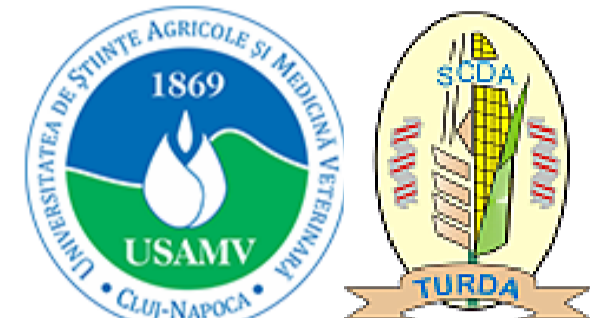


Xenobiotics in *Phaseolus vulgaris*Edward MUNTEAN<sup>1,2</sup>, Nicoleta MUNTEAN<sup>3</sup>, Marcel DUDA<sup>1</sup>, Rajmund MICHALSKI<sup>4</sup><sup>1</sup>University of Agricultural Sciences and Veterinary Medicine Cluj-Napoca, Romania<sup>2</sup>Agricultural Research & Development Station Turda, Romania<sup>3</sup>Regional Center of Public Health Cluj Napoca, National Institute of Public Health, Romania<sup>4</sup>Institute of Environmental Engineering, Polish Academy of Science, Zabrze, Poland

## Introduction

Controlling the contamination of crop plants with pollutants has raised increasing interest in recent years; among the investigated pollutants, heavy metals and polycyclic aromatic hydrocarbons (PAHs) are of particular interest because some of them represent risks for human health due to their toxicity and/ or carcinogenicity [2].

PAHs and heavy metals are ubiquitous in the environment; the contamination of crop plants with these is their entrance point in the food chain, generating health risks for consumers [1, 3]. Common bean (*Phaseolus vulgaris* L.) is one of the most important food legumes in the world, representing ~50% of the grain legumes for direct human consumption; hence, it is one of the major portals of entrance in the food chain for xenobiotics from the environment [1].

## Aims

The major objective of this research is to establish the degree of contamination of common bean with the xenobiotics lead, cadmium, copper, zinc and 15 priority PAH in the conditions of experimental cultures carried out during three years in three locations with different pollution patterns: a reference, non-polluted site, close to Jucu de Jos (experimental field of USAMV Cluj-Napoca, at 46 ° 52'16 "N / 23 ° 45'27" E), a site contaminated by diffuse sources (a high traffic road in Cluj-Napoca at 46 ° 45'57 "N / 23 ° 34'01" E) and a site with historical contamination caused by SC Sometra SA Copsa Mica, located in Șeica Mare (46 ° 01'52 "N / 24 ° 09'39 "E).

