Say it with flowers: pesticides in cut blooms marketed in the UK.

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1 INTRODUCTION

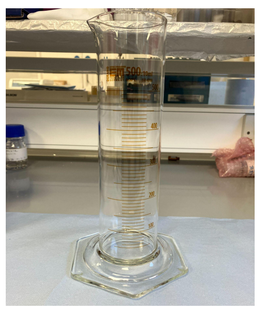
The potential hazards of pesticide residues on cut flowers have been known for almost half a century, following a study of organophosphate pesticides on floriculture products imported into the United States from Colombia and Guatemala (Morse *et al.* 1979). Subsequently, there has been a focus not only on the potential human health impacts of pesticides in floriculture at the point of use (Taylor, D.A. 2006) but also on the risks to florists working in the handling and retailing of cut flowers (Toumi *et al.* 2016; 2017). The German Federal Institute for Risk Assessment (BfR 2021) has criticised these studies on the basis that analysis of homogenised whole or part cut flowers may not reflect the easily mobilised or "wipe off" proportion of applied pesticides most relevant to exposure to pesticides through handling. Accordingly this study reports on pesticides removed from a selection of cut flowers by simple rinsing of whole blooms, followed by LCMS analysis of the rinsate, as opposed to flower homogenates.

2 METHODOLOGY

We purchased 11 bouquets from UK retail shops and specialist florists, focusing as far as possible on flowers of known origin. In addition, we also analysed a sample of locally-grown organic cut flowers (roses). A sub-sample of 100 g of stem, head and leaf of the flowers were selected at random from each bouquet and rinsed with 300 mL deionised water for 30 seconds in order to collect any pesticides deposited on the surface of the flowers. Substances were isolated from the rinse water using an automated solid-phase extraction (SPE) system with hydrophilic-lipophilic balanced (HLB)polymeric cartridges. Extracts were concentrated and analysed using a reverse-phase liquid chromatography (LC) - orbitrap high-resolution mass spectrometry (HR-MS) system, enabling quantitative analysis for over 250 pesticide active ingredients (Casado *et al.* 2018). For two of the bouquets, selected at random, we carried out duplicate extractions and analyses of two separate 100g sub-samples from the same bouquet.

3 PESTICIDES EXTRACTION PROCESS

30 seconds mild rinsing of 100 g of head, leaf and stem with 300 mL of DI water.



Water samples were filtered through glass fibre filters (GF/F; 0.7 µm) and acidified (pH=3) with formic acid (FA).
A system blank and pesticide spiked QC sample were included alongside each batch of four sample extracts.

Automated solid phase extraction with Autotrace

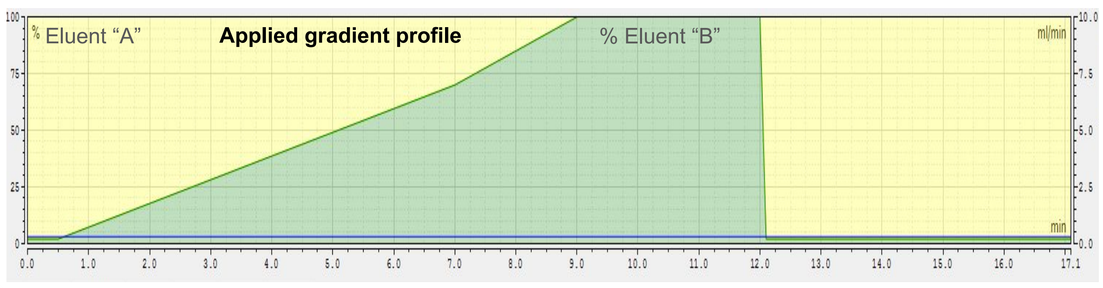
Extraction steps with HLB sorbent:

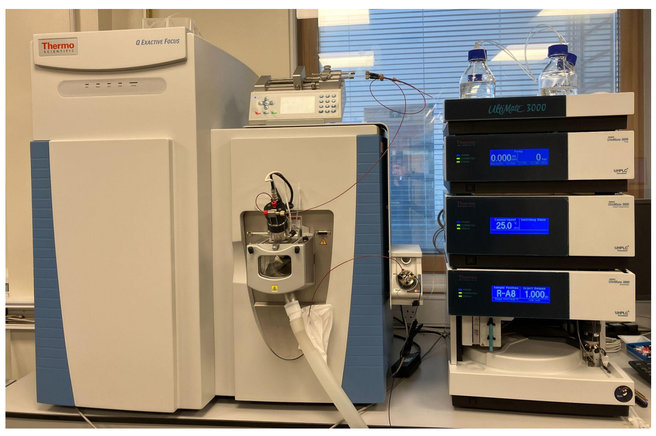
1) Cartridge conditioned with 10 mL of methanol.
2) Cartridge conditioned with 10 mL of ultrapure water adjusted to pH=3 with formic acid.
3) 300 mL of each acidified rinsate sample were loaded on the Oasis HLB cartridge (flow rate: 5 mL min^{-1}).
4) Cartridge was dried under a gentle nitrogen flow.
5) The HLB sorbent was then eluted with 10 mL of methanol.
6) This 10 mL extract was blown down using a TurboVap (N_2 flow 1.8 L min^{-1}, T= 40°C) to a final volume of 1 mL in MeOH.

