

1 **Ornamental plants on sale to the public are a significant source of pesticide**  
2 **residues with implications for the health of pollinating insects.**

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10 **Abstract**

11 Garden centres frequently market nectar- and pollen-rich ornamental plants as “pollinator-friendly”,  
12 however these plants are often treated with pesticides during their production. There is little  
13 information on the nature of pesticide residues present at the point of purchase and whether these  
14 plants may actually pose a threat to, rather than benefit, the health of pollinating insects. Using mass  
15 spectrometry analyses, this study screened leaves from 29 different ‘bee-friendly’ plants for 8  
16 insecticides and 16 fungicides commonly used in ornamental production. Only two plants (a *Narcissus*  
17 and a *Salvia* variety) did not contain any pesticide and 23 plants contained more than one pesticide,  
18 with some species containing mixtures of 7 (*Ageratum houstonianum*) and 10 (*Erica carnea*) different  
19 agrochemicals. Neonicotinoid insecticides were detected in more than 70% of the analysed plants,  
20 and chlorpyrifos and pyrethroid insecticides were found in 10% and 7% of plants respectively.  
21 Boscalid, spiromoxamine and DMI-fungicides were detected in 40% of plants. Pollen samples collected  
22 from 18 different plants contained a total of 13 different pesticides. Systemic compounds were  
23 detected in pollen samples at similar concentrations to those in leaves. However, some contact  
24 (chlorpyrifos) and localised penetrant pesticides (iprodione, pyroclastrobin and prochloraz) were also  
25 detected in pollen, likely arising from direct contamination during spraying. The neonicotinoids  
26 thiamethoxam, clothianidin and imidacloprid and the organophosphate chlorpyrifos were present in  
27 pollen at concentrations between 6.9 and 81 ng/g and at levels that overlap with those known to  
28 cause harm to bees. The net effect on pollinators of buying plants that are a rich source of forage for  
29 them but simultaneously risk exposing them to a cocktail of pesticides is not clear. Gardeners who  
30 wish to gain the benefits without the risks should seek uncontaminated plants by growing their own  
31 from seed, plant-swapping or by buying plants from an organic nursery.

32

33

34 **Capsule summarising main findings (requested by journal)**

35 Many plants that might be bought by gardeners as “bee-friendly” contain multiple pesticides,  
36 including neonicotinoid insecticides, at levels likely to be harmful to bees.

37 **Introduction.**

38 In many countries there is widespread concern regarding the health of populations of certain insect  
39 pollinators including honey bees (*Apis mellifera*) and bumble bees (*Bombus sp*). As a result numerous  
40 studies have focussed on the impact of environmental stressors, including exposure to pesticides, on  
41 the health of wild bees. In particular, exposure to neonicotinoid insecticides has been cited as one of  
42 a number of causes for concern as they are widely used systemic agrochemicals which have been  
43 shown to contaminate pollen and nectar of crop plants and nearby wildflowers (Fairbrother et al.,  
44 2014; Botías et al., 2015; Goulson et al. 2015), and consequently can be detected in bees (Botias et al.  
45 2017), their hives or nests (e.g. David et al. 2016). In addition, environmentally relevant concentrations  
46 of some neonicotinoids can have deleterious effects on bee mortality, foraging, homing, navigation,  
47 and queen survival (Pisa et al. 2015; Godfray et al., 2015; Stanley et al., 2016). There is now a  
48 consensus that bee declines are the result of the combined effects of multiple stressors (Goulson et  
49 al. 2015), within which exposure to pesticides plays a significant role (Arena and Sgolastra, 2014;  
50 Rundlöf et al., 2015; Williams et al. 2015).

51 The neonicotinoid insecticides are one of many classes of pesticides that can contaminate  
52 bees and their colonies. For example, 37 insecticide and fungicide chemicals were detected in honey  
53 bees and hive products in France (Lambert et al., 2013) and 121 agrochemicals and their metabolites  
54 were detected in hive wax and pollen collected by honey bees in the United States (Mullin et al., 2010).  
55 In the UK, pollen collected by bee species also contained a wide range of pesticides, including the  
56 fungicides carbendazim, boscalid, flusilazole, metconazole, tebuconazole and trifloxystrobin as well as  
57 the neonicotinoids thiamethoxam, thiacloprid and imidacloprid (David et al., 2016). These studies  
58 suggest that many bee species are likely to be chronically exposed to mixtures of multiple pesticides,  
59 including insecticides and fungicides, throughout their development and adult life, particularly when  
60 residing in intensively-managed arable and horticultural landscapes (e.g. Roszko et al. 2016).

61 Although fungicides exhibit low toxicity to invertebrates, some laboratory studies have shown  
62 that simultaneous exposure to demethylation-inhibiting (DMI) fungicides can increase the toxicity of  
63 some neonicotinoids by up to 1000-fold (Iwasa et al., 2004; Schmuck et al., 2003). DMI fungicides such  
64 as tebuconazole and metconazole inhibit cytochrome P450 (CYP P450) mediated ergosterol  
65 biosynthesis in fungi and are thought to inhibit P450 enzymes in insects which are important for  
66 detoxification of insecticides (Schmuck et al. 2003). Synergistic effects of DMI fungicides with the  
67 cyanoguanidine neonicotinoids, thiacloprid and acetamiprid, are most apparent as these insecticides  
68 are (in the absence of the fungicide) rapidly metabolised in insects to less toxic metabolites (Johnson,  
69 2015). Other pesticide combinations, e.g. neonicotinoids and pyrethroids, have been reported to  
70 affect bee mortality and colony performance (Gill et al., 2012) possibly due to additive actions on  
71 cholinergic signalling (Palmer et al., 2013). Sub-lethal concentrations of some fungicides and  
72 neonicotinoids can also cause immune suppression in bee species resulting in increased susceptibility  
73 to pathogens (reviewed in Sánchez-Bayo et al., 2016). The interaction of exposure to more complex  
74 pesticide mixtures and other stressors, such as pathogen infections, on bee health have yet to be  
75 studied.

