Polyaromatic hydrocarbon contamination of fruits sold in areas with polluted air

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Abstract

The aim of this research was to find out the levels of polyaromatic hydrocarbons (PAHs) that may be present on the surface of fruits sold in areas where these compounds would be abundant in the environment; a busy city area. It is important to be aware of the levels of PAHs on these foods because their ingestion may lead to the development of cancers. EU's PAH4 were measured using HPLC-FL after sample preparation by solid phase extraction. The levels detected were compared to the allowed levels in the EU Commission Regulation No 835/2011. The results obtained from the investigation reveal that there is a well observable difference between the two fruits investigated (nectarine and apricot). This suggests strongly that the difference in chemical composition of the fruits is an important factor in absorbing pollutants.

Keywords: PAHs, fruit peel, air pollution

Összefoglaló

Kutatásunk célja az volt, hogy feltérképezzük a nagyvárosban, forgalmas környezetben, szennyezett levegőn, kültéren árusított gyümölcsök felületi poliaromás szénhidrogén (PAH) szennyezettségét. A PAH-ok között erősen rákkeltő vegyületek is akadnak, amelyek a táplálékkal az emésztőrendszerbe kerülve ott rosszindulatú daganatos megbetegedéseket indukálhatnak. Az EB 835/2011 rendeletben rögzített négy vegyület (EU PAH4) vizsgálata történt meg fluoreszcens HPLC-s módszerrel, különböző külső, illetve belső helyszíneken árusított nektarin, illetve sárgabarack esetén. Jól megfigyelhető különbséget sikerült körvonalazni a kültéren, illetve a beltéren árusított gyümölcsök PAH szennyezettsége között. Az előbbiek magasabb PAH terheltsége szoros összefüggésben lehet a légszennyezettséggel.

Kulcsszavak: PAH-ok, gyümölcs héj, légszennyezettség

Introduction

Fruits are sold in a variety of different venues and a variety of different ways, in cities one of the greatest differences is whether they are sold indoors or outdoors. A danger for fruit sold outdoors in urban areas is that of contamination from local pollution in the city. The greatest source of air pollution at street level in cities comes from the fumes from vehicles' combustion engines. Polycyclic aromatic hydrocarbons, or PAHs, are described as a large class of organic compounds containing two to seven fused aromatic rings containing carbon and hydrogen atoms. They are formed and released during incomplete combustion or burning of organic matter. With the high amount of traffic in dense areas like cities there will be a high level of PAHs in the atmosphere and so the level of deposition of PAHs on surfaces will also be high. Human exposure to combustion products containing carcinogenic PAHs has long been associated with cancer induction. This is why it is important to learn of the levels of PAHs in foods sold in areas of pollution.

In order to do this a comparative analysis of fruit samples purchased in areas of Budapest with heavy traffic was carried out. The levels of PAHs were detected in nectarines and apricots bought in different outlets around the same area. HPLC and UV spectroscopy were used to analyse the prepared samples. Six main PAHs were identified to detect and compare between samples.

Material and method

It was decided that the best approach was to comparatively analyse two different fruits (apricots and nectarines) sold in different shops and stalls in the same area of Budapest. The samples to be tested were to be from both internally displayed sources, such as supermarkets and shops, and also externally displayed sources such as stalls or shop fronts on streets. An additional set of apricots was received from Kecskemét, the Neumann János University's pilot farm, grown near to roads with heavy traffic and the military airfield.

Preparation of samples

Each sample was separated and labelled. Of the 11 sets of samples, each was divided into washed and unwashed samples. The washed samples were rinsed under running cold tap water for 20 seconds, the unwashed simply remained as they were when purchased. Each sample was then weighed, destoned and homogenised using a blender.

From the homogenized fruits, 3 x 15 g were measured from into a 50 ml centrifuge tube. 100 µl 30 mg/mL TPP solution was added as surrogate standard, then the sample was extracted with 20 ml of toluene/acetone 2:1 mixture by 2-minute intensive shaking. A spoonful of NaCl was added in order to increase the polarity of acetone-layer, and the sample was shaken again for 1 min. After this the sample was centrifuged at room temperature for 10 mins at 8,000 g.

The upper layer (toluene) was removed, and 3x6 ml from it were evaporated to dryness at 55 ºC in the same glass tube under gentle nitrogen stream. The sample was reconstituted in 500 µl ACN, filtered through 0.22 µm membrane filter, then analysed.

