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Abstract: Agriculture is considered as the main source of water contamination by pesticides. However, food packaging or processing industries are also recognized as relevant point sources of contamination by these compounds, not yet investigated in depth. The objective of this work has been to improve current knowledge about the presence and concentration of pesticides in the effluent of a food processing industry, as well as to investigate their main transformation products (TPs). An analytical strategy combining target and suspect analysis has been applied to provide an evaluation of the effluents. The methodology involves solid-phase extraction (SPE) of wastewater samples followed by (i) liquid chromatography quadrupole-linear ion trap tandem mass spectrometry (LC-QqLIT-MS/MS) for quantitative target analysis and (ii) liquid chromatography coupled to quadrupole-time-of-flight high resolution mass spectrometry (LC-QTOF-HRMS) to identify non-target pesticides and possible TPs. The results revealed the presence of 17 of the target pesticides analysed and 3 additional ones as a result of the suspect screening performed by HRMS. The TPs were investigated for the pesticides found at the highest concentrations: imazalil (7038-19802 ng/L), pyrimethanil (744-9591 ng/L) and thiabendazole (341-926 ng/L). Up to 14 TPs could be tentatively identified, demonstrating the relevance of this type of studies. These data provide a better understanding of the occurrence of pesticides and their TPs in agro-food industrial effluents.

Determination of pesticide levels in wastewater from an agro-food industry: target, suspect and transformation product analysis.

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HIGHLIGHTS

- Analysis of pesticides in wastewater effluent of an agro-food industry was carried out
- Imazalil, pyrimethanil, thiabendazole, propiconazole and etoxazole were detected at the highest concentrations
- Presence of imazalil, pyrimethanil and thiabendazole TPs was also evidenced in the effluents.
- Imazalil and cyprodinil concentrations can eventually pose a risk for the environment

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2	industry: target, suspect and transformation product analysis.
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27 Agriculture is considered as the main source of water contamination by pesticides. 28 However, food packaging or processing industries are also recognized as relevant point 29 sources of contamination by these compounds, not yet investigated in depth. The 30 objective of this work has been to improve current knowledge about the presence and 31 concentration of pesticides in the effluent of a food processing industry, as well as to 32 investigate their main transformation products (TPs). An analytical strategy combining 33 target and suspect analysis has been applied to provide an evaluation of the effluents. 34 The methodology involves solid-phase extraction (SPE) of wastewater samples 35 followed by (i) liquid chromatography quadrupole-linear ion trap tandem mass 36 spectrometry (LC-QqLIT-MS/MS) for quantitative target analysis and (ii) liquid 37 chromatography coupled to quadrupole-time-of-flight high resolution mass 38 spectrometry (LC-QTOF-HRMS) to identify non-target pesticides and possible TPs. 39 The results revealed the presence of 17 of the target pesticides analysed and 3 additional 40 ones as a result of the suspect screening performed by HRMS. The TPs were 41 investigated for the pesticides found at the highest concentrations: imazalil (7038-19802 42 ng/L), pyrimethanil (744-9591 ng/L) and thiabendazole (341-926 ng/L). Up to 14 TPs 43 could be tentatively identified, demonstrating the relevance of this type of studies. 44 These data provide a better understanding of the occurrence of pesticides and their TPs 45 in agro-food industrial effluents.

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47 Keywords: Pesticides; transformation products; industrial wastewater; target and
48 suspect analysis; agro-food industry.

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52 Pesticides are mainly used to protect plants against harmful organisms and pests. 53 However, due to their extensive use and inherent toxicity, they have been identified as a 54 long-term hazard for different environmental compartments, especially for water 55 resources (Kuzmanović et al., 2015). Agricultural practices are considered as the main 56 source of water contamination by pesticides (Cahill et al., 2011; Papadakis et al., 2015), 57 but in recent years, other point sources have aroused growing interest, such as effluents 58 from municipal wastewater treatment plants (WWTPs) or agro-food industries (Cahill et 59 al., 2011; Köck-Schulmeyer et al., 2013). Of particular relevance are the latter. The 60 agro-food industry is the main manufacturing industry in Europe, representing 14% of 61 the total turnover, more than 836,000 million euros. In Spain, the food and beverage 62 industry represent the second most important economic activity in Spain (National 63 Statistics Office of Spain, 2007). Most processing operations steps in agro-industry are 64 water-based. Thus, food processing or packaging industries consume large volumes of 65 water in several steps of their production processes, washing of raw product, washing 66 after peeling, size reducing, blanching and fluming, filling, sanitation clean-up, cooking 67 or processed product cooling, being among the largest producers of spent process 68 wastewater, which often contain large amounts of pesticides (Karas et al., 2016a). In 69 fruit-packaging plants, fungicides are applied at particularly dense solutions (0.6–2 g/L) for the control of fungal infestations of fruits during storage (Karas et al., 2016a, 2016b; 70 71 Łozowicka et al., 2016). In food processing industries, fruits and vegetables undergo 72 washing steps before processing, releasing pesticide residues into the washing water 73 (Ponce-Robles et al., 2017). In both cases, these practices result in the production of 74 high volumes of pesticide-contaminated wastewaters (Karas et al., 2016b), which are

not properly managed in many cases. In the absence of on-site treatment systems, agrofood industries often discharge their wastewaters into municipal WWTPs, which have
limited removal capacity (Bueno et al., 2012). Previous studies have demonstrated the
persistence of pesticides in treated wastewaters after conventional secondary or tertiary
treatments (Barco-Bonilla et al., 2010; Cahill et al., 2011; Campos-Mañas et al., 2017;
Köck-Schulmeyer et al., 2013; Ponce-Robles et al., 2017; Singer et al., 2010),
highlighting the need for developing more efficient treatment systems.

82 Although the presence of pesticides in industrial effluents has already been reported 83 (Carra et al., 2015; Ponce-Robles et al., 2017), to our knowledge there are no studies 84 addressing an analytical characterization of these effluents. Most of them are focused on 85 selected fungicides such as imazalil, thiabendazole, ortho-phenylphenol or antioxidants 86 such as diphenylamine (Karas et al., 2016a, 2016b; Łozowicka et al., 2016; Peris-87 Vicente et al., 2016) and reveal that many of these chemicals persist after the treatment 88 processes and return to the environment (Köck-Schulmeyer et al., 2014). Therefore, 89 pesticides occurrence in industrial effluents and their persistence and transformation 90 during their treatment demand more research and better quantification to obtain a 91 reliable risk assessment (Kuzmanović et al., 2015) and improve wastewater treatments 92 (Barco-Bonilla et al., 2010; Bueno et al., 2012; Cahill et al., 2011; Campos-Mañas et 93 al., 2017; Köck-Schulmeyer et al., 2013; Ponce-Robles et al., 2017; Singer et al., 2010). 94 An issue of special interest is the study of the transformation products (TPs) generated 95 when industrial wastewater, containing high levels of pesticides, are subjected to 96 treatments. There is still a lack of knowledge about the formation and input of these TPs 97 in the environment, even though they can be more toxic than the parent compounds 98 (Martínez Vidal et al., 2009).