76 Most studies of exposure of bees to pesticides have focussed on agricultural environments.  
77 However, recent studies have revealed that pollen and nectar collected by wild bees (*Bombus sp*)  
78 located in gardens in urban environments also often contained a complex mixture of pesticides,  
79 including neonicotinoids and fungicides (Botias et al., 2017; David et al., 2016). One source of pesticide

80 use in urban areas may arise from spraying horticultural chemicals to protect ornamental plants prior  
81 to or after flowering. However, many ornamental plants are also treated with systemic pesticides prior  
82 to purchase and there is little information as to whether these pesticides persist in plant tissues long  
83 enough to contaminate pollen during flowering after purchase. However, a recent report published  
84 by Greenpeace described the pesticides found in the leaves of 35 popular ornamental garden plants  
85 sourced from garden centre in 10 European (but not UK) countries; pesticide residues were found in  
86 97% of these flowering plants (Reuter, 2014).

87 The aim of this study was to determine whether bee attractive flowering plants purchased  
88 from major retailers in the UK were a source of toxic pesticides with the potential to contaminate bees  
89 and other pollinators via exposure to their pollen or nectar. Analytical methods were developed to  
90 quantify a complex mixture of insecticides and fungicides in plant tissues. Where possible, we analyse  
91 levels of pesticides separately in leaves, pollen and nectar. Levels of pesticides in leaves and pollen  
92 were compared to identify compounds which were either readily translocated to pollen or had directly  
93 contaminated it during recent pesticide applications. This is the first study to provide data on the  
94 potential for exposure of bees to pesticides arising from the purchase of ornamental plants intended  
95 for UK gardens or parks.

96

## 97 **MATERIALS AND METHODS**

### 98 **Chemicals and reagents**

99 Certified standards of carbendazim, thiamethoxam, thiamethoxam-d3, clothianidin, clothianidin-d3,  
100 imidacloprid, imidacloprid-d4, acetamiprid, thiacloprid, carboxin, boscalid, spiroxamine, silthiofam,  
101 epoxiconazole, tebuconazole, flusilazole, prochloraz, metconazole, pyraclostrobin, trifloxystrobin,  
102 fluoxastrobin,  $\lambda$ -cyhalothrin, iprodione, propiconazole, chrysene, pyrene,  $\alpha$ -cypermethrin and also  
103 formic acid, ammonium formate, magnesium sulphate, sodium chloride and Supel<sup>TM</sup> QuE  
104 PSA/C18/ENVI-Carb<sup>TM</sup> (ratio 1/1/1) were obtained from Sigma-Aldrich UK. Certified standards of  
105 chlorpyrifos, chlorothalonil, carbendazim-d3, tebuconazole-d6 and trans-permethrin-d6 were  
106 purchased from LGC standards UK and prochloraz-d7 and carbamazepine-d10 from QMX Laboratories  
107 Limited UK. Spin filters (PVDF membrane, pore size 0.2  $\mu$ m) were purchased from Fisher Scientific UK.  
108 All pesticide standards were >99 % compound purity (except spiroxamine, 98.5 %;  $\lambda$ - cyhalothrin,  
109 97.8%; chlorothalonil, 98.5%; propiconazole, 98.4%; chrysene, 98.5%) and deuterated standards were  
110 >97 % isotopic purity. HPLC-grade acetonitrile, toluene, methanol and water were obtained from  
111 Rathburn Chemicals, Walkerburn, UK. Individual standard pesticide (native and deuterated) stock  
112 solutions (1 mg/ml) were prepared in acetonitrile. Calibration points were prepared weekly from stock  
113 solutions in H<sub>2</sub>O/ACN (70:30) for LC analysis and in toluene for GC analysis. All solutions were stored  
114 at -20 °C in the dark.

115

### 116 **Choice of plants and analytes**

117 Popular bee-attractive ornamental plants were purchased from local garden centres located in the  
118 East Sussex area (Table 1). Foliage, nectar and pollen samples were collected during flowering, which  
119 varied between May and July according to plant species. Foliage samples were obtained for 29  
120 different species or varieties, and pollen and nectar for 18 and 11 of these species/varieties  
121 respectively.

122 Pesticides for analysis were chosen as the most widely used in the UK, based on data from the  
123 Department for Food, Environment and Rural Affairs, (DEFRA) and also from a reports of pesticides

124 commonly detected in glasshouse crops grown or exported to the UK (Garthwaite et al., 2009; Goulds,  
125 2012; Reuter, 2014). These included five neonicotinoid, two pyrethroids and one organophosphate  
126 insecticide as well as 16 fungicides (see Supplementary Table S1).

