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# Food safety review of UK cereal grain for use in malting, milling and animal feed

By

E. D. Baxter, N. Byrd and I. R. Slaiding

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Campden BRI, Centenary Hall, Coopers Hill Road,

Nutfield, Surrey RH1 4HY

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# 1. Abstract

This project aimed to investigate the occurrence of key contaminants in UK-grown wheat, barley and oats in order to demonstrate safety for use for milling, malting and animal feed, and the extent of compliance with legal and guideline limits. Samples of each type of grain were collected from harvests 2005, 2006, 2007 and 2008, either immediately after harvest, or after a period of storage. Relevant contaminants were identified by regular "horizon scanning" of official publications and the scientific and agricultural literature, together with a steering committee consisting of representatives of the relevant Trade Associations, the HGCA and scientists from the contract laboratories involved in the project. The contaminants selected were mycotoxins (aflatoxins, Fusarium toxins and ochratoxin A), pesticides, including some growth regulators and desiccants, and certain heavy metals.

Analytical results showed that the overwhelming majority of samples complied with legal and guideline limits. Levels of heavy metals and pesticides were in most cases well within legal limits, and did not vary substantially from season to season. Aflatoxins were absent from all samples tested. The other storage mycotoxin investigated, ochratoxin A, although quite common in most sample types, was generally detected only at low concentrations and did not vary significantly from year to year, suggesting that mould growth and toxin synthesis was being adequately controlled, presumably as a result of good storage practice. Fusarium mycotoxins, which are produced during growth in the field, showed significant seasonal variations, overlying what appears to be an increasing trend over the years surveyed. This observation is complicated by the fact that the earlier years of the project were dry while the later years were wet, so a definitive conclusion cannot be drawn. It is certain, however, that the prevalence of certain Fusarium toxins (particularly T-2 and HT-2 toxins), has increased in the UK.

The horizon scanning exercise identified polycyclic aromatic hydrocarbons and masked mycotoxins as emerging issues for cereals, and these are being investigated in other HGCA-funded projects (an extension project to RD 2004-3100 for PAHs and RD 2008-3572 "Food safety review of UK cereal grain for use in malting, milling and animal feed" for masked mycotoxins).

## 2. Project Summary

The aim of this project was to investigate the occurrence of key contaminants in UK-grown wheat, barley and oats in order to demonstrate safety for use for milling, malting and animal feed, as well as the extent of compliance with legal and guideline limits. Throughout the project a "horizon scanning" exercise was carried out, looking at legislation, publications from official bodies such as the UK Food Standards Agency, the European Food Safety Authority (EFSA), and the World Health Organisation's Joint Expert Committee on Additives and Contaminants (JECFA), as well as the scientific, agricultural and medical press, in order to identify emerging issues and trends. The contaminants investigated were selected on the basis of this literature survey, in consultation with a steering committee consisting of representatives of the relevant Trade Associations (the Agricultural Industries Confederation (AIC); the National Association of British and Irish Millers (nabim); the Maltsters Association of Great Britain (MAGB)) together with the HGCA and scientists from the contract laboratory involved in the project. Samples of milling and feed wheat, malting and feed barley, feed oats, wheatfeed, oatfeed and pelleted malt culms were collected from harvests 2005, 2006, 2007 and 2008, either immediately after harvest, or after a period of storage. Contaminants sought included;

- Mycotoxins – aflatoxins, ochratoxin A, Fusarium toxins
- Pesticides – storage insecticides, growth regulators and desiccants
- Metals/metalloids – aluminium, arsenic, cadmium, copper, lead, mercury

The results showed that the overwhelming majority of samples tested were compliant with legal and guideline limits, indicating that UK-grown cereals provide a safe source of raw materials for the milling, malting and animal feed industries.

Of the twenty-two pesticides detected, only three were detected with any regularity. These were the storage insecticide pirimiphos-methyl, the growth regulator chlormequat and the desiccant glyphosate. All samples were well below legal limits for food and feed grain. There was no consistent trend in residues from year to year except for glyphosate, where, as expected, incidence was noticeably higher in wet seasons. However, even in the wettest year, the highest residue detected was less than 10% of the EU's Maximum Residue Limit (MRL).

Levels of metals and arsenic were relatively low in all samples with the exception of one sample of wheat which exceeded the legal limit for cadmium. There was little variation in levels from year to year.

Aflatoxin was not detected in any samples, supporting the long-held observation that UK climatic conditions are not conducive to the formation of this mycotoxin in cereals in the field.

The storage mycotoxin ochratoxin A was relatively common in all cereal types but concentrations were low in most whole grain samples, with no obvious seasonal variations. This suggests that grain storage is in general well controlled. Occasional samples of both wheat and barley were found to exceed legal limits: on re-sampling these frequently gave much lower results. Heterogeneity of mould infection, and consequently of mycotoxin contamination, is a well–recognised problem, particularly with bulks of cereals, and the official sampling method (which involves taking 10kg samples, themselves consisting of an aggregate of a defined number of several subsamples) was designed to counteract this. The malting barley/malt pairs included in this project were sampled according to this official method, but discrepancies between repeat samples were still encountered, indicating that even the rigorous official sampling method does not entirely overcome the problem of heterogeneity.

Unlike the storage mycotoxins, levels of Fusarium toxins (particularly deoxynivalenol (DON), T-2 and HT-2 toxin and zearalenone (ZON)) varied significantly from year to year, with DON and ZON being higher in wet years. Levels of both of these mycotoxins were higher in wheat than in barley or oats, and although most samples complied with legal limits for food grains, and guideline limits for feed materials, in wet years some samples of both milling and feed wheat exceeded relevant guidelines for ZON in food grains or in complete feedstuffs for sensitive species such as pigs. Overlying the seasonal variations was an apparent trend for incidence of Fusarium toxins in general to increase over the period of the project. This was particularly clear for DON and ZON. However, the observation is complicated by the fact that the earlier years of the project were dry while the later years were wet, so a definitive conclusion cannot be drawn.

T-2 and HT-2 have historically not been found in UK-grown wheat and barley. However, data from earlier HGCA projects shows these toxins appearing around 2004 and becoming increasingly prevalent in 2005 and 2006. This has been linked with the appearance in Europe of a newly identified species of Fusarium, *Fusarium langsethiae*, which can colonise wheat, barley and oats. Since then, levels of T-2 and HT-2 have declined somewhat in the UK, although not in the rest of the EU. Since this period has coincided with wet weather and high levels of other, more aggressive Fusarium species which produce predominantly DON, the longer term prognosis for levels of T-2 and HT-2 in UK cereals remains unclear. The data gathered during this project have been presented to the European Commission regularly at their Fusarium Forum, held at the beginning of each year in Brussels. The Commission has repeatedly stated its intention to set legal limits for T-2 and HT-2 toxins in cereals, but, in the light of the available evidence (from this project together with that presented by other European researchers), legislation has again been postponed because of the lack of certainty as to what achievable levels will be in the EU. It is evident that continued monitoring of these mycotoxins will remain a priority.

The potential presence of masked mycotoxins in raw and processed cereals has recently emerged as an issue in the EU. The term “masked mycotoxins” refers to mycotoxins which are bound to other residues – mainly glucose or acetyl residues – and are therefore not detected by conventional analyses. Most studies to date relate to masked DON species, since these are the only ones where reference compounds are available to allow accurate analysis and quantification, but there is no reason why other mycotoxins should not also occur in a bound form. The concern is that these masked mycotoxins could provide a reservoir of undetected toxin which is converted to the free form during food processing or even in the human body after consumption. This project has provided substantial data for acetylated DON, confirming that it can occur in UK grain, but at relatively low levels compared with those of the free DON. However, analytical methods for DON bound to glucose were not available for use within this current project. Suitable methods have now been developed and will be used within a subsequent HGCA project (RD 2008-3572) to investigate DON-3-Glc in UK cereals. This project will also develop analytical methods for ergot alkaloids and investigate their presence in UK-grown cereals, in response to concerns expressed by expert EC Committees about an apparent

increase in the incidence of ergot infestations in food and feed cereals in Europe and the inadequacy of current methods which only measure whole sclerotia rather than the alkaloids themselves.

Another emerging issue identified by this project is that of polycyclic aromatic amines (PAHs). PAHs are a large group of structurally related compounds, many of which are carcinogenic to animals, which can be formed when organic material is burnt. JECFA and EFSA have suggested that drying processes could contribute to the loading of PAHs in foodstuffs and that the use of direct driers should therefore be avoided. There is very little reliable data on the occurrence of PAHs in UK cereals, and this has therefore been investigated in an extension to this current project (RD 2004-3100) and will be reported separately.

# 3. Project Report

## 3.1 Introduction

The overall aim of this project, which began in January 2006 and finished at the end of June 2009, has been to support and maintain the wholesomeness and acceptability in domestic and export markets of UK-grown cereal grain for use in the malting, milling and animal feed industries. Its specific objectives were:

- To monitor the incidence of key contaminants in UK-produced cereals destined for malt, milling and animal feed in order to demonstrate the safety and legal compliance of UK-produced cereals and cereal products and to highlight any problem areas.
- To identify any emerging issues or legislation which could impact on the safety of cereal-based foods or on their acceptability in key markets. Samples of known provenance will be stored to provide an archive of appropriate samples for use in reacting to emerging cereal contaminant issues**.**
- To provide robust data on the incidence and concentration of key contaminants in UK-grown cereals which can be used both to inform discussions on proposed legislation and to also to assure customers of the wholesomeness of UK-grown cereals and cereal products.

The project builds on the foundations provided by earlier HGCA projects *(Baxter, 2003, 2006a, b; Salmon, 2006),* which have established systems to maintain the wholesomeness of UK cereals for key markets. In addition to "horizon scanning" to identify emerging issues or trends which might impact on the safety or acceptability of UK-grown cereals for key markets, monitoring systems have been set up in order to provide data on levels of a range of potential contaminants in UK malting barley, malt, milling wheat and cereal-based animal feed materials. A significant database relating to food safety for UK cereals has now been built up, covering 40 contaminants in total (13 mycotoxins, 23 pesticides and 4 metals), and extending from the 1999 harvest to the 2008 harvest. Over this period, definite trends in the occurrence of mycotoxins, particularly those produced by *Fusarium* moulds, have become evident. The current project, which ran from January 2006 to June 2009, has therefore focused particularly on the *Fusarium* mycotoxins.

The information obtained from project RD 2004-3100 has been made available to growers, processors and their customers (for example, via the HGCA and the MAGB web sites) and to government, including the UK's Pesticides Safety Directorate (now a part of the Chemicals Regulation Directorate) and the FSA, as well as the European Commission.

## 3.2 Materials and Methods

### 3.2.1 Samples

Samples of (1) commercial milling wheat, feed wheat, wheatfeed; (2) malting barley, malts prepared from those barleys, malt culm pellets and (3) feed oats and oat feed were taken by the companies and sent to Campden BRI for analysis. Sampling and analysis was overseen by a steering committee drawn from the relevant trade associations (AIC, MAGB and nabim) together with representatives from HGCA and Campden BRI. This committee met in August each year and decided on the analytes to be tested for in samples from the coming harvest based on results from previous years and risk factors such as the prevailing weather conditions. Two main tranches were collected each year;

(a) Immediately after harvest (September): these were usually analysed for *Fusarium* toxins, ochratoxin A and glyphosate. Selected samples were also analysed for heavy metals
(b) After 6 months storage (March): these were analysed for ochratoxin A, Aflatoxins (selected feed samples only) and storage pesticides.

However, there were some exceptions:

- From 2007 harvest onwards, the malting barley/malt pairs were collected in October after only 2 months storage. This was to allow the results to be included in an EU-wide survey of malting barleys and malts reported to the Commission's Fusarium Forum, held each year around January-February. These samples (10 kg each) were collected using the recommended sampling protocols for official surveillance *(EC, 2006).*
- An additional tranche of milling wheat was collected in January and analysed for ochratoxin A only.
- Not all samples in each tranche were tested for all analytes specified. The number to be tested was agreed by the steering group, based on the risk of that analyte occurring in that sample type.

- Malt culm pellets were not collected in 2008.

A summary of the samples collected is shown in Table 1.

**Table 1. Samples collected**

| Year | Type | Date collected | No. of samples | Analytes sought |
|---|---|---|---|---|
| **2005 stored** | Malting barley | Mar 06 | 18 | Fus. tox., OA, Pesticides |
| | Malt | Mar 06 | 18 | Fus. tox., OA, Pesticides |
| | Feed barley | Mar 06 | 23 | OA, Pesticides |
| | Malt culm pellets | Mar 06 | 6 | OA |
| | Milling wheat | Jan 06 | 54 | OA, Pesticides |
| | Feed wheat | Mar 06 | 24 | OA, Pesticides, Metals |
| | Wheat feed | Mar 06 | 4 | OA, Afla., pesticides, Metals |
| | Feed oats | Mar 06 | 8 | OA, Pesticides |
| | Oat feed | Mar 06 | 8 | OA, Pesticides |
| **2006 fresh** | Malting barley | Sept 06 | 20 | Fus. tox., OA, Growth regs. |
| | Feed barley | Sept 06 | 8 | Fus. tox., |
| | Milling wheat | Sept 06 | 40 | Fus. tox., OA |
| | Feed wheat | Sept 06 | 10 | Fus. tox., |
| | Wheat feed | Sept 06 | 11 | Fus. tox., |
| | Feed oats | Sept 06 | 7 | Fus. tox., |
| | Oat feed | Sept 06 | 6 | Fus. tox., |
| **2006 stored** | Malting barley | Mar 07 | 20 | Fus. tox., OA |
| | Malt | Mar 07 | 20 | Fus. tox., OA |
| | Feed barley | Mar 07 | 18 | OA, Pesticides |
| | Malt culm pellets | Mar 07 | 6 | Fus. tox., OA, Afla., |
| | Milling wheat | Jan 07 | 47 | OA, Pesticides |
| | Milling wheat | Mar 07 | 56 | OA, Pesticides |
| | Feed wheat | Mar 07 | 30 | OA, Pesticides, Fus. tox. |
| | Wheat feed | Mar 07 | 7 | OA, Pesticides, Fus. tox |
| | Feed oats | Mar 07 | 10 | OA, Pesticides |
| | Oat feed | Mar 07 | 9 | Oa, Pesticides, Afla. |
| **2007 fresh** | Malting barley | Sept 07 | 40 | Fus. tox., OA, Glyphosate |
| | Feed barley | Sept 07 | 11 | Fus. tox., Glyphosate |
| | Malt culm pellets | Sept 07 | 6 | Fus. tox., OA, Afla., Pesticides |
| | Milling wheat | Sept 07 | 50 | Fus.tox., Glyphosate, Metals |
| | Feed wheat | Sept 07 | 13 | Fus.tox., Glyphosate, Metals |
| | Wheat feed | Sept 07 | 15 | Fus.tox., Glyphosate, Metals |
| | Feed oats | Sept 07 | 11 | Fus. tox. |
| | Oat feed | Sept 07 | 9 | Fus.tox. |
| **2007 stored** | Malting barley | Oct 07 | 20 | Fus. Tox., OA |
| | Malt | Oct 07 | 20 | Fus. Tox., OA |
| | Feed barley | Mar 08 | 25 | OA, Pesticides |
| | Milling wheat | Jan 08 | 51 | OA |
| | Milling wheat | Mar 08 | 53 | OA, Pesticides |
| | Feed Wheat | Mar 08 | 21 | OA, Pesticides |
| | Wheat feed | Mar 08 | 8 | OA, Pesticides |
| | Feed oats | Mar 08 | 7 | OA, Pesticides |
| | Oat feed | Mar 08 | 7 | OA, Pesticides |

**Table 1 (continued). Samples collected 2008 harvest**

| Year | Type | Date collected | No. of samples | Analytes sought |
|---|---|---|---|---|
| **2008 fresh** | Malting barley | Sept 08 | 36 | Fus. Tox., Glyphosate, Metals |
| | Feed barley | Sept 08 | 12 | Fus. Tox., Glyphosate |
| | Milling wheat | Sept 08 | 50 | Fus. Tox., OA, Glyphosate |
| | Feed wheat | Sept 08 | 11 | Fus.tox., Glyphosate |
| | Wheat feed | Sept 08 | 18 | Fus. Tox., |
| | Feed oats | Sept 08 | 9 | Fus. Tox., |
| | Oat feed | Sept 08 | 9 | Fus. Tox., |
| **2008 stored** | Malting barley | Oct 08 | 19 | OA, Pesticides |
| | Malt | Oct 08 | 19 | OA, Pesticides |
| | Feed barley | Mar 09 | 26 | OA, Pesticides |
| | Milling wheat | Jan 09 | 52 | OA |
| | Milling wheat | Mar 09 | 50 | OA, Pesticides |
| | Feed wheat | Mar 09 | 40 | OA |
| | Wheat feed | Mar 09 | 10 | OA |
| | Feed oats | Mar 09 | 8 | OA, Pesticides |
| | Oat feed | Mar 09 | 10 | OA, Pesticides |

### 3.2.2 "Horizon scanning" for emerging issues

Scientific literature and government publications in the UK, the EU, and other countries representing major customers or cereal suppliers (such as Canada, Australia and Japan) were scanned regularly in order to identify emerging issues. The information gained was used to inform decisions on which analytes to test for in which matrices.