99 Monitoring of pesticides in wastewater effluents requires the application of sensitive 100 and selective analytical tools to minimise matrix effects and improve detectability of 101 compounds at the ng/L level. Solid-phase extraction (SPE) followed by liquid 102 chromatography tandem mass spectrometry (LC-MS/MS) is the analytical strategy more 103 frequently used (Campos-Mañas et al., 2017). However, a more complete evaluation of 104 the problem requires the use of wide-scope methodologies that allow the identification 105 of non-target pesticides and even their TPs (Llorca et al., 2016). Thus, suspect screening 106 and non-target strategies are required, which include the use of high-resolution mass 107 spectrometry (HRMS) and accurate mass measurements (Agüera et al., 2014, 2017; 108 Bletsou et al., 2015).

The aim of this study was to investigate the occurrence and concentration of pesticides and their TPs in an agro-food industrial effluent using a combined strategy based on target analysis by LC-MS/MS (29 compounds) and a suspect screening by LC-HRMS (805 compounds and 86 TPs). The obtained results were compared with those found in effluents from an urban WWTP. To our knowledge, this is the first time that a this type of analytical evaluation of an agro-food industrial wastewater effluent is reported.

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116 2. Materials and methods

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118 2.1. Chemicals and reagents

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High purity (> 97%) analytical pesticide standards and ¹³C-caffeine, used as surrogate
standard for the SPE quality control, were purchased from Sigma-Aldrich (Steinheim,
Germany). Individual stock standard solutions were prepared at 1000 mg/L in methanol
(MeOH) or acetonitrile (AcN) and stored in amber glass vials at -20°C. Multi-

124 compound working solutions were prepared by appropriate mixture and dilution of the
125 stock standard solutions in AcN. AcN and MeOH, HPLC grade, formic acid (purity,
126 98%) and sodium hydroxide (NaOH, >99%) were supplied by Fluka (Buchs, Germany).
127 Milli-Q water used for LC-MS/MS analysis was generated from a Direct-Q Ultrapure
128 Water System from Millipore (Bedford, MA, USA) with a specific resistance of 18.2
129 MΩ/cm and total organic carbon (TOC) of 2 mg/L. Water HPLC grade used for LC130 HRMS analysis was purchased from Fluka.

131

132 2.2. Sample collection and SPE extraction

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134 Industrial wastewater samples were collected from a food processing industry, located 135 in Almería (southeast of Spain). The industrial plant has a processing capacity of more 136 than 120,000 tons of fruits and vegetables per year to produce seasonal products, such 137 as orange juice, gazpacho and vegetable creams. The process water and the rest of wastewater generated are treated on-site (125.000 m^3 /year), by using a sequencing batch 138 139 reactor (SBR) with activated sludge. The SBR operates in 8-h cycles, which include 140 feed (1 h), aeration/reaction (4 h) and settling of the activated sludge (3 h). Finally, 160 141 m^3 of treated effluent is removed. Grab samples of this effluent (2 L) were collected in 142 pre-rinsed amber glass bottles and stored at 4°C in the dark until analysis, within 24 h. 143 Urban wastewater samples were collected from a municipal WWTP (El Bobar, Almeria 144 city, southeast of Spain), which have a capacity of 315000 population equivalents. The 145 water line consists of pre-treatment, primary treatment, a conventional activated sludge biological treatment and a final decantation and produces 11.594.704 m³/year. The 146 147 sampling period was during May and December 2017.

148 An SPE procedure was applied to the samples. Prior to extraction, samples were 149 filtered by 0.45-µm glass microfiber filters (Whatman, Buckinghamshire, UK) and the 150 pH was adjusted to 8 with 20% NH₄OH. Then, 100 mL of sample were spiked with the surrogate standard (¹³C-caffeine) and extracted using Oasis HLB (6 cc, 200 mg; Waters, 151 152 Miliford, MA, USA) cartridges in an automated SPE extractor Dionex[™] AutoTrace[™] 153 280 (Thermo Fisher Scientific, Sunnyvale, CA, USA). SPE cartridges were conditioned 154 with 6 mL of MeOH and 5 mL of Milli-Q water at pH 8. After the sample loading, 155 cartridges were dried with N₂ for 30 min. The elution of the analytes was performed 156 with 2 x 4 mL of MeOH collected in glass tubes. The eluted sample was dried under a 157 gentle N₂ stream and reconstituted with 1 mL of MeOH. Prior to injection, 1:10 dilution 158 was applied to the extract with Milli-Q water. An aliquot of the organic extract was 159 stored in the freezer (-20°C) till analysis by LC-HRMS.

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161 2.3. LC-QqLIT-MS/MS target analysis

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163 Target pesticide analyses were performed using a 1200 HPLC system (Agilent 164 Technologies, Wilmington, DE, USA) coupled to a hybrid quadrupole/linear ion trap 165 (QqLIT) mass spectrometer (5500 Q-TRAP®, Sciex, Foster City, CA, USA). A Kinetex 166 C18 column (150 x 4.6 mm, 2.6-µm particle size, Phenomenex, Torrance, CA, USA) 167 was used for the chromatographic separation of the target compounds. Eluent A was 168 Milli-Q water (0.1% formic acid) and eluent B was MeOH, which were used in an 169 optimised gradient as follows: initial conditions, 20% B for 0.5 min; within 3 min, 170 linear gradient from 20% to 50% B; within 7 min, from 50% to 90% B and within 9.5 171 min from 90% to 100% B. The gradient was kept at 100% B for 4.5 min and at 14.01 172 min the initial conditions were reached again and maintained constant for a reequilibration time of 7 min. The total run time was 21 min. The sample injection
volume was 10 µL and the flow rate was 0.5 mL/min.

175 The mass spectrometer was equipped with a TurboIon Spray source operated in 176 positive and negative electrospray ionization modes in the same run (+ESI and -ESI, 177 respectively). Source settings were: ion spray voltage (IS), 4500 V (+ESI) and -4500 V 178 (-ESI); source temperature, 550°C; CAD gas, medium; ion source gas 1, 50 psi; ion source gas 2, 40 psi and curtain gas, 25 (arbitrary units). N₂ was used as nebuliser gas, 179 180 curtain gas and collision gas. The precursor ion, ionisation mode and MS/MS 181 parameters (declustering potential, DP; collision energy, CE; entrance potential, EP; cell 182 exit potential, CXP) were optimised for each compound by direct infusion of individual 183 standard solutions in MeOH (10 μ g/L). Analyses were done in the multiple reaction 184 monitoring (MRM) mode with Schedule MRMTM Algorithm. The MRM detection 185 window was set at 40 s and the target scan time (TST) at 0.5 s. Confirmation of the 186 analytes in the samples was carried out according to the European Union (EU) 187 guidelines for pesticide residue analysis SANTE/11813/2017 (European Commission, 188 2017a) by the presence of two SRM transitions (two products ions) at the correct 189 retention time (RT) and presenting the correct SRM2/SRM1 ratio. The RT of each 190 analyte in the samples should correspond to that of the calibration standard with a 191 tolerance of ± 0.1 min and the ratios of selected ions relative to the most intense ion 192 (SRM1) should not deviate more than 30%.