127

### 128 **Sample collection**

129 Replicate foliage samples consisted of 10 g of leaves manually gathered from either individual or  
130 several plants depending on leaf size and stored at -70 °C for later analyses. Prior to extraction, leaves  
131 were ground with liquid nitrogen followed by manual homogenisation using a micro-spatula. Pollen  
132 samples from the same plants were isolated from flowers which had been frozen at -70°C. Flowers  
133 were gently defrosted and dried in an incubator at 37 °C for 24 hours to facilitate pollen release from  
134 the anthers. After drying, flowers were brushed over food strainers to separate pollen from anthers  
135 and sifted through multiple sieves of decreasing pore size (from 250 to 45 µm). For some species  
136 where pollen was difficult to isolate from flowers, it was manually sampled by tweezers or both pollen  
137 and anthers were analysed together in order to obtain a sufficient amount of sample material.  
138 Collection of nectar from flowers was performed through capillary action into glass 5 µl calibrated  
139 micropipettes, which were then sealed with putty and stored at -70 °C until analysis. Where there  
140 was not enough nectar and pollen material to analyse three replicates per species/variety, then  
141 composite samples were collected from the same plants sampled for leaf foliage.

142

### 143 **Sample extraction**

144 A QuEChERS method suitable for analysis of multiple pesticides in plant tissues was adapted from  
145 David et al., 2015 in order to extract pyrethroids, organophosphate and fungicides alongside  
146 neonicotinoids.

147 Leaves: 100 mg of ground leaves were spiked with 250 pg of a mix of the LC internal standards  
148 in ACN (carbendazim-d3, thiamethoxam-d3, clothianidin-d3, imidacloprid-d4, carbamazepine-d10,  
149 tebuconazole-d6 and prochloraz-d7) and 5 ng of a mix of the GC internal standards (pyrene, chrysene  
150 and trans-permethrin-d6) in toluene. 500 µL of acetonitrile with acetic acid 1% was added and the  
151 samples vortexed. After addition of 400 µL of water, the analytes were extracted by mixing on a multi  
152 axis rotator for 10 minutes. Then, 250 mg of a salt mixture (MgSO<sub>4</sub> and sodium chloride; 4:1) was  
153 added and the samples quickly mixed to prevent salt clumping. After centrifugation, the organic phase  
154 was transferred to an Eppendorf vial containing 50 mg of a dispersive solid phase extraction (d-SPE)  
155 phase (PSA/C18/ENVI-Carb). The extract was mixed on a multi axis rotator for 10 minutes and  
156 centrifuged. The supernatant was removed, and the d-SPE phase further extracted with 200 µL of a  
157 solution of ACN/toluene (1/3, vortex 15 s). After centrifugation, the supernatants were combined and  
158 spin filtered. For GC analyses, 200 µL of the extract were transferred to an injection vial, evaporated  
159 with a nitrogen flow and reconstituted with 10 µL of toluene. For LC analysis, 400 µL of the extract  
160 was transferred to a glass tube, evaporated to dryness under vacuum and reconstituted with 50 µL of  
161 ACN/water (30:70).

162 Pollen and nectar: The amount of pollen and nectar used for the extraction was variable  
163 depending on sample availability and ranged between 5-90 mg pollen/sample and 10-50 µL  
164 nectar/sample. Samples were extracted as described above, except that the water (400µL) was added  
165 prior to the initial acetonitrile extraction.

166

### 167 **GC-MS/MS analysis**

168 GC-MS/MS analysis were carried out using a Trace GC Ultra, Thermo Scientific linked to an ion trap  
169 mass spectrometer (ITQ1100, Thermo Scientific) operating in splitless mode. Compounds were  
170 separated on an Agilent DB-5MS UI column (30 m × 0.25 mm, 0.25- $\mu$ m film thickness) using helium as  
171 the carrier gas (99.996% purity) at a flow rate of 1.3 ml/min. The injector and transfer line were set at  
172 250 °C and 300 °C respectively, the source at 250 °C. The column was held at 95 °C for 6 min after  
173 injection and then programmed at 12 °C/min to 320 °C and held for 4 min. The mass spectrometer  
174 was operated in the electron ionization mode (EI, 70 eV) and analytes were detected using MS/MS  
175 mode. Analyte precursor and fragment ions and their associated IS used for quantitation are reported  
176 in Table S2. GC-MS/MS spectra were analysed on Xcalibur v1.2 software (Thermoquest-Finishingan).  
177 Concentrations were determined using a least-square linear regression analysis of the peak area ratio  
178 (analyte to IS) versus the analyte concentration using a matrix-matched calibration curve.

179

### 180 **UHPLC-MS/MS analysis**

181 UHPLC-MS/MS analyses were carried out using a Waters Acquity UHPLC system coupled to a Quattro  
182 Premier triple quadrupole mass spectrometer from Micromass (Waters, Manchester, UK). Samples  
183 were separated using a reverse phase Acquity UHPLC BEH C18 column (1.7  $\mu$ m, 2.1 mm × 100 mm,  
184 Waters, Manchester, UK) fitted with a ACQUITY UHPLC BEH C18 VanGuard pre-column (130 Å, 1.7  $\mu$ m,  
185 2.1 mm × 5 mm, Waters, Manchester, UK) and maintained at 24 °C. Injection volume was 20  $\mu$ l and  
186 mobile phase solvents were 95 % water, 5 % ACN, 5 mM ammonium formate, 0.1 % formic acid (A)  
187 and 95 % ACN, 5 % water, 5 mM ammonium formate, 0.1 % formic acid (B). The initial ratio (A/B) was  
188 90:10 and separation was achieved using a flow rate of 0.15 ml/min with the following gradient: 90:10  
189 to 70:30 in 10 min, from 70:30 to 45:55 at 11 min, from 45:55 to 43:57 at 20 min, from 43:57 to 0:100  
190 at 22 min and held for 8 min prior to return to initial conditions and equilibration for 5 min.