### 3.2.3 Analysis of mycotoxins

Mycotoxins in barley (malting and feed) and in oats were analysed at the Nutfield site, while those in wheat (milling and feed) were analysed at the Campden site.

*Fusarium toxins: Trichothecenes and zearalenone*

Trichothecenes (including deoxynivalenol, nivalenol, T-2 and HT-2) were analysed by one of two in-house procedures. Samples from the 2005 and 2006 harvests and fresh samples from the 2007 harvest were analysed by a GC-MS procedure based on a published method *(Patel et al, 1996)*. In this the main trichothecenes (DON,3 and 15 acetyl-DON, NIV, Neosolaniol, Diacetoxyscirpenol, Fusarenone-X, HT-2 toxin and T-2 toxin were extracted using acetonitrile/water, partially purified using trichothecene

clean-up columns, then derivatised and analysed by GC-MS. The limit of quantification for each trichothecene was 5 µg/kg.

Stored samples from the 2007 harvest and samples from the 2008 harvest were analysed by a LC-MS/MS procedure. The mycotoxins were extracted using acetonitrile/water, partially purified using trichothecene clean-up columns, then separated and quantified by liquid chromatography-mass spectrometry. The limit of quantification for each trichothecene in this procedure was 1 µg/kg at the BRI site and 10µg/kg at the Campden site.

Zearalenone was analysed by an in-house procedure based on a published method *(Patel et al, 1996).* After extraction with acetonitrile/water, specific immunoaffinity columns were used for the clean-up stage. Detection and quantification was by HPLC at the Nutfield site and LC-MS/MS at the Campden site. The limit of quantification is 2 µg/kg. Both Campden BRI sites participate in FAPAS proficiency tests and Z scores are available on request.

*Ochratoxin A*

Ochratoxin A was analysed by an in-house procedure. After extraction with acetonitrile/water, specific immunoaffinity columns were used for the clean-up stage. Detection and quantification was by HPLC with fluorescence detection. Both sites have UKAS accreditation for this analysis and participate in FAPAS proficiency tests. Z scores are available on request. The limit of quantification is 0.1 µg/kg.

*Aflatoxins*

Aflatoxins B1, B2, G1 and G2 were analysed by an in-house procedure based on a published method *(Patel et al, 1996).* After extraction with acetonitrile/water, specific immunoaffinity columns were used for the clean-up stage. Detection and quantification was by HPLC with post-column derivatisation and fluorescence detection. Both sites participate in FAPAS proficiency tests for aflatoxins and Z scores are available on request. The limit of quantification is 0.1 µg/kg for each toxin.

### 3.2.4 Analysis of pesticides

*Storage pesticides:* Cereal storage pesticides were analysed by an in-house method. After extraction with acetone/methanol the extract was purified by gel permeation chromatography. The fraction containing pesticide residues was recovered, concentrated

and injected into a gas chromatograph-mass spectrometer to separate and quantify residues. Both sites have UKAS accreditation for these analyses and also participate in FAPAS proficiency tests. Z scores are available on request. The limit of quantification was 10 µg/kg.

**Table 2. Storage insecticides and selected field fungicides included in the pesticide screening.**

| Type | Active ingredient | EU MRL (mg/kg) |
|---|---|---|
| **Post harvest insecticides**<br><br>(NB not necessarily registered in the UK for that use) | Bifenthrin | 0.5 |
| | Chlorpyrifos | 0.2 |
| | Chlorpyrifos-methyl | 3 |
| | Cypermethrin | 0.2 |
| | Deltamethrin | 2 |
| | Diazinon | 0.02 |
| | Dichlorvos | 0.01 |
| | Etrimfos | Withdrawn[1] |
| | Fenitrothion | 0.5[2] |
| | Fenvalerate | 0.2 |
| | Lindane | 0.01 |
| | Malathion | 8 |
| | Methacrifos | 0.05 |
| | Permethrin | 0.05 |
| | Piperonyl butoxide | none |
| | Pirimiphos-methyl | 5 |
| **Field fungicides (Nutfield site only)** | Azoxystrobin | 0.3 |
| | Cyprodinil | Barley 3<br>Oats 2<br>Wheat 0.5 |
| | Kresoxim-methyl | 0.05 |
| | Trifloxystrobin | Barley 0.3<br>Oats 0.02<br>Wheat 0.05 |

[1]Limit of detection applies [2]Applies until June 2009

*Glyphosate: Nutfield site:* Glyphosate was analysed by an in-house method. After extraction with ammonium hydroxide the extract was evaporated to dryness and derivatised with 9-fluorenylmethyl chloroformate. Glyphosate was separated and quantified by HPLC with fluorescence detection. The limit of quantification was

0.5 mg/kg. *Campden site:* Solvent extraction was followed by solid phase extraction. Detection and quantification was by LC-MS/MS *(Granby et al, 2003).* The limit of quantification varied from 0.025 mg/kg in 2006 to 0.05 mg/kg in 2007 and 2008.

*Growth regulators:* Chlormequat and mepiquat were analysed by an in-house method based on a published procedure *(Vahl et al, 1998)*. This method forms the basis of the BSI standard (draft) EN 15055. Samples were extracted with methanol/water then partially purified with C18 solid phase clean-up. Residues were separated and quantified by electrospray mass spectrometry (LC-MS/MS). The limit of quantification was 0.01 mg/kg.

### 3.2.5 Analysis of heavy metals

All metal analysis was carried out at the Campden site. Until 2008, a standard AAS method was used. Samples were ashed, then dissolved in acid and analysed by atomic absorption spectroscopy. From 2008 onwards inductively coupled plasma mass spectroscopy (ICP-MS) was used. Samples were digested by microwave oven and then analysed by ICP-MS. The limit of quantification was 0.01mg/kg for each element.

## 3.3 Results and discussion

### 3.3.1 Mycotoxins

#### Storage mycotoxins: ochratoxin A (OA)

**Milling wheat samples** were tested for ochratoxin A immediately after harvest in 2007 and 2008, and in stored samples from 2005, 2006, 2007 and 2008 harvests in January and March. Results are shown in Table 3. The incidence of contamination was relatively low, generally less than 10%. Actual concentrations were also generally low, with mean levels ranging from <0.1 (the limit of detection) to 0.44 µg/kg. The highest concentration (10.4 µg/kg, twice the legal limit in the EU, and confirmed on re-analysis) was detected in a sample tested in January 2009 which was found to have come from the 2007 harvest.

There was no consistent relationship between storage time and incidence (one of the freshly harvested tranches had the highest incidence rate of 12%). Neither was there any obvious relationship between incidence and mean or maximum concentrations.

There was no evidence to show that wheat samples which originated outside the UK were more or less likely to contain ochratoxin A, although there were too few samples for the results to be statistically significant.

**Malting barley** samples showed a similar picture (Table 4). Incidence was somewhat higher than in wheat, generally in the range 10 – 30%, with the highest incidence being in malts from barleys harvested in 2008. Despite the higher incidence, actual concentrations were slightly lower than those in wheat, with means ranging up to 0.33 µg/kg and a maximum of 5.3 µg/kg.

Freshly harvested samples contained less OA than did stored samples but, as with the milling wheat, there was no obvious relationship between incidence and mean or maximum concentrations. Neither was there any evidence of any consistent increase in OA incidence or concentration during the malting process.

**Compliance.** The overwhelming majority of milling wheat, malting barley and malt samples complied with legal limits in the EU. Occasional samples of each were found to exceed the EU legal limits of 5 µg/kg for OA in raw cereals and 3 µg/kg in processed cereals destined for food use (Table 5). Most of these were only slightly above the limits, and, after re-sampling, lower, compliant values were obtained in most cases.

## Ochratoxin A

**Table 3. Ochratoxin A in milling wheat (results given in µg/kg as is; LOD = 0.1 )**

| Type | 2005 Harvest | | | 2006 Harvest | | | 2007 Harvest | | | 2008 Harvest | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | % > LOD | Mean | Max | % > LOD | Mean | Max | % > LOD | Mean | Max | % > LOD | Mean | Max |
| Freshly harvested | Not done | | | Not done | | | 2 | 0.13 | 4.2 | 12 | 0.14 | 1 |
| Sampled January | 0 | 0.05 | <0.1 | 4.5 | 0.28 | 8.9 | 8 | 0.12 | 1.8 | 8 | 0.44 | 10.4* |
| Sampled March | 4 | 0.29 | 4.7 | 10 | 0.08 | 0.5 | 4 | 0.06 | 0.5 | 6 | 0.09 | 1.1 |

**this sample was submitted as a part of the 2008 tranche but when investigated this was found to be from the 2007 harvest*

**Table 4. Ochratoxin A in malting barley and malts (results given in µg/kg as is; LOD = 0.1 )**

| Type | 2005 Harvest | | | 2006 Harvest | | | 2007 Harvest | | | 2008 Harvest | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | % > LOD | Mean | Max | % > LOD | Mean | Max | % > LOD | Mean | Max | % > LOD | Mean | Max |
| Freshly harvested | Not done | | | 5 | 0.05 | 0.1 | 11 | 0.08 | 0.6 | Not done | | |
| Stored Malting barley | 22 | 0.11 | 0.6 | 15 | 0.33 | 5.3 | 20 | 0.22 | 2.3 | 21 | 0.12 | 1 |
| Malts from stored barleys | 22 | 0.08 | 0.5 | 30 | 0.31 | 3.8 | 10 | 0.12 | 1 | 42 | 0.11 | 0.5 |

**Table 5. Legal limits (LL) and guideline levels (GL) for storage mycotoxins in food and feed cereals in the EU**

| Matrix | Ochratoxin A (µg/kg) | | Status |
|---|---|---|---|
| **Unprocessed cereals** | 5 | | LL *(EC,2006c)* |
| **Processed cereals/products** | 3 | | LL *(EC,2006c)* |
| **Feed materials** | 250 | | GL *(EC, 2006b)* |
| **Complementary & complete feedingstuffs for pigs** | 50 | | GL *(EC, 2006b)* |
| **Complementary & complete feedingstuffs for poultry** | 100 | | GL *(EC, 2006b)* |
| **Matrix** | **Aflatoxin (µg/kg)** | | **Status** |
| | **B1** | **Total** | |
| **Cereals & cereal products (except maize)** | 2 | 4 | LL *(EC, 2006c)* |
| **Feed materials** | 20 | - | LL *(EC, 2002)* |
| **Complete feedingstuffs (except those listed below)** | 20 | - | LL *(EC, 2002)* |
| **Complete feedingstuffs for dairy animals** | 5 | - | LL *(EC, 2002)* |
| **Complete feedingstuffs for calves & lambs** | 10 | - | LL *(EC, 2002)* |
| **Complete feedingstuffs for pigs & poultry** | 20 | - | LL *(EC, 2002)* |
| **Complementary feedingstuffs for cattle, sheep & goats except for dairy & young animals** | 20 | - | LL *(EC, 2002)* |
| **Complementary feedingstuffs for pigs & poultry** | 20 | - | LL *(EC, 2002)* |
| **Other complementary feedingstuffs** | 5 | - | LL *(EC, 2002)* |

**Feed Cereals.** Incidence of OA was generally significantly higher in feed cereals than in those destined for food use, with, in some years, the majority of samples of malt culms, wheatfeed and oatfeed containing detectable residues (Table 6). Actual concentrations were generally moderate, with mean values in any category not exceeding 3 µg/kg. However, the range of concentrations was wider than for food cereals, with several samples containing more than 10 µg/kg. The highest, 64 µg/kg, found in a sample of feed wheat, exceeded the recommended guidelines for OA in complementary and complete feedingstuffs for pigs (Table 5).

**Storage mycotoxins: aflatoxins;** Aflatoxins were not detected in any of the samples tested, from any harvest.

**Table 6. Ochratoxin A in stored feed grains (results given in µg/kg as is; LOD = 0.1 )**

| Type | 2005 Harvest | | | 2006 Harvest | | | 2007 Harvest | | | 2008 Harvest | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | % > LOD | Mean | Max | % > LOD | Mean | Max | % > LOD | Mean | Max | % > LOD | Mean | Max |
| **Feed barley** | 17 | 0.96 | 13.5 | 39 | 2.4 | 18.3 | 60 | 1.63 | 21 | 25 | 0.35 | 6.8 |
| **Malt culm pellets** | 100 | 0.77 | 1.8 | 100 | 0.35 | 0.6 | 100 | 0.6 | 1.2 | Not done | | |
| **Feed Wheat** | 4 | 0.05 | 0.1 | 7 | 0.66 | 17.8 | 16 | 0.28 | 3.9 | 15 | 1.9 | 64 |
| **Wheatfeed** | 0 | 0.05 | <0.1 | 71 | 0.27 | 0.6 | 86 | 0.77 | 1.5 | 90 | 0.77 | 4.3 |
| **Feed Oats** | 38 | 0.34 | 1.1 | 40 | 0.07 | 0.3 | 43 | 0.1 | 0.2 | 63 | 0.52 | 1.4 |
| **Oatfeed** | 63 | 0.59 | 2.2 | 100 | 3 | 13.8 | 100 | 2 | 9 | 70 | 2 | 11 |

## Field mycotoxins: Fusarium toxins -Trichothecenes

**Milling wheat:** deoxynivalenol (DON) was by far the most common of the trichothecenes detected in wheat, with the majority of samples containing quantifiable amounts (Table 7).

### Table 7. DON, NIV, T-2 and HT-2 in freshly harvested milling wheat (results given in µg/kg as is; LOD = 10)

| Toxin | 2006 Harvest | | | 2007 Harvest | | | 2008 Harvest | | |
|---|---|---|---|---|---|---|---|---|---|
| | % > Max LOD | Mean | | % > Max LOD | Mean | | % > Max LOD | Mean | |
| **DON** | 70 | 48 | 332 | 96 | 172 | 1190 | 98 | 249 | 1120 |
| **NIV** | 12.5 | 7.7 | 38 | 34 | 13 | 164 | 28 | 8.6 | 46 |
| **T-2** | 2.5 | 5.5 | 24 | All <10 | 5 | <10 | All <10 | 5 | <10 |
| **HT-2** | 7.5 | 6.6 | 50 | All <10 | 5 | <10 | All < 10 | 5 | <10 |

*3- and 15- acetyl-DON, diacetoxyscirpenol, fusarenone-X and neosolaniol were not detected in any samples*

Incidence appeared to be climate-related, with a clear increase from 74% in 2006 (which was a dry year) to 96 and 98% in 2008 and 2009 respectively (both of which were wet years). There was also a corresponding increase in toxin concentrations, both mean and maximum levels, from a mean of 48 µg/kg in 2006 to 249 µg/kg in 2008. Maximum concentrations were greater than 1000 µg/kg in both 2007 and 2008, although the EU limits of 1750 µg/kg for durum wheat and 1250 µg/kg for other wheat (Table 8) were not exceeded.

