Bioconcentration factor estimates of polycyclic aromatic hydrocarbons in grains of corn plants cultivated in soils treated with sewage sludge

Lourival Costa Paraíba *, Sônia Cláudia Nascimento Queiroz, Aline de Holanda Nunes Maia, Vera Lúcia Ferracini

Embrapa Meio Ambiente — Embrapa Environment, CxP. 69, CEP 13820-000, Jaguariúna, São Paulo, Brazil

ARTICLE INFO

ABSTRACT

This study presents a model to simulate the organic substance concentrations in corn grains assuming that the substances in soil solution are absorbed via the transpiration stream by plants growing in soils fertilized with sewage sludge (SS). The model was applied and validated using soil and corn grain samples from a long-term field experiment with six successive yearly applications of SS to the soil. The following polycyclic aromatic hydrocarbons (PAHs) were simulated and evaluated in soil and grain samples: acenaphthene, acenaphthylene, anthracene, benz(a)anthracene, benz(a)pyrene, benz(b)fluoranthene, benz(g,h,i)perylene, benz(k)fluoranthene, chrysene, dibenz(a,h)anthracene, fluoranthene, fluorene, indeno(1,2,3-c,d)pyrene, naphthalene, phenanthrene and pyrene. The PAH bioconcentration factors (*BCF*) in corn grains ranged from 1.57 to 10.97 L kg^{-1}. Polycyclic aromatic hydrocarbons with low soil distribution coefficients and high values of transpiration stream concentration factors (*TSCF*) are more likely to be absorbed by corn plants and accumulated in grains. It was possible to estimate and observe that highly lipophilic PAH molecules (heavy PAHs) show lower accumulative potential in corn grains than the less lipophilic ones (light PAHs). Sewage sludges containing significant concentrations of light PAHs with two, three or four benzene rings should be avoided as fertilizers in alimentary field crops.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of non-polar hydrophobic organic compounds comprised of two or more fused benzene rings. Those containing up to four fused benzene rings are known as light PAHs; and heavy PAHs are those containing more than four rings. Heavy PAHs are more stable and toxic compared to the light ones (Wenzl et al., 2006), which are more volatile, water soluble and less lipophilic compounds (Ferrarese et al., 2008). According to the Scientific Committee on Food (2002), fifteen PAHs showed clear evidences of mutagenicity or genotoxicity in somatic cells of *in vivo* experimental animals.

The PAH physical–chemical properties such as water solubility, molecular weight and vapor pressure are mainly defined by the number of double bonds, which is in turn dependent on the number of benzene rings. PAHs may be introduced into the environment through natural processes such as plant biomass combustion (Meyers and Ishiwatari, 1993). However, the anthropogenic processes generate much higher PAH amounts during wood pyrolysis activities for coal production; oil transport, storage and refining operations; domestic and industrial residue incineration; field and forest burning; energy produced via fossil-fuel burning; kerosene pyrolysis to and from benzene, toluene and other organic solvents; and vehicle motor emissions, particularly those from diesel. Regions near to urban and industrialized centers are the most affected by PAH pollution originated from petroleum or pyrolysis (WHO, 1998; Environment Canada, 1994). According to US-EPA (1993), the sixteen most toxic PAHs to aquatic and terrestrial life are: acenaphthene, acenaphthylene, anthracene, benz(a)anthracene, benz(a)pyrene, benz(b)fluoranthene, benz(g,h,i)perylene, benz(k)fluoranthene, chrysene, dibenz(a,h)anthracene, fluoranthene, fluorene, indeno(1,2,3-c,d)pyrene, naphthalene, phenanthrene and pyrene.

Human exposure to PAHs may occur via processed foods, contaminated water and green vegetables. Fismes et al. (2002) demonstrated that lettuce, potato and carrot plants can absorb PAHs from contaminated soils; Camargo and Toledo (2002) found significant PAH levels in grapes, apples, pears, tomatoes, cabbages and lettuces grown in Brazilian rural areas nearby urban centers; Zohair et al. (2006) observed PAH-contaminated potatoes and carrots from plants grown in organic cultivation systems. Farhadian et al. (2010) studied polycyclic aromatic hydrocarbons in grilled meat. The highest concentrations of PAHs were detected in charcoal grilled followed by flame-gas and oven grilled dishes. Kulhánek et al. (2005) used models, statistical regressions and the PAH bioconcentration factors in foods to estimate the risk of human PAH intake via contaminated fruits, tubers and vegetables, in order to regulate the maximum food PAH

level in the European Community. Collins et al. (2006) described the main processes involved in the organic compound (including PAHs) accumulation by roots, leaves and fruits. Chouychai et al. (2007) studied the phenanthrene and pyrene phytotoxicity in corn and peanut plants and concluded that corn plants can be used to phytoremediate contaminated soils, meaning that corn plants are able to take up and accumulate several PAHs from soil solution.

Sewage sludge (SS) is a complex organic by-product of the wastewater treatment process. Large amounts of SS are constantly produced and the disposal routes are a matter of worldwide concern and an environmental problem. This material is supposed to be potentially useful in agricultural land amendment or degraded area recovery due to its rich nutrient composition, especially in organic matter (OM), nitrogen (N) and phosphorus (P) (Fernandes et al., 2005a). However, there are risks and benefits associated with SS use in soils, since it contains not only OM, N and P, but also metals, microorganisms and pollutant organic compounds such as the PAHs (Tsutiya et al., 2001; Alcantara et al., 2009). In general, the pollutant substances are associated with uncontrolled mixtures of domestic and industrial wastes or with the waste treatment process used (Oleszczuk, 2006). SS used as a fertilizer might contaminate crops, soils, superficial and underground waters with nitrates, heavy metals, pathogens, various classes of organic compounds and persistent organic compounds (Mantovi et al., 2005; Kinney et al., 2006; Alcantara et al., 2009). In Brazil, the use of SS in agriculture is regulated through the directive CONAMA 357/2005 (CONAMA, 2006).

There is little information on PAH uptake by plants from SS-treated soils, but there is evidence of plant accumulation of organic contaminants as a result of continuous SS addition to agricultural soils. Research results have shown correlations between PAH concentrations in several plant shoots and roots and soil PAH concentrations (Oleszczuk and Baran, 2005; Oleszczuk, 2006). Oleszczuk and Baran (2005) investigated during three years the PAH absorption by *Salix viminalis* and concluded that the residue concentrations found in leaves and stems were associated with the PAH content of SS added to the soil as fertilizers. The continuous PAH accumulation in soils as a consequence of the various human activities (Jones et al., 1989; Oleszczuk, 2006) is also a matter of great concern and represents risk of plant contamination (Oleszczuk and Baran, 2005; Tao et al., 2006).

