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Decline of Pesticide Residues from Barley to Malt

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Abstract

The fate of dinitroaniline herbicides (pendimethalin and trifluralin), organophosphorous insecticides (fenitrothion and malathion), and pyrimidine (nuarimol) and triazole (myclobutanil and propiconazole) fungicides from barley to malt has been determined. Several samples for residue analysis were taken after each stage of malting (steeping, germination, and kilning). Pesticide residues analysis were carried out by GC/ITMS in SIM mode. Pesticides decline along the process although in different proportions. The carryover of residues after steeping was 45-85%. A good correlation ($r>0.92$) was observed between percentages removed after steeping and the P_{OW} values of pesticides. The amount remaining after malting ranged from 13 to 51% for fenitrothion and nuarimol, respectively. Steeping was the most important stage in the removal of pesticide residues (52%) followed by germination (25%), and kilning (drying and curing, 23%). During malt storage (3 months) the fall in pesticide residues was not significant. Applying the standard first-order kinetics equation ($r>0.95$), the half-lives obtained for the pesticides during malt storage varied from 244 to 1,533 days for myclobutanil and nuarimol, respectively.

Keywords: *Barley, malt, malting, malt storage, pesticide residues.*

Introduction

Brewing is the production of alcoholic beverages through fermentation. This is the method used in beer production, although the term can be used for other drinks. Four raw materials are required for beer production: barley, hops, water and yeasts. The quality of these raw materials has a decisive influence on the quality of the final product (Kunze, 2004).

Because of their high content of starch and storage proteins, barley grains represent an attractive source of nutrients for insects and microbial pathogens. The vulnerability of the grain to insect and pathogen attack would be expected to increase during germination, when amino acids, fermentable carbohydrates, nitrogenous bases, and other degradation products of reserve polymers accumulate in the starchy endosperm (Fincher and Stone, 1993). In consequence, several pests and diseases can attack cereal crops, and good weed control is essential if the crop is to make efficient use of moisture, and to prevent weed seeds from contaminating the harvest (Domínguez, 2004). Additionally, barley with a moisture content of above 14 % may be attacked by fungi during storage especially by species *Aspergillus* and *Penicillium*. Most fungi produce secondary metabolites, some of which cause gushing, a very severe quality defect where the beer spontaneously gushes from a bottle on opening. It is therefore important that malting barley is stored under conditions which prevent fungal growth (DMG, 1999). For this reason, pesticides are widely used in different combinations at many stages of cultivation and also during post-harvest storage. The problem is that traces of these pesticides may remain in the beer produced from the treated ingredients, although the residues may also come from the soil itself, and the water used.

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2 65 Malt is germinated barley. Other cereals, such as sorghum or wheat,
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4 66 can be malted, but these processes are less common. Common malting
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6 67 operations involve four basic stages: barley intake, drying and storage;
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8 68 steeping; germination; and kilning (Bamforth and Barclay, 1993). Drying
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10 69 enhances the storage properties of barley. It is necessary only in those
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12 70 climates where barley would otherwise be put into storage at moisture
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14 71 content in excess of 16%. The process commences with the steeping of
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16 72 barley in water to achieve a moisture level sufficient to activate metabolism
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18 73 in the embryonic and aleurone tissues, leading in turn to the development
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20 74 of hydrolytic enzymes. Germination is generally targeted to generate the
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22 75 maximum available extractable material by promoting endosperm
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24 76 modification through the development, distribution, and action of enzymes.
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26 77 Finally, after a period of germination sufficient to achieve even modification,
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28 78 the "green malt" is kilned to arrest germination and stabilize the malt by
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30 79 lowering moisture levels, typically to less than 5%.
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37 80 During malting, some residues of pesticides having $\log K_{ow} > 2$ (as $\log$
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39 81 P) can remain on malt indicated by some authors (Miyake et al. 2002;
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41 82 Collins and Armitage, 2006). If pesticide residues are present on the malt
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43 83 they can pass into the wort after mashing and boiling in different
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45 84 proportions, depending on the process used, although it should be noted
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47 85 that the removal of material in the form of 'trub' and spent grains tends to
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49 86 reduce the level of pesticides, which are often relatively insoluble in water
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51 87 (Hack et al. 1997; Miyake et al. 1999; Navarro et al. 2005, 2006).
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53 88 Therefore, it is important to ascertain the contamination load of barley and
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55 89 how pesticide residues evolve during the malting process. The ingredients
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57 90 used for brewing must not be allowed to act as a source of unacceptable
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59 91 contaminants that represent a risk for the beer consumer and animals.
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According, the objective of this research was to know the fate of several pesticides commonly used on barley from this cereal to malt for assist maltsters in preventing the occurrence of pesticide levels higher than those allowed.