4 ANALYSIS WITH LC-ESI-Q-ORBITRAP-MS SYSTEM

HPLC parameters:

Eluent "A": 2% methanol, 0.1% FA and 5 mM ammonium formate in water
Eluent "B": 2% water, 0.1% FA and 5 mM ammonium formate in methanol
Flow rate: 300 µL min^{-1} | Column: Accucore aQ C18 (100 × 2.1 mm, 2.6 µm)
Injection volume: 1 µl | C18 guard column (10 × 2.1 mm, 2.6 µm)
Column oven: 25°C





Mass spectrometer:

HESI-II electrospray, quadrupole mass filter, HCD collision cell, C-trap and high-resolution Orbitrap mass analyser

Positive/negative measurement mode:

- sheath gas flow 40 a.u.
- auxiliary gas flow at 10 a.u. and 350°C
- spray voltage 3.3 V
- capillary temperature 325°C

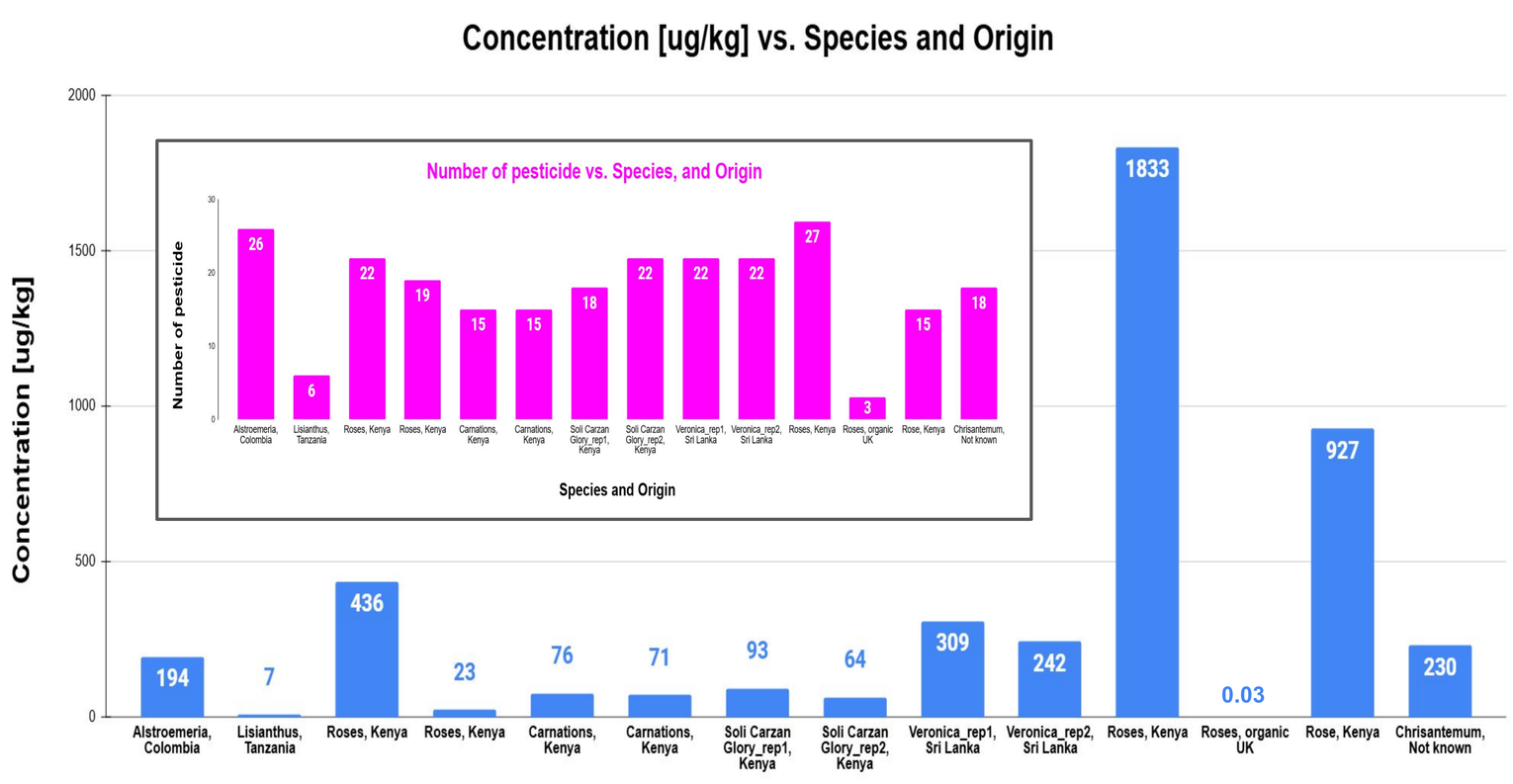
Full-scan:

- data at a resolution of 70 000 (FWHM at 200 Da)
- 80 –1000 Da scan range
- maximum injection time of 200 ms or the time for an AGC target of 1.0E6

dd-MS2 spectra for precursor ions in the inclusion list

- fragmented at a stepped collision energy of 15, 30, 45 eV
- resolution of 17 500, maximum injection time of 100 ms or the time for an AGC target of 5.0E4

5 RESULTS OF PESTICIDE CONTENT



6 SUMMARY

Overall, 67 different pesticides were identified and quantified from the 12 bouquets, the majority being insecticides or fungicides. The number of compounds detected on individual bouquets ranged from 3 to 27, with total combined concentrations ranging from 0.03 µg/kg (for a locally sourced, organically grown rose) to 1833 µg/kg (for a bouquet of roses imported from Kenya). In some cases, the high concentrations of pesticides recovered in the rinsates necessitated dilution of extracts by 20 X or even 200 X in order to remain in the linear calibration range for some compounds. Of the 67 pesticide active ingredients detected across all samples, 28 (≅42%) are prohibited from use in the EU (including acephate, carbendazim, dimethomorph and dinotefuran), while a further 4 (≅6%) are currently not approved for use in the EU. The fact that we recovered such a range of pesticides from the outer surfaces of the blooms and stems with a simple deionised water rinse suggests that human exposure from handling flower bouquets could well be significant.

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