The process of substance accumulation in an organism in relation to the substance concentration in the external medium is called bioconcentration. The bioconcentration factor (*BCF*) is defined as the substance partition coefficient between the organism and the external medium, that is, it is calculated as the quotient between the organism and the external medium substance concentrations. Therefore, the *BCF* describes the organism substance accumulative potential or the organism substance bioconcentration in a specific medium (Paraíba, 2007; Paraíba and Kataguiri, 2008).

When food products originated from soil-grown plants and the substance concentration in the soil solution is known, the *BCF* value allows estimating the daily substance intake through daily food product intake (vegetables, fruits, tubers, etc). When food/substance *BCF* is known and the daily substance admissible intake is also known, it is possible to estimate maximum admissible or tolerable substance limits in the soil used to produce food (Trapp et al., 2003; Kulhánek et al., 2005; Trapp, 2007; Paraíba, 2007; Paraíba and Kataguiri, 2008).

Many PAHs were found in SS samples obtained from Wastewater Treatment Plants in Brazilian cities (Tsutiya et al., 2001). In the State of São Paulo, the use of SS in agriculture is regulated through the technical directive P4230, created by CETESB (1999) — a government environmental sanitation agency — which limits the residue disposal in soils, according to the heavy metal and nitrogen soil contents, the crop nutrient demands and the soil nitrogen mineralization rate. In other Brazilian States, the use of SS in agriculture is regulated through the directive CONAMA 357/2005 (CONAMA, 2006).

Mathematical models might predict and prevent high toxic substance levels in field crops (fruits, tubers, vegetables, and grains) treated with pesticides or cultivated in polluted soils and indicate that organic substances must be systematically monitored through good crop management programs. Several mathematical models have been developed to simulate organic substance uptake by plants (Trapp and McFarlane, 1995; Trapp et al., 2003; Trapp, 2007; Paraíba, 2007; Paraíba and Kataguiri, 2008).

The aim of the present study was to use a mathematical model to estimate the values of corn grain-PAH bioconcentration factors (BCF) of plants grown in soils previously amended with SS for long periods, and also, to compare the estimates with experimentally measured data. In this model, it was assumed that the PAH transport from soil to corn grains occurs through the plant xylem/phloem flow and it is calculated using a steady state equation expressing the compound mass balance in the soil–plant system (Trapp and McFarlane, 1995). To achieve the objectives of this study, sixteen PAHs of concern to be monitored in food, according to US-EPA (1993), were selected. And methods of residue analysis using a gas chromatograph coupled to a mass spectrometer (CG/MS) were developed for the determination of selected PAHs in soil and corn grain samples. Soil and corn grain samples were obtained from an experimental area of Embrapa Meio Ambiente (Embrapa Environment), where a long-term experiment was carried out with corn plants grown in soils amended with SS for six consecutive years (Fernandes et al., 2005a,b; Dynia et al., 2006; Alcantara et al., 2009).

2. Material and methods

2.1. Hypothesis for the PAH-corn grain model

The model was built assuming that PAHs are degraded, dissipated, diluted and transformed in the soil–plant system according to first order kinetics due to plant growth and development, PHAs dissipation and degradation in the soil and PAH transformation through plant metabolism. It was also assumed that PAH uptake, transport and accumulation by corn plants are via plant transpiration stream from the contaminated soil solution (Trapp and McFarlane, 1995; Trapp et al., 2003; Paraíba, 2007).

2.2. PAH-BCF-corn grain model development

2.2.1. Corn plant PAH concentration

The plant PAH uptake kinetics in the soil–plant system was estimated by the equation:

$$\frac{dC_p}{dt} = \frac{Q_x TSCF}{M_p} \times \frac{dC_w}{dt} - \frac{Q_x C_p}{M_p(f_l k_{lw} + f_c k_{cw})} - \left(k_g + k_e\right)C_p \qquad (1)$$

where C_p ($\mu g\,kg^{-1}$) is the plant tissue concentration, Q_x ($L\,day^{-1}\,ha^{-1}$) is the average daily soil solution volume transpired by corn plants per hectare, $TSCF$ is the PAH concentration factor in the plant transpiration stream, M_p ($kg\,ha^{-1}$) is the mature corn plant total fresh biomass, C_w ($\mu g\,L^{-1}$) is the soil solution PAH concentration, k_g (day^{-1}) is the corn plant growth rate, and k_e (day^{-1}) is the corn plant PAH dissipation rate. The coefficients k_{lw} and k_{cw} are the PAH lignin–water and cellulose–water partition coefficients, respectively. The constants f_l and f_c are the lignin and cellulose volumetric fractions in corn plant tissues, respectively.

The transpiration stream concentration factor (*TSCF*) was estimated by the expression $TSCF = \frac{11}{11 + 2.6^{\log k_{ow}}}$ (Dettenmaier et al., 2009). The PAH lignin–water partition coefficient (k_{lw}) was estimated by $k_{lw} = 10^{(-0.04 + 0.74 \times \log k_{ow})}$ (Trapp et al., 2001). The cellulose–water partition coefficient (k_{cw}) was estimated by $k_{cw} = 10^{(\log k_{ow} - 2.6)}$

(Jonker, 2008), where $\log k_{ow}$ is the logarithm of PAH octanol–water partition coefficient (k_{ow}).

The PAH concentration in the corn plant rhizosphere was supposed to dissipate according to a first order kinetics: $C_s(t) = C_s(0)e^{-k_s t}$, where $C_s(0)$ (µg kg^{-1}) is the initial soil PAH concentration, C_s (µg kg^{-1}) is the current soil concentration and k_s (day^{-1}) is the dissipation rate. The k_s value was estimated using the expression $k_s = 0.693 / t_{1/2}$, where $t_{1/2}$ (day) is PAH half-life in the soil. The plant dissipation rate was estimated by $k_e = 16 \times k_s$ (Juraske et al., 2008). The PAH concentration in soil solution was estimated through the equation:

$$C_w(t) = \frac{\rho_{wt} C_s(0) e^{-k_s t}}{(\rho_s k_d + f_\theta + f_\delta k_{aw})} \quad (2)$$

where $C_w(t)$ (µg L^{-1}) is the soil solution PAH; ρ_{wt} (kg L^{-1}) and ρ_s (kg L^{-1}) are the soil densities at humid and dry basis, respectively; f_θ and f_δ coefficients are the soil water and air volumetric fractions at soil field capacity, respectively; k_{aw} coefficient, is the dimensionless constant of Henry's law estimated by $k_{aw} = (v_p m_w)/(s \times 8.314 \times T)$, where v_p (Pa) is the vapor pressure, m_w (g mol^{-1}) is the molar mass, s (mg L^{-1}) is PAH water solubility and $T = 298$ K at room temperature. The k_d (L kg^{-1}) constant is the PAH soil distribution coefficient estimated by $k_d = f_{om} \times 10^{(0.52 \log k_{ow} + 0.64)}$, where f_{om} is the soil organic matter volumetric fraction (Briggs, 1981).