191 MS/MS was performed in the multiple reaction monitoring (MRM) using ESI in the positive mode, and  
192 two characteristic fragmentations of the protonated molecular ion  $[M + H]^+$  were monitored (Table  
193 S2). The declustering potential (DP, 0–40 V) and collision energy (CE, 10–40 eV) were optimised for  
194 each analyte. Other parameters were optimised as follows: capillary voltage –3.3 kV, extractor voltage  
195 8 V, multiplier voltage 650 V, source temperature 100 °C, desolvation temperature 300 °C. Argon was  
196 used as collision gas (P collision cell,  $3 \times 10^{-3}$  mbar), and nitrogen as desolvation gas (600 l/h). Mass  
197 calibration of the spectrometer was performed with sodium iodide. Data were acquired using  
198 MassLynx 4.1 and the quantification was carried out by calculating the response factor of pesticides  
199 to their respective IS. Concentrations were determined using a least-square linear regression analysis  
200 of the peak area ratio versus the concentration ratio (analyte to IS).

201

### 202 **Method validation**

203 For method validation, daffodil leaves were chosen as a test matrix as an initial analysis revealed that  
204 no pesticides were detected in this species. Method recoveries and precision were evaluated by  
205 spiking control leaves, and the method performance acceptability criteria from EU guidelines were  
206 used for assessment (EU, SANCO/12571/2013). Leaf samples (100 mg) were used for the recovery  
207 experiments and to prepare matrix-matched standard solutions for calibration. For recovery  
208 experiments, leaves samples (four replicates) were spiked at two concentration levels of the analytes:  
209 1 and 10 ng/g for UHPLC-MS/MS and 100 and 1000 ng/g for GC-MS/MS analyses. After extraction of  
210 the analytes from the spiked samples, 250 pg of the IS mix used for UHPLC-MS/MS plus 5 ng of the IS  
211 mix used for GC-MS/MS analyses were added. Calibration solutions were prepared using non-spiked  
212 leaf extracts and consisted of six points of each test analyte equivalent to 0.5, 1, 5, 10, 25 and 50 ng/g

213 together with 2.5 ng/g of IS mixture for UHPLC-MS/MS and 10, 50, 100, 250, 500 and 1000 ng/g  
214 together with 50 ng/g of IS mixture for GC-MS/MS. The repeatability of the method was determined  
215 as the intra-day relative standard deviation (RSD %) of repeated extractions ( $n = 4$ ) of a matrix extract  
216 spiked at the two concentrations used in recovery studies. The sensitivity of the method was  
217 calculated in terms of method detection and quantification limits (MDL and MQL, respectively) which  
218 were determined from spiked samples which had been extracted using the QuEChERS method. MDLs  
219 were determined as the minimum amount of analyte detected with a signal-to-noise ratio of 3, and  
220 MQLs as the minimum amount of analyte detected with a signal-to-noise ratio of 10.

221 Linearity was evaluated both in solvent and matrix, using matrix-matched calibration curves  
222 prepared as described above. The effect of the matrix was evaluated by comparison of the slopes of  
223 the calibration curves in solvent only (ACN/H<sub>2</sub>O; 30:70 for UHPLC-MS/MS and toluene for GC-MS/MS)  
224 and in the matrix. The percent increase or decrease of the matrix-matched calibration curve was  
225 measured in relation to the solvent-only curve as described in other studies (Bueno et al., 2014;  
226 Walorczyk, 2014).

227

### 228 **Quality control**

229 One workup sample (i.e. using extraction methods without the matrix) per batch was injected at the  
230 beginning of the analytical run to ensure that no contamination occurred during the sample  
231 preparation. Solvent samples (ACN/H<sub>2</sub>O (30:70) and toluene for UHPLC-MS/MS and GC-MS/MS  
232 respectively) were also injected between sample batches to ensure that there was no carryover.  
233 Identification of pesticides in samples was determined by comparing expected retention time and the  
234 ratio of the two transitions (primary/secondary) with standard solutions. Quality control samples  
235 (QCs, i.e. standard solutions) were injected every 10 samples to monitor the sensitivity changes during  
236 the analysis of each batch.

### 237 **Statistical analyses.**

238 The relationship between pesticide concentrations in leaves and pollen were determined using  
239 Pearson's correlation coefficient after a  $\log_{10}$  transformation of the data.

240

## 241 **Results and discussion**

### 242 **Performance of the analytical methods**

243 The developed analytical method allowed the quantification of pesticides belonging to many different  
244 agro-chemical classes (Table S3). The d-SPE sorbents were effective in removing matrix interferences  
245 but required an additional toluene extraction to avoid retention of planar analytes. Care was taken to  
246 ensure extraction solvents were acidic or neutral to avoid losses of chlorothalonil, which is sensitive  
247 to an alkaline environment. To avoid losses of chlorpyrifos via volatilisation, extracts for GC analyses  
248 were concentrated in a nitrogen stream at atmospheric pressure rather than using a vacuum. The  
249 linearity, precision and bias of the method were all satisfactory and recoveries of analytes were  
250 between 71-124%. A significant matrix effect was observed for three GC-MS/MS analytes  
251 (chlorothalonil, chlorpyrifos and iprodione) and a matrix-matched calibration curve was used for an  
252 accurate quantification of these compounds. Other analytes were quantified using standards  
253 prepared in solvents. The MQL values for the compounds analysed with UHPLC-MS/MS were between  
254 0.14 and 5.9 ng/g, and for GC-MS/MS compounds were between 44 and 230 ng/g. Overall, these

255 results show that this method can be used to efficiently recover mixtures of insecticides and fungicides  
256 in leaf samples with high precision.

