

**Biocide levels in surface and groundwater at IPPC licensed wood  
preservation sites in Ireland**

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**This project is submitted in part fulfilment of  
the HETAC requirements for the award of  
Degree of Master of Science in Environmental Protection**

**June 2009**

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## ABSTRACT

The reason the project was undertaken was to assess the level of compliance at Integrated Pollution Prevention Control (IPPC) licensed sites using copper azole based wood preservatives. It was found during the project that there is an issue with biocide levels reported in surface-water and groundwater, namely tebuconazole and propiconazole at these sites, the results of the environmental audit and statistical analysis of available downstream and upstream results, indicate that at sites in agricultural areas that there is a probable outside contribution to surface-water levels at certain IPPC licensed sites. In terms of surface-water monitoring at these sites, where external sources of pesticides might be suspected based on upstream sampling, results suggest that copper analysis is a more robust indicator of compliance.

The main finding from the environmental audit was that the level of compliance has improved since 2007 and achieving surface-water and groundwater compliance is well within the grasp of site operators provided they follow the manufactures instructions on use of the product. The case study demonstrated that there are still historical issues associated with the previous use of Chromated Copper Arsenate (CCA) at a number of sites, remediation is on-going and with the recent move to the copper azole, which has temperature independent fixation properties, the on-site situation should improved provided that manufacturer's instructions are followed.

The main conclusions reached were:

- On-site practice in terms of the manner in which timber is presented prior to treatment, post treatment holding times of 48 hours and storage is critical to ensuring compliance with surface-water limits for copper and biocides.
- Site monitoring points should include up-stream or up gradient sample points for surface-water and groundwater sampling.
- The draft Code of Practice for the Operation of Timber Preservation Plants in an Environmental Conscious Manner, TQBI, 1996, should be revisited by relevant industry bodies and issued formally.

## ACKNOWLEDGEMENTS

I would like to thank my wife Maura, my daughter Catherine and baby James for their understanding and support, which on occasion involved testing the robustness of my PC hardware during the writing up stage of the MSc programme.

Also I would like to thank Arch Timber Protection management for sponsoring me and for the co-operation I received from timber treaters during the on-site auditing. I would like to thank Thomas Sexton and staff at regional EPA offices for their assistance during the project

Special thanks must go my brother Dr Mark Harvey for his help and guidance in compiling the statistics section of the project.

Finally I extend my thanks to Noel Connaughton the course co-ordinator and Ossian Geraghty my supervisor for steering me in the right direction.



## GLOSSARY OF TERMS

American Wood Protection Association Standard (AWPA).

Arch Timber Protection (ATP).

Best Available Technique (BAT).

Best Available Technology not Entailing Excessive Cost (BATNEEC).

Biocidal Products Directive 98/8/EC (BPD).

British Wood Preserving and Damp Proofing Association (BWPDA).

Building Research Establishment (BRE).

Chromated Copper Arsenate (CCA).

Copper azole –copper azole ie tebuconazole and propiconazole.

Copper quaternary ammonium chloride (ACQ).

Environmental Protection Agency (EPA).

Environmental Quality Standard (EQS).

Enviros – Environmental consultants used by EPA.

European Chemical Bureau (ECB).

Gas Chromatography (GC).

High Performance Liquid Chromatography (HPLC).

Integrated Pollution Prevention Control (IPPC)

Interim Guidance Value (IGV).

International Programme on Chemical Safety (IPCS).

Irish Forest Industry Chain (IFIC).

kgf/cm<sup>2</sup> measure of pressure kilograms force per square centimetre.

Light organic solvent preservatives (LOSP).

Low pressure gas chromatography/mass spectrometry (LP-GC/MS).

National Standards Authority of Ireland (NSAI).

Nordic Wood Preservation Council (NTR).

O’Callaghan Moran & Associates (OCM).

Organisation for Economic Co-operation and Development (OECD).

Pesticide Control Service (PCS).

Pollution Prevention and Control Regulations (PPCR).

Sterol demethylation inhibitor (DMI).

Tanalith<sup>®</sup> E – copper azole formulation marketed by Arch Timber Protection.

Technical Environmental Regulatory Affairs (TERA).

Timber Quality Bureau of Ireland (TQBI).

Tributyltin oxide (TBTO).

United States Geological Survey (USGS).

Wood Marketing Federation (WMF).

Wood Protection Association (WPA).

Woodspec – specifiers guide prepared by WMF and COFORD.