Data were acquired using Analyst Software 1.5.1 and processed with MultiQuant3.0.1 software (Sciex).

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196 *2.4. Validation study of the target approach*

198 The validation study was carried out using industrial wastewater samples. As it was not 199 possible to find blank samples, industrial wastewater samples were previously analysed, 200 and subtraction of the present pesticides was applied. Matrix-matched calibration curves 201 were used for the quantitative analysis. The analytical method was validated in terms of 202 linearity, trueness (recovery), precision (expressed as intra-day and inter-day precision), 203 method detection and quantification limits (MDL and MQL, respectively), and matrix 204 effect (ME). The linearity was studied by analysing spiked wastewater extracts obtained 205 by the proposed SPE method in the range from 10 to 1000 ng/L (10, 50, 100, 500, 1000 ng/L). Satisfactory linearity was assumed when the determination coefficients (R^2) were 206 207 higher than 0.990. The MDLs and MQLs were estimated considering signal-to-noise 208 (S/N) ratios of 3 and 10 for SRM2 and SRM1, respectively.

209 The ME was calculated comparing the slopes of matrix-matched and pure solvent 210 calibration curves according to the following equation: ME (%) = [(Slope of calibration for a state of calibration for a state of calibration for a state of the state of th211 curve in matrix/Slope of calibration curve in solvent)-1] x 100 (Barco-Bonilla et al., 212 2010). Negative values indicate a signal suppression effect and positive values a signal 213 enhancement. The recovery studies (n=3) were carried out by analysing spiked 214 wastewater effluent samples at three concentration levels (50, 500 and 1000 ng L^{-1}). 215 Method precision (intra-day and inter-day precision) was calculated as the relative 216 standard deviation (RSD) of the recoveries obtained. Acceptable mean recoveries were 217 considered in the range 70–120%, with an associated RSD $\leq 20\%$ (European 218 Commission, 2017a). Exceptionally, lower recoveries could be accepted provided the 219 RSD was $\leq 20\%$.

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221 2.5. LC-QTOF-MS/MS suspect screening analysis

223 Chromatographic separation was carried out in an Agilent 1260 Infinity system 224 equipped with a Poroshell 120 EC-C18 column (4.6 x 50 mm; 2.7-µm particle size, 225 Agilent Technologies, Santa Clara, CA, USA). Water 0.1% formic acid (phase A) and 226 AcN (phase B) were used as eluents. Elution gradient at 0.5 mL/min flow rate was as 227 follows: from 10% B (1 min) to 100% in 9 min and kept constant for 4 min before 228 returning to initial conditions. The total run time was 22 min. Injection volume was 10 229 μ L. The LC system was connected to a hybrid quadrupole time of flight mass 230 spectrometer (QTOF) (Sciex TripleTOF 5600⁺) equipped with a DuoSpray ion source 231 operated in positive mode. The equipment worked via TOF-MS survey scan followed 232 by Information Dependent Acquisition (IDA). Scanned mass range was from m/z 50 to 233 1000, for both full scan MS and MS/MS experiments. The IDA experiments were 234 launched for ions exceeding a peak intensity threshold of 1000 cps and dynamic 235 background subtraction was activated. An accumulation time of 100 ms was used for 236 each scan. Collision energy of 30 eV with a ± 15 eV spread was used for MS/MS 237 fragmentation. MS data were processed using MasterViewTM software version 1.1, 238 PeakViewTM and AnalystTM TF 1.5 (Sciex).

239 The suspect screening workflow used two suspect lists containing the monoisotopic 240 masses of the selected analytes. One list was composed of 805 pesticides using the lists 241 available on the NORMAN Suspect List Exchange website (NORMAN Network, 242 2018a) and a previously published database (Gómez-Pérez et al., 2012). The other list included 86 TPs from imazalil, thiabendazole and pyrimethanil (Table A.1) obtained 243 244 using literature and two (in silico) prediction tools: PathPred (Bletsou et al., 2015; 245 Kyoto University, 2018) and EAWAG-BBD pathway prediction system (EAWAG, 246 2018). The "xenobiotics biodegradation (bacteria)" option was set for PathPred. The 247 settings for EAWAG-BBD were: Show biotransformations: aerobic; Show levels: 6;

248 Show Products in a Level: 10; Show Products containing "C": 4+. The requirements for 249 peak extraction were an intensity threshold higher than 1000 cps and a S/N >10 (a 250 default extraction window of 20 mDa was used). A procedural blank was also applied as 251 control sample. Further peak reduction was based on the following criteria set in the sample processing by MasterView[™]: mass accuracy error <5 ppm for the molecular ion 252 253 $[M+H]^+$ and an isotopic ratio difference (IRD) below 10%, together with the formula 254 assignment software (Formula FinderTM). The freely accessible MassBank database 255 (NORMAN Network, 2018b) was used to increase identification confidence. A library 256 fit >70% and the presence of at least two characteristic MS/MS fragments with a mass 257 error <5 ppm was used as positive identification criteria. In addition, a difference of ± 2 258 min of the RT when compared with a home-made RT prediction model was also useful 259 for positive proposal. This prediction model was previously used in our laboratory 260 (Martínez-Piernas et al., 2018) and was based on a strategy already reported (Chiaia-261 Hernandez et al., 2014). Final confirmation of the positive findings was obtained based 262 on RT and MS/MS fragmentation of the purchased analytical standard.

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264 2.6. Hazard Quotient calculations

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The hazard quotient (HQ) was calculated as the ratio predicted or measured environmental concentration (PEC or MEC)/predicted no-effect concentration (PNEC). The individual concentrations obtained from the monitoring data were used as MEC values instead of PEC values obtained from exposure models (Table A.2). The PNEC was calculated using the long-term No-Observed Effect Concentration (NOEC) values. When the NOEC was not available, the short term lethal/effect median values, LC_{50} or EC₅₀, were used. In all cases, an appropriate assessment factor (AF) [PNEC = (NOEC or LC_{50} or EC_{50} / AF] (Vryzas et al., 2009) was applied in order to consider the extrapolation from single species toxicity to ecosystem toxicity and its associated uncertainty. The Pesticides Properties Database (University of Hertfordshire, 2018) was used to obtain the ecotoxicological data (NOEC, LC_{50} , EC_{50}); for cyprodinil, data was obtained from the Pesticide Action Network Pesticide Database (Pesticide Action Network, 2018).