257

### 258 **Identity of pesticide residues in leaves**

259 Plants supplied by all 5 retailers contained pesticide residues. Of the 29 different ornamental plants  
260 that were analysed, only two varieties (*Narcissus* and a *Salvia* variety) did not contain any residues of  
261 the pesticides targeted in this study (Table 1). Of the remainder, 23 varieties contained more than one  
262 pesticide with some varieties containing a mixture of 7 (*Ageratum houstonianum*) and 10 (*Erica*  
263 *carnea*) different insecticides and fungicides. Within the insecticides, neonicotinoids were detected in  
264 more than 70% of the analysed plants, whereas chlorpyrifos and pyrethroids were detected in 10%  
265 and 7% of plants respectively (Figure 1). It is likely that the higher prevalence of neonicotinoids is at  
266 least in part due to their higher persistence compared to the other insecticide classes currently in use  
267 (Bonmatin et al. 2015). Our results also indicate that neonicotinoids are widely used for treatment of  
268 ornamental plants and their residues could contaminate gardens and parks. In addition, boscalid,  
269 spiroxamine and DMI-fungicides were detected in more than 38% of plants indicating widespread  
270 treatment of ornamentals with these pesticides.

271 Mean neonicotinoid concentrations in leaves of the different plants varied from (mean  $\pm$  SD)  
272  $1.7 \pm 1.9$  ng/g for thiacloprid to  $25 \pm 34$  ng/g for thiamethoxam (Table 2). Mean concentrations of  
273 other insecticides were far higher, at  $121 \pm 27$  and  $844 \pm 205$  ng/g for the pyrethroids cyhalothrin and  
274 cypermethrin respectively, and  $207 \pm 93$  ng/g for the organophosphate chlorpyrifos. Of the fungicides,  
275 mean leaf concentrations of boscalid, prochloraz, pyraclostrobin and carbendazim were between  $46$   
276  $\pm 64$  and  $88 \pm 83$  ng/g and iprodione was  $2344 \pm 3550$  ng/g. In general, concentrations of individual  
277 pesticides varied widely between the different plant varieties which was likely due to variations in  
278 timing and types (foliar or soil applied) of treatment applied. However, the data indicates that leaves  
279 of ornamental plants are contaminated with complex mixtures of insecticides and fungicides which  
280 were present from ng/g to  $\mu\text{g/g}$  concentrations.

281

### 282 **Pesticides residue in pollen and nectar**

283 Pollen samples from 18 plant varieties were collected and these contained a total of 13 different  
284 pesticides (Table 3 and S4). Compared to contact and penetrant pesticides, systemic compounds were  
285 detected in pollen samples with higher frequency and, with the exception of acetamiprid, were  
286 present in pollen at similar concentrations to leaves. There was a significant correlation between the  
287 concentrations of all the systemic pesticides quantified in the leaves and pollen of individual plants  
288 (Pearson's  $r=0.780$ ,  $p < 1.1 \times 10^{-9}$   $n=42$  plant replicates). These results suggest that systemic pesticides,  
289 such as carbendazim and the neonicotinoid insecticides, easily contaminate the plant pollen and their  
290 residues are still available to pollinator insects when ornamental plants reach the gardens. In addition,  
291 some contact (chlorpyrifos) and localised penetrant pesticides (iprodione, pyroclastrobin and  
292 prochloraz) were also detected in pollen (Table 3). However, these pesticides may have been applied  
293 by spray and some of the plants were already in flower when purchased (Table S4) so pollen may have  
294 already been directly contaminated during pesticide application. No significant correlation ( $p < 0.05$ )  
295 were observed between leaf and pollen concentrations of pesticides classified as local penetrants  
296 ( $n=19$ ), acropetal penetrants ( $n=12$ ) or as contact action ( $n=6$ ).

297 The finding of residues of imidacloprid, carbendazim and pyroclastrobin in pollen samples  
298 supports recent work where these pesticides were frequently detected in pollen collected from  
299 bumble-bees nests located in the same urban area of S.E UK where our samples were purchased



300 (David et al., 2016) and suggests that ornamental plants are a potential source of contaminated pollen  
301 to pollinator insects.

302 Nectar samples from only 11 different plant species/varieties were collected, due to the  
303 difficulty of collecting enough volume for the chemical analysis. However, concentrations of all target  
304 analytes were below MDL except for the neonicotinoids where acetamiprid was detected in just one  
305 species below MQL of 0.14 ng/g, and thiacloprid detected in one species below MQL of 0.15 ng/g  
306 (Table S4). Imidacloprid was detected in five species/varieties, but only in one plant at concentration  
307 higher than MQL (1.2 ng/g) of 5.7 ng/g. The data confirms that nectar concentrations of some  
308 neonicotinoids were low in this study, likely due, in part, to the small quantities of nectar available for  
309 analysis. Previous studies have found that concentrations of neonicotinoids in nectar are often (but  
310 not always) lower than those found in pollen (Bonmatin et al. 2015; Mogren & Lundgren 2016).

