Detection of Natural and Accidental Contamination of Spices and Herbs

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Objectives of the study

- Elaboration and validation of high resolution mass spectrometric methods (HPLC-q-Orbitrap) for analysis of organic contaminants in spices;
- Efficiency comparision between high resolution mass spectrometric techniques and triple quadrupole methods
- Practical application of elaborated methods for analysis of spices / herbs samples

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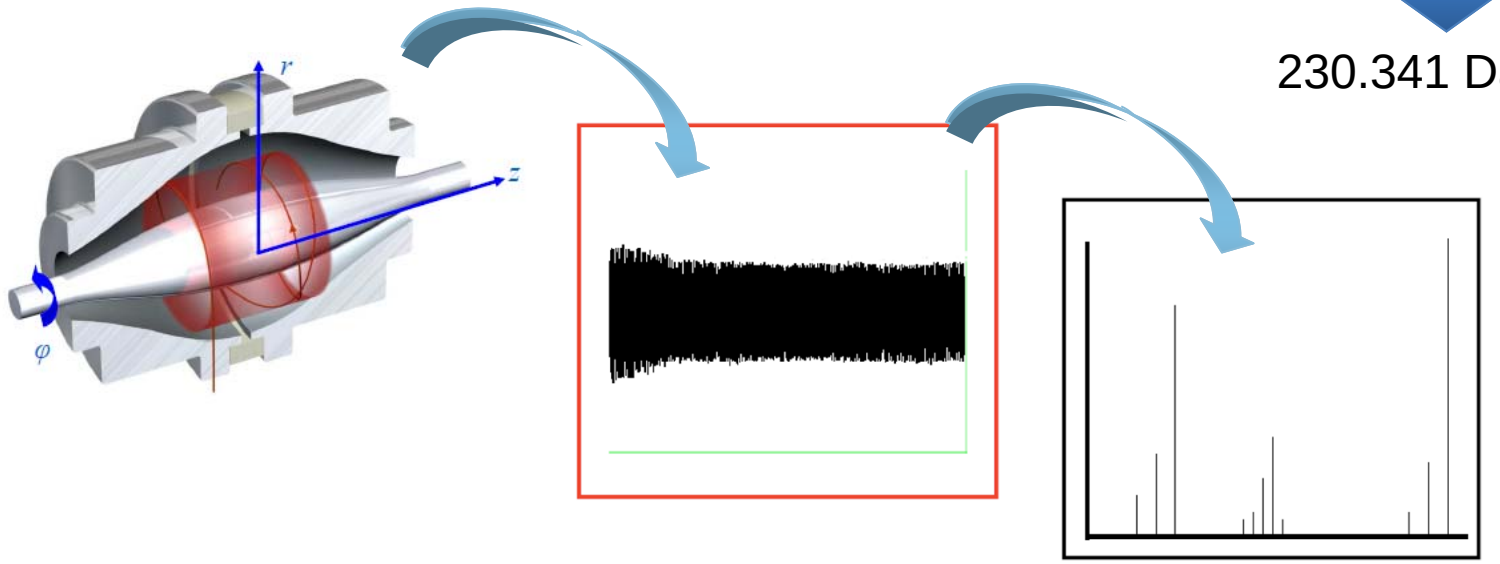
Advantages of high resolution mass spectrometry

- Simultaneous scanning of a wide range of contaminants
- Possibilities of the retrospective analysis
- High selectivity & sufficient sensitivity

230 Da or
230 Da > 175 Da

230.341 Da



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I Determination of chemical contaminants

Analysis by **contaminants using UHPLC-QqQ-MS/MS and UHPLC-q-Orbitrap:**

- ✓ **AZO DYES**
- ✓ **PESTICIDES**
- ✓ **MYCOTOXINS**

SAMPLE PREPARATION

HERBS

SPICES

Purification

- Water /MeCN (1:1 v/v);
- MgSO4 / NaCl / Sodium citrate dehydrate/Sodium citrate sesquihydrate.

Organic fraction exclusion

- Vortexing (1 min);
- Rapid shaking (10 min);
- Centrifugation (5 min);
- Freezing out MeCN fraction;
- Evaporation;
- Reconstituition in water/ MeOH (50:50 v/v).

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II Determination of chemical contaminants

Analysis by **contaminants using UHPLC-QqQ-MS/MS and UHPLC-q-Orbitrap:**

- ✓ **AZO DYES**
- ✓ **PESTICIDES**
- ✓ **MYCOTOXINS**

SAMPLE ANALYSYS

HERBS SPICES

PURIFIED EXTRACT

- 100 mm × 2.1 mm ,2.6 µm Kinetex C18
- Elution: 0.1 % HCOOH (A) / 100% MeOH (B)
- Flow rate of 0.3 mL min^{-1}
- Injection volume of 10 µL

Thermo QExactive UHPLC-q-Orbitrap
AB Sciex 5500 UHPLC-QqQ-MS/MS

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III Determination of chemical contaminants

Analysis by **inductively coupled plasma – mass spectrometry (ICP–MS):**

- ✓ **Toxic metals (As, Cd, Pb, Ni, Sn)**
- ✓ **Micro and macro elements**

SAMPLE PREPARATION

HERBS SPICES

0.3 g matrix
+
8 mL HNO_3 konc.
+
2 mL H_2O_2
(2-6h)

Acid digestion

- **Microwave digestion**
- **Dilution**

ICP-MS analysis

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Comparison of Orbitrap-MS and QqQ-MS/MS

- Equivalent linearity (R^2 > 0,94) and recovery (70 – 120%)
- RSD for both methods were in the range of 8-15%
- The Orbitrap MS system demonstrated at least by 10% better sensitivity for **86** out of 134 pesticides. The sensitivity of UHPLC-QqQ-MS/MS was by 10% better only for **8** pesticides out of 134.
- No substancial differences in efficiencies (precision, accuracy) of analytical techniques for mycotoxins was observed, except for selectivity