279 The most sensitive species (worst-case scenario) was used for the PNEC calculation, 280 and three trophic levels (phytoplankton, zooplankton and fish) were considered. 281 Regardless of the species chosen for the calculation and according to the Technical 282 Guidance Document on Risk Assessment of the European Commission (European 283 Comission Joint Research Centre, 2003), an AF of 1000 was used provided one short 284 term assay at one trophic level was available. An AF of 100 was applied in the case 285 ecotoxicological data with either fish or zooplankton from one long-term assay were 286 available. Finally, the AF of 50 and 10 were used in the calculations in the case of existing two or three long-term assays, respectively. 287

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289 3. Results and discussion

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291 *3.1. Target method validation*

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The optimised MS/MS conditions for the pesticides studied, including SRM transitions and retention times, are listed in Table A.3. 28 out of 29 compounds investigated showed higher response in positive ionisation mode (+ESI), and the protonated molecule $[M+H]^+$ was selected as precursor ion. The analytical method developed showed a satisfactory performance. Linearity of the analytical response yielded R² 298 values ≥ 0.993 for all compounds in matrix. Linearity range was from 10-1000 ng/L 299 (10, 50, 100, 500, 1000 ng/L). MDLs were lower than 10 ng/L in all cases and MQLs 300 ranged from 0.5 ng/L (metalaxyl) to 40 ng/L (diuron). Good recoveries were obtained 301 for most compounds, ranging from 80 to 110%. Only chlorpyriphos and quinoxyfen, 302 yielded recoveries lower than 61% at all the concentration levels tested, but with 303 adequate RSD values so they were accepted. Quinmerac and mecoprop showed low 304 recoveries only at the lowest concentration levels studied (50 and 500 ng/L), with 305 adequate performance at higher concentrations. Method precision yielded in all cases 306 RSD values $\leq 20\%$ (intra-day and inter-day precision), except for quinmerac (31%) at 50 ng/L, and propamocarb (24%) at 500 ng/L. All validation results are summarized in 307 308 Table A.4.

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310 *3.2.* Application of the target method to industrial and urban wastewater effluents

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The amount of pesticides in the industrial effluents can vary considerably with time due 312 313 to changes in the processed products and the season. Therefore, two one-week 314 monitoring events (in May and December 2017) were carried out, to consider the main 315 food processing activities of the industry: vegetable soups and fruit juice production. An 316 internal quality control procedure was included in every sequence of analysis to check 317 method performance. The procedure involved the analysis of a matrix-matched 318 calibration curve, a reagent blank sample and a spiked wastewater sample. Pure solvent 319 (MeOH) was also injected periodically to confirm the absence of carryover effects.

The concentration values found for each compound are summarised in Table 1. The results showed that 65% of the target pesticides were detected at least in one occasion in the industrial effluent, with 10 of them (38%) present in all samples, regardless of the 323 considered sampling period. Pesticides were found in a wide range of concentrations, 324 from 1.7 ng/L to 19802 ng/L. Fig. 1 shows the extracted ion chromatograms obtained 325 from the analysis of an industrial effluent sample, where the differences in the 326 concentrations for the detected compounds are appreciable. In all cases, the analytes 327 were accurately confirmed with the proposed identification criteria. Imazalil (IMA) was 328 the pesticide that showed the highest concentration levels (7038–19802 ng/L), followed 329 by pyrimethanil (PYR, 744–9591 ng/L) and thiabendazole (TBZ, 341–926 ng/L). The 330 high concentrations detected for these compounds can be explained by the large amount 331 of citrus fruits (mainly oranges) that are processed daily to produce juice, the main 332 production line of the company. PYR and the combination IMA-TBZ are widely used 333 as post-harvest fungicides in citrus and their release to wash water during this 334 processing stage is highly probable. Besides, the maximum residue levels (MRLs) 335 allowed by the European Union for oranges and other citrus fruits is quite high, 5 mg/kg 336 (IMA), 7 mg/kg (TBZ) and 8 mg/kg (PYR) (European Commission, 2019), indicating 337 that they can be legally applied at very high amounts. The high levels of PYR can also 338 be explained by the production of gazpacho, a typical Spanish tomato soup, since PYR 339 is also used in tomato crops. It is important to remark that, unlike the packaging 340 industries, the studied agro-food industry does not apply these pesticides in the factory, 341 but fruits and vegetables are treated before entering the industry by producers. However, 342 the processing of the fruits and vegetables, mainly washing, can removes total or 343 partially residues present on the peel (Bajwa and Sandhu, 2014; Sánchez Peréz et al., 344 2014). The removed pesticide residues are transferred to the water during those washing 345 steps. In fact, it has been reported that depending on the washing treatment, up to 30% 346 of the IMA present in lemon peel can be transferred to water (Vass et al., 2015).

347 Comparing the results of the two sampling campaigns (May and December), the three 348 most concentrated pesticides are the same (IMA, PYR and TBZ) in both cases, which 349 represents a continuous discharge of these compounds to the environment. The agro-350 food industry studied increases the production of *gazpacho* and vegetable soups in May, 351 processing tomato as the main raw product, while in December the production of juice 352 predominates, and oranges are mainly processed. Due to variations in production, some 353 differences were observed in the type and concentration of pesticides identified. 354 Clofenvinphos was only identified in May, while dimethomorph, fenhexamid, 355 imidacloprid and propamocarb were only detected in December. All these pesticides 356 showed average concentrations in the range of 3-85 ng/L and the maximum 357 concentration in no case exceeded 195 ng/L (metalaxyl). Presence of chlorpyriphos (15-358 26 ng/L) and prochloraz (3-20 ng/L), although at low concentrations, is relevant 359 because both compounds are considered as endocrine disruptors in both humans and 360 wildlife (United Nations Environment Programme and the World Health Organization, 361 2013). Chlorpyriphos is used in citrus trees to control specific pests and the MRLs 362 allowed in citrus fruits range from 0.3 to 1.5 mg/kg. Both chlorpyriphos and 363 chlorfenvinphos (5-150 ng/L) are included in the priority substances list (European 364 Parliament and the Council of the European Union, 2008). However, as a reference, 365 mean concentration levels found in the effluents were always below the environmental 366 quality standard (EQS) reported in the EU regulation (European Parliament and the 367 Council of the European Union, 2008). Prochloraz can also be used in citrus trees in 368 combination with TBZ as fungicide and showing a higher MRL (10 mg/kg).

Regardless of the seasonal variations on pesticide profile of the industrial effluent,what it is clear is that the wastewater treatment applied fail in the total removal of the

371 pesticides present in the process water and, consequently, pesticides are continuously372 discharged to the environment at high concentrations.