## **1 AIMS AND OBJECTIVES**

- To assess if there are surface and groundwater contamination issues with pesticides at Integrated Pollution Prevention Control (IPPC) licensed sites using copper azole based wood preservatives.
  - To assess if on-site activities are contributing to the issue.
  - To assess if external factors and activities are a significant factor.
  - To assess surface and ground water emissions on-site at selected sites using the copper azole based wood preservatives.
  - Main actives considered: copper, tebuconazole and propiconazole.
- To select eleven IPPC licensed sites, this represents all IPPC licensed sites using copper azole in the Republic of Ireland.
- To identify likely sources of emissions based on data collected.
- Refer to surface and groundwater data available on-site.
- To identify any on/off-site activities that might contribute to emissions based on data examined and audits carried out.
- Audit on-site activities which will include water sampling procedures.
- To make recommendations based on data collected.
- Information gathered will assist IPPC licensees with their Environmental Management Programmes.

## 1.1 Methodology

Information was gathered from the following sources:

- Discussions with Arch Timber Protection colleagues in the UK.
- Discussions with Irish regulators i.e. Environmental Protection Agency (EPA) and Pesticide Control Service (PCS).
- Discussions with Environmental Managers at sites visited.
- Site visits to 11 IPPC wood treatment facilities, this is a 100% sample of IPPC licensed treaters using copper azole Tanalith<sup>®</sup> E in Ireland.
- Audit of activities on site
  - Audit format was devised using the following documents as benchmark:
    - BATNEEC Guidance Note for Wood Preservation EPA 1994.
    - Code of Practice for the Operation of Timber Preservation Plants in an Environmental Conscious Manner, TQBI, 1996.
    - IPC Regulation Of the Timber Preservation Sector, Jonathan Derham, EPA, 2002.
  - Audit consisted of questions, physical measurements of containment facilities and in the case of surface-water and ground-water analysis results the most up-to-date independent information was used along with results from the O'Callaghan Moran & Associates (OCM) and EPA Reports for each site.
  - If the information was not available or forthcoming reference was made to EPA held files at regional offices.
  - At two sites where there was a gap in analytical results water samples were taken and analysed off-site.
- One site was selected as a case study in terms of monitoring procedures, groundwater survey and site investigation procedures.

## 2 LITERATURE REVIEW

### 2.1 Introduction

The objective of this literature review was to look at the present status of the wood preservation sector in Ireland, the range of wood preservatives used and properties of active ingredients in the formulations discussed and environmental aspects of licensed activities. The review will also refer to the regulatory background, the compliance requirements and methodology of measuring compliance through water monitoring and on-site environmental auditing.

### 2.2 Background to wood preservation sector in Ireland

The Irish forestry and forest products sector has an annual value of 1.2 billion euro. The total forest cover in Ireland is estimated to be 724,245 hectares, of which 77% is coniferous softwood, Magner (2009, 90). The main species is Sitka spruce (*Picea sitchensis*), which is classified as a non durable timber, Woodspec (2007, 321) and is widely used for construction and fencing purposes in Ireland, from the annual round wood harvest of 3 million m<sup>3</sup> the yield of sawn fencing is 266,000m<sup>3</sup> and 164,000m<sup>3</sup> of round stakes, Magner (2009, 90), a majority of this fencing material will require preservative treatment if used in accordance with Irish Standards.

The unique growing conditions in Ireland give rise to high yielding plantations of *Picea sitchensis* which in terms of density and permeability render it uniquely suitable for pressure treatment and subsequent use in ground contact situations. In Ireland work by the Wood Technology Centre, Strainer Treatment Test, Anon. (2006, 8) has shown that pre-dried home-grown *Picea sitchensis* complies consistently with the penetration requirements of I.S. 436:2007, National Standards Authority of Ireland (2005) and B.S. 8417:2003, British Standards Institution (2003), where 6mm penetration of wood preservative into the spruce sapwood is required for ground contact use in order to achieve an anticipated service life of 15 years.

When you look at the European Union, which is predominately a coniferous softwood market, it was estimated that 18 million m<sup>3</sup> per annum of timber was pressure treated, Connell (2004, 1).

In 1996 prior to the introduction of Section 8.3 of the Environmental Protection Agency (EPA) licensing schedule there were according to Enterprise Ireland (1996) 94 treatment plants operational in Ireland, 41% were high pressure plants using Chromated Copper Arsenate (CCA). The EPA estimated that in 2005 there was 50 IPPC licensed plants while it was reported by Sexton (2007) following the change from CCA to copper organics, the number had reduced to 46 active plants with eleven licensees using copper azole and eight on copper quaternary ammonium chloride (ACQ). The remainder of the licensed operators are using low pressure systems with metal free preservatives with either a solvent or water-based carrier.