Incidence of nivalenol (NIV) also increased substantially in wetter years, from 12.5% in 2006 to around a third of samples in 2007 and 2008 (Table 7). Changes in concentration were less marked, with mean concentrations increasing from 7.7 µg/kg in 2006 to 13 µg/kg in 2007 but falling back to 8.6 µg/kg in 2008. Maximum values in 2007 were skewed by one very high value of 164 µg/kg, otherwise there was only a relatively small increase from 38 µg/kg in 2006 to 46 µg/kg in 2008. There was little

correlation between DON and NIV concentrations (Figure. 1) except in 2007, when the calculation was skewed by the one very high value.

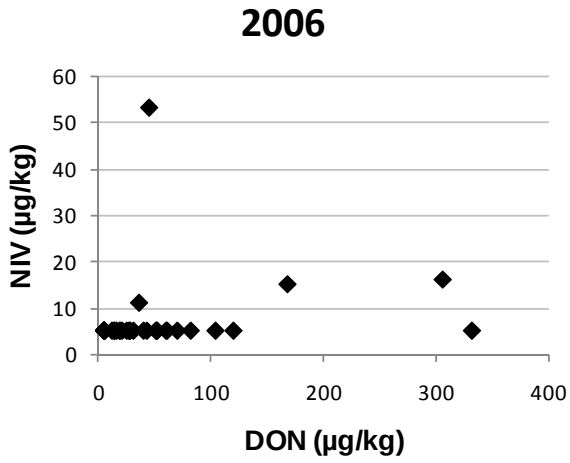
**Table 8. Legal limits and Guideline Levels for the trichothecene deoxynivalenol (DON) in food and feed cereals in the EU**

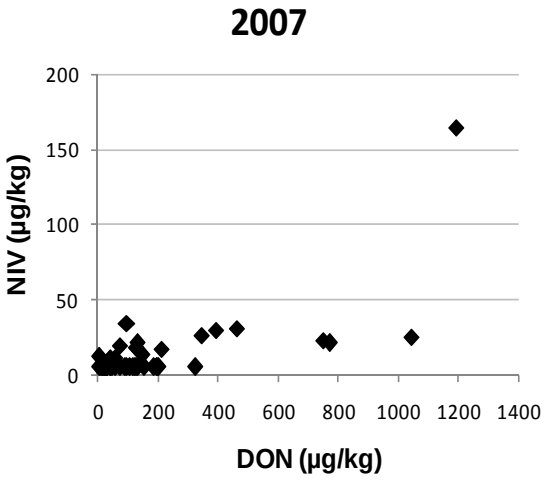
| Matrix | DON (µg/kg) | Status |
|---|---|---|
| **Unprocessed cereals for food (except durum wheat, oats and maize)** | 1250 | LL *(EC, 2006c)* |
| **Unprocessed durum wheat and oats** | 1750 | LL *(EC, 2006c)* |
| **Feed cereals and cereal byproducts** | 8000 | GL *(EC, 2006b)* |
| **Complete and complementary feedingstuffs (except for those listed below)** | 5000 | GL *(EC, 2006b)* |
| **Complete and complementary feedingstuffs for pigs** | 900 | GL *(EC, 2006b)* |
| **Complete and complementary feedingstuffs** | 2000 | GL *(EC, 2006b)* |

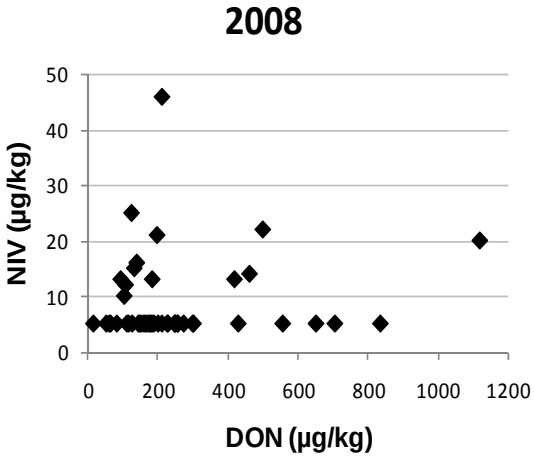
Incidence of T-2 and HT-2 toxins was low: only 7.5% of samples contained detectable levels in 2006, and no samples were positive in 2007 or 2008. The mean concentration in 2006 was around 6 µg/kg, similar to that of NIV, but, at 74 µg/kg, the maximum for T-2 + HT-2 combined was significantly higher than that of NIV.

The other trichothecenes sought, - 3- and 15- acetyl-DON, diacetoxyscirpenol, fusarenone-X and neosolaniol, were not detected in any samples (note however, that the limit of quantification for all trichothecenes was higher than for the malting barley samples).

**Fig. 1. Correlation between DON and NIV in milling wheat**




**Correlation coefficients**

**2006: 0.17** **2007: 0.71**
**2008: 0.12**

**Malting barley:** freshly harvested barleys were analysed using the GC-MS method with a limit of quantification of 5 µg/kg. Matched pairs of stored malting barleys plus the malt prepared from them were collected in March in 2005 and 2006, but subsequently in October/November to allow data to be included in a Europe-wide survey and reported to the European Commission. Results are therefore available for samples from the 2005 harvest as well as 2006, 2007 and 2008. These samples were analysed by the LC-MS/MS method with a quantification limit of 1 µg/kg.

As with milling wheat, DON was the mycotoxin detected most frequently in most years, although in 2006 the incidence of both T-2 and HT-2 toxins exceeded that of DON (Table 9). While the actual incidence of DON in barley was lower than that in wheat, there was a similar clear increase in the incidence of DON across the period of the project, from 35% in 2006 to 78% in 2008 (freshly harvested samples). Mean and maximum concentrations also increased substantially over the same period, from 3.4 to 72µg/kg for mean values and from 33 to 381µg/kg for maximum values. These concentrations, however, remained significantly lower than those in wheat, and all were well below legal limits.

The incidence of NIV also increased steadily over the duration of the project, from 10% for freshly harvested barley in 2006 to 64% in 2008. Means and maximum values also increased significantly, from 4.2 to 15µg/kg for mean values and from 22 to 137µg/kg for maximum values. These concentrations are on a par with those found in wheat. Correlation between DON and NIV was, as in wheat, highly variable from year to year (Figure 2).

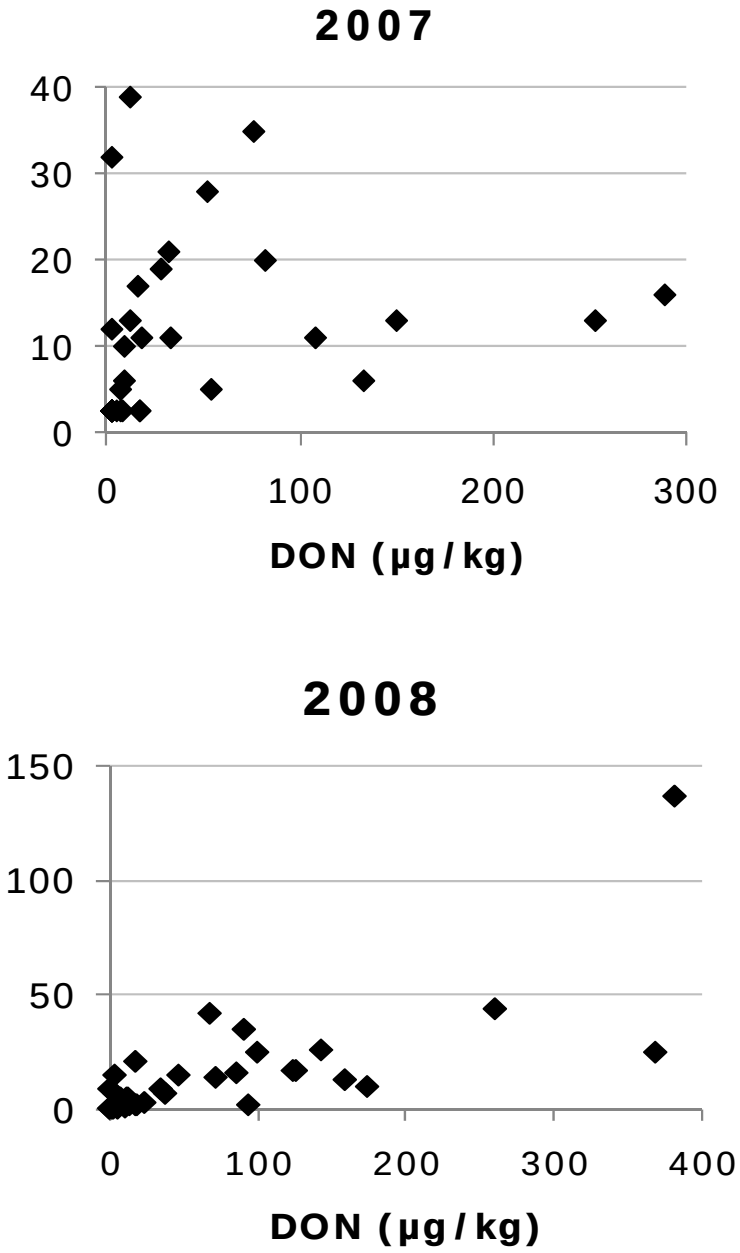
The incidence of T-2 and HT-2 toxins was noticeably higher in barley than in wheat, although the difference was less obvious when the lower limit of detection in barley was taken into account. As observed in previous studies, T-2 was not detected in the absence of HT-2, and concentrations of HT-2 were almost always higher than those of T-2. However, incidence of both toxins declined steadily from 2006 to 2008. This followed the sharp increase from previous years which was reported in HGCA Project Reports 380 and 387 and was also evident in the stored samples from the 2005 harvest. Mean and maximum concentrations did not follow the incidence trend as clearly, remaining broadly similar from year to year. There was some evidence of an inverse relationship between the incidence of DON and that of HT-2 toxin (Figure 3).

**Table 9. DON, NIV, T-2 and HT-2 in malting barley and malts**

| Type | 2005 Harvest | | | 2006 Harvest | | | 2007 Harvest | | | 2008 Harvest | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | % > LOD | Mean | Max | % > LOD | Mean | Max | % > LOD | Mean | Max | % > LOD | Mean | Max |
| **Freshly harvested** | Not done | | | | | | | | | | | |
| **DON** | | | | 35 | 5.4 | 33 | 60 | 11.7 | 289 | 78 | 72 | 381 |
| **NIV** | | | | 10 | 4.2 | 22 | 53 | 9.8 | 39 | 64 | 15 | 137 |
| **T-2** | | | | 50 | 4.5 | 13 | 5 | 3.3 | 25 | 3 | 2.5 | 5 |
| **HT-2** | | | | 90 | 10.6 | 30 | 28 | 5.5 | 28 | 11 | 3 | 9 |
| **Stored Malting barley** | | | | | | | | | | | | |
| **DON** | 35 | 9.9 | 33 | 25 | 3.6 | 14.1 | 60 | 36 | 312 | 68 | 55 | 418 |
| **NIV** | 11 | 3.4 | 12 | 30 | 1.8 | 10 | 45 | 8.5 | 39 | 53 | 9.6 | 45 |
| **T-2** | 11 | 2.8 | 5 | 55 | 2.1 | 7.5 | 20 | 3.3 | 9 | 5 | 1.2 | 8 |
| **HT-2** | 33 | 4.4 | 15 | 80 | 4.8 | 14.1 | 20 | 4.3 | 18 | 5 | 2.5 | 16 |
| **Malts from stored barleys** | | | | | | | | | | | | |
| **DON** | 39 | 4.3 | 10 | 0 | 0.8 | 4.3 | 60 | 44 | 399 | 79 | 97 | 490 |
| **NIV** | 0 | 2.5 | <5 | 10 | 0.6 | 2.2 | 0 | 0.5 | <1 | 16 | 2.1 | 13 |
| **T-2** | 0 | 2.5 | <5 | 0 | 0.5 | <1 | 0 | 0.5 | <1 | 0 | 0.5 | <1 |
| **HT-2** | 0 | 2.5 | <5 | 25 | 1.0 | 3.9 | 0 | 0.5 | <1 | 0 | 0.5 | <1 |

Notes: (1) results given in µg/kg as is
(2) Limit of quantification decreased from 5 µg/kg in 2005 to 1 µg/kg in 2008, but in all cases the incidence is calculated as the % of samples >5 µg/kg to allow long term trends to be ascertained.
(3) Diacetoxyscirpenol, fusarenone-X and neosolaniol were not detected in any samples

**Fig. 2. Correlation between DON and NIV in malting barley**

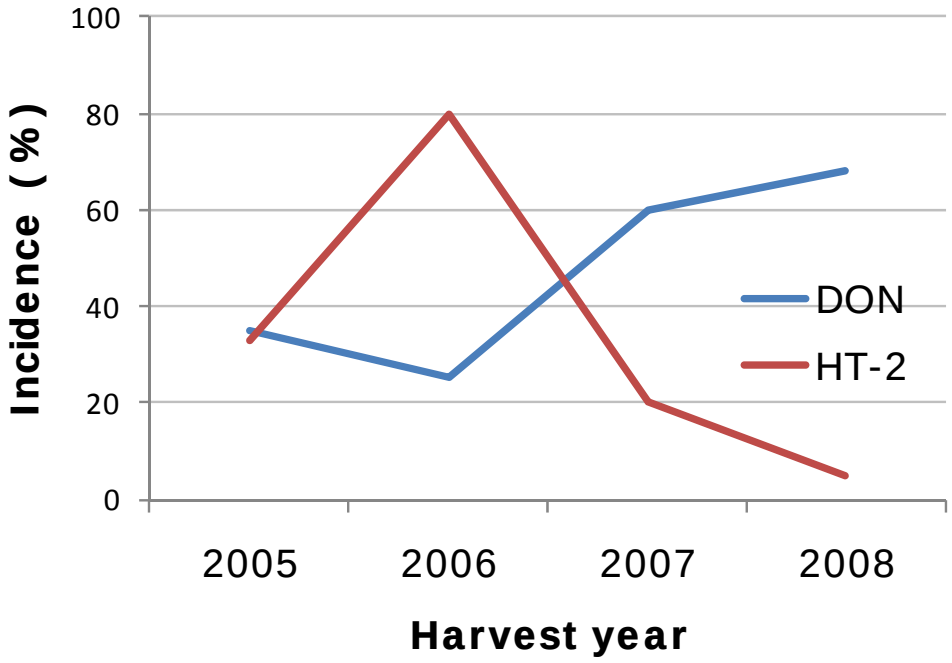



**Correlation coefficients**

| | |
|---|---|
| **2007** | **0.2643** |
| **2008** | **0.7347** |

*(In 2006 too few samples contained detectable DON or NIV for a valid calculation)*

**Fig. 3. Incidence of DON and HT-2 toxin in malting barley**




***Note that barleys from the 2005 harvest were stored for approximately 6 months before sampling and analysis. All other samples were from freshly harvested grain.***

**Barley and malt pairs:** In general, malts contained less trichothecenes than the barleys from which they were prepared, indicating that toxin was usually lost during the commercial malting process (Table 9 and Figures 4-7). This was especially evident with T-2 and HT-2 toxins, where there were substantial losses during malting. With the wetter seasons of 2007 and 2008, occasional malt samples were found to contain higher levels of DON than the starting barley, but this did not occur with T-2 or HT-2. It is not certain whether this is due to the well recognised heterogeneity of mycotoxin distribution in cereals (although these were 10kg samples, taken according to the EU Recommended Official sampling procedure *(EC, 2006a)* or whether it indicated *de novo* synthesis of DON during the malting process.

Plots of toxin concentrations in barleys and in the corresponding malts are shown in Figures 4 – 7. These demonstrate clearly the reduction in toxin concentration after malting, but also suggest that there is no clear correlation between barley and malt concentrations. Correlation coefficients are given in Table 10 below. These range from less than 0.1 to 0.79, which suggests that it is not possible to determine a reliable reduction factor which would predict levels in malt from those in the barley.