311

### 312 **Implications for toxicity to non-target insects**

313 The presence of pesticides residues in ornamental plants could be a threat to non-target insects such  
314 as insect pollinators, which may be exposed to pesticides by ingestion of contaminated pollen and  
315 nectar or through contact with residues on pollen and leaves after spraying. Many ornamental plants  
316 are a rich source of flowers in urban environments and bees and other pollinator insects are usually  
317 highly attracted to these plants and therefore could be exposed to a complex mixture of different  
318 agrochemicals. Indeed, many gardeners are keen to encourage wildlife such as pollinators in their  
319 garden and may deliberately purchase plants such as those we tested to provide forage for bees,  
320 butterflies and hoverflies.

321 Are the concentrations we describe sufficient to cause harm to pollinators? Calculation of the  
322 amount of pollen a honey bee would need to consume to receive the LD50 (Table 3) suggests that  
323 honeybees are unlikely to receive a lethal dose, at least in the short term. For example, to receive a  
324 lethal dose a honeybee would need to consume 0.32g of pollen containing the mean concentration of  
325 clothianidin found in samples. Given that a honeybee weighs approximately 0.1g, and consumes up  
326 to 29 mg per day (Schmidt et al. 1987), it would take at least ten days to receive a lethal dose.  
327 However, the concentrations found here overlap with those found to cause significant sublethal  
328 effects on bees, something that has been studied extensively in neonicotinoids. Where detected, the  
329 mean concentrations of imidacloprid, clothianidin and thiamethoxam in pollen were 6, 11 and 11  
330 ng/g, respectively. These values are similar to or slightly higher than residues typically found in pollen  
331 of treated crops (Bonmatin et al. 2015) that have been found to have measurable impacts on  
332 pollinators. For example, bumblebees nests fed on imidacloprid in pollen at 6 ng/g (plus in nectar at  
333 0.7 ng/g) grew more slowly and produced 85% fewer queens than control nests (Whitehorn et al.  
334 2012). This same concentration significantly reduced pollen collection in bumblebees (Feltham et al.  
335 2014). Following field exposure to thiamethoxam at up to 1.6 ng/g in pollen, bumblebee nests grew  
336 less and produced significantly fewer queens (Goulson 2015). In honeybees, exposure to just 1 ng/g  
337 of clothianidin significantly impaired the immune response allowing viruses to replicate more quickly  
338 (Di Prisco et al. 2013). Thus the concentrations of individual neonicotinoids found in our study are  
339 certainly well within the range found to have measurable impacts on bees, and at worst exceed  
340 concentrations that cause harm by an order of magnitude.

341 Unlike neonicotinoids, chlorpyrifos is more toxic via contact rather than consumption  
342 (honeybee LD50s 72 ng for contact exposure and 240 ng for oral consumption, Table 3). Thus  
343 pollinators may be exposed via contact with foliage and petals as well as contact with and  
344 consumption of pollen. Some residues in foliage and pollen were relatively high (up to 273 and 163

345 ng/g), but how this would translate into total exposure of a foraging bee is not clear. The same is true  
346 of the pyrethroids, which were found in few plants but at high concentrations, and are also more toxic  
347 via contact exposure (Table 3).

348 Pollinators feeding on the flowers we studied are likely to be simultaneously exposed to a  
349 cocktail of chemicals. A recent study on the effects of exposure of bees to pairs of pesticides concluded  
350 that most pesticides act additively (Spurgeon et al. 2016), so we might attempt to assess the total  
351 effect of exposure to a pesticide cocktail by summing the individual effects of each chemical. However,  
352 there is evidence that DMI fungicides, which were detected in 38% our samples, act synergistically  
353 with insecticides (Iwasa et al., 2004; Schmuck et al., 2003). Residues of the DMI fungicide prochloraz  
354 as well as five other fungicide structures were detected in pollen samples and the effect of exposure  
355 to these complex mixtures is currently unknown.  
356

## 357 **Conclusion**

358 The results of our screening reveal that ornamental plants are widely treated with a mixture of  
359 insecticides and fungicides and that significant residues of these chemicals are still present in the plant  
360 tissues when they reach retailers and gardens. In particular, the neonicotinoid insecticides and the  
361 fungicides boscalid, spiroxamine and prochloraz were frequently detected while pyrethroid and  
362 organophosphate insecticides were found infrequently but sometimes at high concentrations. The  
363 concentrations of individual chemicals found overlap with and sometimes considerably exceed those  
364 known to do measureable harm to bees. Residues of pesticides in plants bought by members of the  
365 public will decline over time, and unless large numbers of contaminated plants are bought and planted  
366 together, it is likely that the total residues to which pollinators are exposed will be diluted by their also  
367 feeding on other, uncontaminated plants nearby. Many ornamental plants are bought in spring, which  
368 may provide a pulse of exposure of bees to pesticides at a critical time in the early development of  
369 bumblebee colonies and when honey bees colonies are normally undergoing rapid growth. With the  
370 current state of knowledge, we are not able to evaluate whether the net effect of planting 'pollinator-  
371 friendly' flowers contaminated with pesticides is likely to be positive or negative. However, it is clear  
372 that levels of pesticides found in some plants may well be sufficient to do harm, and the purchaser  
373 currently has no way of knowing what residues are in the different plants on sale. All of the retailers  
374 we tested were selling plants containing highly variable combinations of potentially harmful  
375 chemicals, so that any purchaser is playing 'Russian roulette' with their garden pollinators. In these  
376 circumstances, the safest option for a gardener wishing to encourage pollinators would be to buy  
377 plants from an organic nursery, grow plants from seed, or plant-swap with friends and neighbours that  
378 do not use pesticides. Alternatively, the horticultural industry might consider adding data on pesticide  
379 exposure to plant labels so that consumers could make an informed choice.