The framework legislation in the European Union is the Integrated Pollution Prevention and Control Directive (IPPC, 96/61/EC) and considers emissions to land, air and water. The Department of Environment in Ireland have interpreted this EU Directive by setting a license threshold of “10 tonnes of preservative per day”. This particular interpretation of the directive is unique to Ireland in terms of regulation of the preservation sector and contrasts with our nearest neighbours in the UK and Northern Ireland where wood preservation plants using water-based preservatives are effectively exempt from IPPC licensing, this regulatory situation has the potential to impact on competitiveness within the sector and has been raised as a key issue by the timber industry with Department of Environment, Wood Marketing Federation (2008).

The EPA, which is the regulatory authority for the timber preservation industry, view on the industry is outlined in their Office of Enforcement Report, EPA Office of Enforcement (2006, 7) where a listed objective of the Agency in relation to the sector was to “tackle the persistent land and groundwater issues associated with the timber preservation industry”. Sexton (2007) reported that 26% of licensees sampled had pesticide levels in surface and ground-waters which had exceeded the Dangerous Substances and Drinking Water Regulations respective limits. The pesticides detected were tebuconazole and propiconazole which are secondary biocides that are present in the wood preservatives, Tanalith<sup>®</sup> E (copper azole), Vacsol<sup>®</sup> Aqua (triazole permethrin) and Osmose Clearchoice (triazole permethrin).

In terms of IPPC licensing of the wood preservation sites in other European countries the focus tends to be on the use of heavy metals like copper and organic solvent based preservatives. In the UK the regulatory authorities licensing applies to use of light organic solvent preservatives (LOSP) and potential air emissions of volatile organic carbons, Anon. (2004, 6). In Norway there is reported to be monitoring for copper levels near wood preservation facilities, 15 plants are identified but no information relating to non-compliance is reported, Bergfald & Co. (2005, 80).

### 2.3 Wood Preservation Overview

Wood has innumerable uses and "...is an indispensable part of the material structure upon which civilisation rests..", Roosevelt (1905 cited in Wilkinson, 1979, 7). Timber preservation is not a new idea and a famous transporter of livestock is reported to have treated the Ark with pitch, Noah (1905 cited in Wilkinson, 1979, 21) however it was only in the 1800's that scientific timber preservation was born following the development of pressure impregnation by Bethell using the coal tar derived creosote, Wilkinson (1979). In 1933 the first water-based CCA formulation was developed by Dr Sonti Kamesan in India which demonstrated excellent performance up until it was replaced by copper organics following the restrictions and phase-out arising from the Marketing and Use Directive 76/76/EC in 2001, Connell (2004, 4). Developments have tended to rely on the replacement of arsenic in CCA with alternative active ingredients such as copper azoles and ammonium copper quaternary (ACQ).

At the Scandinavian Wood Preservation Conference, Edlund (1998 cited in Connell 2004, 2) identified the need for field tests as a key requirement for evaluating the performance in ground of different wood preservatives. He highlighted the importance of bench-marking the performance of new generation copper organics against traditional CCA which had a proven track record worldwide.

Archer & Preston (2006) recognised the need for "co-biocides" to work alongside copper, this is especially true when treated timbers are potentially exposed to copper tolerant brown rot fungi in-service, this issue was highlighted by Suttie *et al.* (2002, 9)

“when brown rot is dominant then a higher concentration of the copper is required or additional active ingredients are required”. Archer & Preston (2006) concurred with this view “in terms of wood preservatives and incident of copper tolerance the focus has been on brown rot basidiomycetes especially in the genus *Poria*”. Bravery *et al.* (2007, 25) gave practical guidance “the main fungi in this genus, which is commonly known as wet rot, are *Amyloporia xantha*, *Fibroporia villanti* and *Poria placenta*, *Fibroporia* in particular can cause extensive damage”.

The wood preservation standard used in the UK is BS 8417:2003, section 4.2.4 which, when addressing other preservatives, refers to the variable performance of new generation preservatives “as different molecules are susceptible to different forms of depletion data from field trials may provide a sound basis for deriving recommended loadings rather than relying on extrapolated laboratory data”. This issue was addressed by Lebow (2004, 3) “because a wood preservative must protect against a range of organisms while simultaneously resisting environmental degradation at least three to five years of test stake exposure in multiple locations is needed to demonstrate the potential for long term efficacy in ground contact applications”.

In the UK the Building Research Establishment (BRE) carried out a review of the new generation preservatives available on the market and Suttie *et al.* (2002, 2) concluded that “the evidence available from field trials across the world indicates that 1.5 times as much copper azole and 3 times as much ammonium copper quaternary (ACQ) is required to give equivalent performance to CCA”. Suttie (2009) reaffirmed the critical importance of field data and recommends that preservative loadings should be adjusted when field trial data becomes available.