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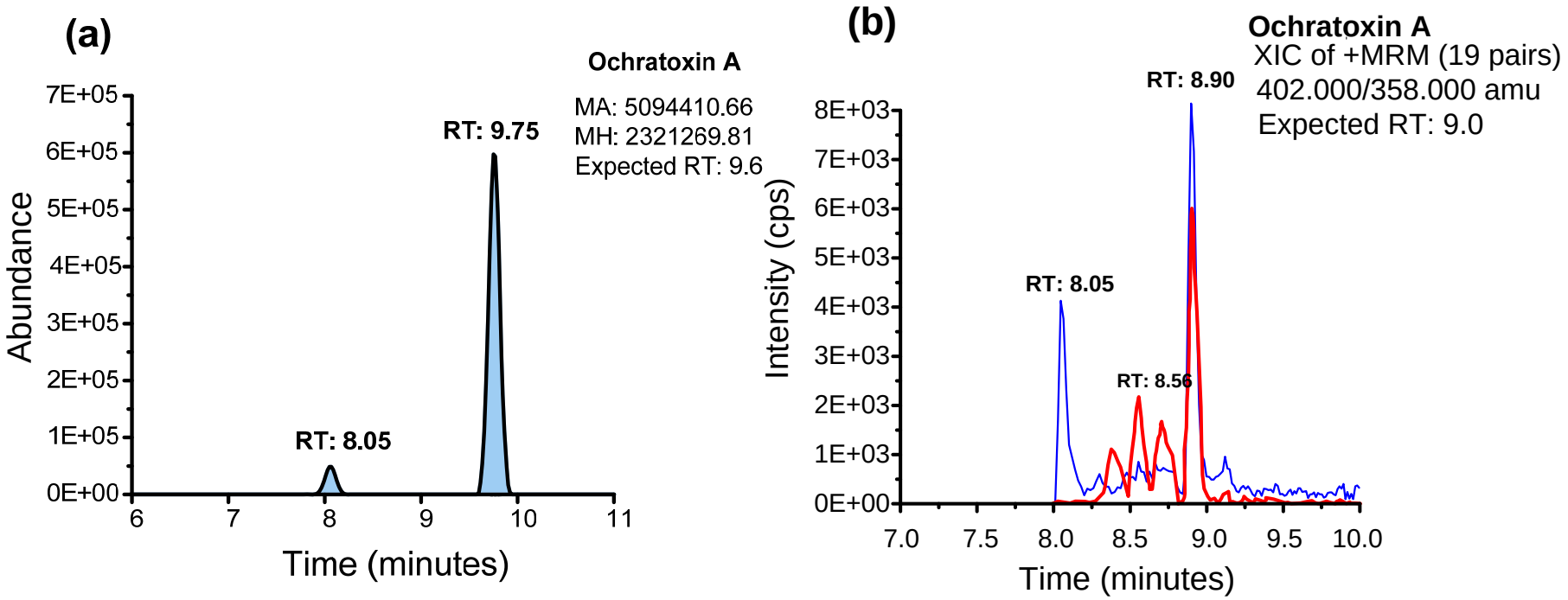
Comparison of Orbitrap-MS (a) and QqQ-MS/MS (b)



Better peak shape and low baseline drift was obtained for chromatograms obtained by the Orbitrap-MS detector (OTA :**a**), compared to the high asymmetry and high noise level of the QqQ-MS (OTA: **b**)

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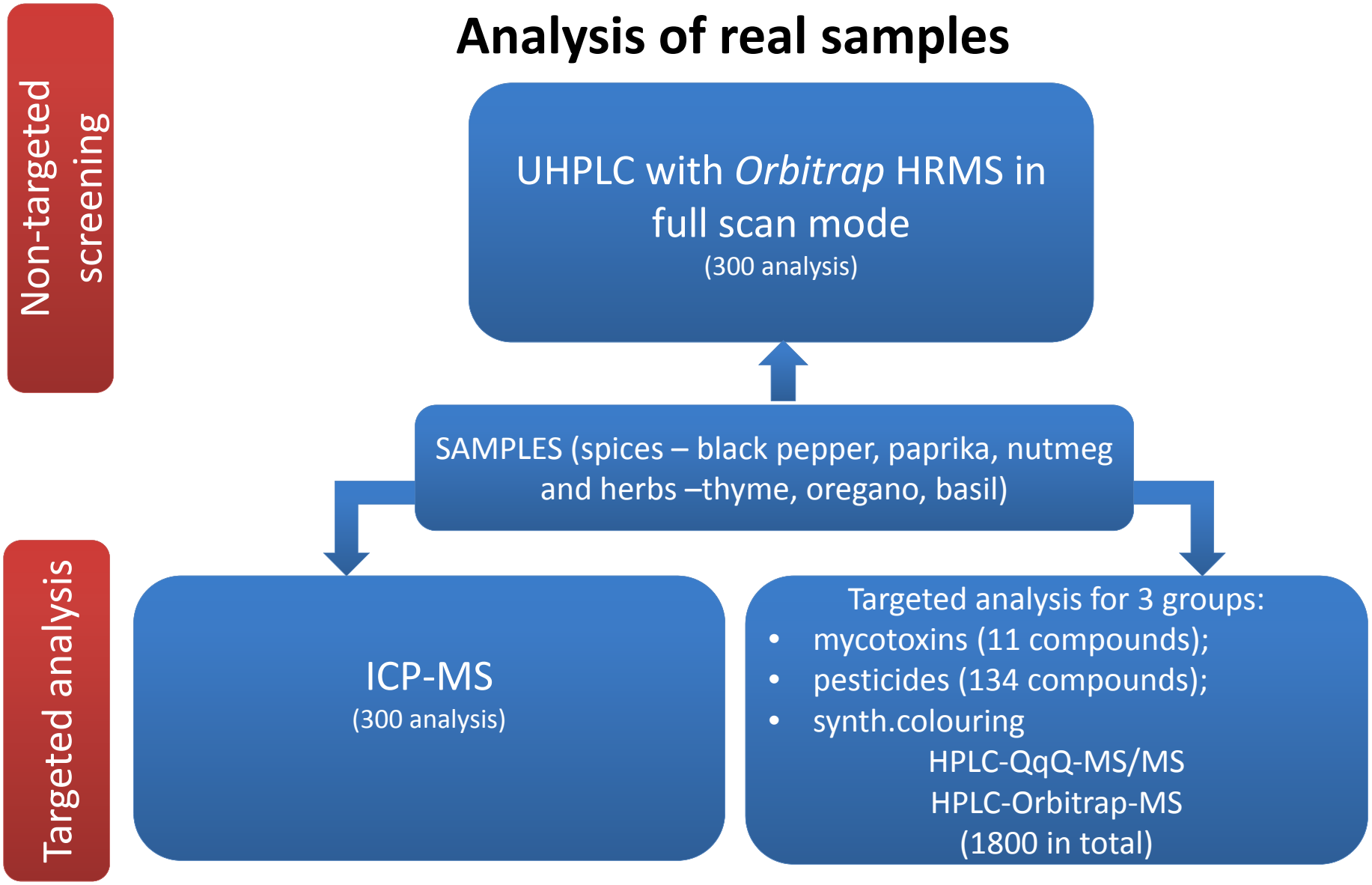
Analysis of real samples