Material and Methods

Pesticides and reagents. Pesticide standards with purity higher than 98% were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Table 1 shows the pesticides used and their main physicochemical characteristics (Tomlin, 2003). Stock standard solutions of 100 µg/ml were prepared by exact weighing and dissolving in acetone and finally stored in the dark at 4 °C. Working standard solutions were prepared freshly by dilution in the same solvent. Solvents for pesticide residue analysis (*n*-hexane, dichloromethane, and acetone) were supplied by Scharlau Chemie S.A. (Barcelona, Spain). Helium (99.99% purity) was purchased from Abelló Linde S.A. (Barcelona, Spain).

Raw material and malting process. Barley (11% moisture), two-row spring malting barley (*Hordeum distichum*) was obtained from the Brewers Estrella de Levante Fábrica de Cerveza S.A. (Murcia, Spain). Barley grains (100 g, n=3), once spiked with the pesticides (0.2-1 mg/kg) were subjected to the process according to the common malting operations (steeping; germination; and kilning) after evaporation of the spiking solvent (3 h). The process commences with the steeping of barley by water immersion (300 ml at 15°C) followed by aeration until the water content of the grain reaches to achieve a sufficient moisture level (42-44%). The water used for the steeping process (EC -dS m⁻¹ at 25 °C-, 0.93; pH, 8.22; Dissolved Solids (mg/L), 771.2; Alkalinity (mg/L), 184.3; Trihalomethanes

($\mu\text{g/L}$), 45.2 and pesticides below detection limit) was obtained from the municipal network. After approximately 24 h, the first visible sign of germination was the appearance of the root, as a white "chit". The grains were then transferred to malting beds where germination was performed at $15\pm 1^\circ\text{C}$ over a period of around four days. The speed of germination was controlled by temperature and aeration of the malt bed, while moisture content was maintained by spraying. The grain bed was regularly turned to prevent grains matting together. Finally, after a period of germination, the "green malt" was kiln dried from 50 to 85°C over 24 h in a forced flow of hot air to arrest germination and stabilize the malt by moisture level of 4-5% and then the malt was "cured" increasing temperature to $90\text{-}100^\circ\text{C}$ and reducing the speed of air flow. At the end of kilning the malt was cooled to arrest colour formation and to stabilize enzyme levels. Finally, the brittle malt rootlets were separated and the rest milled. Figure 1 shows the experimental procedure for malting process.

Samples and sampling methods. Different samples (barley grains, steeped grains, steeping water, green malt, dried malt, and cured malt) were taken during malting process (Figure 1). Bearing in mind the yields obtained after the different elaboration steps, the total residual amount present in each vessel was calculated, as shown in Table 2. The total amount present in barley grains (100%) was considered to be the starting point to study the dissipation of the pesticides. To know the dissipation of pesticide residues from stored malt four samples (0, 30, 60, and 90 days) were taken, starting the study when the cured malt was cooled and milled.