This variation in efficacy and performance is illustrated in the published ground contact loadings for use in Scandinavia, Nordic Wood Preservation Council (2008) which are derived from five years field data from two Swedish independent test sites, copper azole is approved at 16 kg/m<sup>3</sup> while ACQ products are approved at 36 kg/m<sup>3</sup> for in ground contact use (class A).



This trend is similar in the US where data reviewed in the American Wood Protection Association Standard (AWPA) on ground contact approvals, which are also based on field results, indicate that the preservative loadings for ACQ based preservatives are twice that of copper azole, AWPA (2008, 25). The recently published Irish standards by the National Standards Authority of Ireland (2005 and 2007) for timber fencing components I.S. 435:2005 and I.S. 436:2007 refer to the need for 10 years independent field data from test sites in Europe to support the loadings used for ground contact situations.

The independent field study information and published approved wood preservative loadings in Scandinavia and US indicate that of the CCA alternative new generation wood preservatives used in Ireland that copper azole formulations can be used at half the preservative loading required for ammonium copper quaternary (ACQ) when used in ground contact situations, when field data is used as the basis for that standard. This differentiation in wood preservative efficacy has consequences when you look at load minimisation and use of metals and biocides in the environment, the environmental aspects of the various wood preservatives is explored later in this review section.

#### ***2.4 Copper azole wood preservatives***

At the start of the 1980s Hickson Timber Products (now Arch Timber Protection) identified through laboratory screening tests and extensive field trials that copper and triazole active ingredients could offer a viable alternative to CCA. The main active ingredients in Tanalith<sup>®</sup> E are copper carbonate, tebuconazole and propiconazole, Arch Timber Protection (2004). The ratio of actives as presented by Enviro (2003, 11) in their treated timber classification report on a percentage weight/weight basis in the preservative was copper carbonate 20%, propiconazole 0.2% and tebuconazole at 0.2%.

Gray and Dickinson (1998, 65-79) recognised that “in terms of the efficacy adsorption of copper is important to the performance of timber preservatives, especially against soft rot fungi *Chaetomium globosum* where cation exchanged copper is thought to prevent the initiation of soft rot attack in the cell wall”. The importance of protection

against soft rot in critical timber components like bridges was identified by the US Department of Transportation (2004, 19) “this fungal decay organism causes a gradual degradation from the surface inward and primarily attack cellulose and hemicellulose and are more prevalent in very wet environments, in agricultural soils. Because the attack occurs on the surface, soft rot damage can be particularly important where members are used in bending or where exposed to windy conditions”. The efficacy of waterborne metal preservatives is driven by fixation which is a process that reduces the leaching of a preservative component and is defined by Cooper *et al.* (1993, 7) as “the state of chemical components of preservative wood or other substrate when all chemical reactions are complete”.

Archer & Preston (2006) described the complex reaction between copper and wood components as “in chemical terms copper fixation involves ion exchange with acidic groups (e.g. carboxylic acid and phenolic OH groups) present in lignin, hemicellulose and wood extractives”. Mitsuhashi (2007, 19) describes the role of copper which is “broadly toxic to fungi, causing membrane disruption and inhibiting many important enzymatic reactions. Low levels of copper are less effective against insect attack and high levels are effective against most insects”.

Grundlinger and Exner (1990, 3) were the first to identify the potential wood preservative properties of the organic biocide, tebuconazole, “which is an un-leachable, light and heat stable compound that provides protection against copper tolerant fungi”. It was reported by Kugler *et al.* (2008) that tebuconazole and propiconazole complement each other in terms of their efficacy against basidiomycete fungi which cause brown rot. Grundlinger and Exner (1990, 3) outlined the biological tests that assess performance against basidiomycete decay fungi is EN113 and these tests indicate toxic values for *Coniophora puteana* is 0.08 – 0.13 kg/m<sup>3</sup> active ingredient.

#### **2.4.1 Ammonium copper quaternary (ACQ) based wood preservatives**

ACQ products are based on copper plus a quaternary ammonium chloride organic biocide and is available in ammoniacal or amine form with different quaternary compounds, in Ireland the ACQ based product approved by the Pesticide Control

Service (PCS) is AC500 and is marketed by Osmose, Connell (2004, 7). In terms of active ingredients Enviros. (2003) reports that AC500 contains 16.53% copper carbonate, 4.75% benzalkonium chloride (BAC) and 5% boric acid. In terms of approvals based on field data AC500 is not approved for ground use in Scandinavia, NTR (2008).

