alternative means for conservation of green areas which also helps the recharge of aquifers in rural areas such as Xochimilco, Tlalpan, Magdalena Contreras, Milpa Alta and Tláhuac (Grupo Produce 2006).

The research was conducted in Tlahuac (situated 19° 20′ and 19° 12′ north; 98° 56′and 99° 04′ west) at a mean altitude of 2,500 m mean, an area in the template region of Mexico. Rain falls almost exclusively between June and

R. O. Salinas · G. D. González (✉) · B. S. Bermudez · R. G. Tolentino · S. Vega y León
Laboratorio de Análisis Instrumental, Departamento de Producción Agrícola y Animal, Universidad Autónoma Metropolitana Unidad Xochimilco, Calzada del Hueso 1100, Colonia Villa Quietud, 04960 Coyoacán, México D.F., Mexico
e-mail: guppyabanico@gmail.com; gdiaz@correo.xoc.uam.mx

Table 1 Individual PAHs (μg/g) in apple crops in Mexico City (n = 4 for each season)

Compounds	Sample sites											
	Tlahuac						Milpa alta					
	Dry months 2008	Dry months 2009	Mean	Wet months 2008	Wet months 2009	Mean	Dry months 2008	Dry months 2009	Mean	Wet months 2008	Wet months 2009	Mean
Nap (2)	–	1.01 ± 1.76	0.51 ± 0.88	–	–	–	–	***	–	–	–	–
Acy (3)	0.14 ± 0.20	–	0.07 ± 0.10	0.13 ± 0.19	–	0.07 ± 0.09	–	***	–	0.21 ± 0.30	–	0.10 ± 0.15
Ace (3)	0.21 ± 0.30	–	0.11 ± 0.15	0.60 ± 0.85	–	0.30 ± 0.42	–	***	–	0.85 ± 1.20	–	0.43 ± 0.60
Flu (3)	0.32 ± 0.46	–	0.16 ± 0.23	0.79 ± 1.11	–	0.39 ± 0.56	0.49 ± 0.69	***	0.24 ± 0.34	0.61 ± 0.85	–	0.31 ± 0.43
Phe (3)	0.49 ± 0.69	–	0.25 ± 0.35	1.24 ± 1.25	2.67 ± 2.81	1.95 ± 2.03	1.54 ± 2.17	***	0.76 ± 1.08	1.06 ± 1.50	–	0.53 ± 0.75
Ant (3)	3.80 ± 3.31	1.20 ± 2.08	2.50 ± 2.70	0.78 ± 1.10	1.40 ± 2.42	1.09 ± 1.76	5.13 ± 0.77	***	2.56 ± 0.38	0.76 ± 1.08	3.54 ± 0.32	2.15 ± 0.70
Fla (4)	3.45 ± 3.34	0.10 ± 0.17	1.78 ± 1.75	3.05 ± 3.66	–	1.53 ± 1.83	3.48 ± 3.33	***	1.74 ± 1.67	2.48 ± 3.50	0.01 ± 0.01	1.24 ± 1.76
Pyr (4)	2.77 ± 1.10	–	1.39 ± 0.55	2.30 ± 2.97	–	1.15 ± 1.48	3.76 ± 0.07	***	1.87 ± 0.03	1.88 ± 2.65	–	0.94 ± 1.33
BaA (4)	1.79 ± 1.83	–	0.90 ± 0.92	5.64 ± 7.01	24.78 ± 29.34	15.21 ± 18.71	2.10 ± 2.97	***	1.04 ± 1.48	3.54 ± 5.01	0.59 ± 0.83	2.07 ± 2.92
Cry (4)	0.94 ± 0.75	1.09 ± 1.88	1.02 ± 1.32	0.88 ± 1.25	7.24 ± 2.72	4.07 ± 1.99	0.49 ± 0.41	***	0.24 ± 0.20	1.18 ± 1.66	1.15 ± 1.63	1.16 ± 1.64
BbF (5)	1.05 ± 0.36	–	0.53 ± 0.18	3.58 ± 2.37	–	1.79 ± 1.18	0.98 ± 0.80	***	0.49 ± 0.40	2.95 ± 1.03	–	1.47 ± 0.52
BkF (5)	0.82 ± 0.25	0.52 ± 0.91	0.68 ± 0.58	3.91 ± 5.52	–	1.95 ± 2.76	2.50 ± 2.00	***	1.25 ± 1.00	5.03 ± 7.12	2.44 ± 3.45	3.74 ± 5.28
BaP (5)	6.07 ± 7.95	–	3.04 ± 3.98	3.04 ± 2.23	3.59 ± 6.22	3.31 ± 4.22	2.48 ± 2.73	***	1.24 ± 1.37	3.61 ± 1.76	0.68 ± 0.95	2.14 ± 1.36
Ind (6)	0.50 ± 0.71	3.04 ± 5.26	1.77 ± 2.99	–	1.22 ± 2.12	0.61 ± 1.06	0.34 ± 0.48	***	0.17 ± 0.24	–	2.32 ± 3.27	1.16 ± 1.64
DaA (5)	0.67 ± 0.95	–	0.34 ± 0.48	–	5.75 ± 4.06	2.88 ± 2.03	1.61 ± 2.28	***	0.81 ± 1.14	–	7.09 ± 10.02	3.54 ± 5.01
Bghi (6)	1.39 ± 1.97	–	0.70 ± 0.98	–	1.41 ± 2.44	0.71 ± 1.22	–	***	–	–	–	–
PAHs total	24.48 ± 15.37	6.96 ± 7.71	15.75 ± 11.54	25.94 ± 25.06	48.07 ± 37.16	37.01 ± 31.11	24.90 ± 13.18	***	12.41 ± 6.59	24.16 ± 24.16	17.80 ± 0.45	20.98 ± 12.31