**Table 10. Correlation coefficients for DON and HT-2 in barleys and in the corresponding malts**

| Harvest year | DON | HT-2 |
|---|---|---|
| **2005** | 0.79 | 0.26 |
| **2006** | 0.02 | 0.71 |
| **2007** | 0.18 | 0.48 |
| **2008** | 0.61 | 0.46 |

**Other trichothecenes:** the related trichothecenes diacetoxyscirpenol, fusarenone-X and neosolaniol were also sought. None of these mycotoxins was detected in any of the samples tested. However, 3- and 15-acetylated DON were detected in some samples of malting barley and malt in 2007 and 2008 using the LC-MS/MS method, which has a lower limit of detection than GC-MS (Table 11). Wheat and feed grains were not tested using this method, but there is no reason to expect that they would differ significantly from malting barley. The results shown in Table 11 suggest that the incidence of acetylated DONs increases when concentrations of DON itself are higher,

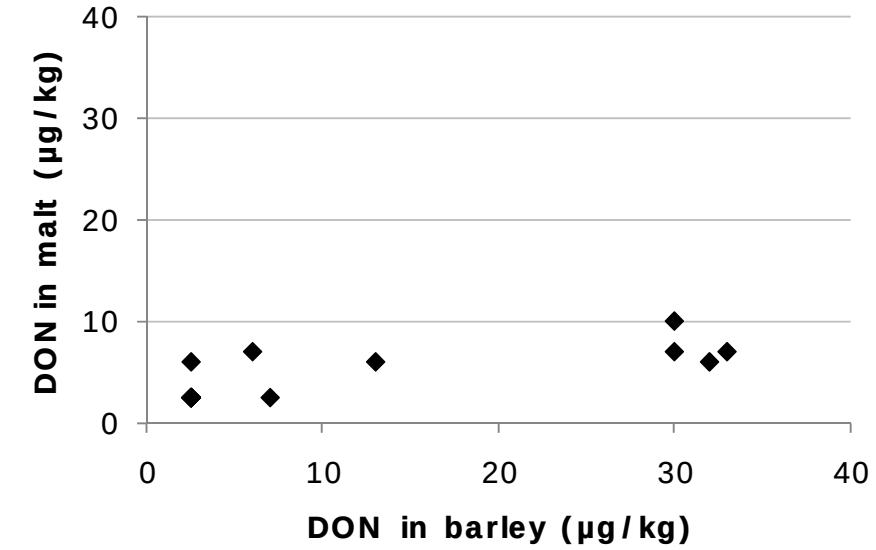
and that processed grains (such as malt) contain slightly more than raw grain. Relative concentrations were, however, significantly lower than those reported by Lancova et al *(2008),* who found that barley containing 238µg/kg of DON (similar to the highest levels found in our samples from 2007 and 2008) also contained 140µg/kg of acetyl DON. It is possible that the difference is due to the fact that Lancova's samples were artificially inoculated with Fusarium mould in the field and that the malting was carried out on a small scale, possibly in conditions which did not closely approximate to commercial malting.

**Table 11. 3+15-Acetylated DON species in barleys and their corresponding malts**

| Harvest year | | Barley | Malt |
|---|---|---|---|
| 2005 | Incidence (%>5) | 0 | 0 |
| | Mean (µg/kg) | 2.5 | 2.5 |
| | Maximum (µg/kg) | <5 | <5 |
| 2006 | Incidence (%>2) | 0 | 0 |
| | Mean (µg/kg) | 1 | 1 |
| | Maximum (µg/kg) | <2 | <2 |
| 2007 | Incidence (%>2) | 25 | 55 |
| | Mean (µg/kg) | 1.2 | 5.4 |
| | Maximum (µg/kg) | 6 | 32 |
| 2008 | Incidence (%>2) | 10 | 21 |
| | Mean (µg/kg) | 2.8 | 11 |
| | Maximum (µg/kg) | 19 | 69 |

**Figure 4. Trichothecenes in barley and malt pairs: 2005 harvest**

**DON**




**HT-2 Toxin**

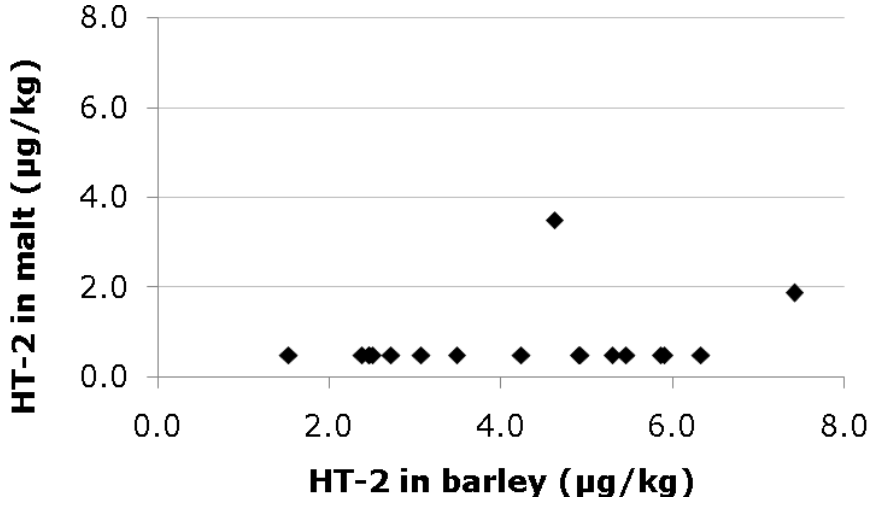
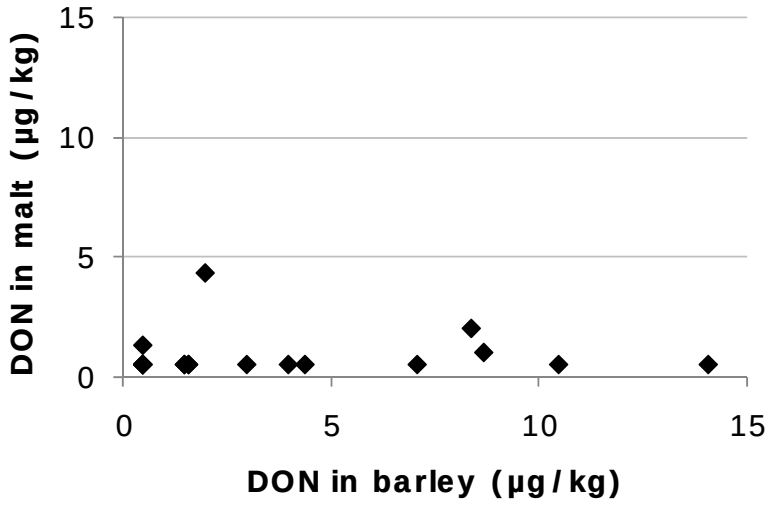


**Figure 5. Trichothecenes in barley and malt pairs: 2006 harvest**

**DON**




**HT-2 Toxin**

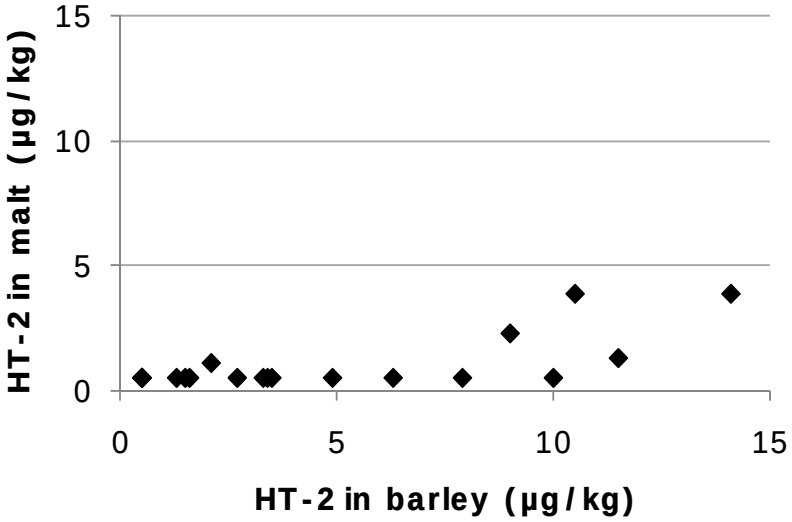
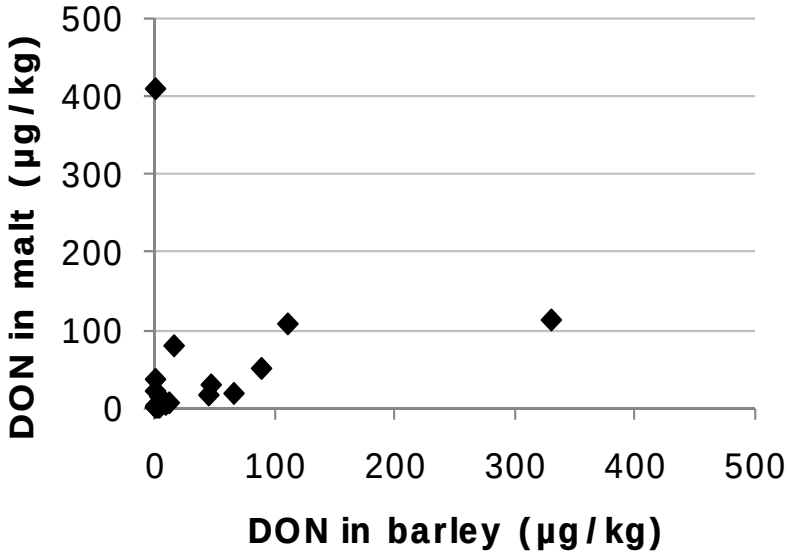


**Figure 6. Trichothecenes in barley and malt pairs: 2007 harvest**

**DON**




**HT-2**

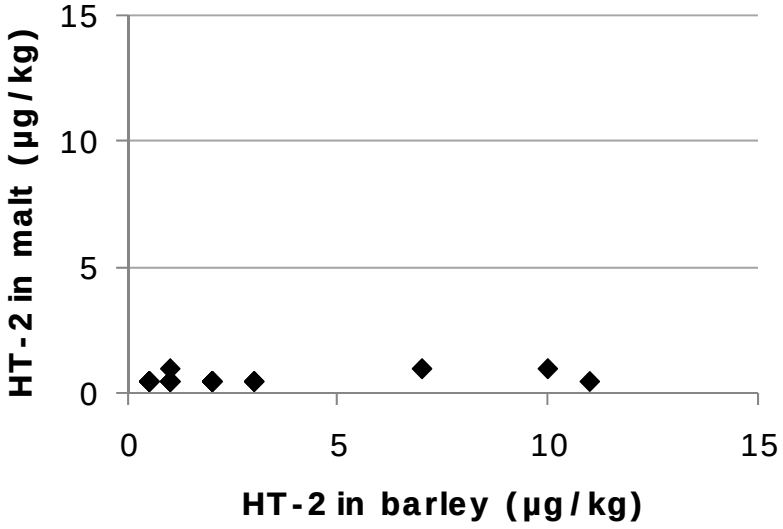
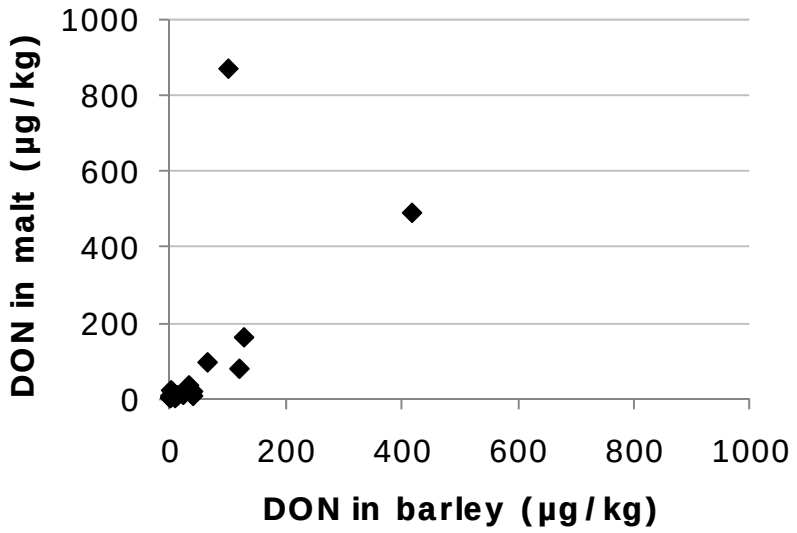
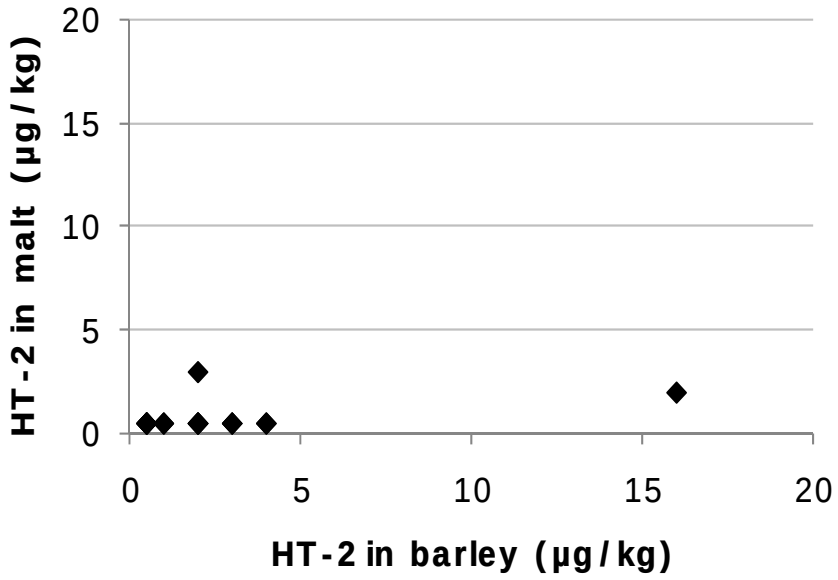


**Figure 7. Trichothecenes in barley and malt pairs: 2008 harvest**

**DON**




**HT-2**



**Feed Grains:** results for feed grains are shown in Table 12. The following general points can be made;

- Feed barley: incidence trends were similar to those in malting barley. Concentrations were also in the same range as those in malting barley. All were well below the Guideline levels for DON in animal feed (Table 7).
- Malt culm pellets, like wheatfeed and oatfeed, are compounded and, in addition to malt rootlets (culms), contain a higher proportion of undersized grains and barley/malt husk than whole grain samples. Contaminants which are predominantly present on the surface of grains, such as many pesticides and mycotoxins, can therefore accumulate in these pellets. The incidence of mycotoxins was, as expected, generally higher than in either raw barley or malt. This was especially noticeable for T-2 and HT-2 in 2007 samples, suggesting that there was ongoing contamination of malting barley and malt with these toxins, albeit at concentrations below the detection limit.
- Feed wheat; incidence of DON was slightly lower than that in milling wheat. Mean and maximum concentrations were, however, similar to those in milling wheat. Most samples were well below guideline levels, except for a few which exceeded the recommended guidelines for pig feed (Table 7). In contrast, the incidence and concentrations of NIV, T-2 and HT-2 were noticeably higher than those in milling wheat.
- Wheatfeed: incidence of DON, NIV, T-2 and HT-2 toxins was high in each harvest year. Concentrations of each toxin were also higher than in feed wheat, with some samples in 2007 and several in 2008 exceeding the guideline values for pig feed (Table 7). However, no samples exceeded the guidelines for other animal feeds.
- Feed oats: both incidence and concentrations of DON were similar to those in barley and significantly lower than in wheat. However, NIV was detected frequently and concentrations were generally higher than those in wheat. T-2 and HT-2 toxins were very common in the oat samples, and concentrations were also significantly higher than in the other cereals tested. There was some evidence of a decline in incidence from 2006 to 2008, but it was less marked than in the other cereals.
- Oatfeed: most samples tested contained significant quantities of DON and NIV although none exceeded guideline limits. Levels of T-2 and HT-2 were particularly high.