The AC800 product is approved for ground contact use in Scandinavia at a loading of 36 kg/m<sup>3</sup>, this ACQ formulation has a similar ratio of copper to BAC actives with the exception of boric acid which is not present in the formulation, Osmose Sweden AB (2002). The other ACQ product used in Scandinavia is Kemwood ACQ which is approved at similar loadings to AC800 and is based on copper at 9.5% and BAC at 4.8%, Edlund (2002, 4).

#### **2.4.2 Copper HDO based wood preservatives**

This copper-based product is supplied in Europe by Dr Wolman and is based on copper bis-N-cyclohexyldiazoniumdioxy (Cu-HDO), Freeman *et al.* (2003, 11). The products approved in Scandinavia are Wolmanit CX-8 and CX-10, NTR (2008) and are not listed as being used in Ireland by IPPC licensed treaters, Sexton (2007).

#### **2.5 Wood Preservation Process**

A pressure treatment is defined in the Arch Training Manual “as one in which timber is placed in a closed cylinder and preservative fluid is forced into the wood by artificially applied high pressure - usually 10-14 kgf/cm<sup>2</sup> (approximately 11 bar). When preservation by high pressure is carried out, the pre-treatment moisture content of the timber must be below 28% moisture content”.

A typical high pressure treatment process cycle is outlined below in Figure 1.

Source: Arch Timber Protection (2001, ch. 3).

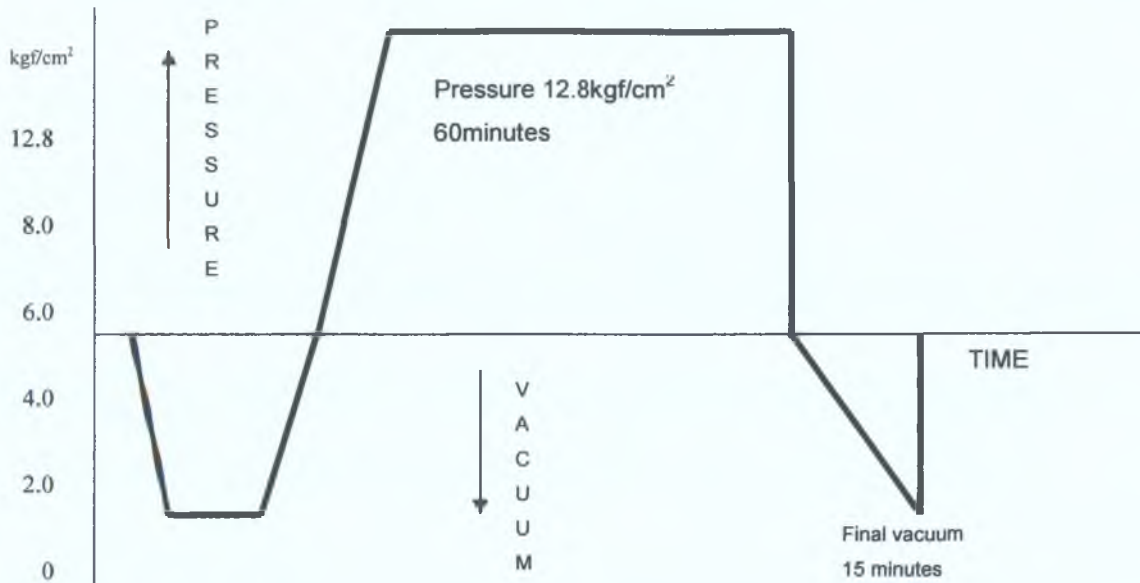


FIGURE 1: TREATMENT PROCESS.

An initial vacuum is applied to the charge, and held at 600mm Hg or above, this vacuum removes air from the timber cells. Then, without releasing the vacuum, the cylinder is flooded with preservative solution and a pressure of a minimum of 12.8 kgf/cm<sup>2</sup> is applied to the timber in the vessel. The pressure in the vessel is released, the treatment cylinder is then emptied of solution and a second or final vacuum is applied.

On release of this final vacuum, a final recovery phase removes excess solution, the timber is ready to be removed from the cylinder. The duration of initial vacuum and pressure periods will differ according to the differences in permeability between timber species and end use of the timber. The treated timber is then held within a contained area for a period of 48 hours, as shown in Plate 1, Arch Timber Protection (2001, 16). The Material Safety Data Sheet has the following wording “treated wood must be held until surfaces are dry within a bunded area on a site which is maintained to prevent loss of treatment product to the environment”, Arch Timber Protection (2007, 8).

It is important to consider that post treatment drying is influenced by a number of factors; climatic conditions, air drainage, species of timber, cross sectional area, pre-treatment moisture content, manner in which timber is presented and actual treatment process parameters. The TERA Update G1/08 gives guidance to treaters in terms of improving post treatment drying, Arch Timber Protection (2008, 2).