380 Recently, most attention has been focussed on the negative effects of environmental  
381 pesticide pollution as a result of agricultural uses. However, our results suggest that applications of  
382 pesticides to ornamental plants are also contributing to the exposure of pollinating insects to harmful  
383 chemicals.  
384

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**Table 1: Number of pesticides detected in leaves of different ornamental plants.**

Common name	Species and variety	Retailer	Insecticides	Fungicides
Achillea	<i>Achillea millefolium</i> 'Desert Eve Deep Rose'	B&Q	1	3
Ageratum	<i>Ageratum houstonianum</i>	Aldi	3	4
Allium	<i>Allium hollandicum</i>	Wyevale	2	1
Bellflower	<i>Campanula portenschlagiana</i>	Wyevale	0	2
Catmint	<i>Nepeta cataria</i> 'Six Hill Giant'	Wyevale	2	3
Catmint	<i>Nepeta cataria</i> 'Walkers low'	Wyevale	1	2
Coreopsis	<i>Coreopsis grandiflora</i> 'Early Sunrise'	B&Q	1	3
Cosmos	<i>Cosmos bipinnatus</i> 'Casanova Violet'	Homebase	4	1
Crocus	<i>Crocus vernus</i> 'Golden Yellow'	Wyevale	1	1
Daffodil	<i>Narcissus jonquilla</i> 'Tete-a-Tete'	Wyevale	0	0
Dahlia	<i>Dahlia x hybrida</i> 'Gallery Art Fair'	Staverton's	0	1
Dahlia	<i>Dahlia x hortensis</i> 'Bishop of Llandaff'	Wyevale	1	0
Dahlia	<i>Dahlia x hybrida</i> 'Mystic Dreamer'	B&Q	2	2
Dutch iris	<i>Iris tingitana</i> x <i>I. xiphium</i>	Wyevale	1	3
Foxgloves	<i>Digitalis purpurea</i> 'Dalmatian White'	Wyevale	1	1
Grape hyacinth	<i>Muscari armeniacum</i>	Wyevale	1	5
Heathers	<i>Erica carnea</i>	Wyevale	5	5
Lavender	<i>Lavandula stoechas</i> 'Victory'	Wyevale	0	3
Lavender	<i>Lavandula angustifolia</i>	Wyevale	0	1
Lavender	<i>Lavandula stoechas</i> 'Papillon'	Wyevale	0	3
Salvia	<i>Salvia longispicata</i> x <i>S. farinacea</i> 'Mystic Spires'	Staverton's	1	0
Salvia	<i>Salvia nemerosa</i> 'Sensation Deep Rose'	Homebase	0	0
Scabious	<i>Scabiosa columbaria</i> 'Pink Mist'	Wyevale	1	1
Scabious	<i>Scabiosa columbaria</i> 'Butterfly Blue'	Homebase	3	2
Strawberry	<i>Fragaria</i> x <i>ananassa</i> 'Toscana F1'	Homebase	2	2
Thistles	<i>Cirsium atropurpureum</i>	Wyevale	2	1
Verbena	<i>Verbena x hybrida</i>	Aldi	3	3
Veronica	<i>Veronica spicata</i>	Staverton's	2	4
Wallflower	<i>Erysimum linifolium</i> 'Bowles's Manve'	Wyevale	1	1

485 **Table 2: Concentration of pesticides detected in leaves of different ornamental plant species or**  
 486 **varieties.**

Pesticide	Number of plant species/ varieties where the pesticide was detected (% of total plants analysed) <sup>a</sup>	Mean ± SD (ng/g)	Median (ng/g)	Range (ng/g)
Thiacloprid	14 (48)	1.0 ± 1.8	0.28	0 - 6.4
Boscalid	14 (48)	37 ± 61	7.7	0 – 223
Spiroxamine	12 (41)	0.65 ± 0.85	0.34	0 - 3.5
Imidacloprid	11 (38)	3.9 ± 8.4	0.36	0 – 29
Prochloraz	9 (31)	59 ± 99	3.5	0 – 308
Pyroclastrobin	7 (24)	39 ± 66	3.1	0 – 257
Acetamiprid	6 (21)	7.5 ± 21	0.04	0.04 – 85
Iprodione	5 (17)	1966 ± 3549	327	3.7 – 10593
Thiamethoxam	4 (14)	16 ± 35	0.77	0.09 – 119
Carbendazim	3 (10)	54 ± 79	9.6	1.2 - 213
Chlorpyrifos	3 (10)	108 ± 127	19	19 - 328
Chlorothalonil	2 (7)	486 ± 416	364	0 - 1190
Fluoxastrobin	2 (7)	8.0 ± 17	0.19	0.09 - 41
Tebuconazole	2 (7)	0.16 ± 0.23	0.09	0 - 0.60
Clothianidin	1 (3)	9.3 ± 4.9	11	3.8 - 13
λ-Cyhalothrin	1 (3)	121 ± 33	105	99 - 158
Cypermethrin <sup>b</sup>	1 (3)	844 ± 251	805	616 - 1113
Propiconazole	1 (3)	0.65 ± 1.1	0	0 - 2.0
Trifloxystrobin	1 (3)	0.27 ± 0.04	0.24	0.24 - 0.32

487 Mean, median and range value were calculated using the concentrations measured in all the plant  
 488 species/varieties where a specific compound was detected. The concentrations over the MDL but  
 489 below the MQL were assigned the MDL value, whilst concentrations below the MDL were considered  
 490 to be zero.