Assuming Eq. (2), and supposing that $C_w(0) = \frac{\rho_{wt} C_s(0)}{(\rho_s k_d + f_\theta + f_\delta k_{aw})}$ is known, and that $C_p(0) = 0$, thus, Eq. (1) is solved by:

$$C_p(t) = \frac{A C_w(0)}{(B - k_s)} \left[e^{(-k_s t)} - e^{(-Bt)} \right] \quad (3)$$

where, A (L kg day^{-1}) and B (day^{-1}) constants are given by $A = \frac{Q_f TSCF}{M_p}$ and $B = k_e + k_g + \frac{Q_x}{M_p(f_l k_{lw} + f_c k_{cw})}$. The A constant represents the PAH total uptake rate by corn plants and the B constant, the PAH total dissipation rate, both in the soil–plant system.

2.2.2. PAH concentration in corn grains

Using Eq. (3), the corn grain PAH concentration was estimated by the equation:

$$C_g(t > t_e) = \frac{\rho_w}{\rho_g} Q_f C_p(t) = \frac{\rho_w A Q_f C_w(0)}{\rho_g (B - k_s)} \left[e^{(-k_s t)} - e^{(-Bt)} \right] \quad (4)$$

where $C_g = C_g(t > t_e)$ (µg kg^{-1}) is the corn grain PAH concentration and Q_f (L kg^{-1}) is the average sap flow value necessary to produce 1.0 kg fresh corn grains, estimated by $Q_f = d_w 20$, where d_w is the corn grain water volumetric fraction (Trapp et al., 2003); ρ_w (kg L^{-1}) and ρ_g, (kg L^{-1}) are the soil solution (water) and corn grain densities, respectively; t_e (day) is the initial time of corn grain filling period, because $C_g(t) = 0$ when $t \leq t_e$.

2.2.3. PAH bioconcentration factor — BCF — in corn grains

The bioconcentration factors (BCF) were estimated as the quotient between the grain and the soil solution PAH concentrations (Eq. (2)), according to the expression:

$$BCF(t_h > t_e) = \frac{C_g(t_h)}{C_w(t_h)} \quad (5)$$

where BCF (L kg^{-1}) is the PAH bioconcentration factor in corn grains and t_h (day) is the final time of corn grain filling period or days after sowing.

Eq. (5) demonstrates that BCF depends on the PAH total uptake rate and total elimination rate in the soil–plant system; PAH half-life and distribution coefficient in the soil; PAH air–water partition coefficient; soil air, water and organic matter volumetric fractions; soil solution, humid and dry soil densities; corn grain density; plant transpiration stream rate and total fresh biomass; phloem sap flow rate necessary to produce 1.0 kg fresh corn grains; cellulose and lignin volumetric fractions and plant growth rate. Thus, the BCF value depends on the properties and characteristics of PAHs, soil, corn plants and grains.

2.2.4. Soil and plant samplings in the field experiments

Field experiments were carried out in a clay texture distroferric Red Oxisol (sand loam Rhodic Oxisol, Typic Haplustox) at the experiment station of Embrapa Environment, at Jaguariúna City, São Paulo State, Brazil (22° 41′ S latitude, 47° W longitude and 570 m elevation). The PAH residue determinations in soil and corn grain samples were made in the Laboratory of Pesticide and Contaminants Residues of Embrapa Environment. Four field plots were randomly selected from a long-term experiment, in which SS was added to the soil as fertilizer source for corn production for six consecutive years. From each plot, three soil samples from the 0–20 cm depth layer and three corn samples at the fresh stage were collected for the PAH analysis of residues in grains. Samples were prepared for analysis as follows: soil samples were air-dried at room temperature and corn grains were oven-dried at 70 °C and ground in a laboratory grain-mill (1 mm sieve).

2.2.5. PAH determination in soil and corn grain samples

2.2.5.1. Standards and reagents. A standard solution obtained from ChemService (West Chester, PA, USA) was used, containing 2.0 mg mL^{-1} of each PAH studied in dichloromethane: benzene (50:50, v/v). Dichloromethane and n-hexane (pesticide residual degree) were obtained from Tedia Company Inc.; anhydrous sodium sulfate from J.T. Baker; and alumina (80–200 mesh) from Fisher Scientific.

2.2.5.2. PAH extraction. 10 g of dry soil and 5 g of ground corn grains were transferred to 250 ml-centrifuge tubes; 20 mL of dichloromethane (DCM) was added and the sample was shaken for 30 min, centrifuged and the organic supernatant was preserved; this procedure was repeated with 20 mL of n-hexane; the collected organic extract was submitted to evaporation to reduce the volume to 3 mL.

2.2.5.3. PAH clean-up. The soil extract was cleaned up using a 1.5 cm diameter glass column containing 2 g of alumina (activated Al$_2$O$_3$) and 1.0 g of anhydrous sodium sulfate (Na$_2$SO$_4$). The soil extract was transferred into the glass column and PAHs were eluted with 10 mL of n-hexane: DCM (19:1, v/v), and after, with 15 mL of n-hexane: DCM (1:2, v/v). All the percolate was collected and evaporated to reduce the volume to 1 mL. The corn grain extract was cleaned up using silica gel column conditioned with 40 mL of cyclohexane; the PAHs were eluted with 85 mL of cyclohexane and the percolate collected was evaporated to reduce the volume to 1 mL.

2.2.5.4. Quantification. PAHs were quantified using the method of external standardization. An 80 mg L^{-1} dichloromethane standard stock solution was used to prepare the 1.0 mg L^{-1} diluted standard solution. Afterwards, the work solutions were prepared by means of successive dilutions in n-hexane and they were used to determine the detector linearity, fortify samples and obtain the standard analytical curves.