PLATE 1: TYPICAL TREATMENT PLANT LAYOUT

### 2.5.1 Low Pressure Water-based Preservative Systems

Low pressure double vacuum treatments provide for the treatment of low hazard classes (i.e. above ground and protected from the elements) and are designed to give a protective envelope of preservative around the timber. Homebond (2005) describes that the low pressure process normally uses organic solvent or micro-emulsion preservatives. Woodspec (2008, 66) recommends that “these preservatives are not designed for use in ground contact or below damp proof course (DPC) and if used externally they should receive a surface coating”. This preservative system is designed for treatment of truss, timber frame and external joinery products and is not suitable for treating fencing timbers, Arch Timber Protection (2008).

Sexton (2007) reported that there were 17 low pressure plants IPPC licensed and operational in Ireland. The main active ingredients in Osiose Clearchoice 415E (16 plants) and Vacsol Aqua (1 plant) are, as reported by Enviro (2003, 8-10) to be

tebuconazole, propiconazole and permethrin, the ratio of actives % weight/weight in the 415E preservative was propiconazole 0.15% and tebuconazole at 0.15%.

This 2007 EPA/OCM study concluded that permethrin was not detected at elevated levels at IPPC licensed sites assessed however the study did not indicate if the presence of tebuconazole and propiconazole was linked to sites using low pressure or high pressure systems.

## ***2.6 Environmental Aspects of Wood Preservatives***

Environmental and health concerns have been raised in the past about the use of the active ingredients which were present in CCA wood preservatives however once the chemicals are fixed in the timber the field performance is difficult to question, the Irish Forest Industry Chain (IFIC) submission to the European Commission in 2001 gave a good summary of the complex issues with CCA, IFIC (2001).

CCA alternatives, like copper azole, have been developed and introduced to the market relatively recently, in wood preservation terms. They are proprietary products, limited information has been published on the formulations currently being used in Ireland. The main conclusions drawn by Lebow (1996, 2-8) in relation to CCA was that the time for fixation varied with wood species, specimen size, retention and most important parameter being temperature.

Wilkinson (1979, 140) outlined the development of CCA in the 1920s when Heinrich Brüning discovered that chromium undergoes reaction mechanisms that enhances deposition of soluble salts. Work by Hughes (1995, 7) indicated that with the copper azole formulation, i.e. Tanalith<sup>®</sup> E, the fixation mechanism immediately after treatment is temperature independent over the temperature range 5-21<sup>0</sup> C, this is in contrast to the situation with the CCA formulation where rate of fixation was driven by temperature. This feature of CCA had the potential to cause surface-water and groundwater compliance issues particularly during the winter months with low temperatures and high rainfall levels.

### 2.6.1 Leaching studies on new generation preservatives

Lebow (2004, 3) concluded that “CCA alternatives will release copper into the environment at a rate greater than or equal to that of CCA however copper is associated with fewer mammalian health concerns than with arsenic or chromium. In terms of the aquatic impacts of copper it can be toxic to aquatic organisms particularly to the larval stages of invertebrates. The active ingredients are initially water soluble in the treating solution but become resistant to leaching when placed in the wood”.

Aston (2004, 4) outlined the approach being taken in relation to leaching studies “there has been a number of initiatives through the Organisation for Economic Co-operation and Development (OECD), EU, American Wood Preservers Association (AWPA) and other organisations to devise appropriate leaching procedures that can predict both expected long term efficacy of the treatment and potential impacts of leachate on human health and environment. In 2000 the OECD established an Expert Group to prepare an Emission Scenario Document (ESD) that would describe the ways in which wood preservatives were applied and the end uses to which the treated timber was put. These scenarios were published on the European Chemical Bureau (ECB) website”.

The issue of assessing leaching from treated timber is a very complex subject with a range of data from different preservatives and loadings being derived from laboratory and field tests. Aston (2004, 4) urged a certain degree of caution when drawing conclusions from leaching studies “although numerous laboratory studies and small-sized field studies have been conducted to evaluate the effect of various parameters on preservative fixation and leaching, these studies often have little applicability to in-service leaching rates”.

Laboratory based leaching studies carried out by Waldron and Cooper (2002) “predict that ACQ treated timber will have higher leaching rates compared to CCA and copper azole but copper azole will continue to leach copper at a measurable rate for a longer time than with CCA”. Recent field based leaching studies by Cooper *et al.* (2005, 6) looked at preservative levels in soil below treated decking components after eight years in service, the results indicated that copper leaching from timber treated with

copper HDO (CX8) and ammonium copper quaternary (ACQ) was more than twice that from timber treated with copper azole at similar initial retentions. Mitsuahhi (2007, 28) concluded in her review “leaching of components from copper azole treated wood is small and primarily occurs immediately after the initial exposure of the treated member as unfixed components are removed from the wood surface”.