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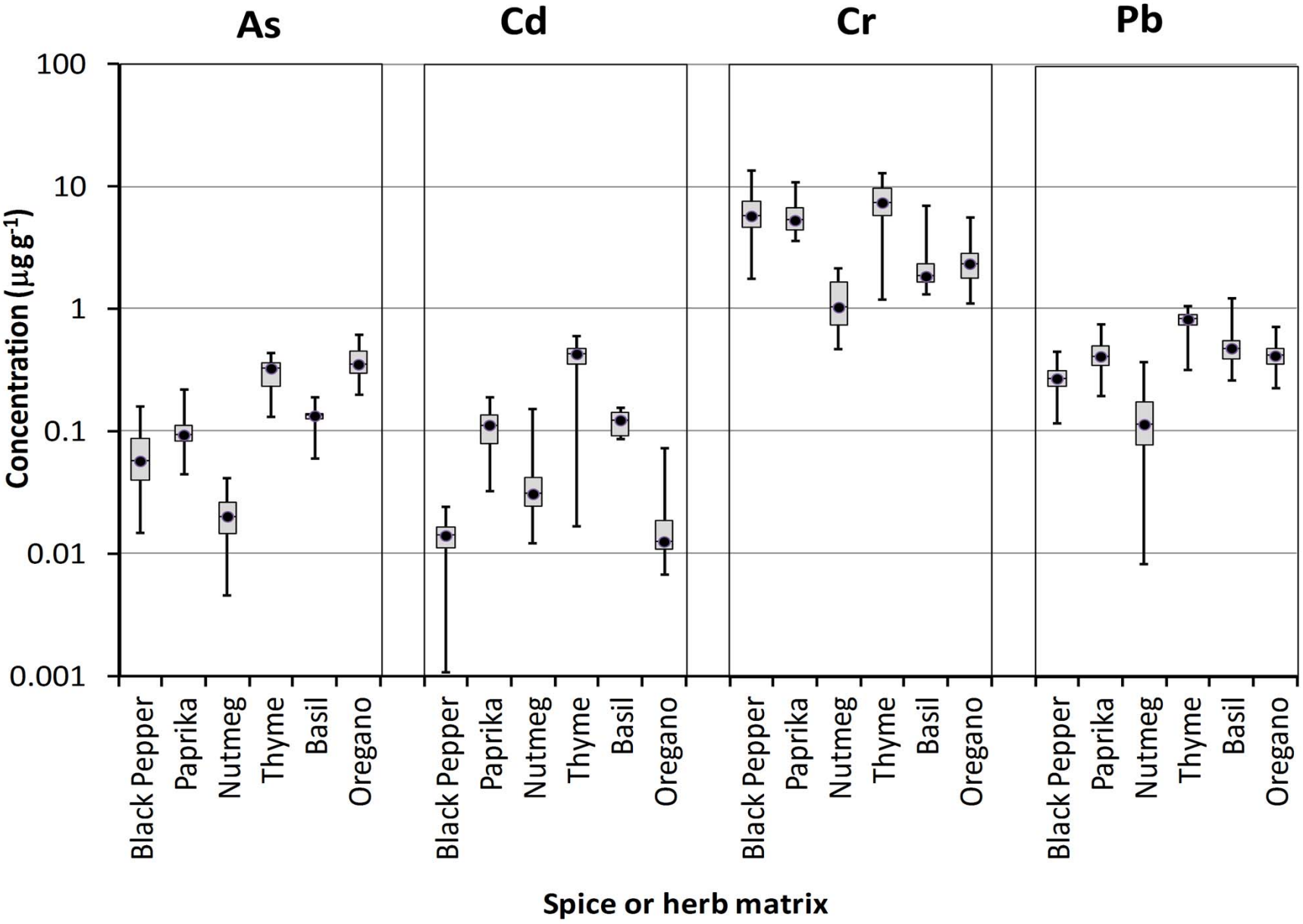
Toxic elements concentrations in spices/herbs



Toxic elements concentrations in spices/herbs

The concentrations of toxic metallic elements in several samples exceeded the permissible levels set for condiments according to WHO 2013, especially in the case of Pb and Cd in thyme and chromium in 68% of all condiment samples.

However, exposure assessment results indicate that the determined heavy metal concentrations are far below the levels of concern, thus do not pose an acute threat to consumer health, even in case of thyme.

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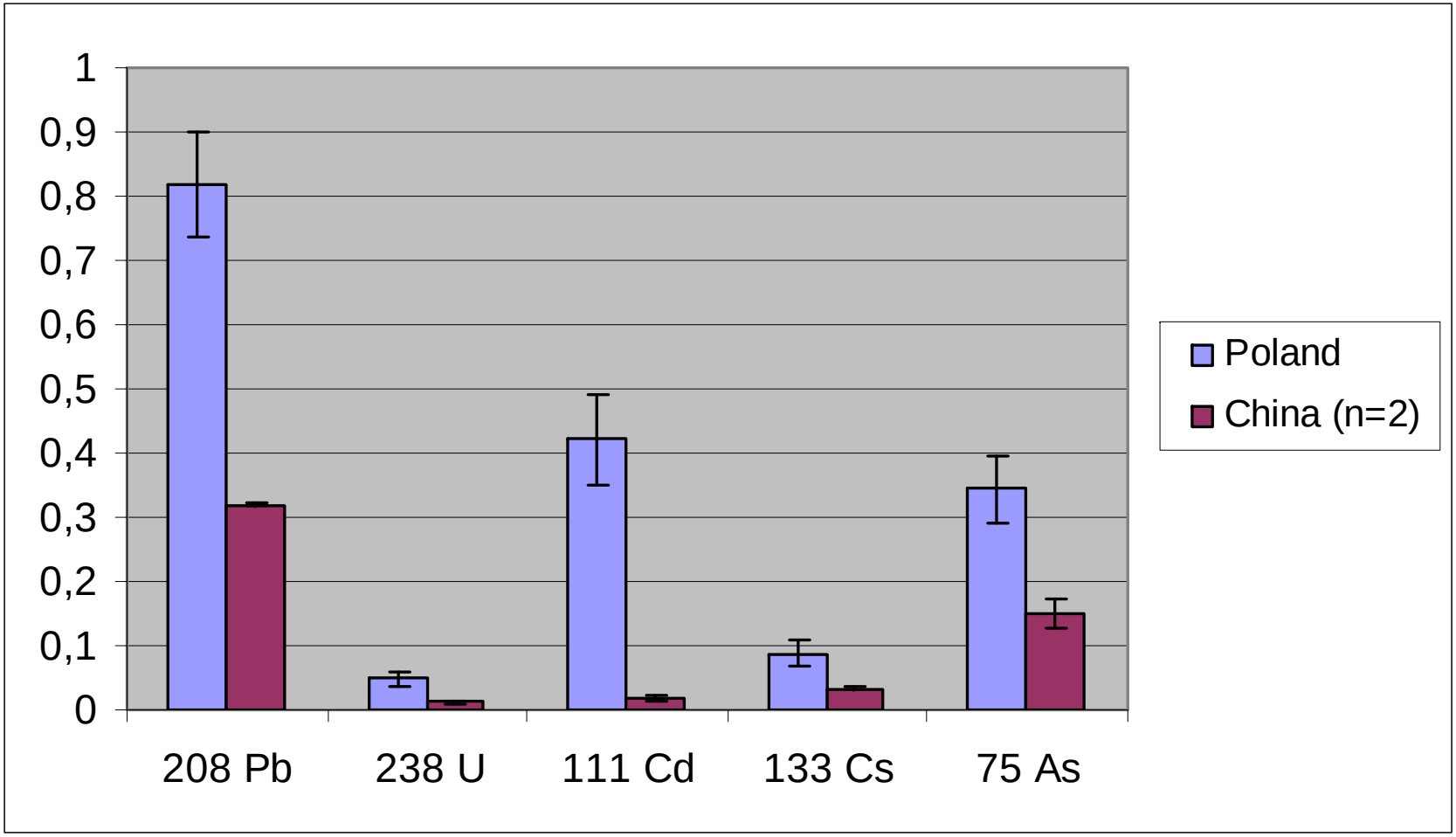
Thyme