– Not detected, *** Not determinated due ill over crop

August with a mean precipitation mean of 534 mm. Mean monthly maximum temperatures range from 14°C in January to 22.8°C in May. The study site was composed mainly of grassland and pine forest. Milpa Alta (situated 19° 13′ and 19° 04′ north; 98° 57′ and 98° 10′ west) is the second largest delegation of the Federal District by surface area. It is a mountainous area with a mean altitude of 2,500 m and is in the a cold template region. Rainfall is abundant and the mean temperature is 14°C. The principal vegetation is trees, mainly different species of pine. Typically in the rurally populated hills, slopes have a 15% gradient although slopes of 25% gradient also are quite common 25.

High levels of air contamination in the city can influence the quality of the food produced in these relatively rural areas near the city and it is necessary to monitor organic contaminants in vegetables and fruits produced (Escobedo et al. 2000). The main objective of this study was to determine concentration of PAHs on apples and the source of this contamination in dry and wet months.

Materials and Methods

We collected a composite sample (2 kg) of apple for each location from an area of approximately 1,500 m^2 during both dry and wet months. The samples were conserved in aluminum foil in order to avoid possible contamination by traffic and other sources during transportation and were then stored frozen at −5°C. The apple samples were peeled then crushed and homogenized. Soxhlet extraction was used to extract 10 g of sample mixed with anhydrous sodium sulfate, using a solvent mix of hexane-dichloromethane (1:1). Extraction time was 8 h after which the organic extracts were evaporated in a rotary evaporator to 5 mL (Samsoe et al. 2002). Chromatographic columns were prepared with silica gel and aluminum oxide deactivated with deionized water (5%) and topped with anhydrous sodium sulfate. The samples were passed through the columns then the PAHs eluted with a mixture of hexane-dichloromethane (9:1 and 1:1). The organic extract was concentrated in a rotary evaporator to 1 mL and transferred to a vial for gas chromatographic analysis according to EPA method 8100.

The concentrations and profiles of PAH compounds were analyzed using a Perkin Elmer AutoSystem gas chromatograph (Column HP-5, 30 m, 0.35 mm ID, 0.25 μm film thickness). The oven temperature was initially set at 90°C and held for 0 min then ramped at 8°C/min to 180°C (1 min), then ramped at 5°C/min to 245°C (0 min), and ramped at 2°C/min to a final temperature of 300°C (0 min). Detector and injector temperature were 320°C. The carrier gas was high purity helium (99.99%). A sample of 1 μL was injected in splitless mode.