373 The optimised analytical method was also applied to the analysis of effluent samples 374 from a municipal WWTP located in the same province with the aim of comparing 375 pesticide loads in the effluents of both industrial and urban WWTPs. The results 376 showed the occurrence of a greater number of pesticides in the urban effluent (88% 377 target compounds) but with lower average concentrations, below 286 ng/L in all cases. 378 Table 1 reports the results obtained. Only 5 compounds (carbendazim, clofenvinphos, 379 imidacloprid, metalaxyl and tebuconazole) were present in all samples. The individual concentration levels ranged from 1 ng/L up to 1357 ng/L in the case of imidacloprid, 380 381 which had the highest concentration and frequency of detection. Considering the 382 average total charge of pesticides (sum of all the individual concentrations of the 383 detected pesticides), this total concentration of pesticides was remarkably lower in 384 urban (1181 ng/L) than in industrial (20628 and 13619 ng/L) effluents. Acetamiprid, 385 diuron, imidacloprid, IMA and PYR showed the highest average values, with IMA and 386 PYR also the most relevant in the industrial effluent. Typically, washing of fruits and 387 vegetables before consumption is also a domestic practice, which can explain the 388 presence of these compounds. The neonicotinoids imidacloprid and acetamiprid, which 389 are allowed for certain crops, were also found at significant concentrations in urban 390 effluents. These compounds are a cause for concern due to the toxic effects on bees, and 391 the EU is restricting their use (European Commission, 2017b).

392

393 3.4. Suspect screening analysis by LC- QTOF-MS/MS

395 A suspect screening strategy was applied to extend the scope of the analysis to 396 pesticides and TPs not included in the target study. Two suspect lists were created 397 including accurate mass information of selected compounds. The first list focused on 398 the identification of pesticides and included 805 LC-amenable candidates. The second 399 list aimed to detect TPs of the three most relevant compounds identified by the target 400 method, namely IMA, PYR and TBZ. Considering the high concentrations found for 401 these pesticides, it would be more likely to find TPs at measurable concentrations for 402 them in the evaluated real samples. A total of 86 TPs were selected (Table A.1) based 403 on a literature review and using computational (in silico) prediction tools, such as the 404 PathPred or EAWAG-BBD pathway prediction system (Bletsou et al., 2015; EAWAG, 405 2018).

406 Based on these lists, peaks fulfilling pre-set criteria described in Section 2.5 (intensity 407 >1000 cps; S/N >10; signal 10 times higher than in the control sample) were 408 investigated throughout the chromatogram and filtered considering mass accuracy (<5 409 ppm) and isotope ratio difference (IRD <10%). At this stage, 79 suspect pesticides and 410 26 possible TPs were tentatively identified. A manual review of the extracted-ion 411 chromatograms (XIC) allowed reducing the list of positive findings to 38 pesticides and 412 20 TPs. For pesticides, the MS/MS spectra of the potential candidates were compared 413 with commercial databases (Sciex and Mass Bank libraries). A fit higher than 70%, the 414 presence of at least two characteristic MS/MS fragments (mass error <5 ppm) and a 415 difference of ± 2 min on the RT when compared with a home-made RT prediction model 416 were used to reinforce the proposal of tentative candidates. At this point the list of 417 candidates was reduced at 5 pesticides and 14 TPs (Tables 2 and 3).

The final confirmation of the proposed structures was obtained by the acquisition andanalysis of the corresponding analytical standards. Three of the five pesticide

420 candidates, boscalid (23–47 ng/L), etoxazole (161–2014 ng/L) and propiconazole 421 (1884–75950 ng/L) (Fig. 2) could be confirmed while hydroxyquinoline and rotenone 422 were rejected as false positives. Table 2 summarises the values obtained for the 423 identification criteria. Propiconazole and boscalid are fungicides whereas etoxazole is 424 an acaricide widely used in citrus. Considering the use of these pesticides, the results 425 are in accordance with the products processed in this agro-food industry and have 426 evidenced the presence of these three additional pesticides.

427 Regarding TPs identification (Table 3), the proposed structures were not confirmed 428 due to the lack of standards, so they were assigned based on MS/MS information 429 available in literature or by structural elucidation of the MS/MS fragmentation pattern. 430 Although TPs found in literature had been generated by other treatments (photolysis, 431 photocatalysis), their presence in the SBR effluent is not surprising, since it is reported 432 that in many cases, the same TP can be formed from different treatments (Haddad et al., 433 2015). Biotic or abiotic processes which take place in biological treatments can include 434 oxidation, reduction, demethylation, double bond shift, nucleophilic addition, 435 hydroxylation, molecular rearrangements and other transformations in common with 436 other processes (Wick et al., 2011).

437 In the case of TBZ, two TPs could be identified. TBZ-218 ($[M+H]^+$ m/z 218.0383; 438 $C_{10}H_7N_3OS$ corresponded to a frequently reported hydroxylated derivative (Sánchez 439 Peréz et al., 2014; Sirtori et al., 2014), which was even confirmed by the Sciex library as 5-hydroxythiabendazole (95%). TBZ-147 ($[M+H]^+$ m/z 147.0553; C₈H₆N₂O) was 440 441 identified as 1*H*-benzo[*d*]imidazole-2-carbaldehyde, a compound previously reported as 442 derivative of TBZ photolysis (Murthy et al., 1996). The characteristic ion fragment 443 observed at m/z 119.0604 (C₇H₆N₂) corresponded with the benzimidazole moiety after 444 loss of the carbonyl group and was useful for the structure confirmation.

445 Four PYR TPs were detected and their structures explained and justified based on 446 previous literature (Sirtori et al., 2012). PYR-216a and PYR-216b ($[M+H]^+$ m/z 447 $C_{12}H_{14}N_{3}O$) matched with positional isomers 216.1331; corresponding to 448 hydroxylation reactions already reported (Sirtori et al., 2012). That study suggested the 449 structures showed in Table 3, corresponding to the hydroxylation of benzene (PYR-450 216a) and pyrimidine rings (PYR-216b). However, the fragmentation obtained does not 451 provide unequivocal confirmation. PYR-230 ($[M+H]^+$ m/z 230.0924; C₁₂H₁₁N₃O₂) is 452 generated by initial di-hydroxylation of PYR and further oxidation to yield a quinone 453 imine derivative. PYR-136 ($[M+H]^+$ m/z 136.0869; C₇H₉N₃) arises from the pyrimidine 454 ring opening (Fig. 3) and its structure was tentatively identified by the losses of -NH₃ 455 $(m/z \ 119.0604; \ C_7H_6N_2)$ and $-CN_2H_2$ to yield aniline $(m/z \ 94.0651; \ C_6H_7N)$. To our 456 knowledge, PYR-136 has not been previously reported. Additionally, another non-457 previously reported TP, PYR-234 ($[M+H]^+$ m/z 234.1237; $C_{12}H_{15}N_3O_2$), was tentatively 458 identified and its structure explained and justified using the product ions of the MS/MS 459 spectrum (Fig. 3). This compound could correspond with the hydroxylation and opening 460 of the pyrimidine ring before the PYR-136 formation.