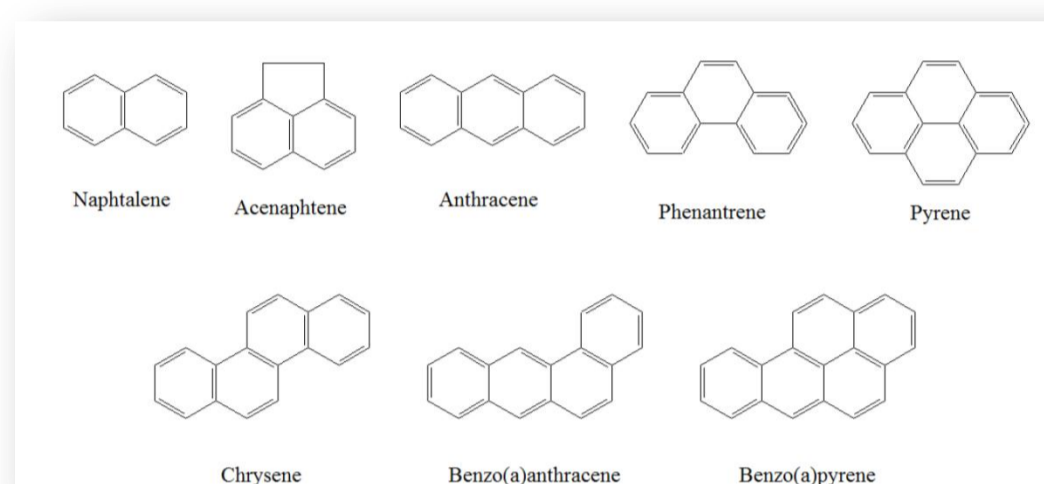


Fig.1 Structures of some representative PAHs

## Materials and methods

**For PAHs' analysis,** *Phaseolus vulgaris*'s grain samples (Ardeleana variety) were processed using ultrasonic assisted extraction, followed by filtration and concentration to dryness: representative samples of ~5 g grains were weighed, grounded and subjected to solid-liquid extraction using 20 mL mixture of hexane: acetone (2: 1), by sonication for 30 minutes in an 30H Elmasonic ultrasonic bath (Elma, Germany), at room temperature. The resulting suspensions were filtered, then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness in a Laborotta 4000 Efficient rotary evaporator (Heidolph, Germany), under vacuum. The obtained residues were dissolved in acetonitrile and injected in the high performance liquid chromatographic (HPLC) system. HPLC analysis was achieved using an Agilent 1100 system (Agilent Technologies Inc., Palo Alto, USA) consisting in a solvent degasser, a quaternary pumping module, an autosampler, a column oven, a diode array detector and a fluorescence detector. The separations were performed with an Envirossep PP column using a gradient with acetonitrile: water (45:55 v/v) [3], at ambient temperature, by injecting 10 μL of samples; quantitative determinations were achieved using the external standard method.

**For heavy metals' analysis,** ~0.5 g grinded samples were accurately weighed and transferred in Teflon reaction vessels; wet digestion was accomplished using 5 mL HNO<sub>3</sub> 65% and 3 mL H<sub>2</sub>O<sub>2</sub> within a Berghoff Microwave Digestion System MWS-3+ (190°C for 2 hours). Measurements were performed using an AA-6300 – Shimadzu double beam atomic absorption spectrophotometer (Shimadzu Corporation, Japan) with both flame and graphite furnace atomization, equipped with deuterium lamp for background correction and hollow-cathode lamps for each of the studied elements.

All determinations were accomplished in triplicate and the averages of 3 measurements for each case were reported.

## Results

- The obtained results revealed a higher share of low molecular weight PAHs, mainly naphthalene, fluorene, acenaphthene and anthracene, high molecular weight PAH contamination being due to dibenzo(a,h)anthracene and indeno(1,2,3-c,d)pyrene.
- The recorded concentrations for total PAH's ranged from 3.06 μg/ kg (Șeica Mare) to 6.97 μg/ kg (Cluj Napoca), the highest levels being those originating from the urban area.
- The maximum average individual PAH's contents were those for low molecular weight compounds, especially for naphthalene (up to 3.72 mg/ kg) and fluorene (up to 2.34 μg/ kg). From high molecular weight PAHs, only dibenzo(a,h)anthracene was detected in all three sites, its concentration ranging from 0.04 to 0.30 mg/ kg.
- The highest content of heavy metals of concern was recorded in samples harvested from the site with historical contamination – Șeica Mare: 0.05 μg Pb/ kg, 0.03 μg Cd/ kg
- The correlation analysis involving PAH contamination of soils on which the studied plants were cultivated and PAH contamination of grains (not detailed here) revealed a weak correlation between these, the most important source of contamination being atmospheric depositions loaded with combustion products of fossil fuels (car traffic from Cluj Napoca).
- The reduced PAH concentrations in the samples from Șeica Mare can be due to the lack of major sources of contamination in that area: the car traffic is very low, the industrial activity is missing and the only sources generating PAH in the area are individual households (wood burning for houses' heating and food preparation, incineration of domestic garbage and the practice of stubble burning – still used in rural areas).