491 <sup>a</sup> for each species/varieties 3 leaf replicates were analysed.

492 <sup>b</sup> detected 3 isomers, quantified as sum of the three peaks on calibration curve obtained from α-  
 493 cypermethrin.

494 The concentrations of the fungicides carboxin, epoxyconazole, flusilazole, metconazole and siltiofam  
 495 were all below MDL.

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**Table 3: Comparison between the mean concentration of pesticides in leaves and pollen of different ornamental plant species or varieties.**

Pesticides grouped by translocation properties in the plant	Leaves (ng/g)	Pollen (ng/g)	LD <sub>50</sub> honey bee <sup>a</sup> (ng/g)		Mass of pollen to give LD50 <sup>d</sup>
	Mean ± SD	Mean ± SD	Oral	Contact	
<b>Systemic</b>					
acetamiprid	8.6 ± 23	0.45 ± 0.23	14,000	7900	31,111
imidacloprid	3.8 ± 9.1	6.9 ± 16	13	61	1.9
thiacloprid	1.2 ± 1.9	0.78 ± 1.1	17,000	36,000	21,794
thiamethoxam	17 ± 35	11.0 ± 16	5	25	0.45
clothianidin	9.3 ± 4.9	11.0 ± 9.3	3.5	39	0.32
carbendazim	54 ± 79	57 ± 98	NA	>50,000	NA
spiroxamine	0.54 ± 0.82	<0.20 <sup>b</sup>	92,000	42,000	5 x 10 <sup>5</sup>
<b>Acropetal penetrant</b>					
boscalid	30 ± 66	0.53 ± 1.1	166,000	>200,000	3 x 10 <sup>5</sup>
fluoxastrobin	8.0 ± 17	<MDL <sup>c</sup>	843,000	>200,000	0
propiconazole	0.65 ± 1.1	<MDL <sup>c</sup>	77,000	50,000	0
tebuconazole	0.16 ± 0.23	<MDL <sup>c</sup>	83,000	>200,000	0
<b>Localized penetrant</b>					
iprodione	2743 ± 4459	252 ± 496	25,000	400,000	99
pyroclastrobin	38 ± 85	9.8 ± 14	73,000	>100,000	7,449
trifloxystrobin	0.27 ± 0.04	<MDL <sup>c</sup>	>200,000	>200,000	0
prochloraz	55 ± 104	4.9 ± 12	60,000	50,000	12,245
<b>Contact</b>					
chlorothalonil	485 ± 416	<MDL <sup>c</sup>	63,000	135,000	0
chlorpyrifos	146 ± 142	81 ± 115	240	72	3.2
cyhalothrin	121 ± 33	<MDL <sup>c</sup>	NA	22	0
cypermethrin	844 ± 251	<111 <sup>b</sup>	64	34	0

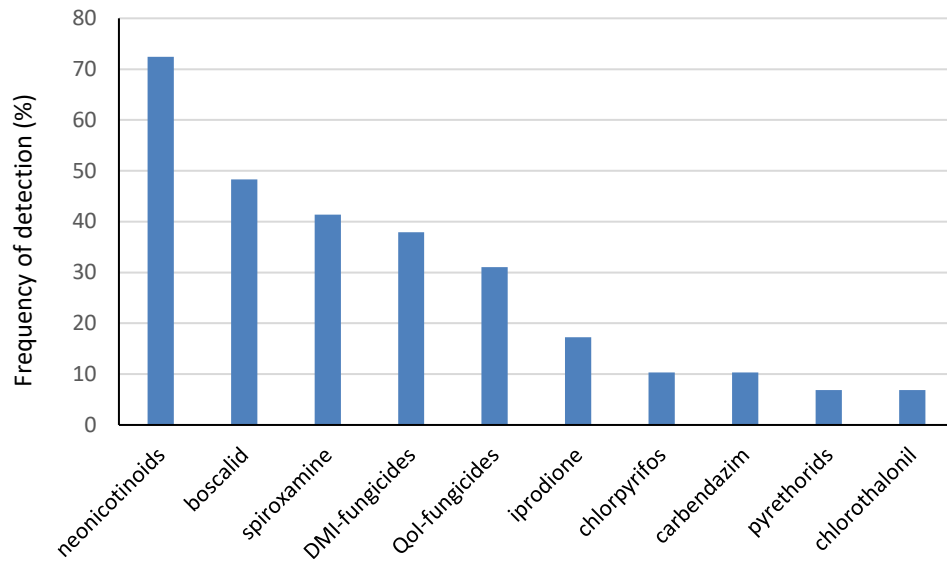
500 Mean concentrations of pesticides were calculated for samples from all plant species/varieties where  
501 there were matching leaf and pollen samples. The concentrations over the MDL but below the MQL  
502 were assigned the MDL value, whilst concentrations below the MDL were considered to be zero. The  
503 number of replicates analysed and the mean values for each plant species/varieties are reported in  
504 Supplementary Table S4.

505 <sup>a</sup> data from Sanchez and Goka 2014.

506 <sup>b</sup> below the MQL in all the analysed samples.

507 <sup>c</sup> below the MDL in all the analysed samples.

508 <sup>d</sup> Mass of pollen (g) a bee would need to consume to obtain the LD50



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**Figure 1: Frequency of detection of different agro-chemical classes in leaves of ornamental plants.**  
Individual pesticides are named when just one pesticide was detected in a particular class.