Laboratory analysis

Measurements were made on a Shimadzu 10A series HPLC system equipped with fluorescence (FL) and ultraviolet (UV) detectors. PAHs were measured by the FL, TPP was measured by the UV detector. A Phenomenex Kinetex® C18 150 x 4.6 mm column (2.6 µm particle size) was used for separation. High-purity water (SUEZ Environment) and HPLC-grade acetonitrile (VWR) were used as eluents A and B, respectively. The flow rate was set to 0.3 mL/min, the ratio of B eluent to 85% during the isocratic elution. The column oven was kept at 35 ºC. The injected volume was 20 µL, each sample was injected three times. One chromatographic run lasted for 20 minutes.

Quantification was done by calibrating with external standard method: solutions with known concentrations of TPP and the six PAHs were measured before the samples, and the areas of corresponding peaks were plotted against the nominal concentration of the given compound and level by the LCSolutions® software of the HPLC system. The lowest level of quantification was 0.25 ng/mL for the PAHs and 0,15 ng/mL for the TPP. Calculations and statistical analysis of data after the primary data processing were done by MS Excel software.

The measurements were carried out by an FL-HPLC at the laboratory of the Department of Food Hygiene in the University of Veterinary Medicine Budapest. The samples were tested for the presence of six PAHs; chrysene, benzo[a]pyrene, benz[a]anthracene and benzo[b]fluoranthene (“*EU PAH4*”), and fluoranthene and dibenzo[a,h]anthracene. The measured levels of these PAHs were then compared to those set in EU Commission Regulation No 835/2011.

Results and discussion

As there are no limits set for fruits in the EU Commission Regulation No 835/2011 it was decided to compare the obtained results against the limits set in section 6.1.3 – "Coconut oil intended for direct human consumption or use as an ingredient in food."

From the results obtained it can be seen that in general the nectarines had a higher PAH level that the apricots. This suggests that the difference in skin and chemical composition of the fruits may be an important factor in absorbing pollutants. From the results it appeared that washing had a positive effect and seems to have reduced the number of PAHs. However, the correlation analysis did not reveal any correlation between washing and the PAH level, therefore, although the washed fruits showed generally lower levels of detectable PAHs this cannot be deemed statistically relevant.

The highest amount of PAHs detected in both fruits was for the X2 samples (see table 1.). Indeed, sample X2NU, a nectarine, had the highest level of PAHs present of all samples and its counterpart, X2AU had the highest level of PAHs in all apricot samples. The area these fruits were purchased in was in close vicinity to Keleti railway station. There is a clear link between the pollution of these samples, displayed externally in the vicinity of this busy station and the trains' diesel-powered engines. This area is well sheltered, and it can be assumed the particles of the fumes expelled from these engines would deposit in the locality.

The results show ultimately that the level of PAHs detected in the samples were under those allowed limits set out in the EU Commission Regulation No 835/2011 section 6.1.3. For a healthy adult it can be suggested that simple washing of the fruits shall be enough for their consumption. For weaker persons, such as the elderly, sick or young infants, peeling should be used as a more effective way of reducing the intake of contamination from these foods.

1. Table. Legend for codes of fruits

1st character	2nd character	3rd character	4th character
place of origin	number of the place	fruit type	washing
X: eXternally sold		A: apricot	U: unwashed
N: iNternally sold		N: nectarin	W: washed
K: from the fields near Kecskemét			

On viewing the results the most notable difference is in the level of detected PAHs between the washed and unwashed, however, as explained this should be not be considered clear cut. The majority of the difference between the unwashed and washed fruits proved to be significant statistically but we cannot know in advance what portion will be removed. Washing may reduce the level of PAHs on the fruit surface but its efficiency cannot be predicted form this.

The next noticeable results are the general differences in the level of PAHs between the fruits. This may ultimately be due to the differences in the biological and chemical make-up of the peel, or exocarp, of the two fruits. Apricots and nectarines are similar fruits but they have slight differences in their exterior surfaces.

In each case, the type of fruit of place of purchase, it was true that fruits sold at internal places had lower PAH levels that those sold externally. So being stored outside in an area with heavy traffic could indeed be deemed to have an effect on the PAH contamination levels of the fruits. However, fruits sold internally were not as free from PAH contamination as may have been expected.

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