Table 1. Average content of xenobiotics from samples harvested from Cluj-Napoca

Analyte	UM	2012	2013	2014
Pb	μg/kg	<b>0,04</b>	0,02	0,01
Cd	μg/kg	N.D.	N.D.	N.D.
Cu	mg/kg	<b>2,63</b>	2,32	2,07
Zn	mg /kg	21,13	<b>27,2</b>	19,55
Naphthalene	μg/kg	3,54	<b>3,72</b>	2,93
Acenaphthene	μg/kg	0,09	0,21	<b>0,39</b>
Fluorene	μg/kg	1,45	<b>1,76</b>	0,72
Anthracene	μg/kg	0,03	0,07	<b>0,20</b>
Dibenzo(a,h)anthracene	μg/kg	0,09	<b>0,22</b>	0,30
Indeno(1,2,3-c,d)pyrene	μg/kg	0,71	<b>0,99</b>	0,68
Total PAHs	μg/kg	<b>5,91</b>	<b>6,97</b>	5,22

Table 2. Average content of xenobiotics from samples harvested from Jucu

Analyte	UM	2012	2013	2014
Pb	μg/kg	0,01	<b>0,02</b>	0,01
Cd	μg/kg	N.D.	N.D.	N.D.
Cu	mg/kg	<b>1,58</b>	1,49	1,07
Zn	mg/kg	39,36	<b>43,25</b>	35,14
Naphthalene	μg/kg	2,15	2,03	<b>2,36</b>
Acenaphthene	μg/kg	<b>0,61</b>	0,32	0,49
Fluorene	μg/kg	1,97	2,19	<b>2,34</b>
Anthracene	μg/kg	<b>0,25</b>	0,21	0,18
Dibenzo(a,h)anthracene	μg/kg	<b>0,04</b>	0,02	N.D.
Indeno(1,2,3-c,d)pyrene	μg/kg	N.D.	N.D.	N.D.
Total PAHs	μg/kg	<b>5,09</b>	4,8	<b>5,37</b>

Table 3. Average content of xenobiotics from samples harvested from Șeica Mare

Analyte	UM	2012	2013	2014
Pb	μg/kg	0,02	<b>0,05</b>	0,01
Cd	μg/kg	0,01	<b>0,03</b>	0,01
Cu	mg/kg	1,46	<b>1,56</b>	1,19
Zn	mg/kg	<b>32,35</b>	29,01	23,51
Naphthalene	μg/kg	1,53	<b>1,42</b>	1,23
Acenaphthene	μg/kg	0,4	0,31	<b>0,44</b>
Fluorene	μg/kg	<b>1,46</b>	1,1	1,41
Anthracene	μg/kg	0,12	0,06	<b>0,08</b>
Dibenzo(a,h)anthracene	μg/kg	<b>0,26</b>	0,12	0,15
Indeno(1,2,3-c,d)pyrene	μg/kg	N.D.	N.D.	N.D.
Total PAHs	μg/kg	<b>3,8</b>	3,06	3,31

Note: N.D. – not detected

## Conclusion

The obtained results revealed low concentrations of the studied xenobiotics in *Phaseolus vulgaris* grains, caused mainly by the pollution generated by car traffic and historical pollution. These data may be useful as a referential in future studies on human exposure to these pollutants.

## References

1. Kobayashi R., Okamoto R.A., Maddalena R.L. and Kado N.Y. (2008). PAHs in edible grain: a pilot study of agricultural crops as a human exposure pathway for environmental contaminants using wheat as a model crop. *Environmental Research*, 107(2), 145-151.
2. Michalski R., Duda M. M., Șerdean P.N., Kernert J., Grygoyc K., Pecyna P., Muntean, E. (2020). Heavy Metals in Several Soybean Varieties Cultivated in the Transylvanian Plain, Romania. *Bulletin UASVM Food Science and Technology*, 77, 1-10.
3. Muntean, N., Muntean, E., Duda, M. (2013). Contamination of some plant origin food products with polycyclic aromatic hydrocarbons. *Bulletin UASVM serie Agriculture*, 70(2), 383-386.