2.2.5.5. Soil and corn grain sample analysis by GC-MS/MS. Sixteen PAHs were analyzed using a gas chromatograph — model 3900 — coupled to a mass spectrometer model 2100 T, and a Restek capillary column (RTX®-5 Sil MS, 30 m × 0.25 mm DI × 0.25 µm). The trap, manifold, transferline and injector temperature were 220 °C, 60 °C, 280 °C and 250 °C, respectively. The oven temperature was initially 50 °C per 1 min; 10 °C min^{-1} until 150 °C per 2 min; 6 °C min^{-1} until 220 °C;

Table 1
Analytical method limits of detection (LOD) and limits of quantification (LOQ) of PAHs in soils, PAH concentrations in soils [dry weight]: minimum, maximum, average and median residual levels and number of soil samples showing PAH levels above the method limits of quantification (>LOQ).

PAH	LOD $\mu g\ kg^{-1}$	LOQ $\mu g\ kg^{-1}$	Minimum $n=12$ $\mu g\ kg^{-1}$	Maximum $n=12$ $\mu g\ kg^{-1}$	Average $\mu g\ kg^{-1}$	Median $n=12$ $\mu g\ kg^{-1}$	Count >LOQ
Acenaphthylene	0.4	1.2	<LOD	<LOD	–	<LOD	n.d.
Acenaphthene	0.4	1.4	<LOD	2.1	2.1	<LOD	3
Anthracene	0.3	1.1	<LOD	3.1	2.2	2.1	6
Benz(a)anthracene	0.4	1.5	<LOD	7.4	3.0	2.3	8
Benz(a)pyrene	2.5	8.4	<LOD	<LOQ	–	<LOQ	n.q.
Benz(b)fluoranthene	1.6	5.4	<LOD	6.5	5.7	5.4	3
Benz(g,h,i)perylene	0.8	2.8	<LOD	6.0	3.6	3.1	6
Benz(k)fluoranthene	1.8	6.0	<LOD	8.5	8.5	<LOD	1
Chrysene	0.4	1.4	<LOD	5.6	3.3	2.6	7
Dibenz(a,h)anthracene	0.9	3.0	<LOD	6.0	4.4	<LOD	4
Fluoranthene	0.2	0.5	<LOD	5.8	3.1	2.6	8
Fluorene	0.4	1.3	<LOD	2.1	1.9	<LOD	2
Indeno(1,2,3-c,d)pyrene	0.9	2.7	<LOD	5.8	4.5	<LOD	5
Naphthalene	0.9	3.0	<LOQ	6.5	4.8	4.6	11
Phenanthrene	0.3	0.9	<LOD	3.3	2.8	2.8	3
Pyrene	0.2	0.5	<LOD	7.5	4.9	4.9	8

N = total number of samples; n.d. = not detected; n.q. = not quantified; <LOD − lower than the limit of detection; <LOQ − lower than the limit of quantification.

4 °C min^{-1} until 286 °C and 10 °C min^{-1} until 300 °C. The acquisition data were obtained in the MS/MS mode.

3. Results and discussion

3.1. Simulation, numerical results and model validation

The limits of detection − LOD ($\mu g\ kg^{-1}$) − and limits of quantification − LOQ ($\mu g\ kg^{-1}$) − of analytical methods used for residual PAH determination in soil and grain samples are presented in Tables 1 and 5. The minimum, maximum, median and average PAH residues in soil are presented in Table 1, as well as the number of SS-treated soil samples showing PAH levels above the method limits of quantification (>LOQ). The physical–chemical characteristics of the sixteen PAHs used in the model to estimate the BCF values are presented in Table 2. The soil, corn plant and grain physical–chemical parameters used in the model to estimate the BCF values are presented in Table 3. BCF values ranged between 1.51 [indeno(1,2,3-c,d)pyrene] and 10.97 L kg^{-1} [anthracene] (Table 4) or equivalently the corn grain PAH concentrations may range between 1.5 and 11 fold the soil solution PAH concentrations.

The experimentally determined soil PAH concentrations were used to estimate the soil solution PAH concentrations C_{w-exp} ($\mu g\ L^{-1}$), making $C_{w-exp} = \frac{\rho_{wt}C_{s-exp}}{(\rho_s k_d + f_\theta + f_\delta k_{aw})}$, where C_{s-exp} ($\mu g\ kg^{-1}$) is the average dry soil PAH concentration (Table 1). The BCF values calculated by means of Eq. (5) and the estimated soil solution concentrations were used to estimate the modeled corn grain PAH concentrations, making $C_{g-mod} = BCF \times C_{w-exp}/(1-d_w)$, where C_{g-mod} ($\mu g\ kg^{-1}$) is the modeled corn grain PAH concentration. The estimates of the soil PAHs distribution coefficient, k_d (L kg^{-1}), transpiration stream concentration factor (TSCF) and soil solution PAH concentrations (C_{w-exp}) are presented in Table 4.

A negative correlation was observed between k_d values and the corn grain BCF values and a positive correlation was found between the TSCF and BCF values (see Table 4). The empirical linear regression model between log k_d (the logarithm of soil distribution coefficient) and log BCF (the logarithm of bioconcentration factor) obtained was: log $BCF = 1.49(\pm 0.10) - 0.45(\pm 0.05 \times \log\ k_d$ with ($n=12$) and $R^2=0.83$, correlation coefficient $= -0.91$ and $p<0.001$, indicating a linear regression and negative correlation between the dependent variable (log BCF) and the independent variable (log k_d). The empirical linear regression model between log TSCF (the logarithm of transpiration stream concentration factor) and log BCF was: log $BCF = 1.11(\pm 0.04) + 0.27(\pm 0.02) \times \log\ TSCF$ with ($n=12$) and

Table 2
Polycyclic aromatic hydrocarbons (PAH) physical–chemical properties applied to the mathematical model to estimate the PAH bioconcentration factor (BCF) in corn grains. # rings: number of aromatic rings; m_w molar mass; s: water solubility; logarithm of octanol–water partition coefficient k_{ow}; v_p: vapor pressure; $t_{1/2}$: half-life in the soil.