461 Five IMA TPs, which were previously reported (Rodríguez-Cabo et al., 2018; 462 Santiago et al., 2013) in literature, have been identified in the wastewater samples. They 463 corresponded to the oxidation of the double bond in the allyl chain of IMA (IMA-331) 464 and further hydrolysis of the ether bond to produce a secondary alcohol (IMA-257), 465 which was positively identify by the Sciex library (96%). The opening of the imidazole 466 ring, previously reported (Rodríguez-Cabo et al., 2018), has been also evidenced by the 467 identification of IMA-273 ($[M+H]^+$ m/z, 273.0556; $C_{12}H_{14}Cl_2N_2O$), IMA-274 ($[M+H]^+$ 468 m/z 274.0396; C₁₂H₁₃Cl₂NO₂) and IMA-188 ([M+H]⁺ m/z 188.0028; C₈H₇Cl₂N), which 469 presented the same MS/MS fragmentation described by the aforementioned work. Two

470 new TPs predicted by the PathPred software were tentatively proposed: IMA-313 471 $([M+H]^+ m/z 313.0505; C_{14}H_{14}Cl_2N_2O_2)$ and IMA-329 $([M+H]^+ m/z 329.0454;$ 472 $C_{14}H_{14}Cl_2N_2O_3$), which correspond to mono- and di-hydroxylated derivatives of IMA. 473 Fig. 4 shows the tentative identification of both compounds by structure elucidation of 474 the product ions in the MS/MS spectrum. The fragment at m/z 239.0137 in the spectrum 475 of IMA-329 confirms that the hydroxylation takes place in the double bond of the allyl 476 chain. On the contrary, the product ion at m/z 271.0026 of IMA-313 suggests the 477 hydroxylation of the imidazole ring, also confirmed by fragments at m/z 188.9866 and 478 174.9706, although available information is not enough to assign the correct position of 479 the hydroxyl group. To our knowledge, this is the first time that these TPs have been 480 found in real wastewater.

In absence of analytical standards and in order to estimate the relevance of the TPs identified, the corresponding peaks were integrated, and their areas compared (Table A.5). The TPs of TBZ were detected in all cases at much lower intensity than their parent compound and the frequency of detection was below 50%, probably because of their low concentration.

In the case of PYR, PYR-216a/b and PYR-136 were present in all the samples, reaching PYR-216a and PYR-230 the highest intensity. In any case, the PYR TPs showed abundances at least one order of magnitude lower than PYR. This also applies to IMA. Except for IMA-329, all the TPs of IMA presented a high frequency of detection (85-100%). IMA-257 was the TP more abundant followed by IMA-331, thus suggesting that the oxidation of the allyl chain is the main degradation route.

492

493 *3.5. Hazard Quotients*

495 The risk quotient (RQ) or HQ are often used to evaluate the risk associated to the 496 introduction of pesticides and other microcontaminants in the aquatic environment 497 through wastewater (Frédéric and Yves, 2014; Santos et al., 2013) as well as their 498 impact in surface water (Palma et al., 2014; Papadakis et al., 2015; Vryzas et al., 2009). 499 Two previous works (Frédéric and Yves, 2014; Santos et al., 2013) reported the 500 calculation of a HQ corresponding to the highest concentration measured in an hospital 501 wastewater effluent for each pharmaceutical compound founded. In our study, the HQ 502 has been used to identify potentially hazardous compounds and take into account the 503 individual risk of these compounds identified in the agro-food industry wastewater 504 samples, applying a similar strategy as described in previous studies (Frédéric and 505 Yves, 2014; Mendoza et al., 2015; Papadakis et al., 2015; Vryzas et al., 2009). HQ is 506 usually expressed as the ratio MEC/PNEC.

507 This strategy was applied to determine median and maximum or extreme HQs for 508 each pesticide (HQ_m, HQ_{ex}) using the median and extreme concentrations from the 509 monitoring study, respectively. HQ <1 would indicate that the compound does not show 510 significant concentrations as to pose a relevant risk for the environment. Table A.2 511 details the ecotoxicological data used to calculate the HQ for each pesticide.

512 The HQs of etoxazole and propiconazole were in the range 1-10 for median MEC, 513 indicating a probable adverse or moderate risk, but considering the extreme MEC, HQs 514 >10, anticipating a high risk. The insecticides chlorfenvinphos and chlorpyrifos showed 515 HQex of 1.49 and 1.86, respectively, representing a moderate risk (Table A.2). Some 516 pesticides showed HQs higher than 10 for MEC_m and MEC_{ex}: the fungicides IMA (31.8 517 and 46.1, respectively) and cyprodinil (13.1 and 29.6 respectively), which is normally 518 considered as a high risk for aquatic organisms (Mendoza et al., 2015). Other 519 compounds showing HQs in the range 0.1-1 were boscalid, prochloraz (only the HQ_{ex}), 520 pyrimethanil and TBZ. The rest of pesticides present did not pose any hazard for the521 environment, with HQs < 0.1.

Although HQ values cannot be used directly as an exposure concentration since the effluents released in receiving surface water systems are diluted by the large volumes of the receiving water bodies, they can be considered as a reference to highlight the compounds with higher potential impact. It is also important to consider that a continuous discharge of these pesticides can lead to their accumulation, depending on the characteristics of the receiving water and the weather conditions.

528

529 4. Conclusions

530 The presence of pesticides and their TPs in the wastewater effluent of an agro-food 531 industry has been demonstrated in this study. The combination of target and suspect 532 analytical strategies has allowed a characterization of the effluents. The fungicides IMA 533 (7038–19802 ng/L), PYR (744–9591 ng/L), TBZ (341–926 ng/L) and propiconazole 534 (1884-75950 ng/L) and the acaricide etoxazole (161-2014 ng/L) showed the highest 535 concentration levels. Up to 14 TPs of the pesticides IMA, PYR and TBZ were also 536 identified. The comparison between urban and industrial wastewater stresses the 537 importance of controlling agro-food industry wastewater effluents, which represent a 538 relevant hotspot of pesticide discharge into the environment. The environmental risk 539 assessment based on the calculation of HQs revealed that cyprodinil, etoxazole, imazalil 540 and propiconazole can eventually represent a risk for the environment. The reduction of 541 the levels of the compounds with higher HQs should be put under consideration in 542 future upgrading of wastewater treatment of agro-food industries.

543

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545

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- 551
- 552 Appendix A. Supplementary data
- 553
- 554 Supplementary data associated with this article can be found, in the online version.
- 555

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- 754 Figure captions
- Fig. 1. Extracted ion chromatograms obtained from the analysis of an industrial WWsample.
- **Fig. 2.** Pesticide suspect screening identification and confirmation: propiconazolesuspect analysis by LC-QTOF-MS.
- Fig. 3. Tentative identification by structure elucidation of the product ions of
 transformation products (a) PYR-234 and (b) PYR-136 obtained in their MS/MS
 spectra.
- 762 Fig. 4. Tentative identification by structure elucidation of the product ions of
- transformation products (a) IMA-313 and (b) IMA-329 obtained in its MS/MS spectra.

Table 1

Summary of the results obtained in agro-food industry wastewater and urban wastewater.