Elemental compostion depending on origin



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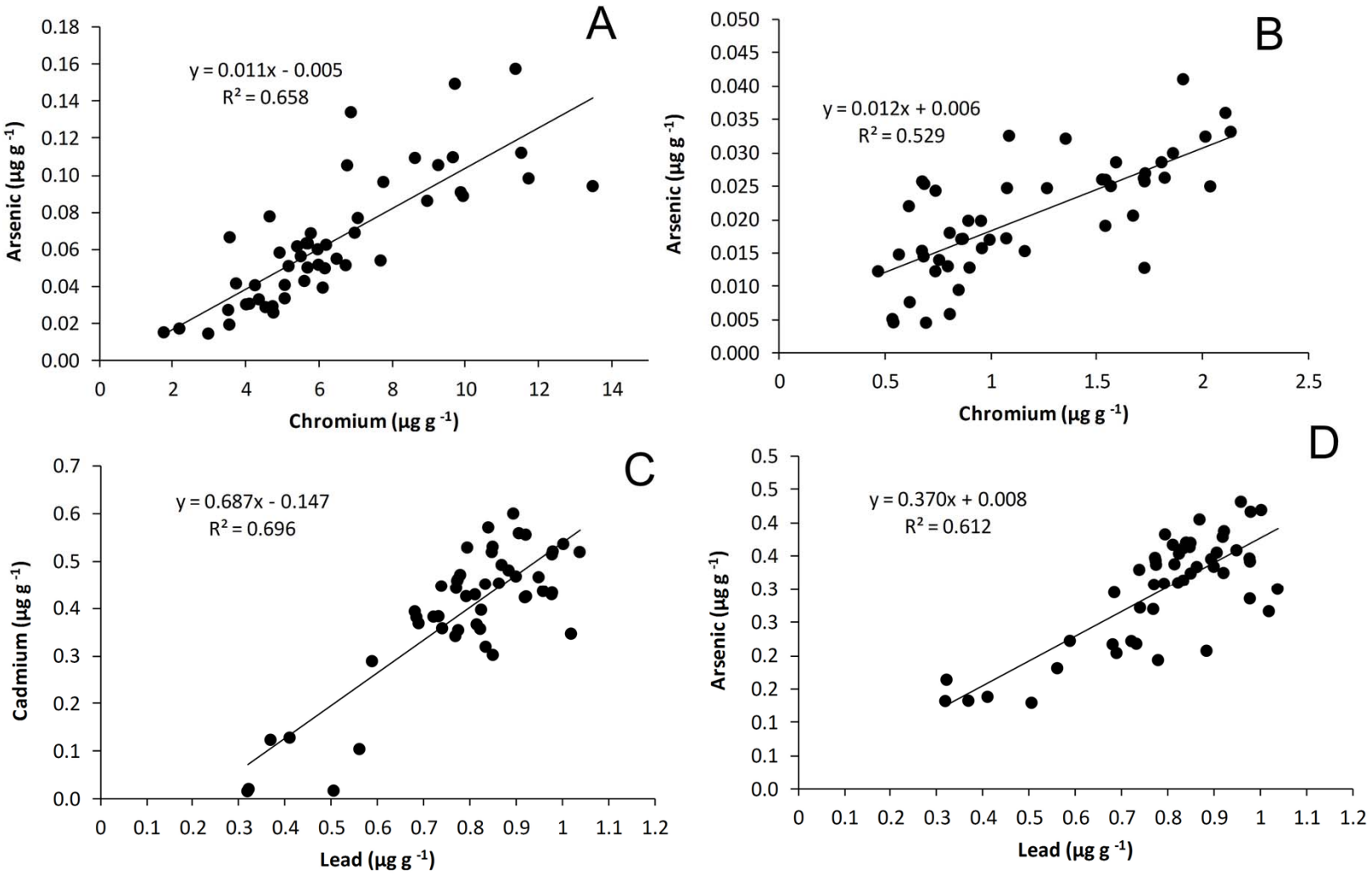
Correlation of the toxic element content



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Chemical contaminants in spices/herbs

➢ Low level of mycotoxins

•Black pepper and basil were the only matrices in which we did not find any traces of mycotoxins above the LOD.

•Only one sample of nutmeg was determined to contain ochratoxin A at a level close to ML (14 µg kg^{-1}) and one sample contained 25 µg kg^{-1} of FB1

•Mycotoxins were detected in 10% and 30% of all basil and thyme samples, respectively (most frequently found - zearalenone and deoxynivalenol).

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Chemical contaminants in spices/herbs

➢ The high content of pesticides

•The residues of 24 pesticides were detected in 59% of the analysed condiments. The number of detected pesticide residues ranged from none in nutmeg to sixteen compounds present at trace or elevated levels in thyme.