PAH	# Rings	m_w[a] g mol^{-1}	s[a] mg L^{-1}	logk_{ow}[a]	v_p[a] Pa	$t_{1/2}$[b] day
Aenaphthene	3	154	3.90	3.92	2.87×10^{-1}	102
Aenaphthylene	3	152	16.10	3.94	8.91×10^{-1}	60
Athracene	3	178	0.04	4.45	8.71×10^{-4}	460
Benz(a)anthracene	5	228	0.01	5.76	2.80×10^{-5}	670
Benz(a)pyrene	6	252	0.00	6.13	7.32×10^{-7}	530
Benz(b)fluoranthene	5	252	0.00	5.78	6.67×10^{-5}	610
Benz(g,h,i)perylene	6	276	0.00	6.63	1.33×10^{-8}	650
Benz(k)fluoranthene	5	252	0.00	6.11	1.29×10^{-7}	2140
Crysene	4	228	0.00	5.81	8.31×10^{-7}	990
Dibenz(a,h)anthracene	5	278	0.00	6.75	1.27×10^{-7}	940
Fuoranthene	4	202	0.26	5.10	1.23×10^{-3}	60
Fuorene	3	166	1.69	4.18	8.00×10^{-2}	60
Ideno(1,2,3-c,d)pyrene	6	276	0.00	6.70	1.67×10^{-8}	178
Naphthalene	2	128	31.00	3.30	1.13×10^{-0}	48
Penanthrene	3	178	1.15	4.46	1.61×10^{-2}	200
Pyrene	4	202	0.14	4.88	6.00×10^{-4}	1870

[a]Values from SRC (2010) and [b]Howard et al. (1991).

Table 3
Soil, corn plant and grain physical–chemical parameters applied to the model to estimate the polycyclic aromatic hydrocarbons (PAH) bioconcentration factor (BCF) in corn grains.

Parameter	Symbol	Value	Unity
Total daily volume of water lost by plant transpiration[a]	Q_x	5.0×10^4	L day^{-1} ha^{-1}
Plant fresh biomass[a]	M_p	2.0×10^4	kg ha^{-1}
Plant growth rate[a]	k_e	0.71	day^{-1}
Corn grain cellulose volumetric fraction[b]	f_c	0.25	g g^{-1}
Corn grain lignin volumetric fraction[b]	f_l	0.06	g g^{-1}
Phloem sap flow rate necessary to produce 1.0 kg fresh corn grains	Q_f	3.0	L kg^{-1}
Corn grain density[b]	ρ_g	1.2	kg L^{-1}
Soil solution density[c]	ρ_w	0.98	kg L^{-1}
Soil water volumetric fraction[c]	f_θ	0.25	g g^{-1}
Soil air volumetric fraction[c]	f_δ	0.16	g g^{-1}
Soil organic matter volumetric fraction[c]	f_{om}	0.027	g g^{-1}
Dry soil density[c]	ρ_s	1.3	kg L^{-1}
Humid soil density[c]	ρ_{wt}	1.5	kg L^{-1}
Plant age at grain harvest (days after sowing)	t_h	120	day

[a]Values from Bergamaschi et al. (2005), [b]Rosa et al. (2004) and [c]Dynia et al. (2006).

Table 4
Polycyclic aromatic hydrocarbons (PAH) parameters: soil sorption coefficients (k_d), transpiration stream concentration factor (TSCF), bioconcentration factor in corn grains (BCF) and observed soil solution concentrations ($C_{w-\exp}$).

PAH	k_d L kg^{-1}	TSCF	BCF L kg^{-1}	$C_{w-\exp}$ µg L^{-1}
Acenaphthene	13	0.346	10.11	n.d.
Acenaphthylene	13	0.338	8.48	0.20
Anthracene	24	0.173	10.97	0.16
Benz(a)anthracene	117	0.012	4.40	0.08
Benz(a)pyrene	182	0.005	3.10	n.q.
Benz(b)fluoranthene	119	0.012	4.29	0.07
Benz(g,h,i)perylene	330	0.001	2.00	0.02
Benz(k)fluoranthene	177	0.005	3.42	0.06
Chrysene	124	0.011	4.33	0.06
Dibenz(a,h)anthracene	381	0.001	1.83	0.02
Fluoranthene	53	0.055	4.16	0.14
Fluorene	18	0.253	7.71	0.15
Indeno(1,2,3-c,d)pyrene	359	0.009	1.51	0.02
Naphthalene	6	0.590	8.22	1.28
Phenanthrene	25	0.171	9.69	0.17
Pyrene	41	0.084	9.30	0.23

n.d. = not detected; n.q. = not quantified.

$R^2 = 0.90$, correlation coefficient $= -0.95$ and $p < 0.001$, indicating a linear regression and positive correlation between the dependent variable, log TSCF, and the independent variable, log TSCF. Consequently, the PAHs with low k_d and high TSCF values will most likely be found in corn grains. Such compounds usually present two, three or four benzene rings and $3.3 \leq \log k_{ow} \leq 5.81$.

The PAH limits of detection (LOD) and the limits of quantification (LOQ) in corn grains (Table 5), the observed corn grain PAH concentrations (Table 5) and the expected corn grain PAH concentrations (Table 4) can be used to qualify this model (Fig. 1). Fig. 1 illustrates the correlation between the measured PAH concentrations, $C_{g-\exp}$, and the modeled PAH concentrations, C_{g-mod}, limits of detection (LOD) and limits of quantification (LOQ) in corn grains.

The modeled PAH concentrations values, C_{g-mod}, indicated that acenaphthylene (acy), anthracene (ant), fluoranthene (flt) and fluorene (flr) are detectable but not quantifiable in corn grains, and that naphthalene (nap), phenanthrene (phe) and pyrene (pyr) are quantifiable (Fig. 1). However, the benz(a)anthracene (bza), benz(a)pyrene (bzy), benz(b)fluoranthene (bzk), benz(g,h,i)perylene (bzp), benz(k)

fluoranthene (bzk), chrysene (chr) and dibenz(a,h)anthracene (dba) are not detectable in corn grains (Fig. 1).

The results of the twelve corn grain samples analysis (Table 5) showed that: anthracene was not detected; fluoranthene was quantified in two samples; fluorene and naphthalene were detected but not quantified; phenanthrene was quantified in nine samples and pyrene in just one sample; and also, as predicted by the model, benz(a)anthracene, benz(a)pyrene, benz(b)fluoranthene, benz(g,h,i)perylene, benz(k)fluoranthene, chrysene and dibenz(a,h)anthracene were not detected in any of the corn grain samples. Therefore, for soils showing PAH concentrations close to the ones presented in Table 1, the BCF estimates will allow indicating which PAHs can or cannot be detected and quantified in corn grains. All detected or quantified PAHs in corn grains presented two, three or four benzene rings [$3.3 \leq \log k_{ow} \leq 5.81$] (acenaphthylene, chrysene, fluoranthene, fluorene, naphthalene, phenanthrene and pyrene) as indicated by the model. Besides, it was possible to estimate and observe that highly lipophilic PAH molecules (heavy PAHs) show low accumulative potential in corn grains and those less lipophilic ones (medium affinity to lipids or light PAHs) with two, three or four benzene rings may accumulate in corn grains.