The effect of leaching on exposed pine decking was analysed by Kennedy and Collins (2001, 13) and concluded that “rates of leaching from decks during 300 days service varied widely between preservative components ranging from  $0.029 \text{ mg m}^{-2} \text{ d}^{-1}$  for tebuconazole, corresponding rates for CCA elemental components varied from 0.52 to  $1.4 \text{ mg m}^{-2} \text{ d}^{-1}$ ”, the results of this short study indicated that the co-biocide, tebuconazole, performed well when compared to traditional CCA, which is the benchmark wood preservative formulation in field trials.

Longer term depletion studies in Sweden by Edlund and Jermer (2002, 9) where treated timber members used above ground were analysed after five years in-service indicates that 85% of copper and 60% tebuconazole remained for the copper azole formulation tested. It should be noted that these studies referenced looked at timber treated with earlier formulations of Tanalith<sup>®</sup> E which were based on copper and tebuconazole while the formulation used in Ireland now are based on copper, tebuconazole and propiconazole, Enviros (2003, 11). In terms of likely loadings of biocides in Tanalith<sup>®</sup> E treated timber Table 11 in the Enviros report referred to loadings of 0.000016 kg of preservative per kg of treated timber for tebuconazole and propiconazole, based on a sapwood loading in the treated timber of  $16 \text{ kg/m}^3$ .

### **2.6.2 Classification of treated timber waste off-cuts**

One of the on-site handling issues with pressure treated timber is the waste classification of treated timber off-cuts and treated timber that has reached the end of its useful service life. The Environmental Protection Agency commissioned Enviros to assess Norway spruce (*Picea abies*) treated with a range of wood preservatives and Enviros (2003, 15) concluded that timber treated with Tanalith<sup>®</sup> E (copper azole) “should be classified as non-hazardous, where the uptake rate of preservative is known to be below  $9.5 \text{ kg/m}^3$ ”.



This threshold refers to overall  $\text{kg/m}^3$  loading for the full spruce cross section, the maximum loading achieved in the Wood Technology Centre, Strainer Treatment Test, Anon. (2006, 10) was  $1.05 \text{ kg/m}^3$  for treated spruce timbers so it is technically difficult to reach this threshold of  $9.5 \text{ kg/m}^3$  in practice with home-grown spruce in Ireland.

## 2.7 *Properties of Copper*

Natural sources of copper exposure include windblown dust, volcanoes, decaying vegetation, forest fires and sea spray, International Programme on Chemical Safety IPCS (1998, sec 1.3). Fay *et al.* (2006) described the background levels of metals in Irish soils “soils of the central north eastern area of Ireland, (immortalised by Patrick Kavanagh), consist mainly of gleys which have been derived from Lower Palaeozoic greywacke and shale have a significant volcanic mineral content and high levels of copper and chromium in the soil profile”.

Copper ores are mined, smelted and refined to produce many industrial and commercial products. McGrath and McCormack (1999, 13) collated information on Irish soils and noted “elevated levels of copper in soil have been reported in Wicklow and are linked to mining in the Avoca Valley”. The IPCS (1998) described the main copper uses “i.e. cooking utensils, pipes, fertilizers, bactericides, fungicides, algacides and antifouling paints and wood preservatives”.

The normal method of analysis for copper is Atomic Absorption Spectrometry, APHA (2005, 3-72), there are 29 laboratories registered in Ireland, EPA Register (2007) that can analyse for copper however for trace amounts in surface-water and groundwater the favoured method is inductively coupled plasma mass spectrometry (ICP-MS), ALcontrol (2007).

### 2.7.1 Environmental factors

OCM (2007) reported background levels of copper in natural freshwater sediments range from 16 to 5,000 mg/kg (dry weight) and in groundwater, 2.5 µg/litre is the global average. The IPCS (1998) dossier on copper reported background levels “in marine sediments range from 2 to 740 mg/kg (dry weight and copper concentrations in uncontaminated soil were reported to be 30 mg/kg (range 2-250 mg/kg).”