•The maximum residue levels of pesticides were exceeded in 10% of oregano and 46% of thyme samples (cymoxanyl and dimethoate).

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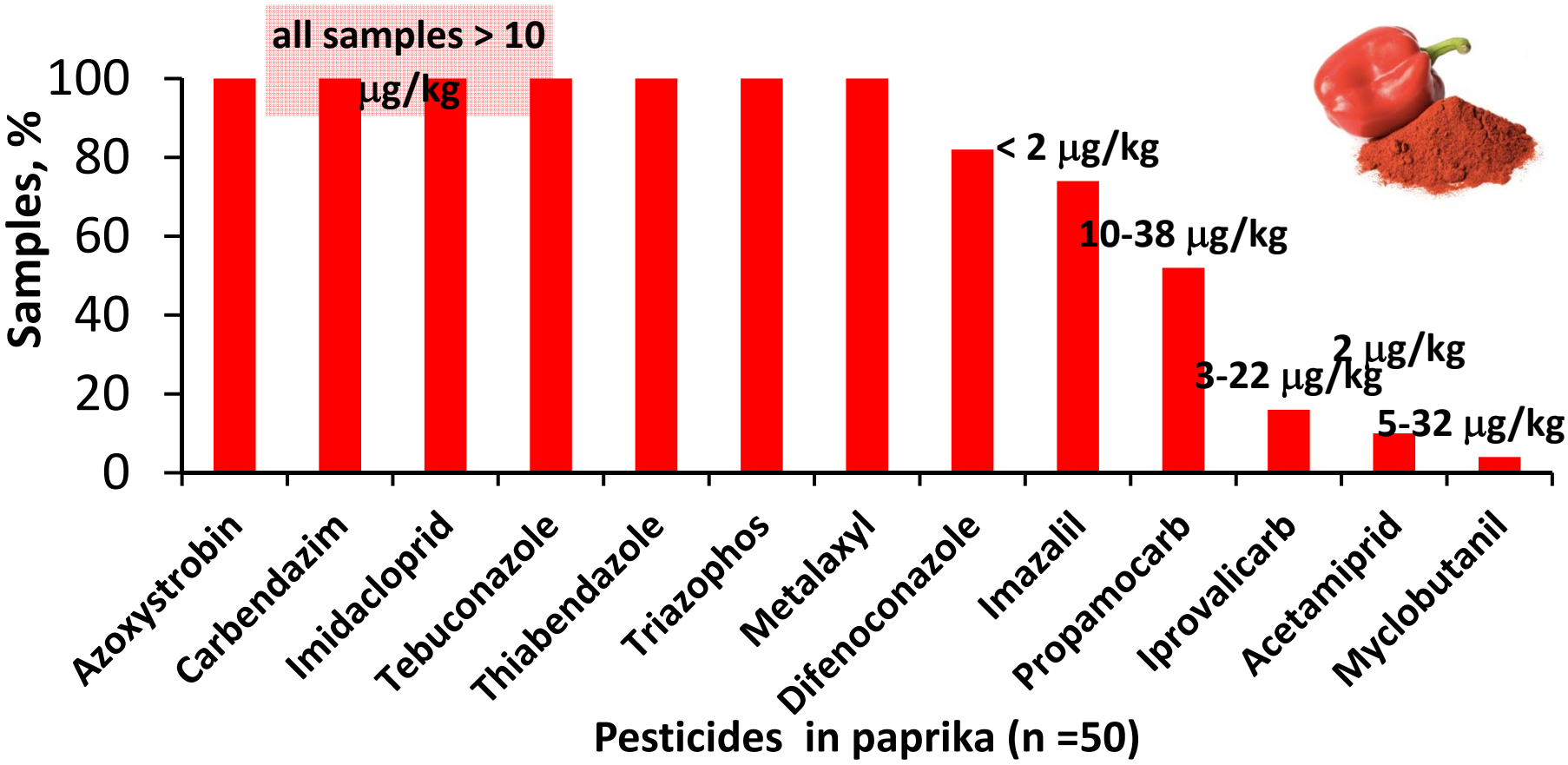
Pesticide concentrations determined in paprika



The highest concentrations (24-38 µg/kg) were determined for propamocarb in 6 samples and for carbendazim (47-70 µg/kg)

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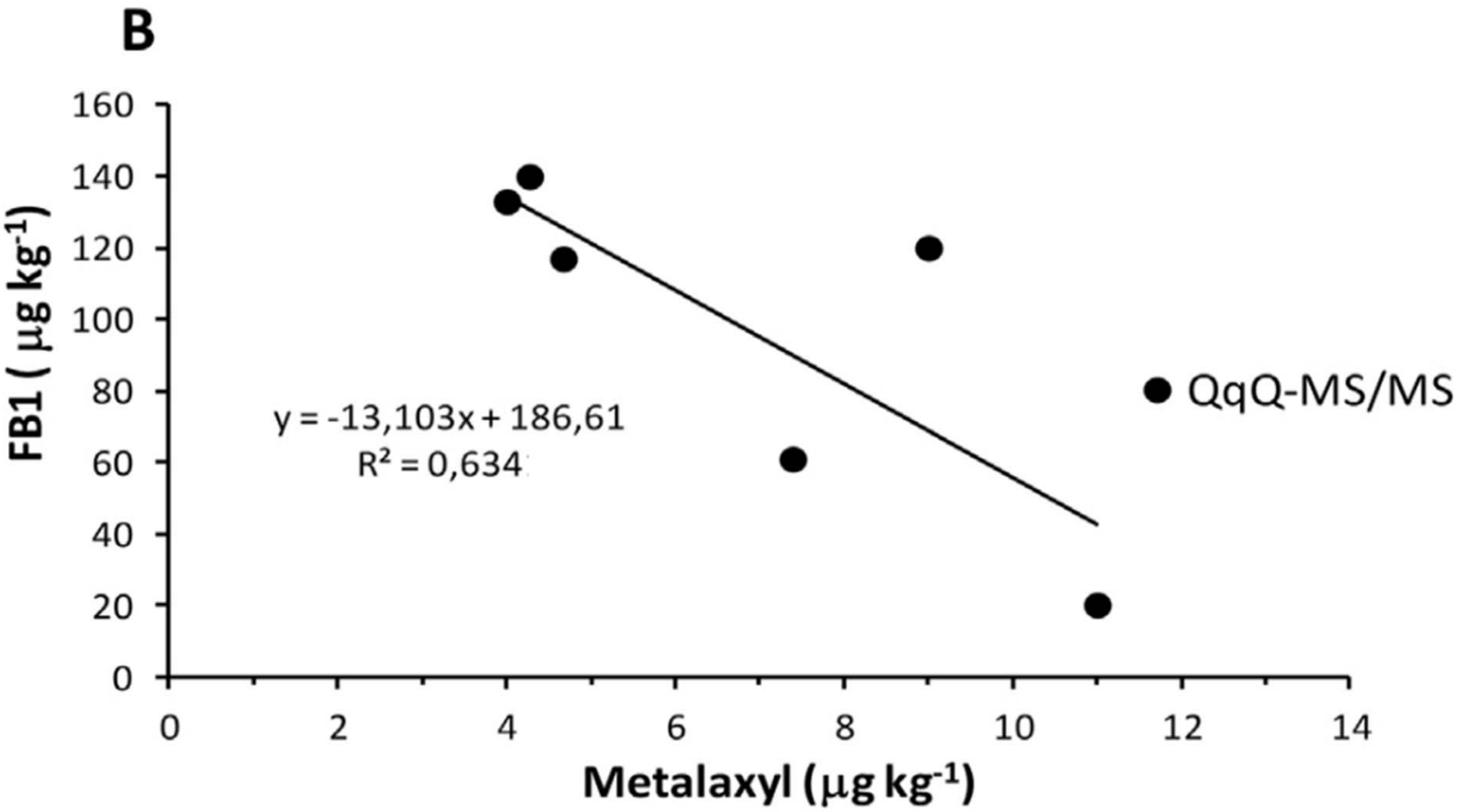
Pesticide residues determined in spices and herbs.