Extraction procedures. Water samples (20 ml) were placed in a 100 ml glass flask with hermetic closing, with 40 ml of *n*-

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2 144 hexane+dichloromethane (1+1, v/v) and 2 g of anhydrous NaCl. The flasks
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4 145 were introduced into an ultrasonic bath (Ultrasons 613, Selecta) with
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6 146 distilled water for 10 min and the liquid was passed through Phase
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8 147 Separator Paper (Albet 302, 15 cm Ø). Finally, the organic phase was
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10 148 concentrated by rotary vacuum evaporation (35 °C) to dryness and
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12 149 redissolved in 10 ml of acetone and injected into the GC/MS system in the
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14 150 conditions specified previously. For barley and malt, samples (5 g) were
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16 151 homogenized at 8,000 rpm for 5 min in a high-speed electric mixer
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18 152 (Polytron-Aggregate, Kinematica) with 10 ml of distilled water and 20 ml of
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20 153 n-hexane. After this time, 20 ml of dichloromethane were added and the
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22 154 mixture was centrifuged for 10 min at 3,000 rpm. The liquid phase was
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24 155 quantitatively transferred to a glass funnel provided with a phase separator
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26 156 paper. After filtration, the organic phase was concentrated through rotary
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28 157 vacuum evaporation to dryness and redissolved in 10 ml of acetone
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35 **Pesticide analysis.** A Finnigan Trace Ultra GC (Thermo Electron
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37 159 Corporation, USA) with split-splitless injector, AS2000 Autosampler and
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39 160 directly coupled by a transfer line to a Finnigan Polaris Q Ion Trap MS
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41 161 (Thermo Electron Corporation) was used. Updated Dell ChemStation
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43 162 application with Xcalibur™ software was used to control and automate many
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45 163 features of the GC/ITMS system. The Rtx®-5MS (Restek, USA) fused silica
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47 164 capillary column (30 m x 0.25 mm x 0.25 µm film thickness) contained 5 %
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49 165 diphenyl, 95 % dimethyl polysiloxane as liquid-phase. The oven
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51 166 temperatures were programmed as follows: column oven: initial 70 °C, hold
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53 167 1 min, programming rate 10 °C/min (70 to 160 °C), hold 2 min; 5 °C/min
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55 168 (160 to 250 °C), hold 0 min; 30 °C/min (250 to 280 °C) and hold 4 min at
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57 169 280 °C for a total run time of 35 min. The injector and MS transfer line were
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60 170 operated at 230 and 275 °C, respectively. The IT operation conditions were:

acquisition mode Sequential FS (50-400 m/z) & SIM range mode (exact mass ± 0.4 amu), multiplier 1788, ion source temperature 230 °C, emission current 250 μ amp, AGC 50. The carrier gas was He at 1.2 ml min⁻¹. The sample (2 μ l) was injected in the splitless mode (60 s). Identification of the pesticides was based on the retention time of the target ion and on the three qualifier-to-target ion ratios. The qualifier-to-target ion percentage was then determined by dividing the abundance of the selected qualifier ion (Q) by the target ion (T) and multiplying by 100. Quantitation was achieved by linear regression against calibration standards (2-3,000 ng/mL) and using the GC ChemStation software.

Results and Discussion

Analytical determination. Pesticides were identified by their R_t values and their qualifier-to-target abundance ratios. Isomers of propiconazole and nuarimol are not well distinguished by GC-MS. The criteria for identification were based on the retention times and the target-to-qualifier ion ratios using their respective m/z values. Linear calibration curves were obtained for all the pesticides in different concentration ranges (2-3000 ng/mL). The correlation coefficients derived from the linear regressions were higher than 0.99, with strong correlation between concentration and area for all the studied compounds. The interday repeatability was calculated using the relative standard deviation (RSD) for 10 successive injections of a mixture of the pesticides and was in the range of 3.8-8.1%. Detection limits (LODs) were calculated using signal-to-noise ratio of 3 for all the investigated compounds and ranged from 0.2-8 pg for trifluralin and malathion, respectively.