When the soil solution PAH concentration is known and it is originated from SS addition to the soil, the BCF value allows estimating the corn grain PAH concentration and also determining the SS-PAH maximum limits. According to the Brazilian Association of Corn Industry, the corn intake per capita of Brazilian people is around 18 kg year^{-1} (≈ 0.05 kg day^{-1}) (Abimilho: http://www.abimilho.com.br/noticias/noticias07.htm). In this study, the corn grain samples presented a total PAH level of 31.51 µg kg^{-1} (dry weight basis). Considering the average corn grain total PAH value of 35 µg kg^{-1} and the average corn grain daily intake of 0.05 kg day^{-1} per capita, it is possible to estimate the PAH daily intake — DI (µg kg^{-1} day^{-1} b.w.$^{-1}$) — by the expression $DI = \frac{0.05 \times totalPAH}{70}$, resulting in an estimated total PAH daily intake per capita of 0.025 µg kg^{-1} day^{-1} b.w.$^{-1}$ (2.5×10^{-5} mg kg^{-1} day^{-1} b.w.$^{-1}$), for corn grains produced in PAH soil level conditions similar to those shown in Table 1.

The maximum residue level (MRL) allowed for different PAHs has been defined by the Agency for Toxic Substances and Disease Registry (ATSDR, 2010). According to the human oral exposition duration to anthracene, fluoranthene and fluorene, the MRL for these substances are 10, 0.4 and 0.4 mg kg^{-1} day^{-1}, respectively. Consequently, the total PAH levels in grains of corn plants cultivated in soils with similar PAH levels do not negatively implicate the grain quality for human consumption. The

Table 5
Analytical method limits of detection (LOD) and limits of quantification (LOQ) of PAHs in corn grains, PAHs concentrations in corn grains [dry weight]: minimum, maximum, average and median residual levels; and number of corn grain samples showing PAH levels above the method limit of quantification (>LOQ).

PAH	LOD µg kg^{-1}	LOQ µg kg^{-1}	Minimum $n = 12$ µg kg^{-1}	Maximum $n = 12$ µg kg^{-1}	Average µg kg^{-1}	Median $n = 12$ µg kg^{-1}	Count >LOQ
Acenaphthylene	0.7	2.4	<LOD	<LOQ	–	<LOD	n.q.
Acenaphthene	0.8	2.8	<LOD	<LOQ	–	<LOD	n.q.
Anthracene	0.6	2.2	<LOD	<LOD	–	<LOD	n.d.
Benzo(a)anthracene	0.9	3.0	<LOD	<LOD	–	<LOD	n.d.
Benzo(a)pyrene	5.0	16.8	<LOD	<LOD	–	<LOD	n.d.
Benzo(b)fluoranthene	3.2	10.8	<LOD	<LOD	–	<LOD	n.d.
Benzo(g,h,i)perylene	1.6	5.6	<LOD	<LOD	–	<LOD	n.d.
Benzo(k)fluoranthene	3.6	12.0	<LOD	<LOD	–	<LOD	n.d.
Chrysene	0.8	2.8	<LOD	<LOQ	–	<LOD	n.q.
Dibenzo(a,h)anthracene	1.8	6.0	<LOD	<LOD	–	<LOD	n.d.
Fluoranthene	0.3	1.1	<LOQ	1.12	1.1	<LOQ	2
Fluorene	0.8	2.6	<LOD	<LOQ	–	<LOD	n.q.
Indeno(1,2,3-c,d)pyrene	1.7	5.4	<LOD	<LOD	–	<LOD	n.d.
Naphthalene	1.8	6.0	<LOD	<LOQ	–	<LOQ	n.q.
Phenanthrene	0.6	1.8	<LOQ	4.2	3.0	2.9	9
Pyrene	0.3	1.1	<LOD	1.4	1.4	<LOQ	1

N = total number of samples; n.d. = not detected; n.q. = not quantified; <LOD − lower than the limit of detection; <LOQ − lower than the limit of quantification.
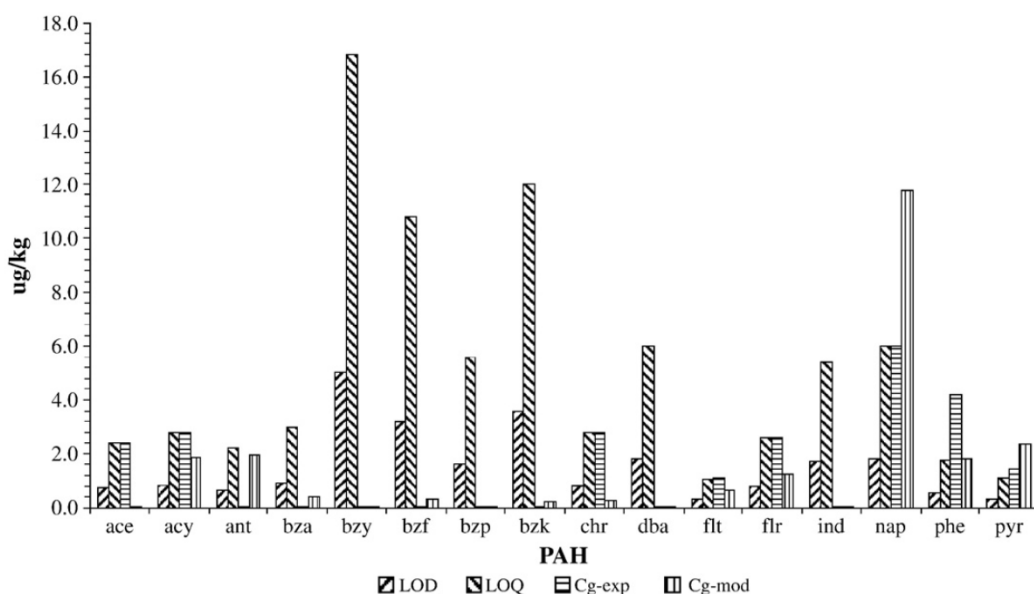
Fig 1. Correlation between the measured, C_{g-exp}, and modeled, C_{g-mod}, PAH concentrations, the PAH limits of detection, LOD, and PHA limits of quantification, LOQ, in corn grains: acenaphthene (ace), acenaphthylene (acy), anthracene (ant), benz(a)anthracene (bza), benz(a)pyrene (bzy), benz(b)fluoranthene (bzf), benz(g,h,i)perylene (bzp), benz(k) fluoranthene (bzk), chrysene (chr), dibenz(a,h)anthracene (dba), fluoranthene (flt), fluorene (flr), indeno(1,2,3-c,d)pyrene (ind), naphthalene (nap), phenanthrene (phe), and pyrene (pyr).

government Company of Environmental Sanitation (CETESB) of São Paulo State, Brazil (http://www.cetesb.sp.gov.br/Solo/relatorios/tabela_va-lores_2005.pdf) has established the naphthalene maximum residue limit (MRL) of 30 µg kg^{-1} for agricultural soils.