Spice / Herb	Contaminated samples	Pesticide compound, mean concentration (concentration range), MRL from EC database, µg kg^{-1}
Black Pepper	49	carbendazim, 8.0 (4.0-14.9), 100; metalaxyl, 12.2 (5.7-25.4), 100
Nutmeg	0	No compounds determined
Basil	27	diazinon, 5.7 (0.8-9.4), 20; malathion, 6.4 (1.6-11.2), 20; metalaxyl, 8.0 (3.3-14.0), 2,000
Oregano	30	carbendazim, 2.2 (1.5-4.0), 100; dimethoate and omethoate, 14.9 (3.0-51.6), 20; fenthionsulfoxide, 9.4 (2.9-32.0), 10; monocrotophos, 7.9 (2.1-20.4), 20
Thyme	41	acetamiprid, 7.0 (3.0-11.0), 3,000; cymoxanil, 51.6 (20.0-78.0), 50; cyproconazole, 18.5 (10.0-27.0), 50; difenoconazole, 31.0 (31.0), 20,000; dimethoate, 64.4(35.0-85.0), 20; flusilazole, 16.0 (16.0), 20; metalaxyl, 29.8 (16.0-42.0), 2,000; methoxyfenozide 5.0 (5.0), 4,000; 20; oxadixyl, 10.0 (6.0-14.0), 10; pirimiphos-methyl, 11.8 (5.0-20.0), 50; propamocarb, 15.3 (2.3-50.0), 30,000; tebuconazole, 85.7 (10.0-603.0), 50; tetraconazole, 56.0 (13.0-171.0), 20; thiacloprid 3.0 (2.0-4.0), 5,000; thiamethoxam 3.0 (3.0), 1,500

Dependence of fumonisin B1 level on the content of metalaxyl content in paprika



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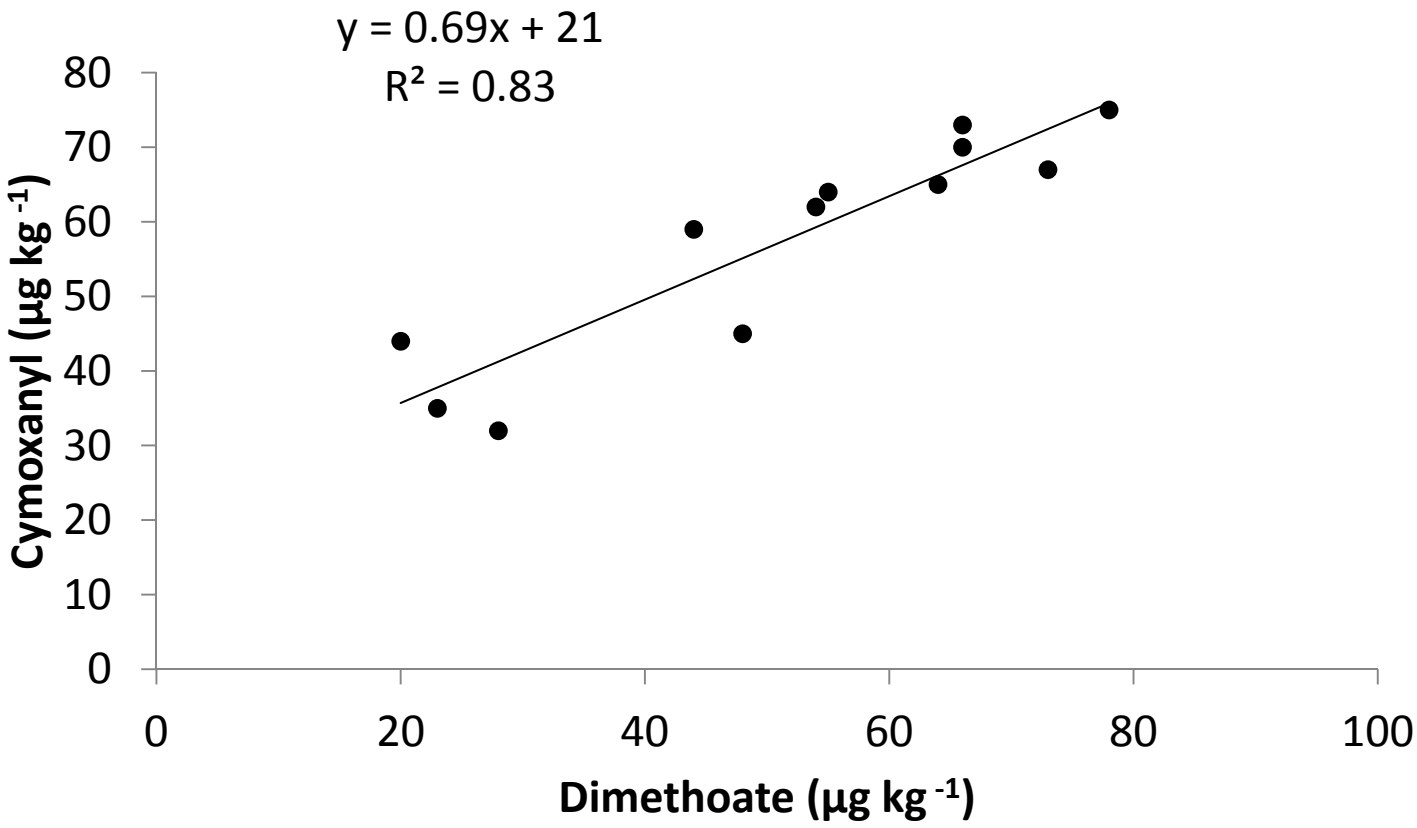
Correlation between the content of cymoxanyl and dimethoate in thyme