**Table 12. DON, NIV, T-2, and HT-2 in freshly harvested feed grains (results given in µg/kg as is; LOD = 5 )**

| Type | 2006 Harvest | | | 2007 Harvest | | | 2008 Harvest | | |
|---|---|---|---|---|---|---|---|---|---|
| | % > LOD | Mean | Max | % > LOD | Mean | Max | % > LOD | Mean | Max |
| **Feed barley** | | | | | | | | | |
| **DON** | 38 | 7.2 | 27 | 27 | 6 | 18 | 92 | 40 | 270 |
| **NIV** | 12.5 | 5.2 | 24 | 10 | 7.3 | 56 | 58 | 27 | 102 |
| **T-2** | 38 | 5.2 | 12 | 0 | 2.5 | <5 | 8 | 1.25 | 8 |
| **HT-2** | 50 | 12 | 28 | 18 | 3.7 | 12 | 8 | 3.5 | 32 |
| **Malt culm pellets** | | | | (stored) | (stored) | (stored) | Not done | | |
| **DON** | 100 | 22 | 44 | 100 | 188 | 342 | | | |
| **NIV** | 0 | 2.5 | <5 | 83 | 25 | 85 | | | |
| **T-2** | 50 | 16 | 37 | 83 | 5 | 12 | | | |
| **HT-2** | 83 | 40 | 113 | 83 | 9 | 19 | | | |
| **Feed Wheat** | | | | | | | | | |
| **DON** | 50 | 17 | 58 | 85 | 160 | 809 | 91 | 426 | 1297 |
| **NIV** | 60 | 9.5 | 49 | 92 | 52 | 199 | 91 | 49 | 198 |
| **T-2** | 10 | 3.7 | 14 | 8 | 3.1 | 10 | 9 | 11 | 66 |
| **HT-2** | 20 | 5.7 | 19 | 8 | 4.1 | 24 | 9 | 11 | 66 |
| **Wheatfeed** | | | | | | | | | |
| **DON** | 100 | 207 | 974 | 80 | 377 | 926 | 100 | 900 | 1760 |
| **NIV** | 82 | 34 | 176 | 100 | 46 | 95 | 94 | 52 | 105 |
| **T-2** | 55 | 16 | 60 | 20 | 3.3 | 8 | 6 | 5.8 | 88 |
| **HT-2** | 82 | 27 | 129 | 47 | 6.7 | 17 | 28 | 8.7 | 105 |
| **Feed Oats** | | | | | | | | | |
| **DON** | 63 | 24 | 149 | 0 | 2.5 | <5 | 44 | 31 | 267 |
| **NIV** | 75 | 29 | 99 | 73 | 74 | 268 | 67 | 94 | 385 |
| **T-2** | 100 | 94 | 156 | 91 | 79 | 188 | 55 | 28 | 148 |
| **HT-2** | 100 | 291 | 621 | 91 | 389 | 867 | 55 | 36 | 180 |
| **Oatfeed** | | | | | | | | | |
| **DON** | 67 | 67 | 336 | 44 | 16 | 42 | 100 | 95 | 214 |
| **NIV** | 67 | 92 | 299 | 100 | 127 | 302 | 100 | 195 | 355 |
| **T-2** | 100 | 311 | 497 | 100 | 285 | 738 | 89 | 171 | 420 |
| **HT-2** | 100 | 1085 | 1675 | 100 | 1174 | 4664 | 89 | 282 | 696 |

## Field mycotoxins: Fusarium toxins - Zearalenone (ZON)

**Milling wheat:** Zearalenone was analysed in all freshly harvested samples of milling wheat from each harvest. Results are shown in Table 13. There was a clear increase in incidence from 2006 to 2008, and mean and maximum values also increased over the same period, and some samples exceeded the legal limit of 100 µg/kg for feed cereals (other than maize) in the EU (Table 14).

**Table 13. Zearalenone in milling wheat** *(results given in µg/kg as is; LOD, 2 )*

| Type | 2006 Harvest | | | 2007 Harvest | | | 2008 Harvest | | |
|---|---|---|---|---|---|---|---|---|---|
| | % > LOD | Mean | Max | % > LOD | Mean | Max | % > LOD | Mean | Max |
| **Freshly harvested** | 5 | 1.4 | 13 | 26 | 3.2 | 43 | 82 | 26 | 125 |

**Table 14. Some Legal Limits (LL) and Guideline Levels (GL) for Zearalenone in food and feed cereals in the EU**

| Matrix | ZON (µg/kg) | Status |
|---|---|---|
| **Unprocessed cereals for food (except maize)** | 100 | LL *(EC, 2006c)* |
| **Cereals for direct human consumption, cereal flour, bran and germ as end products for direct human consumption (except categories otherwise specified)** | 75 | LL *(EC, 2006c)* |
| **Processed cereal-based foods (except maize based foods) and baby foods for infants and young children** | 20 | LL *(EC, 2006c)* |
| **Feed Materials:**<br>**Cereals and cereal products** | 2000 | LL *(EC, 2006c)* |
| **Complete and complementary feedingstuffs for;**<br>• **piglets and gilts**<br>• **sows and fattening pigs**<br>• **calves, dairy cattle, sheep, goat** | <br>100<br>250<br>500 | GL *(EC, 2006b)* |

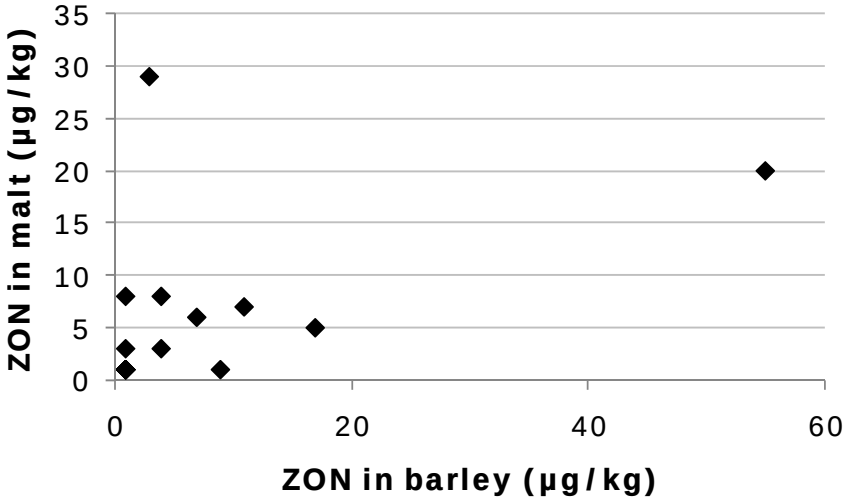
**Malting barley and malts:** Freshly harvested malting barleys from the 2006 harvest were analysed for ZON, when no samples exceeded the limit of detection of 2 µg/kg (Table 15). Freshly harvested samples from subsequent harvests were not tested.

**Table 15. Zearalenone in malting barley and malts** *(results given in µg/kg as is; LOD, 2 µg/kg)*

| Type | 2006 Harvest | | | 2007 Harvest | | | 2008 Harvest | | |
|---|---|---|---|---|---|---|---|---|---|
| | % > LOD | Mean | Max | % > LOD | Mean | Max | % > LOD | Mean | Max |
| **Freshly harvested** | 0 | 1 | <2 | Not done | | | Not done | | |
| **Stored Malting barley** | 5 | 1.1 | 2 | 35 | 4.1 | 24 | 42 | 6.4 | 55 |
| **Malts from stored barleys** | 5 | 1.1 | 3 | 20 | 0.12 | 1 | 47 | 5.2 | 29 |

Stored barleys and the malts prepared from them were analysed from each harvest. As with wheat, incidence in unprocessed barley increased from 2006 to 2008, but was generally lower in barley than that in wheat. Mean and maximum values were also significantly lower than those in wheat, and no samples exceeded legal limits. Overall, malts generally contained less ZON than unprocessed barleys, but there was little correlation between them. Figure 8 compares ZON levels in barleys from the 2008 harvest (which were higher than in 2006 or 2007) and the corresponding malts.

**Figure 8. ZON in barley and malt pairs from the 2008 harvest**



**Feed grains:** Freshly harvested Feed Barley was tested from the 2006 and 2007 harvests. Results are shown in Table 16. Although the incidence was slightly higher than in malting barley, concentrations were low, well below guideline levels for all categories of feed. Both incidence and concentrations of ZON were significantly higher in Malt Culms than in malting barley. In part, this may be because some sites also malted wheat, which would have contributed to the culm samples. However, all samples were below guideline levels.

Freshly harvested Feed Wheat was tested each year, and stored samples from the 2006 harvest only. Both incidence and actual concentrations of ZON were significantly higher than in milling wheat and some samples exceeded guideline levels for feedingstuffs for more sensitive animals such as pigs. The stored samples contained more ZON than freshly harvested samples. Results for Wheatfeed were similar to those for whole feed wheat, with maximum levels being, if anything, slightly lower.

Feed oats contained less ZON than either barley or wheat. Even in 2008, when the incidence of ZON contamination was significantly higher than in previous years, concentrations remained low. The incidence of contamination was noticeably greater in Oatfeed, but again actual concentrations were relatively low, well below the lowest guideline levels set for sensitive animals.

**Table 16. Zearalenone in feed grains** *(results given in µg/kg as is; LOD,2 µg/kg)*

| Type | 2006 Harvest | | | 2007 Harvest | | | 2008 Harvest | | |
|---|---|---|---|---|---|---|---|---|---|
| | % > LOD | Mean | Max | % > LOD | Mean | Max | % > LOD | Mean | Max |
| **Feed barley (Fresh)** | 12.5 | 1.1 | 2 | 18 | 1.6 | 6 | Not done | | |
| **Malt culms** | 33 | 1.7 | 4 | 100 | 39 | 66 | Not done | | |
| **Feed Wheat** | | | | | | | | | |
| **Fresh** | 20 | 4.3 | 33 | 69 | 39 | 342 | 100 | 89 | 210 |
| **Stored** | 42 | 16.3 | 98 | Not done | | | | | |
| **Wheatfeed** | | | | | | | | | |
| **Fresh** | 27 | 3.3 | 24 | 93 | 28 | 151 | 89 | 62 | 214 |
| **Stored** | 43 | 7 | 24 | Not done | | | | | |
| **Feed Oats (Fresh)** | 12.5 | 1 | 2 | 0 | 1 | <2 | 44 | 2.3 | 6 |
| **Oatfeed (Fresh)** | 33 | 1.5 | 3 | 54 | 3.3 | 11 | 100 | 21 | 49 |

### 3.3.2 Pesticides

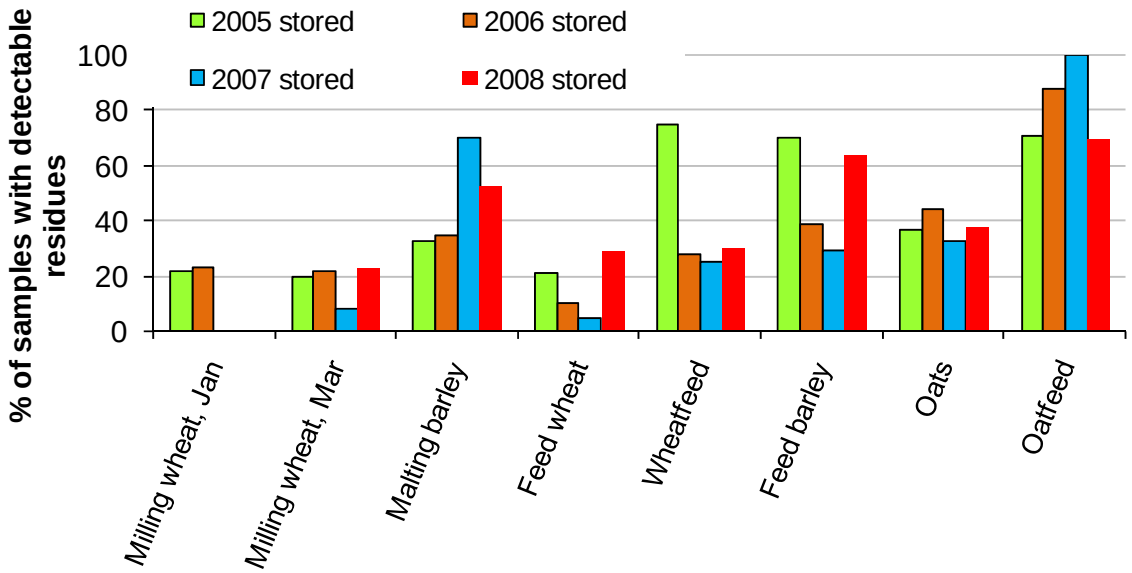
***Storage insecticides and selected field fungicides***

Stored whole grains were tested for a range of pesticides which included all insecticides currently or recently approved for use on stored cereal grain or in cereal stores. At the Nutfield site samples were also analysed for a limited number of field fungicides commonly used on cereals. A list of residues sought is given in the Materials and Methods section, in Table 1.

The percentage of samples in each category of grain which contained detectable residues is shown in Figure 9, where the different coloured columns represent the different harvest years. A few general trends are evident:

- wheat, both milling and feed, was the least likely to contain detectable residues.
- Wheatfeed was slightly more likely to contain detectable residues than feed wheat.
- Oatfeed was most likely to contain detectable residues. (It should be noted, however, that only a few samples of oats and oatfeed were available for analysis each year, so differences are unlikely to be statistically valid).

**Fig. 9. Percentage of samples with detectable residues**



**Nature of Residues detected**

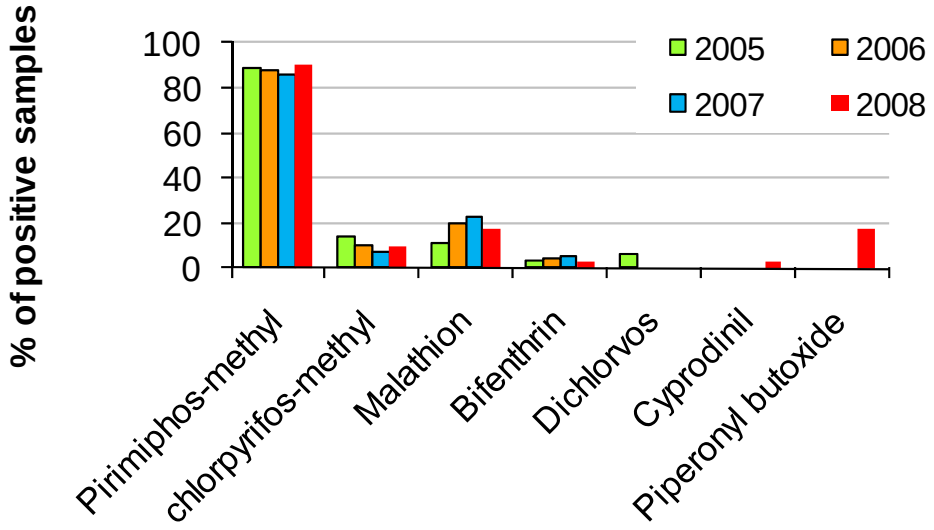
Pirimiphos-methyl was by far the most common residue detected, regardless of sample type (Figure 10). This storage insecticide represented over 80% of residues detected (other than growth regulators – see later).

Chlorpyrifos-methyl and malathion were detected in some 10-20% of samples. Bifenthrin, which is used in a mixture with malathion but at a much lower dose rate was detected in about 5% of samples, almost always in conjunction with malathion. (Neither malathion nor bifenthrin have been accepted onto Annex 1 of Directive 91/414/EEC, and both have now been withdrawn in the EU. Malathion was withdrawn first, in December 2008, and this is reflected in the lower proportion of positive samples from the 2008 harvest compared with the 2006 and 2007 harvests).

Dichlorvos, which has been widely used on stored cereals in many countries, was detected in a few samples from the 2005 harvest, but not in subsequent harvests. This insecticide was withdrawn from use in the EU from 2007.

Piperonyl butoxide, a synergist used with pyrethroid insecticides, was detected in 10-20% of samples in 2008. This may reflect increasing use of the pyrethroid deltamethrin, which was authorised for use on stored cereals and in cereal stores in the UK in 2007. However, residues of deltamethrin itself were not detected.