	Priority substance ^a	EQS ^b (ng/L)	Industrial WW May 2017 (n=7)			Industrial WW December 2017 (n=7)			Urban WW 2017 (n=10)		
Compound			Concentration (ng/L)	Mean ± SD ^c (ng/L)	FD ^d (%)	Concentration (ng/L)	Mean ± SD (ng/L)	FD (%)	Concentration (ng/L)	Mean ± SD (ng/L)	FD (%)
Acetamiprid	-	-	30 - 39	37 ± 3	100	24 - 52	29 ± 10	100	15 - 1228	238 ± 434	90
Atrazine	YES	600	-	-	n.d. ^e	-	-	n.d.	2 - 12	7 ± 7	20
Buprofezin	-	-	-	-	n.d.	-	-	n.d.	1 - 21	11 ± 14	20
Carbendazim	-	-	-	-	n.d.	-	-	n.d.	14 - 103	41 ± 26	100
Chlorfenvinphos	YES	100	5 - 150	18 ± 83	43	-	-	n.d.	4 -39	16 ± 14	100
Chlorpyrifos	YES	30	15 - 20	17 ± 2	86	19 - 26	20 ± 5	100	11-12	12 ± 1	60
Cyprodinil	-	-	17 - 22	19 ± 2	100	8 - 37	11 ± 10	100	14 - 111	40 ± 35	80
Dimethoate	-	-	-	-	n.d.	-	-	n.d.	2 - 29	14 ± 11	70
Dimethomorph	-	-	-	-	n.d.	3 - 9	4 ± 2	100	4-5	7 ± 4	20
Diuron	YES	200	-	-	n.d.	-	-	n.d.	67 - 129	105 ± 23	60
Fenhexamid	-	-	-	-	n.d.	25 - 50	36 ± 10	100	46 - 50	48 ± 3	20
Imazalil	-	-	12140 - 19802	16564 ± 2789	100	7038 - 15592	10723 ± 2916	100	3 - 496	105 ± 173	80
Imidacloprid	-	-	-	-	n.d.	40 - 57	47 ± 12	29	40 - 1357	286 ± 395	100
Isoproturon	YES	300	-	-	n.d.	-	-	n.d.	3 -14	8 ± 4	90
Metalaxyl	-	-	74 - 195	126 ± 52	100	16 - 37	24 ± 9	100	3 -15	7 ± 4	100
Myclobutanyl	-	-	11 - 15	13 ± 2	40	6 - 11	8 ± 3	45	-	-	n.d.
Pirimicarb	-	-	-	-	n.d.	-	-	n.d.	1 -86	15 ± 32	70
Prochloraz	-	-	9 - 20	14 ± 4	57	3 -7	5 ± 1	100	14	14	10
Propamocarb	-	-	-	-	n.d.	28 - 146	58 ± 37	100	1 - 10	7 ± 4	60
Pyrimethanil	-	-	901 - 4877	3358 ± 1382	100	744 - 9591	1780 ± 2988	100	35 - 197	124 ± 78	40
Quinoxyfen	YES	15	-	-	n.d.	-	-	n.d.	-	-	n.d.
Simazine	YES	1000	-	-	n.d.	-	-	n.d.	14	14	10
Tebuconazole	-	-	21 - 38	31 ± 6	100	75 - 86	85 ± 8	100	3 - 21	12 ± 6	100
Terbutryn	YES	6.5	-	-	n.d.	-	-	n.d.	-	-	n.d.
Thiabendazole	-	-	341 - 553	419 ± 86	100	344 - 926	512 ± 227	100	-	-	n.d.

^aAccording to the Water Framework Directive for surface waters [1]; ^bEQS: Environmental quality standard for annual average value (AA-EQS) in "Other surface waters"[2]; ^cSD: Standard deviation; ^dFD: frequency of detection; ^en.d.: not detected.

Table 2Identification information of the candidates identified by the suspect screening

Compound	Boscalid	Etoxazole	H <mark>yi</mark> droxyquinoline	Propiconazole	Rotenone
Formula (M)	$C_{18}H_{12}Cl_2N_2O$	$C_{21}H_{23}F_2NO_2$	C ₉ H ₇ NO	$C_{15}H_{17}C_{12}N_3O_2$	$C_{23}H_{22}O_{6}$
RT ^a (min)	9.70	12.12	5.89	10.22	7.70
$[M+H]^+$ expected (m/z)	343.0399	360.1769	146.0600	342.0770	395.1489
$[M+H]^+$ measured (m/z)	343.0401	360.1772	146.0599	342.0772	395.1481
Mass error (ppm)	0.5	0.7	-0.7	-0.2	-1.8
IRD ^b (%)	3.4	2.5	3.7	1.6	6.6
Score MS/MS library (%)	MassBank (84.6) Sciex (99.4) ChemSpider (82.2)	<u>-Mass Bank (n.a.)</u> ^e Sciex (99.7)	MassBank (95.9) <u>-</u>	Mass Bank (99) Sc <u>i</u> tex (99.8) ChemSpider (94.2)	- Sciex (79.2) ChemSpider (55.4)
More than 2 $\mathbf{PI}^{\text{cd}}_{\text{cd}}$ error < 5 ppm	Vas	ChemSpider (84.3) Vos	ChemSpider (89.9) Vos	Vas	Vos
	Tes	Tes	Tes	1es	Tes
RT prediction ($\pm 2 \text{ min}$)	Yes	Yes	Yes	Yes	Yes
Purchased standard	Yes	Yes	Yes	Yes	Yes
RT confirmation	Yes	Yes	No	Yes	No
Concentration range (ng/L)	161 - 2014	23 - 47	-	1884 - 75950	-

^aRT: Retention time; ^bIRD: Isotope ratio diference; ^en.a.: Data not available; ^{ed}PI: Product ion.

Table 3

Structure, acquisition and chromatographic parameters for thiabendazole, pyrimethanil, imazalil and their transformation products after analysis by LC-QTOF-MS/MS.