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Risk factors, influencing the chemical contamination of spices/herbs

- **Geographic origin** (some of spices/herbs were mixtures of species produced by several countries, e.g. paprika – blend of Brazil and China products)

- **Storage conditions**

- **Treatment** (e.g. cleaning, steam treatment, sun drying)

- **Factor of the harvest year**

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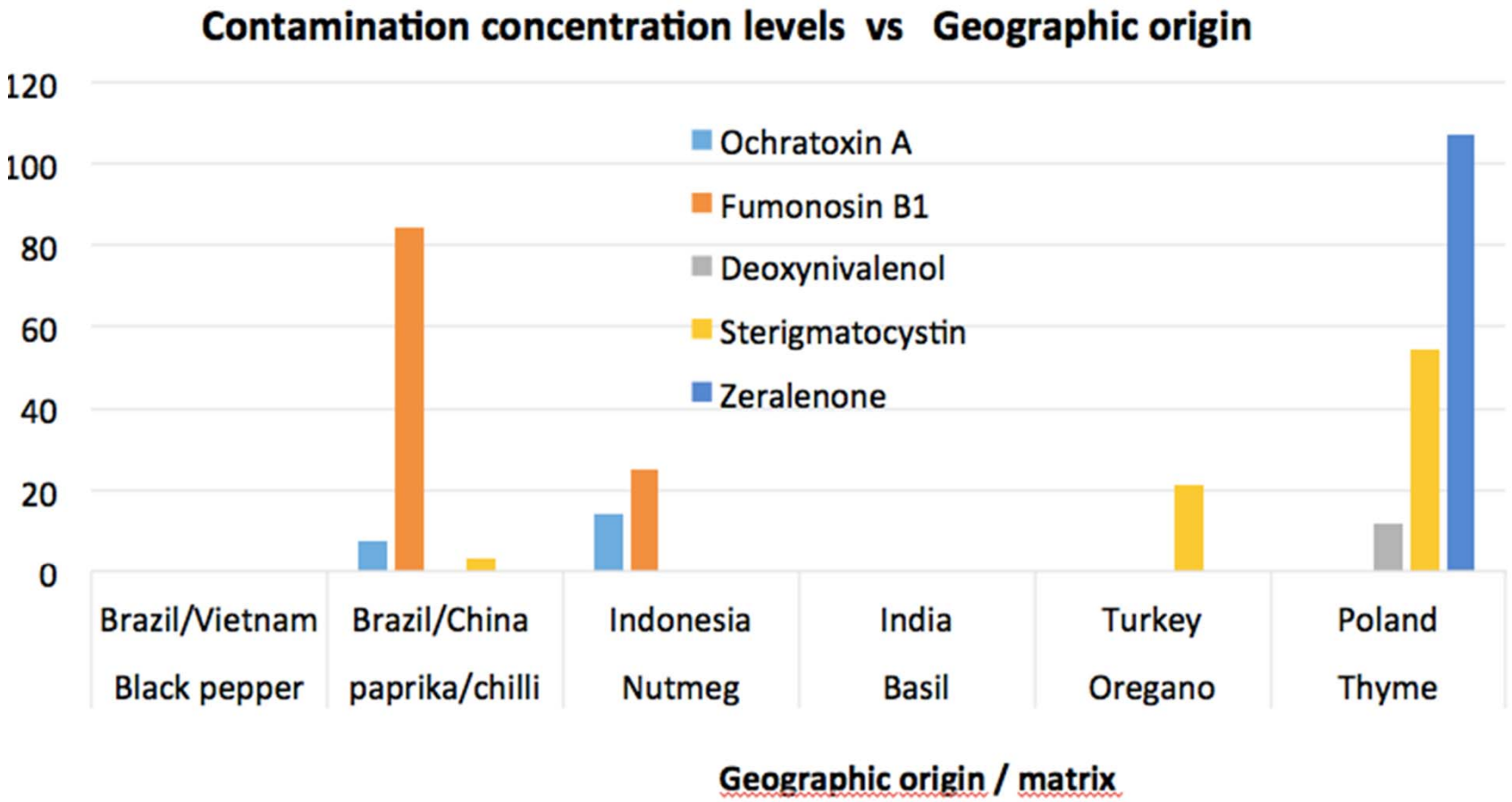