**Fig. 10. Active pesticidal ingredients detected**

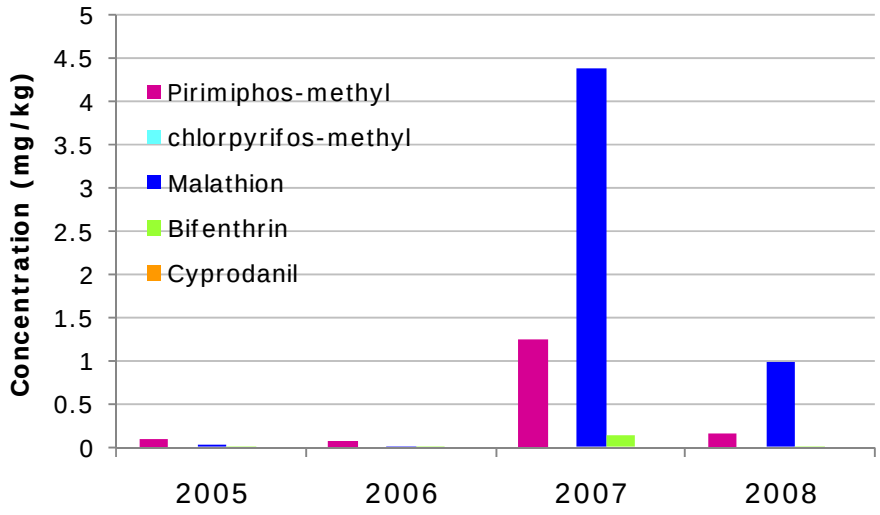


### Concentration of residues detected

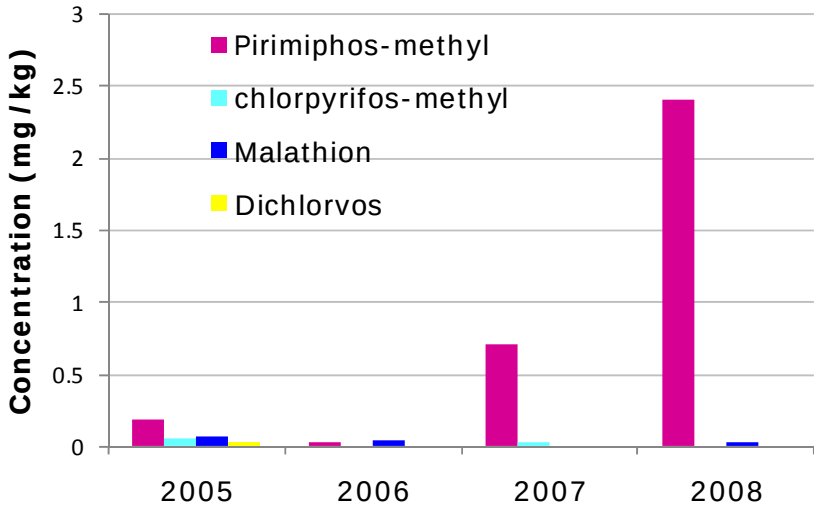
In spite of the frequency of occurrence, the actual concentration of pirimiphos-methyl, and other pesticides, detected was very low. Figure 11 (A – G) shows the maximum concentration of each pesticide detected in the different sample types each year. All were well below the MRLs set in the EU (see Table 1), with the highest concentration detected being 4.38mg/kg of malathion in a sample of malting barley (MRL for malathion in cereals is 8mg/kg). Numerical results for mean and maximum concentrations are given in tables 18-28.

**Fig. 11. Maximum concentrations of pesticides**

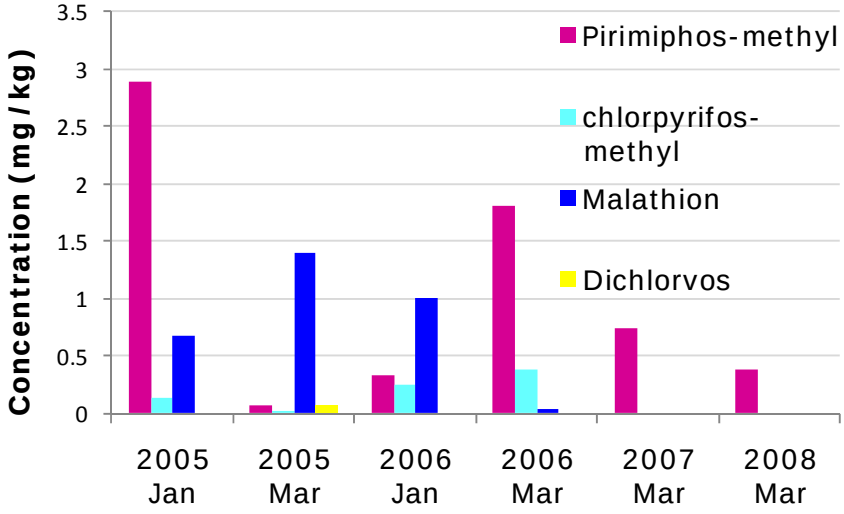
***A. Malting barley***



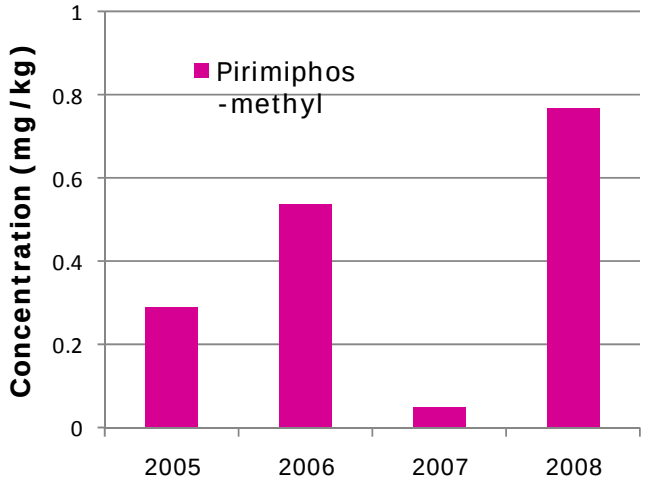

***B. Feed barley***



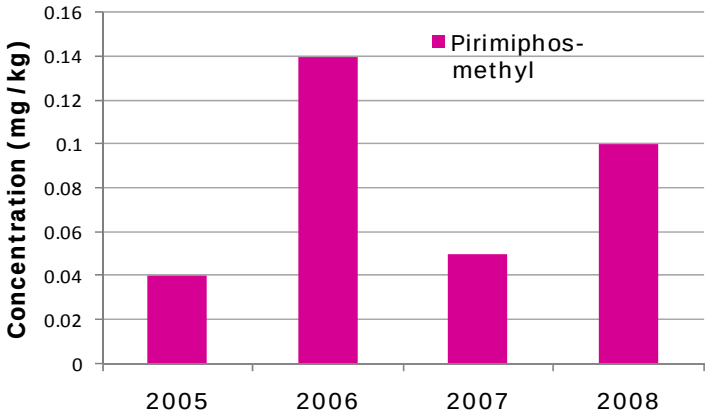
***C. Milling wheat***



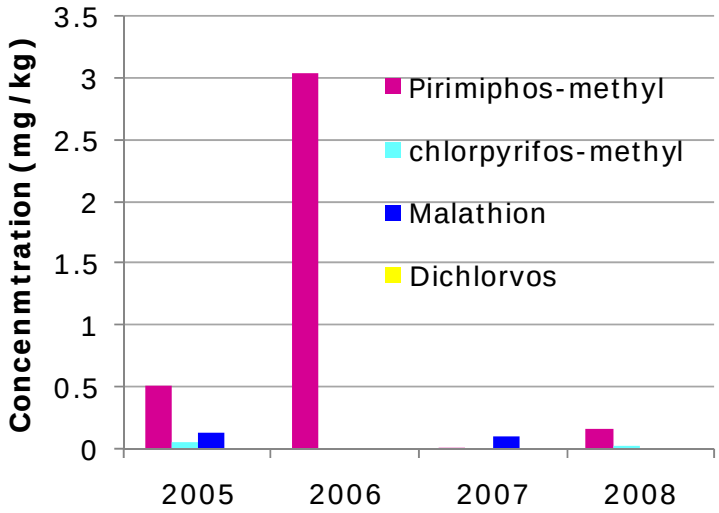

***D. Feed wheat***



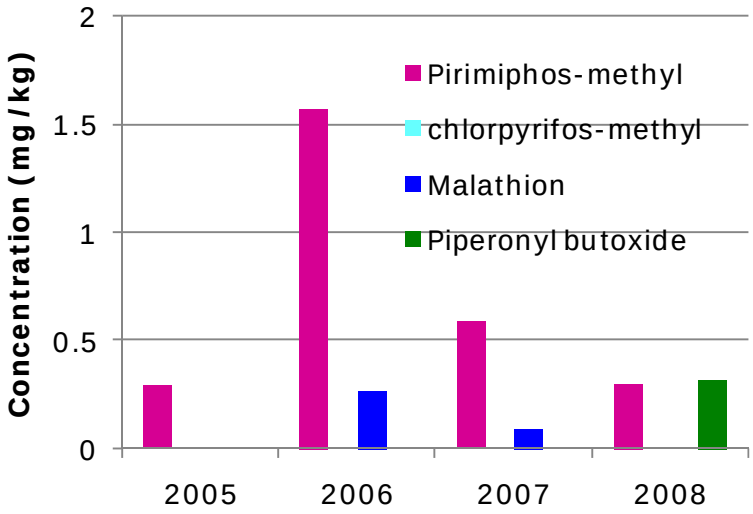

***E. Wheatfeed***



***F. Feed oats***




***G. Oatfeed***



## Concentration of pesticides; detailed results

### *A. Malting barleys*

**Table 17. Stored malting barleys from the 2005 harvest**

| Chemical | LOD mg/kg | % of samples > LOD | Mean* mg/kg | Max mg/kg | EU Legal limits mg/kg |
|---|---|---|---|---|---|
| **Fungicides** | | | | | |
| cyprodinil | 0.01 | 0 | 0.005 | <0.01 | Not yet set |
| azoxystrobin | 0.01 | 0 | 0.005 | <0.01 | 0.3 |
| kresoxim-methyl | 0.01 | 0 | 0.005 | <0.01 | 0.05 |
| trifloxystrobin | 0.01 | 0 | 0.005 | <0.01 | 0.3 |
| **Insecticides** | | | | | |
| bifenthrin | 0.01 | 6 | 0.005 | 0.01 | 0.5 |
| chlorpyrifos | 0.01 | 0 | 0.005 | <0.01 | 0.2 |
| chlorpyrifos-methyl | 0.01 | 0 | 0.005 | <0.01 | 3.0 |
| diazinon | 0.01 | 0 | 0.005 | <0.01 | 0.02 |
| dichlorvos | 0.01 | 0 | 0.005 | <0.01 | 2.0 |
| etrimfos | 0.01 | 0 | 0.005 | <0.01 | 5.0 |
| fenitrothion | 0.01 | 0 | 0.005 | <0.01 | - |
| malathion | **0.01** | **6** | **0.006** | **0.03** | **8.0** |
| methacrifos | 0.01 | 0 | 0.005 | <0.01 | 0.05 |
| pirimiphos-methyl | **0.01** | **22** | **0.02** | **0.11** | **5.0** |
| lindane | 0.01 | 0 | 0.005 | <0.01 | 0.01 |
| cypermethrin | 0.01 | 0 | 0.005 | <0.01 | 0.2 |
| fenvalerate | 0.01 | 0 | 0.005 | <0.01 | 0.2 |
| permethrin | 0.01 | 0 | 0.005 | <0.01 | 0.05 |
| deltamethrin | 0.01 | 0 | 0.005 | <0.01 | 1.0 |

* Mean is calculated by assuming that all samples below the limit of detection contained half that limit. The limit of detection was 0.01 mg/kg for all chemicals.

**Table 18. Stored malts from the 2006 harvest**

| Chemical | LOD mg/kg | % of samples > LOD | Mean* mg/kg | Max mg/kg |
|---|---|---|---|---|
| **Fungicides** | | | | |
| cyprodinil | 0.01 | 0 | 0.005 | <0.01 |
| azoxystrobin | 0.01 | 0 | 0.005 | <0.01 |
| kresoxim-methyl | 0.01 | 0 | 0.005 | <0.01 |
| trifloxystrobin | 0.01 | 0 | 0.005 | <0.01 |
| **Insecticides** | | | | |
| bifenthrin | 0.01 | **10** | **0.006** | **0.01** |
| chlorpyrifos | 0.01 | 0 | 0.005 | <0.01 |
| chlorpyrifos-methyl | 0.01 | 0 | 0.005 | <0.01 |
| diazinon | 0.01 | 0 | 0.005 | <0.01 |
| dichlorvos | 0.01 | 0 | 0.005 | <0.01 |
| etrimfos | 0.01 | 0 | 0.005 | <0.01 |
| fenitrothion | 0.01 | 0 | 0.005 | <0.01 |
| malathion | 0.01 | **10** | **0.006** | **0.01** |
| methacrifos | 0.01 | 0 | 0.005 | <0.01 |
| pirimiphos-methyl | 0.01 | **25** | **0.011** | **0.08** |
| lindane | 0.01 | 0 | 0.005 | <0.01 |
| cypermethrin | 0.01 | 0 | 0.005 | <0.01 |
| fenvalerate | 0.01 | 0 | 0.005 | <0.01 |
| permethrin | 0.01 | 0 | 0.005 | <0.01 |
| deltamethrin | 0.01 | 0 | 0.005 | <0.01 |

* Mean is calculated by assuming that all samples below the limit of detection contained half that limit. The limit of detection was 0.01 mg/kg for all chemicals.

**Table 19. Stored malting barleys from the 2007 harvest**

| Chemical | LOD mg/kg | % of samples > LOD | Mean* mg/kg | Max mg/kg |
|---|---|---|---|---|
| **Fungicides** | | | | |
| cyprodinil | 0.01 | 0 | 0.005 | <0.01 |
| azoxystrobin | 0.01 | 0 | 0.005 | <0.01 |
| kresoxim-methyl | 0.01 | 0 | 0.005 | <0.01 |
| trifloxystrobin | 0.01 | 0 | 0.005 | <0.01 |
| **Insecticides** | | | | |
| bifenthrin | 0.01 | **10** | **0.017** | **0.13** |
| chlorpyrifos | 0.01 | 0 | 0.005 | <0.01 |
| chlorpyrifos-methyl | 0.01 | 0 | 0.005 | <0.01 |
| diazinon | 0.01 | 0 | 0.005 | <0.01 |
| dichlorvos | 0.01 | 0 | 0.005 | <0.01 |
| etrimfos | 0.01 | 0 | 0.005 | <0.01 |
| fenitrothion | 0.01 | 0 | 0.005 | <0.01 |
| malathion | 0.01 | **10** | **0.43** | **4.38** |
| methacrifos | 0.01 | 0 | 0.005 | <0.01 |
| pirimiphos-methyl | 0.01 | **55** | **0.21** | **1.27** |
| lindane | 0.01 | 0 | 0.005 | <0.01 |
| cypermethrin | 0.01 | 0 | 0.005 | <0.01 |
| fenvalerate | 0.01 | 0 | 0.005 | <0.01 |
| permethrin | 0.01 | 0 | 0.005 | <0.01 |
| deltamethrin | 0.01 | 0 | 0.005 | <0.01 |

* Mean is calculated by assuming that all samples below the limit of detection contained half that limit. The limit of detection was 0.01 mg/kg for all chemicals.

**Table 20. Stored malting barleys from the 2008 harvest**

| Chemical | LOD mg/kg | % of samples > LOD | Mean* mg/kg | Max mg/kg |
|---|---|---|---|---|
| **Fungicides** | | | | |
| cyprodinil | 0.01 | **5** | **0.006** | **0.03** |
| azoxystrobin | 0.01 | 0 | 0.005 | <0.01 |
| kresoxim-methyl | 0.01 | 0 | 0.005 | <0.01 |
| trifloxystrobin | 0.01 | 0 | 0.005 | <0.01 |
| **Insecticides** | | | | |
| bifenthrin | 0.01 | **5** | **0.006** | **0.02** |
| chlorpyrifos | 0.01 | 0 | 0.005 | <0.01 |
| chlorpyrifos-methyl | 0.01 | **5** | **0.006** | **0.02** |
| diazinon | 0.01 | 0 | 0.005 | <0.01 |
| dichlorvos | 0.01 | 0 | 0.005 | <0.01 |
| etrimfos | 0.01 | 0 | 0.005 | <0.01 |
| fenitrothion | 0.01 | 0 | 0.005 | <0.01 |
| malathion | 0.01 | **16** | **0.06** | **0.99** |
| methacrifos | 0.01 | 0 | 0.005 | <0.01 |
| Piperonyl butoxide | 0.01 | 0 | 0.005 | <0.01 |
| pirimiphos-methyl | 0.01 | **47** | **0.027** | **0.17** |
| lindane | 0.01 | 0 | 0.005 | <0.01 |
| cypermethrin | 0.01 | 0 | 0.005 | <0.01 |
| fenvalerate | 0.01 | 0 | 0.005 | <0.01 |
| permethrin | 0.01 | 0 | 0.005 | <0.01 |
| deltamethrin | 0.01 | 0 | 0.005 | <0.01 |

* Mean is calculated by assuming that all samples below the limit of detection contained half that limit. The limit of detection was 0.01 mg/kg for all chemicals.