Compound	<u>Structure</u>	RT (min)	Formula [M]	Calculated mass [M+H] ⁺ (m/z)	DBR	Error (ppm)	Identification
TBZ	н	4.31	$C_{10}H_7N_3S$	202.0433	9	1.3	
	N		$C_9H_6N_2S$	175.0324	8	1.4	
			$C_8H_6N_2$	131.0604	7	1.0	
			C_6H_5N	92.0495	5	9.0	
TBZ-218	HO o H	3.09	$C_{10}H_7N_3OS$	218.0383	9	0.3	Sciex (94.6) ^a
			$C_9H_6N_2OS$	191.0290	8	-1.9	(Sanchez Pérez
	N N		$C_8H_6N_2O$	147.0558	7	-5.0	Sirtori et al.
			C ₆ H ₆ O	95.0491	4	-7.8	<u>2014) [34]</u>
TBZ-147	A N O	1.22	$C_8H_6N_2O$	147.0553	7	1.4	(Murthy et al.,
			$C_7H_6N_2$	119.0604	6	1.1	<u>1996) [36]</u>
	Ň H		C_6H_5N	92.0495	5	2.4	
PYR	ц	8.15	$C_{12}H_{13}N_3$	200.1182	8	-1.1	
	H ₃ C N N		$C_{12}H_{10}N_2$	183.0917	9	-2.6	
			$C_{12}H_7N$	166.0651	10	0.4	
	Ť. Ť		$C_9H_6N_2$	143.0604	8	4.4	
	CH_3		$C_6H_6N_2$	107.0604	5	7.7	
PYR-136	H _N N N A	1.80	$C_7H_9N_3$	136.0869	5	-0.5	Not previously
			$C_7H_6N_2$	119.0604	6	-5.7	reported [37]
	йн		C_6H_7N	94.0651	4	1.9	
PYR-230	H ₃ C N N	7.58	$C_{12}H_{11}N_3O_2$	230.0924	9	0.4	(Sirtori et al.,
			$C_{12}H_9N_3O$	212.0818	10	2.2	<u>2012) [37] - </u>
	HO		$\underline{C_{11}}\underline{H_{11}}\underline{N_3}\underline{O}$	<u>202.0980</u>	<u>8</u>	<u>-0.9</u>	
	ĊH ₃		$C_{11}H_9N_3$	184.0869	9	-0.7	
PYR-216a		4.86	$C_{12}H_{13}N_3O$	216.1131	8	-0.6	(Sirtori et al.,
	H ₃ C N N		$C_{12}H_{11}N_3$	198.1026	9	0.1	<u>2012) [37]</u>
			$C_{11}H_{10}N_2$	171.0920	8	-3.9	
	С СН		$C_{11}H_8N_2$	169.0760	9	-4.9	
	CH ₃		$C_8H_6N_2$	131.0612	7	-0.6	
PYR-216b	HaC. N N A	6.95	$C_{12}H_{13}N_3O$	216.1136	8	2.1	(Sirtori et al.,
			$C_{12}H_{11}N_3$	198.1026	9	1.6	<u>2012) [37]</u>
	HONN		$C_{11}H_{10}N_2$	171.0920	8	1.9	
	 CH₃		$C_8H_6N_2$	131.0612	7	6.3	
PYR-234	H ₃ C H	1.77	$C_{12}H_{15}N_3O_2$	234.1237	7	-2.6	Not previously
I	HIG-CH		$C_{10}H_{11}N_{3}O$	190.0975	7	-0.5	reported
	HO		$C_9H_8N_2$	145.0760	7	-4.3	
	HU		$C_7H_6N_2$	119.0604	6	0.2	
	CH ₃		C_6H_7N	94.0651	4	3.2	
IMA	/	7.61	$C_{14}H_{14}Cl_2N_2O$	297.0556	8	0.4	
	o ci		$C_{11}H_8Cl_2N_2O$	255.0086	8	0.2	

			$C_9H_6Cl_2O$	200.9868	6	-1.7	
			$C_7H_{\underline{64}}Cl_2$	158.9763	5	-3.0	
			$C_6H_8N_2$	109.0760	4	5.3	
IMA- 257	он сі	6.20	$C_{11}H_{10}Cl_2N_2O$	257.0243	7	0.8	Sciex (95.5)
			$C_8H_6Cl_2O$	188.9868	5	-0.2	(Rodríguez-
	N.		$C_8H_4Cl_2$	170.9763	6	-2.8	<u>Cabo et al.,</u> 2018: Santiago
	CI		C ₈ H ₅ ClO	153.0102	6	-0.5	$\frac{2010, 5411420}{2013}$ et al., 2013)
	N		C7H5Cl	125.0153	5	3.6	[35]
			$C_3H_4N_2$	69.0447	3	4.5	
IMA-331	ŎН	6.01	$C_{14}H_{16}Cl_2N_2O_3$	331.0610	8	0.5	(Rodríguez-
	HO		$C_{11}H_8Cl_2N_2$	239.0137	8	-2.2	Cabo et al.,
	ç		$C_{11}H_7ClN_2$	203.0371	9	0.2	2018; Santiago
			$C_7H_4Cl_2$	158.9763	5	-1.1	<u>(35)</u>
I	CI		$C_3H_4N_2$	69.0447	3	3.7	
IMA-188	Ň// ÇI	9.18	$C_8H_7Cl_2N$	188.0028	5	0.4	(Rodríguez-
			C ₈ H ₇ ClN	153.0345	5	3.0	Cabo et al.,
	NH L		C_8H_6N	117.0578	6	2.0	<u>2018) [33]</u>
	° CI		C_7H_6	91.0551	5	9.6	
IMA-273	\	7.40	$C_{12}H_{14}Cl_2N_2O$	273.0556	6	0.0	(Rodríguez-
			$C_9H_8Cl_2N_2$	215.0137	6	1.0	$\frac{\text{Cabo et al.}}{2018}$
ļ			$C_8H_7Cl_2N$	188.0028	5	-6.5	<u>2018) [ээ</u>]
	CI		$\mathbf{C}_{11}\mathbf{H}_4\mathbf{\Theta}$	153.0340	10	0.5	
			<u>C₈H₆ClN</u>	<u>152.0262</u>	<u>6</u>	<u>0.3</u>	
			C_8H_6N	117.0573	6	-1.0	
IMA-274		9.21	$C_{12}H_{13}Cl_2NO_2$	274.0396	6	-5.1	(Rodríguez-
			C ₉ H ₇ Cl ₂ NO	215.9977	6	0.1	Cabo et al.,
Į	ŤŢĮ		$C_8H_7Cl_2N$	188.0028	5	0.8	<u>2018) [ээ</u>]
	CI		$C_8H_6Cl_2$	172.9919	5	1.0	
			<u>C₈H₆ClN</u>	<u>152.0262</u>	<u>6</u>	<u>0.9</u>	
			C_8H_6N	117.0578	6	2.0	
IMA-329	OH	6.71	$C_{14}H_{14}Cl_2N_2O_3$	329.0454	8	0.8	Not previously
	OH		$\underline{C_{11}}\underline{H_8}\underline{Cl_2}\underline{N_2}$	<u>239.0137</u>	<u>8</u>	<u>0.7</u>	reported
			$\underline{C_{11}}\underline{H_7}\underline{ClN_2}$	<u>203.0373</u>	<u>4</u>	<u>1.2</u>	
			$C_8H_6Cl_2O$	188.9868	5	-1.8	
			$C_7H_{\underline{64}}Cl_2$	158.9763	4	-3.0	
	CI		C ₈ H ₅ ClO	153.0102	6	-8.3	
			$C_7H_{\frac{75}{2}}Cl$	125.0153	4	-0.4	
IMA-313		6.78	$C_{14}H_{14}Cl_2N_2O_2$	313.0505	8	0.0	Not previously
	OH CI		$C_{11}H_8Cl_2N_2O_2$	271.0036	8	4.5	reported
	N N I		$C_{12}H_{11}ClN_2O_2$	251.0582	8	5.3	
	Ť Į Į		$C_8H_{11}Cl_2N$	192.0341	3	-4.3	
	CI		$C_8H_6Cl_2O$	188.9868	5	-1.3	
			$C_7H_4Cl_2O$	174.9712	5	5.2	

^a Score in percentage indicated by the MS library.









1 Figure captions

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