The naphthalene *BCF* value in corn grains and the MRL defined by CETESB allow estimating the human naphthalene daily intake via corn grain consumption from plants cultivated in soils containing the limit concentration of naphthalene (30 µg kg^{-1}). In fact, knowing the naphthalene *BCF* (8.22 L kg^{-1}, Table 4) and that the limit concentration might provide 48.63 µg of naphthalene per liter of soil solution, it is possible to estimate a corn grain naphthalene concentration of 399.74 µg kg^{-1}, and consequently, a daily naphthalene intake of 0.28 µg kg^{-1} through a daily corn grain consumption of 0.05 kg. Such naphthalene daily intake value is 100 times lower than the RfD value (2.0×10^{-2}) defined by US-EPA (http://www.epa.gov/iris/subst/0436.htm), what means that the MRL, defined by CETESB for this substance in agricultural soils, guarantees high corn grain quality for human consumption.

The present mathematical model allows estimating the PAH bioconcentration factor in corn grains and the equations derived from the model allows estimating the PAH concentrations in corn plants and grains. However, the equations are conservative since their hypotheses neglect the compound volatilization, dissipation and transformation processes into the corn grains. Furthermore, the model did not take into consideration the PAH uptake by leaves; neither through air respiration nor through passive diffusion from the soil particles to the leaf surface. Despite the conservativeness, the model and equations satisfactorily simulated the PAH accumulation in corn grains.

4. Conclusions

The objectives of the present study were to estimate the values of corn grain-PAH bioconcentration factors (BCF) of plants grown in soils amended with SS and to compare the estimates values with experimentally measured values. The mathematical model used satisfactorily estimated the concentration and BCF of polycyclic aromatic hydrocarbons (PAH) in corn grains. The model was experimentally tested and validated, indicating which PAHs might accumulate in grains of corn plants cultivated in PAH-contaminated or

SS-treated soils for long periods. The corn grain PAH bioconcentration factors varied between 1.57 and 10.97 L kg^{-1}. PAHs showing that low soil distribution coefficients and high transpiration stream concentration factors (*TSCF*) were more likely to be absorbed by corn plants and accumulated in grains. Highly lipophilic PAHs (heavy PAHs) showed low accumulative potential in corn grains and lesser lipophilic ones (medium affinity to lipids or light PAHs) with two, three or four benzene rings were more likely to accumulate in corn grains, identified as acenaphthylene, chrysene, fluoranthene, fluorene, naphthalene, phenanthrene and pyrene. Therefore, sewage sludges containing significant concentrations of light PAHs are not recommended as fertilizers for alimentary field crops. The results obtained in the present work evidenced that PAH levels found in corn grains of plants fertilized with sewage sludge might raise potential contamination risks to the food chain. Therefore, additional research on this subject is of high concern and priority in order to achieve an ecologically correct and sustainable agriculture. More research is needed to know better the PAH and Persistent Organic Pollutants (POPs) concentration ranges in sewage sludges of varied origins and the consequent ecosystem impacts before using them as fertilizers in agriculture.

References

Alcantara S, Pérez DV, Almeida MRA, Silva GM, Polidoro JC, Bettiol W. Chemical changes and heavy metal partitioning in an oxisol cultivated with maize (*Zea mays*, L.) after 5 years disposal of a domestic and industrial sewage sludge. Water Air Soil Pollut 2009;203:3-16.

ATSDR, Agency for Toxic Substances and Disease Registry: <http://www.atsdr.cdc.gov/mrls/index.html#bookmark02> (accessed 2010).

Bergamaschi H, Dalmago GA, Comiran F, Bergonci JI, Müller AG, França S, et al. Water deficit and yield in maize crop | [Deficit hídrico e produtividade na cultura do milho]. Pesq Agropec Bras 2005;41(2):243–9.

Briggs GG. Theoretical and experimental relationships between soil adsorption, octanol–water partition coefficients, water solubilities, bioconcentration factors, and the parachor. J Agric Food Chem 1981;29(5):1050–9.

Camargo MCR, Toledo MCF. Avaliação da contaminação de diferentes grupos de alimentos por hidrocarbonetos policíclicos aromáticos. Braz J Food Technol 2002;5: 19–26.

CETESB (1999). Aplicação de Biossólidos de Sistemas de Tratamento Biológico em Áreas Agrícolas — Critérios para Projeto e Operação (P4230). São Paulo, Brazil: Available online at: <http://www.cetesb.sp.gov.br/>.

Chouychai W, Thongkukiatkul A, Upatham S, Lee H, Pokethitiyook P, Kruatrachue M. Phytotoxicity assay of crop plants to phenanthrene and pyrene contaminants in acidic soil. Environ Toxicol 2007;22:597–604.

Collins C, Fryer M, Grosso A. Plant uptake of non-ionic organic chemicals. Environ Sci Technol 2006;40:45–52.

CONAMA, (2006). Conselho Nacional do Meio Ambiente. Resolução no. 375, de 29 de agosto de 2006: define critérios e procedimentos para o uso agrícola de lodos de esgoto gerados em estações de tratamento de esgoto sanitário e seus produtos derivados, e dá outras providências. Available online at: <ftp://ftp.sp.gov.br/ftpcomitepcj/Res-CONAMA-375-06.PDF>.

Dettenmaier EM, Doucette WJ, Bugbee B. Chemical hydrophobicity and uptake by plant roots. Environ Sci Technol 2009;43:324–9.

Dynia JF, Souza MD, Boeira RC. Nitrate leaching in a Typic Haplustox planted with mayze after successive applications of sewage sludge | [Lixiviação de nitrato em Latossolo cultivado com milho após aplicações sucessivas de lodo de esgoto]. Pesq Agropec Bras 2006;41:855–62.