Recoveries from spiked samples varied from 81.2 to 113.5% with RSD from 3.6 to 8.7% and a mean recovery in excess of 89% in all cases. The slopes of the calibration graphs with the standards directly prepared in 2,2,4-trymethyl pentane/toluene (1/1, v/v) and the standard addition calibration graphs obtained from the different samples were similar, confirming the absence of any matrix effect.

The limit of quantitation (LOQ), defined as the lowest fortification level attempted, was lower than 5 ng/g with the exception of malathion (14 ng/g). These limits are, in all cases, below the maximum residue limits (MRLs) established in barley by the Spanish legislation for the studied compounds (BOE, 2004).

Removal and transfer of pesticide residues from barley to malt. Table 2 shows the amount of pesticide residues recovered from the different samples. In all cases, RSDs were lower than 11%. The percentages removed after each stage of the process were calculated against the residue level on grains at the end of the previous stage. As can be seen in Table 2, steeping reduced residue levels significantly; the lowest percentages removed at the end of the steeping process correspond to dinitroaniline herbicides, pendimethalin (10%) and trifluralin (15%). Both are hydrophobic pesticides because their high log P_{ow} (>5) and low solubility (0.2-0.3 mg/l). In consequence, a low proportion of their residues were removed with the steeping water. Regarding to the organophosphorus pesticides, malathion has the lower log P_{ow} (2.75) and the higher water solubility (145 mg/l) of the all studied pesticides. For this, 55% of its residues were removed from the barley grains after steeping while 48% of fenitrothion residues (log P_{ow} = 3.5) were removed in this stage. Others

have shown carry-over of 43% for fenitrothion after steeping process while other organophosphorus insecticide as phentoate remains in lower proportion (27%) as indicated by Miyake et al (2002). On the contrary, other insecticides of the same family as pirimiphos-methyl remain as a high proportion (90%) after steeping (Collins and Armitage, 2006). Fungicide residues were removed from the barley grains (after steeping) in proportions ranging from 30-41% which it is expected bearing in mind their respective coefficients between *n*-octanol and water (P_{ow} values). Miyake et al (2002) found higher percentages of elimination for some azole fungicides, concretely 50, 62 and 76% for propiconazole, triflumizole, and triadimefon, respectively. The results obtained by us are supported by the good correlation ($r>0.92$) between amounts removed after steeping and log P_{ow} of the pesticides used in this study as can be seen in Figure 2. The carryover of hydrophilic pesticides (low log P_{ow}) such as malathion was lower while carryovers of hydrophobic pesticides (pendimethalin and trifluralin) were higher. Miyake et al. (1999) suggest that brewers should pay attention to the residues of hydrophilic pesticides on malt with P_{ow} values <4 because they can be carried over into beer being of special interest the steeping stage of the malting process. The same authors (Miyake et al. 2002) showed that pesticides with log $P_{ow} >2$ can remain on malt. Therefore, the control of pesticides with P_{ow} values ranging from 2-4 must be very important for maltster and brewers.

On the other hand germination was also an important stage on the removal of several pesticide residues. Only for trifluralin (18%) and nuarimol (11%) no more than 20% of their residues were eliminated. Similar findings were found by Miyake et al (2002) working with several insecticides and fungicides. Regarding drying, this stage does not reduce

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2 249 residues in a great extent. Only fenitrothion residues significantly declined
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4 250 (32%) while the removal of the other compounds varied from 6-17%. Some
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7 251 authors (Miyake et al. 2002) show that most of the residues on germinated
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9 252 grain were lower than those on kilned malt which is attributed to the
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11 253 inhibition of the extraction by the moisture present in germinated grains. In
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13 254 our case, germinated grains were air-dried (30 °C) to constant weigh.
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16 255 Finally, curing removed fenitrothion and propiconazole residues in
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18 256 proportions of 39% and 23%, respectively while the losses of the other
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20 257 pesticides ranged from 2-16%. Figure 3 shows the total amounts of
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22 258 pesticide residues removed during the different stages of malting. As can be
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25 259 observed the most important stage in the removal of pesticide residues was
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27 260 steeping (52%) followed by germination (25%), and kilning (drying and
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29 261 curing, 23%)..