**Table 21. Stored milling wheats from the 2005 harvest**

| Chemical | LOD mg/kg | % of samples > LOD | Mean* mg/kg | Max mg/kg |
|---|---|---|---|---|
| bifenthrin | 0.01 | 0 | 0.005 | 0.01 |
| chlorpyrifos | 0.01 | 0 | 0.005 | <0.01 |
| chlorpyrifos-methyl | 0.01 | **2** | **0.005** | **0.02** |
| diazinon | 0.01 | 0 | 0.005 | <0.01 |
| dichlorvos | 0.01 | **2** | **0.006** | **0.07** |
| etrimfos | 0.01 | 0 | 0.005 | <0.01 |
| fenitrothion | 0.01 | 0 | 0.005 | <0.01 |
| malathion | 0.01 | **2** | **0.033** | **1.4** |
| maloxon | 0.01 | 0 | 0.005 | <0.01 |
| methacrifos | 0.01 | 0 | 0.005 | <0.01 |
| pirimiphos-methyl | 0.01 | **18** | **0.013** | **0.06** |
| lindane | 0.01 | 0 | 0.005 | <0.01 |
| cypermethrin | 0.01 | 0 | 0.005 | <0.01 |
| fenvalerate | 0.01 | 0 | 0.005 | <0.01 |
| permethrin | 0.01 | 0 | 0.005 | <0.01 |
| deltamethrin | 0.01 | 0 | 0.005 | <0.01 |

* Mean is calculated by assuming that all samples below the limit of detection contained half that limit. The limit of detection was 0.01 mg/kg for all chemicals.

**Table 22. Stored milling wheats from the 2006 harvest**

| Chemical | LOD mg/kg | % of samples > LOD | Mean* mg/kg | Max mg/kg |
|---|---|---|---|---|
| bifenthrin | 0.01 | 0 | 0.005 | 0.01 |
| chlorpyrifos | 0.01 | 0 | 0.005 | <0.01 |
| chlorpyrifos-methyl | 0.01 | **6** | **0.017** | **0.381** |
| diazinon | 0.01 | 0 | 0.005 | 0.01 |
| dichlorvos | 0.01 | 0 | 0.005 | <0.01 |
| etrimfos | 0.01 | 0 | 0.005 | 0.01 |
| fenitrothion | 0.01 | 0 | 0.005 | <0.01 |
| malathion | 0.01 | **1** | **0.006** | **0.035** |
| maloxon | 0.01 | 0 | 0.005 | 0.01 |
| methacrifos | 0.01 | 0 | 0.005 | <0.01 |
| pirimiphos-methyl | 0.01 | **22** | **0.073** | **1.84** |
| lindane | 0.01 | 0 | 0.005 | 0.01 |
| cypermethrin | 0.01 | 0 | 0.005 | <0.01 |
| fenvalerate | 0.01 | 0 | 0.005 | 0.01 |
| permethrin | 0.01 | 0 | 0.005 | <0.01 |
| deltamethrin | 0.01 | 0 | 0.005 | <0.01 |

* Mean is calculated by assuming that all samples below the limit of detection contained half that limit. The limit of detection was 0.01 mg/kg for all chemicals.

**Table 23. Stored milling wheats from the 2007 harvest**

| Chemical | LOD mg/kg | % of samples > LOD | Mean* mg/kg | Max mg/kg |
|---|---|---|---|---|
| bifenthrin | 0.01 | 0 | 0.005 | <0.01 |
| chlorpyrifos | 0.01 | 0 | 0.005 | <0.01 |
| chlorpyrifos-methyl | 0.01 | 0 | 0.005 | <0.01 |
| diazinon | 0.01 | 0 | 0.005 | <0.01 |
| dichlorvos | 0.01 | 0 | 0.005 | <0.01 |
| etrimfos | 0.01 | 0 | 0.005 | <0.01 |
| fenitrothion | 0.01 | 0 | 0.005 | <0.01 |
| malathion | 0.01 | 0 | 0.005 | <0.01 |
| maloxon | 0.01 | 0 | 0.005 | <0.01 |
| methacrifos | 0.01 | 0 | 0.005 | <0.01 |
| pirimiphos-methyl | 0.01 | **7.5** | **0.023** | **0.74** |
| lindane | 0.01 | 0 | 0.005 | <0.01 |
| cypermethrin | 0.01 | 0 | 0.005 | <0.01 |
| fenvalerate | 0.01 | 0 | 0.005 | <0.01 |
| permethrin | 0.01 | 0 | 0.005 | <0.01 |
| deltamethrin | 0.01 | 0 | 0.005 | <0.01 |

* Mean is calculated by assuming that all samples below the limit of detection contained half that limit. The limit of detection was 0.01 mg/kg for all chemicals.

**Table 24. Stored milling wheats from the 2008 harvest**

| Chemical | LOD mg/kg | % of samples > LOD | Mean* mg/kg | Max mg/kg |
|---|---|---|---|---|
| bifenthrin | 0.01 | 0 | 0.005 | <0.01 |
| chlorpyrifos | 0.01 | 0 | 0.005 | <0.01 |
| chlorpyrifos-methyl | 0.01 | 0 | 0.005 | <0.01 |
| diazinon | 0.01 | 0 | 0.005 | <0.01 |
| dichlorvos | 0.01 | 0 | 0.005 | <0.01 |
| etrimfos | 0.01 | 0 | 0.005 | <0.01 |
| fenitrothion | 0.01 | 0 | 0.005 | <0.01 |
| malathion | 0.01 | 0 | 0.005 | <0.01 |
| maloxon | 0.01 | 0 | 0.005 | <0.01 |
| methacrifos | 0.01 | 0 | 0.005 | <0.01 |
| pirimiphos-methyl | 0.01 | **23** | **0.028** | **0.37** |
| lindane | 0.01 | 0 | 0.005 | <0.01 |
| cypermethrin | 0.01 | 0 | 0.005 | <0.01 |
| fenvalerate | 0.01 | 0 | 0.005 | <0.01 |
| permethrin | 0.01 | 0 | 0.005 | <0.01 |
| deltamethrin | 0.01 | 0 | 0.005 | <0.01 |

* Mean is calculated by assuming that all samples below the limit of detection contained half that limit. The limit of detection was 0.01 mg/kg for all chemicals.

**Table 25. Stored feed grains, 2005 harvest**

| Matrix | Feed barley | | Feed oats | | Oatfeed | | Feed Wheat | | Wheat feed | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Chemical** | **Mean* mg/kg** | **Max mg/kg** | **Mean* mg/kg** | **Max mg/kg** | **Mean* mg/kg** | **Max mg/kg** | **Mean* mg/kg** | **Max mg/kg** | **Mean* mg/kg** | **Max mg/kg** |
| bifenthrin | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 |
| chlorpyrifos | **0.007** | **0.05** | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 |
| chlorpyrifos-methyl | 0.005 | <0.01 | 0.005 | <0.01 | **0.024** | **0.06** | 0.005 | <0.01 | **0.008** | **0.02** |
| diazinon | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 |
| dichlorvos | **0.006** | **0.02** | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 |
| etrimfos | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 |
| fenitrothion | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 |
| malathion | **0.008** | **0.07** | 0.005 | <0.01 | **0.021** | **0.13** | 0.005 | <0.01 | **0.079** | **0.45** |
| methacrifos | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 |
| pirimiphos-methyl | **0.032** | **0.18** | **0.059** | **0.29** | **0.146** | **0.30** | **0.002** | **0.29** | **0.174** | **0.91** |
| lindane | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 |
| cypermethrin | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 |
| fenvalerate | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 |
| permethrin | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 |
| deltamethrin | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 |

* Mean is calculated by assuming that all samples below the limit of detection contained half that limit. The limit of detection was 0.01 mg/kg for all chemicals.

**Table 26. Stored feed grains, 2006 harvest**

| Matrix | Feed barley | | Feed oats | | Oatfeed | | Feed Wheat | | Wheat feed | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Chemical** | **Mean* mg/kg** | **Max mg/kg** | **Mean* mg/kg** | **Max mg/kg** | **Mean* mg/kg** | **Max mg/kg** | **Mean* mg/kg** | **Max mg/kg** | **Mean* mg/kg** | **Max mg/kg** |
| bifenthrin | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 |
| chlorpyrifos | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 |
| chlorpyrifos-methyl | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 |
| diazinon | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 |
| dichlorvos | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 |
| etrimfos | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 |
| fenitrothion | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 |
| malathion | **0.008** | **0.04** | 0.005 | <0.01 | **0.06** | **0.27** | 0.005 | <0.01 | 0.005 | <0.01 |
| methacrifos | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 |
| pirimiphos-methyl | **0.015** | **0.04** | **0.362** | **3.04** | **0.288** | **1.57** | **0.034** | **0.544** | **0.028** | **0.14** |
| lindane | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 |
| cypermethrin | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 |
| fenvalerate | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 |
| permethrin | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 |
| deltamethrin | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 |

* Mean is calculated by assuming that all samples below the limit of detection contained half that limit. The limit of detection was 0.01 mg/kg for all chemicals.

**Table 27. Stored feed grains, 2007 harvest**

| Matrix | Feed barley | | Feed oats | | Oatfeed | | Feed Wheat | | Wheat feed | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Chemical** | **Mean* mg/kg** | **Max mg/kg** | **Mean* mg/kg** | **Max mg/kg** | **Mean* mg/kg** | **Max mg/kg** | **Mean* mg/kg** | **Max mg/kg** | **Mean* mg/kg** | **Max mg/kg** |
| bifenthrin | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 |
| chlorpyrifos | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 |
| chlorpyrifos-methyl | **0.007** | **0.03** | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 |
| diazinon | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 |
| dichlorvos | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 |
| etrimfos | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 |
| fenitrothion | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 |
| malathion | 0.005 | <0.01 | **0.03** | **0.10** | **0.034** | **0.09** | 0.005 | <0.01 | 0.005 | <0.01 |
| methacrifos | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 |
| pirimiphos-methyl | **0.057** | **0.70** | **0.005** | **0.01** | **0.175** | **0.59** | **0.007** | **0.05** | **0.014** | **0.05** |
| lindane | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 |
| cypermethrin | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 |
| fenvalerate | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 |
| permethrin | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 |
| deltamethrin | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 |

* Mean is calculated by assuming that all samples below the limit of detection contained half that limit. The limit of detection was 0.01 mg/kg for all chemicals.

**Table 28. Stored feed grains, 2008 harvest**

| Matrix | Feed barley | | Feed oats | | Oatfeed | | Feed Wheat | | Wheat feed | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Chemical** | **Mean* mg/kg** | **Max mg/kg** | **Mean* mg/kg** | **Max mg/kg** | **Mean* mg/kg** | **Max mg/kg** | **Mean* mg/kg** | **Max mg/kg** | **Mean* mg/kg** | **Max mg/kg** |
| bifenthrin | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | Not done | | | |
| chlorpyrifos | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | | | | |
| chlorpyrifos-methyl | 0.005 | <0.01 | **0.009** | **0.03** | 0.005 | <0.01 | | | | |
| diazinon | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | | | | |
| dichlorvos | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | | | | |
| etrimfos | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | | | | |
| fenitrothion | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | | | | |
| malathion | **0.009** | **0.03** | 0.005 | <0.01 | 0.005 | <0.01 | | | | |
| methacrifos | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | | | | |
| Piperonyl butoxide | 0.005 | <0.01 | 0.005 | <0.01 | **0.042** | **0.32** | | | | |
| pirimiphos-methyl | **0.23** | **0.52** | **0.047** | **0.17** | **0.068** | **0.12** | | | | |
| lindane | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | | | | |
| cypermethrin | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | | | | |
| fenvalerate | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | | | | |
| permethrin | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | | | | |
| deltamethrin | 0.005 | <0.01 | 0.005 | <0.01 | 0.005 | <0.01 | | | | |

* Mean is calculated by assuming that samples below the limit of detection contained half that limit. The limit of detection was 0.01 mg/kg for all chemicals.

***Glyphosate***

Glyphosate is a herbicide which is also authorised for use as a desiccant on cereals, where it may be used immediately before harvesting. The MRL is relatively high – 20 mg/kg – and it is one the residues most frequently reported in official surveys of cereals in the UK and some other northern EU states (the others being pirimiphos-methyl and chlormequat) *(EC, 2005a).* Use of desiccants would be expected to increase in wet years, and there have therefore been concerns that residues could be high in particularly wet years. Selected samples of malting barley and milling wheat from each harvest were therefore analysed for glyphosate, with feed grain being also analysed in 2007 and 2008, both of which were relatively wet harvests. Results are shown in Table 29.

**Table 29. Glyphosate in selected cereals (freshly harvested)**

| Type | 2006 Harvest | | | 2007 Harvest | | | 2008 Harvest | | |
|---|---|---|---|---|---|---|---|---|---|
| | % > LOD | Mean mg/kg | Max | % > LOD | Mean mg/kg | Max | % > LOD | Mean mg/kg | Max |
| **Malting barley** | 0 | 0.25 | <0.5 | 14 | 0.3 | 0.6 | 40 | 0.095 | 0.27 |
| **Milling wheat** | 10 | 0.076 | 1.18 | 60 | 0.22 | 1.25 | 20 | 0.05 | 0.1 |
| **Feed barley** | Not done | | | 18 | 0.33 | 0.9 | 55 | 0.31 | 1.4 |
| **Feed Wheat** | Not done | | | 0 | 0.25 | <0.5 | 27 | 0.08 | 0.23 |

For malting barley, there is a clear increase in the incidence of glyphosate residues from 2006 (a dry year) to 2008 (a wet year). Feed wheat and feed barley show a similar increase from 2007 to 2008. Milling wheat showed a significant increase in 2007, with 60% of samples containing detectable residues, but incidence declined again in 2008. However, the actual concentrations (both means and maxima) found were low across all sample types and for each harvest. The highest concentration detected – 1.4mg/kg in a sample of feed barley, was less than 10% of the EU MRL. There was no evidence of a substantial increase in mean concentrations in wet years compared with the dry harvest of 2006. The overall range of glyphosate concentrations detected was lower than that reported by Griffiths and Mason *(2003)* in their survey of glyphosate in UK-grown wheat, where the highest concentration found was 2.3 mg/kg.

***Plant growth regulators***

The growth regulator chlormequat, alone or in combination with mepiquat, is very widely used on cereals in order to restrict stem elongation and reduce the risk of lodging (which can cut yield and increase the likelihood of mould growth and mycotoxins contamination). It has been cited as one of the most common residues detected on cereals by several EU member states, including the UK *(EC 2005a)*. Selected malting barley and milling wheat samples were tested for both chlormequat and mepiquat in 2006. Results are shown in Table 30. Chlormequat was detected in the majority of samples (60% of barleys and 87% of wheats). Mepiquat was not detected as frequently (20% of barley samples and 13% of wheat samples) but this would be expected from the differing dose rates.