Environment Canada. Canadian Environmental Protection Act Priority Substances List Assessment Report: Polycyclic Aromatic Hydrocarbons. Ottawa, Ontario: Ministry of Supply & Services; 1994.

Farhadian A, Jinap S, Faridah A, Sakar ZI. Determination of polycyclic aromatic hydrocarbons in grilled meat. Food Control 2010;21:606–10.

Fernandes SAP, Bettiol W, Cerri CC, Camargo P. Sewage sludge effects on gas fluxes at the soil–atmosphere interface, on soil δ^{13}C and on total soil carbon and nitrogen. Geoderma 2005a;125:49–57.

Fernandes SAP, Bettiol W, Cerri CC. Effect of sewage sludge on microbial biomass, basal respiration, metabolic quotient and soil enzymatic activity. Appl Soil Ecol 2005b;30:65–77.

Ferrarese E, Andreottola G, Oprea IA. Remediation of PAH contaminated sediments by chemical oxidation. J Hazard Mater 2008;152:128–39.

Fismes J, Perrin-Ganier C, Empereur-Bissonnet P, Morel JL. Soil-to-root transfer and translocation of polycyclic aromatic hydrocarbons by vegetables grown on industrial contaminated soils. J Environ Qual 2002;31:1649–56.

Howard PH, Boethling RS, Jarvis WF, Meylan WM, Michalenko EM. Handbook of environmental degradation rates. Chelsea: Lewis Publishers; 1991.

Jones KC, Stratford JA, Tidridge P, Waterhouse KS, Johnston AE. Polynuclear aromatic hydrocarbons in an agricultural soil: long-term changes in profile distribution. Environ Pollut 1989;56:337–51.

Jonker MTO. Absorption of polycyclic aromatic hydrocarbons to cellulose. Chemosphere 2008;70:778–82.

Juraske R, Antón A, Castells F. Estimating half-lives of pesticides in/on vegetation for use in multimedia fate and exposure models. Chemosphere 2008;70:1748–55.

Kinney CA, Furlong ET, Zaugg SD, Burkhardt MR, Werner SL, Cahill JD, et al. Survey of organic wastewater contaminants in biosolids destined for land application. Environ Sci Technol 2006;40:7207–15.

Kulhánek A, Trapp S, Sismilich M, Janků J, Zimová M. Crop-specific human exposure assessment for polycyclic aromatic hydrocarbons in Czech soils. Sci Total Environ 2005;339:71–80.

Mantovi P, Baldoni G, Toderi G. Reuse of liquid, dewatered, and composted sewage sludge on agricultural land: effects of long-term application on soil and crop. Water Res 2005;39:289–96.

Meyers PA, Ishiwatari R. Lacustrine organic chemistry: an overview of indicators of organic matter sources and diagenesis in lake-sediments. Org Geochem 1993;20 (7):867–900.

Oleszczuk P. Persistence of polycyclic aromatic hydrocarbons (HPAs) in sewage sludge-amended soils. Chemosphere 2006;65:1616–26.

Oleszczuk P, Baran S. Polycyclic aromatic hydrocarbons content in shoots and leaves of willow (*Salix viminalis*) cultivated on the sewage sludge-amended soil. Water Air Soil Pollut 2005;168:91-111.

Paraíba LC. Pesticide bioconcentration modelling for fruit trees. Chemosphere 2007;66: 1468–75.

Paraíba LC, Kataguiri K. Model approach for estimating potato pesticide bioconcentration factor. Chemosphere 2008;73:1247–52.

Rosa JRP, da Silva JHS, Restle J, Pascoal LL, Brondani IL, Alves Filho DC, et al. Evaluation of silages of different corn hybrids (*Zea mays*, L.) by feedlot performance of calves, during the growing phase | [Avaliação da silagem de diferentes híbridos de milho (*Zea mays*, L.) por meio do desempenho de bezerros confinados em fase de crescimento]. Rev Bras Zootec 2004;33(2):302–12.

Scientific Committee on Food. Opinion of the Scientific Committee on Food on the risks to human health of polycyclic aromatic hydrocarbons in food. SCF/CS/CNTM/PAH/29 Final. Brussels: European Commission, Health and Consumer Protection Directorate-General; 2002.

SRC, Syracuse Research Corporation, (2010) <http://www.syrres.com/what-we-do/databaseforms.aspx?id=386> (accessed 10/21/02).

Tao S, Jiao XC, Chen SH, Liu WX, Coveney Jr RM, Zhu LZ, et al. Accumulation and distribution of polycyclic aromatic hydrocarbons in rice (*Oryza sativa*). Environ Pollut 2006;140:406–15.

Trapp S. Fruit tree model for uptake of organic compounds from soil and air. SAR QSAR Environ Res 2007;18(3–4):367–87.

Trapp S, McFarlane JC. Plant contamination: modelling and simulation of organic chemical processes. Boca Raton: CRC Press; 1995.

Trapp S, Miglioranza KSB, Mosbæk H. Sorption of lipophilic organic compounds to wood and implications for their environmental fate. Environ Sci Technol 2001;35: 1561–6.

Trapp S, Rasmussen D, Samsøe-Petersen L. Fruit tree model for uptake of organic compounds from soil. SAR QSAR Environ Res 2003;14:17–26.

Tsutiya MT, Comparini JB, Sobrinho AP, Hespanol I, Carvalho PCTde, Melfi AJ. Biossólidos na Agricultura. São Paulo, Brazil: SABESP; 2001.

US-EPA. Provisional guidance for qualitative risk assessment of polycyclic aromatic hydrocarbons. Washington, DC: U.S. Environmental Protection Agency. Office of Research and Development; 1993 (EPA/600/R-93/089).

Wenzl T, Simon R, Anklam E, Kleiner J. Analytical methods for polycyclic aromatic hydrocarbons (PAHs) in food and the environment needed for new food legislation in the European Union. Trends Anal Chem 2006;25(7):716–25.

WHO. Environmental Health Criteria 202: Selected Non-Heterocyclic Polycyclic Aromatic Hydrocarbons. Geneva: WHO; 1998.

Zohair A, Salim AB, Soyibo AA, Beck AJ. Residues of polycyclic aromatic hydrocarbons (HPAs), polychlorinated biphenyls (PCBs) and organochlorine pesticides in organically-farmed vegetables. Chemosphere 2006;63:541–53.