Identification of PAH compounds were based on matching their retention time with a mixture of PAH standards (Chem Service). The 16 PAH compounds were naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benzo(a)fluorene (BaF), benzo(a)anthracene (BaA), chrysene (Cry), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), indeno(1,2,3-cd)pyrene (Ind), dibenzo(ah + ac)anthracene (DaA), and benzo(ghi)perylene (Bghi). The detection limits were 0.01 μg/g for some compounds.

Quality control was made by analysis of fortified blanks and samples together with the performance of the GC. Recoveries were 80–95% except for naphthalene for which a value of 50% was obtained. Quantification of individual PAHs was made by an external standard method.

Results and Discussion

Dominant compounds in apple were Phe, Ant, Fla, and Flu while those of high molecular weight (5–6 aromatic rings) were present in low concentrations (Tables 1 and 2). In this preliminary monitoring we found temporal changes over apple and cactus stem surfaces according to dry (May and June) and wet (April and July) months and also depending on harvest activities. Many studies have described the domination of high molecular weight compounds, generally between 60% and 90% of the total (Bishnoi et al. 2005). Our results showed approximately equal proportions

Table 2 Average PAH concentrations by compound type (μg/g) in crops from rural areas of Mexico City (n = 4 for each season)

Compound type	Apple Tl 2008 (dry months)	Apple Tl 2009 (wet months)	Apple MA 2008 (dry months)	Apple MA 2009 (wet months)
Low molecular weight (2 aromatic rings)	0.51 (3.1)	– (–)	– (–)	– (–)
Intermediate molecular weight (3–4 aromatic rings)	8.18 (52.0)	25.76 (69.6)	8.45 (68.1)	8.93 (42.6)
High molecular weight (5–6 aromatic rings)	7.06 (44.9)	11.25 (30.4)	3.96 (31.9)	12.05 (57.4)
Total concentration	15.75	37.01	12.41	20.98

Numbers in parentheses represent percent of total concentration of low and high molecular weight compounds in the dry months while the high molecular weight compounds dominated in the wet months.

Figure 1 shows the individual concentrations of PAHs in apple where the dominant compounds were: BaA, BkF, BaP, DaA, Ant, Fla, Pyr and BbF. BaA has a high concentration in Tlahuac with upper values of 6 µg/g for both seasons.

In a few countries there are specific regulations about organic contaminant residues in vegetables, for example in Germany a maximum level of 25 µg/g of total light PAHs (<3–4 aromatic rings) and a maximum level of 5 µg/g of total heavy PAHs (>5 aromatic rings) has been established (Barra et al. 2007). Comparing our data with these limits, the light PAH concentrations in apple crops were below the limit in both dry and wet months while heavy PAH concentrations were above mainly the limit in rain season.

Our results for concentrations on apples was high in concentration levels with respect to a Brazilian study by Rojo and Toledo (2003) who found low concentrations of high molecular weight PAHs with levels of 0.08–4.61 µg/kg. Further, these concentrations compared with contaminated sites that are elevated in concentration, mainly in vegetables from China (Li et al. 2007).

Mo et al. (2009) established that there are high concentrations of PAHs in vegetables grown near industries, in high density urban and highway areas when compared to those grown in rural zones. Nowadays, the consumption of vegetables is an important human exposure pathway for these contaminants. For example, for the Chinese population leaf vegetables such as spinach, cabbage, lettuce, asparagus and cucumber amongst others were considered important.

The presence of HAPs in apple crops probably occurs because of deposition of organic atmospheric contaminants over their surfaces (Kipopoulou et al. 1999; Zohair et al. 2006; Barra et al. 2007). For agricultural land located within a city with high atmospheric contamination similar studies have shown that vegetables and fruits contain higher PAH concentrations in industrial areas than in non-industrial areas because of deposition (dry mainly). This organic contamination has many origins such as incomplete combustion of fossil fuels, garbage, industrial emissions and wood within urban and semi urban zones (Tao et al. 2004; Bishnoi et al. 2005).