**Table 30. Chlormequat and mepiquat in selected cereals (freshly harvested)**

| Type | 2006 Harvest | | | EU MRL mg/kg |
|---|---|---|---|---|
| | % >LOD | Mean mg/kg | Maximum mg/kg | |
| **Malting barley** | | | | |
| **Chlormequat** | 60 | 0.16 | 1.37 | 2 |
| **Mepiquat** | 20 | 0.04 | 0.37 | 3 |
| **Milling wheat** | | | | |
| **Chlormequat** | 87 | 0.12 | 0.52 | 2 |
| **Mepiquat** | 13 | 0.02 | 0.19 | 2 |

Although the incidence of residues was high, actual concentrations were low. Mean values were less than 10% of the EU MRL for chlormequat (around 1% for mepiquat). The highest concentration of chlormequat found (1.37mg/kg in a sample of malting barley) was comfortably below the EU MRL. The range of concentrations found in wheat was very similar to those reported in a previous HGCA-funded survey *(Griffiths and Mason, 2003).*

### 3.3.3 Heavy metals

Previous HGCA surveys *(Baxter, 2003, 2006a, 2006b; Salmon, 2006)* have suggested that UK-grown cereals generally contain only low levels of heavy metals. However, since legal limits or guideline levels have been set for several metals/metalloids in food and feed grain in the EU, it was thought prudent to carry out at least limited checks on these potential contaminants. Wheat, both milling and feed samples, from the 2007 harvest and malting barley from the 2008 harvest were tested for a range of

heavy metals. Initially, samples were tested for arsenic, cadmium, lead and mercury, since legal limits are in place for these elements in food and/or feed. Limits for lead and cadmium in cereals are set by the Contaminants Regulation 1881/2006 *(EC, 2006c)* for food use and by Directive 2002/32 *(EC, 2002)* for use in animal feed. This latter Directive also sets limits for arsenic and mercury. Copper was added to the survey in 2008, following the setting of limits for copper (from copper-containing pesticides) in food and feed grain under the pesticides legislation *(EC 2005b).* These limits can be found in the EU MRL database. Aluminium was added in 2008 following media publicity alleging high levels of this metal in the diet in some EU countries.

The results, shown in Table 31, confirm previous findings. Mean and maximum levels of arsenic and cadmium were largely within the ranges previously reported *(Baxter, 2003, 2006b; Salmon 2006).*

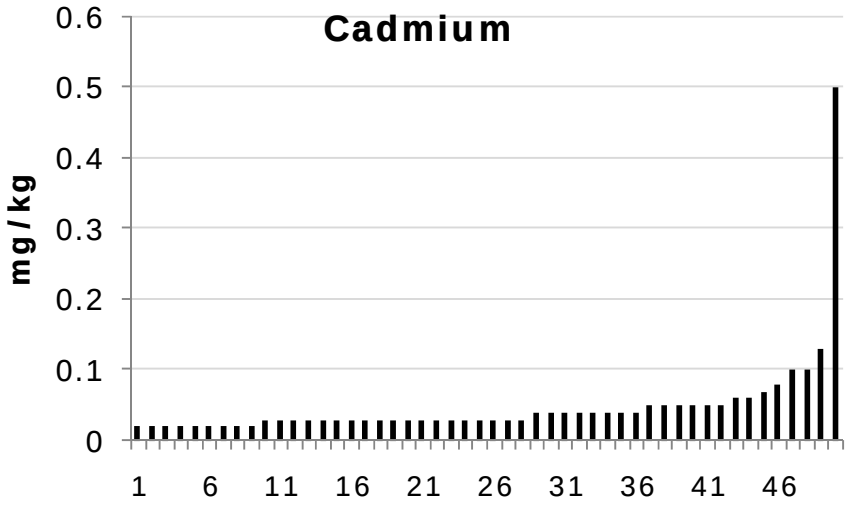
**Table 31. Heavy metals in selected freshly harvested grain samples**

| Grain type | Metal concentration (mg/kg) | | | | | |
|---|---|---|---|---|---|---|
| | As | | Cd | Pb | | Hg |
| **2007 harvest** | | | | | | |
| Milling wheat<br>Mean<br>Maximum | 0.008<br>0.03 | | 0.049<br>0.5 | 0.014<br>0.06 | | 0.005<br><0.01 |
| EU Limit (mg/kg) | UK limit of 1mg/kg in food unless otherwise specified[4] | | 0.2[1] | 0.2[1] | | None set |
| Feed wheat<br>Mean<br>Maximum | 0.014<br>0.06 | | 0.037<br>0.07 | 0.025<br>0.11 | | Not done |
| EU limit;<br>Feed materials<br>Complete feed | 2[2]<br>2[2] | | 1[2]<br>0.5 – 1[2] | 10[2]<br>5[2] | | 0.1[2]<br>0.1[2] |
| **2008 harvest** | | | | | | |
| | Al | As | Cd | Cu | Pb | Hg |
| Malting barley<br>Mean<br>Maximum | 4.12<br>11.1 | 0.013<br>0.03 | 0.014<br>0.03 | 1.77<br>4.6 | 0.013<br>0.03 | 0.005<br><0.01 |
| EU Limit (mg/kg) | None set | UK limit of 1mg/kg in food unless otherwise specified[4] | 0.1[1] | 10[3] | 0.2[1] | None set |

[1] *EC 2006c (Reg 1881/2006)* [2] *EC 2002 (Dir. 2002/32/EC)*
[3] *EU pesticides database* [4] *UK Arsenic in food regs, 1959, SI 831*

One sample of milling wheat exceeded the EU limit for cadmium in wheat. A comparison of the individual results for each sample (Figure 12) confirms that this sample was an outlier, and all the other samples were well within the legal limit.

**Figure 12. Cadmium levels in milling wheat samples from the 2007 harvest**




Levels of copper in malting barley were well below legal limits for cereals. No limits have been set for aluminium in cereals, but levels found in malting barley were within the range reported by MAFF for barley in their multi-element survey of food in the UK *(MAFF, 1994)* and the mean value, 4.12 mg/kg, was lower than that found by MAFF for barley-based foods (6.4 mg/kg). Mercury was not detected in any sample.

Overall, levels of lead in most cereal categories were lower than in previous surveys (Table 32). This may reflect a general reduction in environmental contamination resulting from successive EU legislation relating to lead, for example in fuels.

**Table 32. Comparison of Lead levels in cereals**

| Matrix | Harvest Year | Mean (mg/kg) | Maximum (mg/kg) | Reference |
|---|---|---|---|---|
| **Malting barley** | 1999 – 2001 | 0.03 | 0.08 | Baxter, 2003 |
| | 2008 | 0.013 | 0.03 | This report |
| **Milling wheat** | 2005 | 0.02 | 0.06 | Salmon, 2006 |
| | 2007 | 0.014 | 0.06 | This report |
| **Feed wheat** | 2004-2005 | 0.038 | 0.14 | Baxter, 2006b |
| | 2007 | 0.025 | 0.11 | This report |

### 3.3.4 "Horizon scanning"

During the first two years of this project, it became evident that the dietary intake of polycyclic aromatic hydrocarbons (PAHs) was becoming an emerging issue in the EU. Cereals and cereal products have been identified by the United Nations' Environment Programme as the main contributor to PAH intake from food. In the absence of substantial data, it is considered that the drying process might increase this loading *(JECFA, 2005a, b)*, and there have been moves within the European Commission to ban the use of direct drying processes for cereals and oilseeds, since these are most likely to generate PAHs in the foodstuff being dried *(EFSA, 2008)*. Such a ban would have both cost and environmental implications (in the form of increased fuel usage). The evidence for PAHs in barley and wheat in Western Europe is limited. An extension to the project reported here was therefore set up to allow this topic to be investigated and authoritative data to be obtained. The results of this extension project will be reported in a separate report.

In the last two years of the project the subject of "masked mycotoxins" was identified as an emerging issue. Masked mycotoxins are mycotoxins which are not detected by the standard reference methods for detection and quantification of mycotoxins in foodstuffs because they are bound to other residues, but which could be converted to free mycotoxins by metabolic activity during digestion in the body. They therefore represent a "sink" of potential mycotoxins which is currently not being detected. Food processing could both generate masked mycotoxins or convert them to free toxin. Most published work to date relates to deoxynivalenol (DON) and the species most investigated include the acetyl-DONs and deoxynivalenol-3-glucoside (DON-3-Glc). Initial findings were presented at the European Commission's 6$^{th}$ Fusarium Forum, held in Brussels in 2009 and have also been published in the scientific press *(Lancova et al, 2008; Kostelanska, 2009)*. Some data are available from the current project for the acetyl-DONs in UK cereals (see Section 3.3.1) but not for DON-3-Glc. It has been agreed that this species will be investigated in a subsequent HGCA project, starting in July 2009 (RD-2008-3572).

This project will also include an investigation into ergot alkaloids in cereals, following concerns expressed by EFSA about the risks posed by ergot for human and animal health *(EFSA, 2005)* and the paucity of information on suitable marker alkaloids and the relationship, if any, between the presence of ergot sclerotia and the concentration of individual alkaloids *(SCFCAH, 2005).*

## 3.4 Conclusions

Overall, the data established by this project suggest that the bulk of UK-grown cereals complies with EU and UK legislation and recommendations with regard to the presence of contaminants.

**Mycotoxins:** OA was the only storage mycotoxin detected, supporting the generally accepted understanding that climatic conditions in the UK do not support the formation of aflatoxins in cereals. OA itself was detected regularly, but the incidence in food grains (milling wheat and malting barley) was relatively low, in the range of 10-30%, but with no consistent trend. Incidence in compounded samples (wheatfeed, oatfeed and malt culm pellets) was significantly higher, suggesting that contamination with the causative mould *P verrucosum* was widespread but at a low level, and that toxin synthesis in food grains is being successfully kept in check by storage conditions. The occasional samples which exceeded legal limits were generally much lower when bulks were re-sampled, suggesting that the well- recognised difficulties with obtaining representative samples remain a problem.

The situation with trichothecenes was very different from that of OA. Concentrations of these toxins varied from year to year. Over the short term, concentrations followed changes in climatic conditions. DON was the most common trichothecene in barley and wheat, whilst T-2 and HT-2 toxins predominated in oats. However, the results for malting barley (for which data are available from earlier HGCA surveys – see Baxter 2003 and Baxter 2006a) reveal a long term increase in both DON and T-2 / HT-2 toxins over the last decade (Figure 13). T-2 and HT-2 appeared suddenly in 2004 and this is thought to be related to the spread of a new Fusarium species – *Fusarium langsethiae,* recently identified in the UK and several other EU countries *(Edwards et al, 2009; Imathiu et al, 2009).* There are signs of a decrease in T-2 and HT-2 in 2008, which could be related to the wetter conditions in that year, when other Fusarium species would have been more prevalent. *F langsethiae* has been found to be less aggressive than other Fusarium species in wheat, but there are no data for barley *(Imathiu et al, 2009).*

**Figure 13. A. DON in malting barley over the period 1999 to 2008**

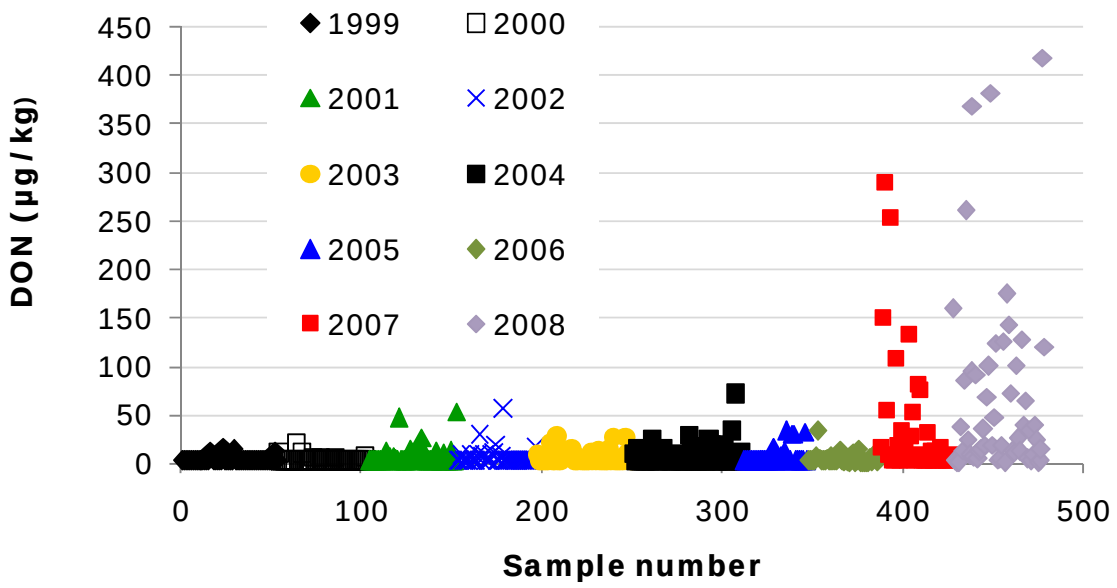
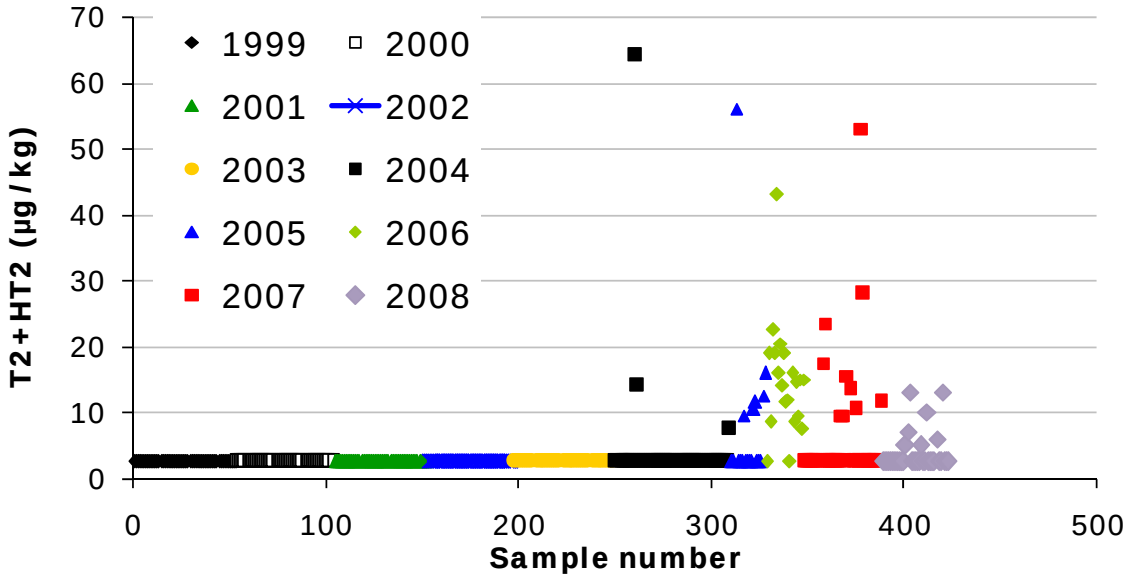



**Figure 13. B. T-2 and HT-2 toxins in malting barley, 1999 - 2008**



**Pesticides:** although many samples tested contained detectable residues of agrochemicals, concentrations were very low, and were invariably well below legal MRLs for all chemicals sought. The residue detected most frequently was the growth regulator chlormequat, which was found in the majority of samples tested. The desiccant glyphosate was also detected quite frequently, although incidence varied widely according to the season, ranging from 0% in dry years to over 50% in wet years. Even in wet years, however, residues did not exceed 10% of the MRL. The only other pesticide detected with any frequency was the storage insecticide pirimiphos-methyl, which was detected in one quarter to just under a half of whole grain samples. In general, incidence of pirimiphos-methyl tended to be higher in compounded samples (such as wheatfeed and oatfeed). Fungicides were rarely detected in any samples. Overall, the generally low concentrations detected for all pesticides relative to legal limits suggested that pesticides in UK-grown cereals are unlikely to present a health hazard.

**Heavy metals:** concentrations of metals were generally low in the samples tested and well below any legal limits, other than for one sample of milling wheat. The ranges of concentrations found were in agreement with other published reports. Overall, it is unlikely that heavy metals in cereals present a health hazard.

**Emerging issues:** masked mycotoxins (that is, mycotoxins which escape detection in conventional analysis because they are bound to other residues) and the potential for drying to contribute PAHs to grain were identified as emerging issues which could impact on the market acceptability or future legislation for grain. Both of these issues are being addressed in separate projects.

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