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33 262 **Loss of pesticide residues from stored malt.** Several models
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35 263 (Timme et al. 1986; Morton et al. 2001) are used to describe the decay of
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37 264 pesticides in different matrices. Probably, the most commonly used model
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40 265 to describe loss of grain protectants is the following equation, where R_t is
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42 266 the residue at time t , R_0 is the residue at time zero and K is the rate
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45 267 constant (Desmarchelier, 1977, 1978):

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$$\ln R_t = \ln R_0 - Kt$$

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51 269 To know the rate of loss of residues in the stored malt, the
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53 270 experimental data (Table 3) were fitted to the above model. Table 4 shows
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55 271 the values derived from the fit. In all cases, there was a good linear
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57 272 correlation between $\ln R_t$ and time ($r \geq 0.95$). Additionally, a perfect
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59 273 correlation ($r > 0.99$) between the analytical and theoretical concentration
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274 calculated (R_0) at 0 days was observed which indicates that the model is

valid. According to the calculated values for the constant rate (K) and half-lives time, the following dissipation rate was observed: myclobutanil> propiconazole> fenitrothion> trifluralin> pendimethalin> malathion> nuarimol.

Conclusions

As result of this research it can be concluded that residues of water soluble pesticides on barley tend to be eliminated in the greatest amount after steeping. Conversely, hydrophobic residues remain in steeped grain which it is supported by the good correlation that exists between the partition coefficients of the octanol-water values of the pesticides and the decline in concentration. Germination and kilning processes also contribute to reduce the residue content of malt although to a lesser extent. Finally, malt storage does not significantly reduce pesticide residues. Therefore, the maltsters should pay special attention to pesticide residues on barley, especially for triazole fungicides as propiconazole, which has been demonstrated to be a strong sterol biosynthesis-inhibiting compound (Navarro et al., 2007).

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Table 1

Principal physical-chemical characteristics of the studied compounds.

Common* and chemical (IUPAC) name	Chemical structure	Molecular formula	Molecular weight	log P _{ow}	Water solubility (mg/l)
Pendimethalin^H					
<i>N</i> -(1-Ethylpropyl)-2,6-dinitro-3,4-dimethylaniline		C ₁₃ H ₁₉ N ₃ O ₄	281.3	5.18	0.3
Trifluralin^H					
2,6-Dinitro- <i>N,N</i> -dipropyl-4-trifluoromethylaniline		C ₁₃ H ₁₆ F ₃ N ₃ O ₄	335.3	5.07	0.2
Fenitrothion^I					
<i>O,O</i> -Dimethyl <i>O</i> -(3-methyl-4-nitrophenyl) phosphorothioate		C ₉ H ₁₂ NO ₅ PS	277.2	3.50	14
Malathion^I					
Diethyl (dimethoxy thioxophosphorylthio) succinate		C ₁₀ H ₁₉ O ₆ PS ₂	330.3	2.75	145
Propiconazole^F					
(±)-1-([2-(2,4-Dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl)-1 <i>H</i> -1,2,4-triazole		C ₁₅ H ₁₇ Cl ₂ N ₃ O ₂	342.2	3.72	100
Myclobutanil^F					
2-(4-chloro-phenyl)-2-(1 <i>H</i> -1,2,4-triazol-1-ylmethyl)-hexanenitrile		C ₁₅ H ₁₇ ClN ₄	288.8	2.94	142
Nuarimol^F					
(±)-(2-Chlorophenyl)(4-fluorophenyl)-pyrimidin-5-yl)methanol		C ₁₇ H ₁₂ ClFN ₂ O	314.7	3.18	26.0

355 *: H: Herbicide; I: Insecticide; and F: Fungicide.