According to scientific reports about organic chemical contamination of crops, wet (aerosols) and dry (particles) deposition are the main sources, more important than other processes such as bioaccumulation, adsorption and translocation (Pimentel et al. 1997). The use of cross plots has been established to identify probable sources, using specific individual PAHs which are resistant to microbial, photochemical and chemical breakdown (Cai et al. 2007). We used the Flu/(Flu + Pyr) and Ant/(Ant + Phe) ratios and the majority of samples fell into the section identifying petroleum (fossil fuel combustion) as the source. This is logical considering the presence of heavy machinery (Tlahuac) and vehicle traffic (Tlahuac and Milpa Alta) and the lack of vegetation combustion (which for example is sometimes used to remove weeds) in the city (Fig. 2). Further our results are consistent with reports in Mexico City of the influence of vehicular traffic and industrial activities on atmospheric contamination and contamination of other environmental compartments such as water, soil, crops and organisms (Marr et al. 2004).

The presence of low molecular weight PAHs (2–3 aromatic rings) is indicative of petroleum (fossil fuel combustion) while high molecular weight PAHs (>4 aromatic rings) are more likely to be derived from organic material combustion (Ma et al. 2008). There are likely to be multiple contamination sources in vegetables and garbage from these conservation terrains.

PAH concentrations in apple crops vary due the influence of the dry and wet seasons (Tables 1 and 2). We found high concentrations of individual PAHs in the dry months

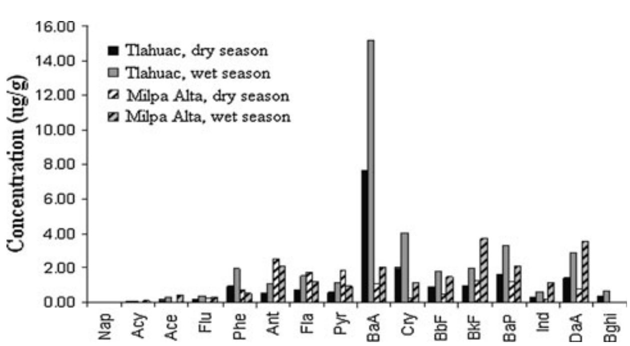

Fig. 1 Comparison of average individual PAH concentrations in apple crops from conservation terrains of Mexico City

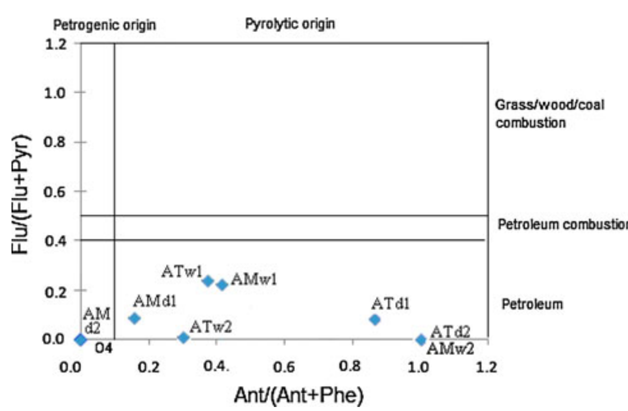

Fig. 2 Cross-plot for Ant/(Ant + Phe) and Flu/(Flu + Pyr) in samples of apple crops from the Tlahuac (AT) and Milpa Alta (AM) areas of Mexico City; where d1 = dry2008, d2 = dry2009, w1 = wet2008 and w2 = wet2009

and lower concentrations and number of PAHs in wet months.

There are few studies available with which to compare our results because most focus on leaf vegetables and grains and also environmental conditions are different. This lack of information suggests that we need to continue this monitoring and it will provide useful data on the contamination of these crops and will help to develop strategies to minimize contamination of the food chain. Cross plot using individual PAH indicators have shown that the origin of these contaminants on apples is mainly fossil fuel combustion with low contributions from vegetation combustion. These results show that atmospheric deposition is the main contamination pathway in these crops due to the problems of air quality in Mexico City.

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