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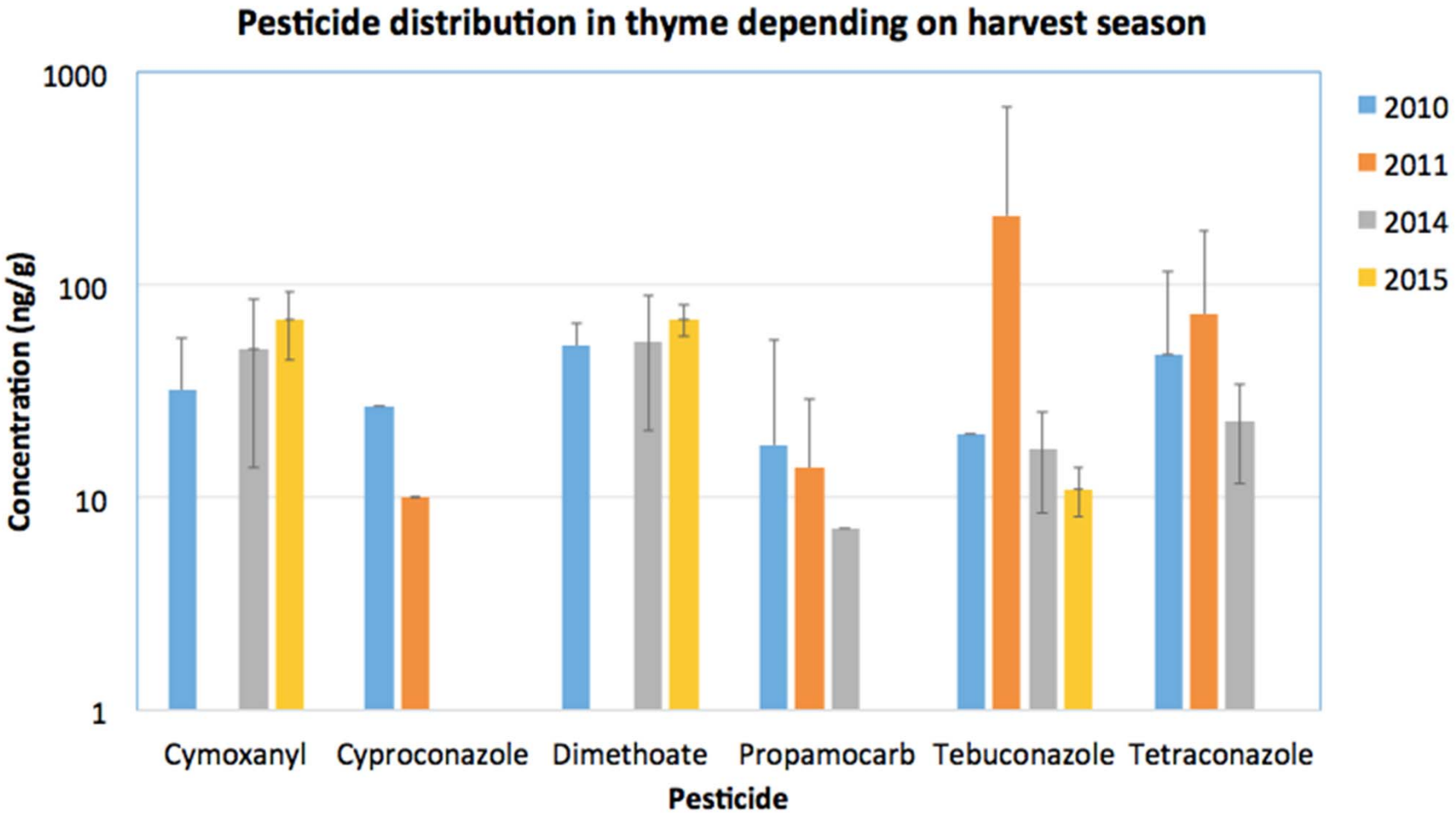

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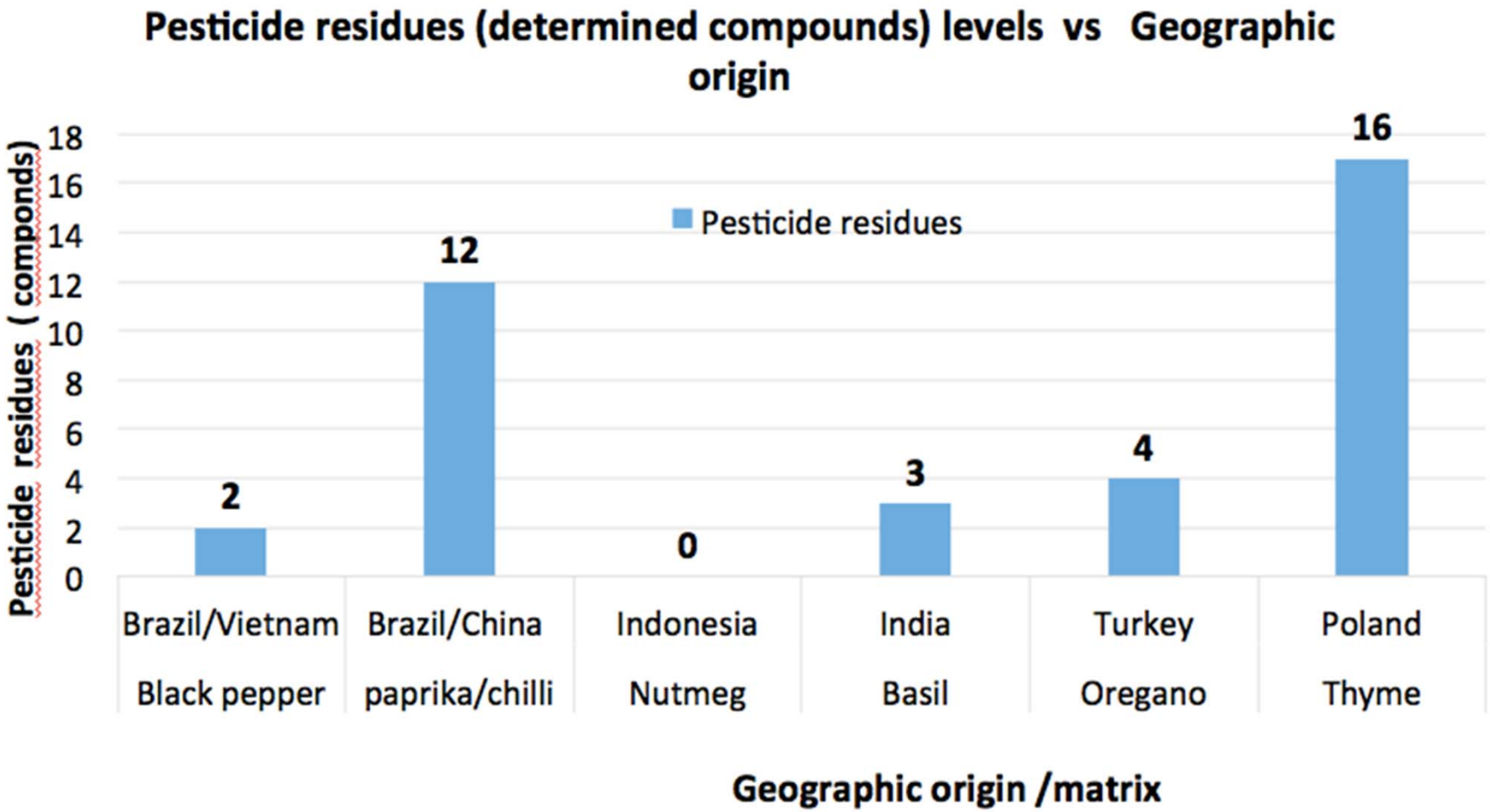

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Conclusions

- **High resolution mass spectrometry has demonstrated at least an equivalent efficiency in comparison to tandem mass spectrometry with provision of additional potential benefits**

- **Analysis of real samples indicated the elevated content of pesticides, especially in samples of thyme.**

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Thanks for your attention!
Questions and comments..

Website: http://www.spiced.eu

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