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Table 2

Mean amount (n=3) of pesticide residues recovered in the whole weight or volume from different samples and percentage remaining during malting.

sample	Mean (µg, as dry) ± RSD and % remaining													
	Pendimethalin		Trifluralin		Fenitrothion		Malathion		Myclobutanil		Nuarimol		Propiconazole	
Barley grains	22.1±6.2	100.0	16.5±4.7	100.0	57.0±8.6	100.0	60.0±3.3	100.0	82.2±2.9	100.0	72.0±5.5	100.0	96.6±8.2	100.0
Steeped grains	18.8±5.8	85.1	13.2±6.9	80.0	29.6±5.1	52.0	27.0±3.3	45.0	48.3±5.5	58.8	46.2±5.6	64.1	53.1±9.5	55.0
Steeping water	2.3±10.7	10.4	2.5±7.9	15.2	26.2±8.8	45.9	32.9±5.3	54.8	33.6±4.6	40.9	25.2±6.5	35.0	39.3±8.3	41.0
Green malt	14.9±6.7	67.4	10.8±9.5	65.5	17.6±4.6	30.9	12.3±4.6	20.5	34.5±8.3	42.0	40.8±9.9	56.7	41.2±6.8	42.6
Dried malt	12.3±9.4	55.6	9.6±4.7	58.2	11.9±2.9	20.9	10.2±8.2	17.0	31.6±2.9	38.4	36.9±8.1	51.5	38.5±6.2	39.8
Cured malt [†]	10.9±5.8	49.3	8.3±3.2	50.3	7.3±5.3	12.8	8.6±9.1	14.3	29.6±7.6	36.0	36.2±4.7	51.1	29.5±9.5	30.5

[†] After milling.

Table 3

Residual levels (n=3) found during malt storage.

sample	Mean $\pm$ RSD (ng/g)						
	Pendimethalin	Trifluralin	Fenitrothion	Malathion	Myclobutanil	Nuarimol	Propiconazole
<i>Milled malt</i>	109 $\pm$ 5.8	83 $\pm$ 3.2	73 $\pm$ 5.3	86 $\pm$ 9.1	296 $\pm$ 7.6	362 $\pm$ 4.7	295 $\pm$ 9.5
<i>Stored malt, 1 month</i>	104 $\pm$ 7.7	81 $\pm$ 10.5	67 $\pm$ 6.1	85 $\pm$ 7.6	274 $\pm$ 15.9	354 $\pm$ 6.6	272 $\pm$ 16.4
<i>Stored malt, 2 months</i>	103 $\pm$ 15.9	78 $\pm$ 8.5	66 $\pm$ 12.2	83 $\pm$ 13.8	246 $\pm$ 3.9	351 $\pm$ 3.4	251 $\pm$ 3.8
<i>Stored malt, 3 months</i>	101 $\pm$ 8.2	74 $\pm$ 6.6	62 $\pm$ 8.6	82 $\pm$ 6.9	231 $\pm$ 8.4	347 $\pm$ 9.8	245 $\pm$ 13.2

Table 4

Dissipation parameters for the pesticide residues during malt storage

Parameter	Pendimethalin	Trifluralin	Fenitrothion	Malathion	Myclobutanil	Nuarimol	Propiconazole
K (days ⁻¹)	7.9×10^{-4}	1.3×10^{-3}	1.7×10^{-3}	5.4×10^{-4}	2.8×10^{-3}	4.5×10^{-4}	2.1×10^{-3}
r	0.951	0.987	0.969	0.996	0.995	0.977	0.977
R_0 (ng/g)	108	84	72	86	296	361	291
$t_{1/2}$ (days)	873	546	413	1291	244	1533	325

Figure Captions

Figure 1: Scheme showing four primary steps of malting process and sample points (*) for pesticide analysis.

Figure 2: Correlation between percentages of pesticides removed ($n=3$) after steeping and their $\log P_{ow}$ values (solid line is 95% confidence interval and dash line 95% prediction interval).

Figure 3: Mean amounts removed ($n=3$) of total pesticide residues into the different stages of malting (error bars are 95% confidence intervals).

Figure 1

Figure 2

Figure 3