### 2.7.2 Toxicology

In terms of copper toxicology Clenaghan *et al.* (2005, 34) reported that “for healthy, non-occupationally-exposed humans the major route of exposure to copper is oral. The mean daily dietary intake of copper in adults ranges between 0.9 and 2.2 mg. A majority of studies have found intakes to be at the lower end of that range. Copper is an essential dietary requirement though at levels above 1 mg/l copper can cause organoleptic (taste) problems”. A summary of LD50 data, median lethal dose that will kill 50% of the tested group, is presented in Table 1.

| Source IPCS (1998)        |              |
|---------------------------|--------------|
| Male rats dermal exposure | >1,124 mg/kg |
| Rabbits                   | >2,058 mg/kg |

TABLE 1: ORAL ACUTE LD50 FOR COPPER

### 2.7.3 Environmental impacts

Archer and Preston (2006) presented data in relation to the potential environmental impacts “in the US the chronic affects criteria for copper ranges from 3.12 µg Cu/L in soft freshwater or 33.3 µg Cu/L in hard water. In a marine environment the chronic criteria is 3.1 µg Cu/L. Copper released to surface water has a strong tendency to adsorb to fine particles and copper in sediment tends to be less toxic than dissolved copper”. A summary of LC50 data is presented in Table 2, LC50 is defined as the “concentration estimated to produce mortality in 50% of a test population over a specific time”, Rand (1985, 4).

| Source IPCS (1998)          |                |
|-----------------------------|----------------|
| Fish LC50 (96 h) for salmon | 60 µg Cu/litre |
| Daphnia LC50 (48 h)         | 5 µg Cu/litre  |

TABLE 2: SUMMARY OF ECO-TOXICITY FOR COPPER

Brooks (2004, 2) gives a summary of the concerns in the US and Canada about the potential effects of copper on salmon and trout populations in river systems if exposed to chronic or acute concentrations of the metal in water, the sensitivity of fish to copper explains the low surface water limits of 0.03mg/l versus 2mg/l for groundwater.

In some cases, drinking-water may make a substantial additional contribution to the total daily intake of copper, particularly in households where corrosive waters have stood in copper pipes. Page *et al.* (2007, 23) report on drinking water quality in Ireland found that “elevated levels of copper were found in three of the 1,115 water supplies monitored and were due to internal domestic plumbing at the sample points”. In Norway Bergfald & Co. (2005, 80) the main source of copper emissions were anti fouling from aquaculture and wood preservation.

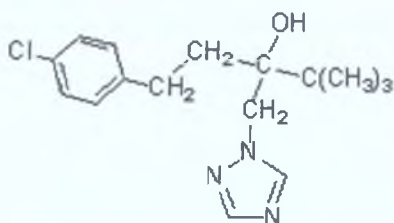
The situation in Ireland was assessed by Clenaghan *et al.* (2005, 33) and they concluded that “environmental issues with copper seemed to be limited with an 82% compliance with the EPA copper standard of 0.03 mg/l for surface waters”. Work carried out by the EPA, Sexton (2007) at IPC licensees indicated that at three wood preservation sites copper level exceeded the Environmental Quality Standard (EQS) for surface waters (limits 0.03 mg/l) and Interim Guidance Value (IGV) standard for groundwater (limit 2.0 mg/l).

## 2.8 Tebuconazole

Tebuconazole is a secondary biocide in copper azole wood preservatives. Courier (2006, 3) gives a history of the development of azole fungicides, tebuconazole based agricultural fungicides were first synthesized in 1981 by the Bayer Pharmacology Department in Wuppertal. It is classified as a sterol demethylation inhibitor (DMI). This bio-chemical mode of action stop all important steps of fungal infection by blocking the precursors of sterols, Dutzmann and Suty-Heinze (2004, 1).

### 2.8.1 Chemical name and structure

Wüstenhöfer *et al.* (1990) presented the full chemical name for tebuconazole, (+)-Alpha-(2-(4-Chlorophenyl)-ethyl)-alpha-(1.1-dimethylethyl)-1H-1.2.4-triazole-1-ethanol.  $C_{16}H_{22}ClN_3O$ . The structure of tebuconazole and summary of properties is presented in Table 3.



| Source: Gründlinger, Roland (1990 p. 2) |  |
|---|--|
| Molecular weight                        | 307.8  |
| Colour                                  | Colourless to light brown powder   |
| Density                                 | 400 g/l  |
| Solubility                              | In water 0.0032 w/w, (20 °C).  |
| Stability                               | Stable to elevated temperatures, and to photolysis and hydrolysis in pure water, under sterile conditions; hydrolysis          |
| Phytotoxicity                           | Good plant compatibility in most crops with any formulation, and achieved in more sensitive crops by appropriate formulations. |

TABLE 3: TEBUCONAZOLE: PHYSICAL CHEMISTRY

Agricultural Trade Names: Beam<sup>®</sup> and Folicur<sup>®</sup> are listed in Crop Protection (2004) as being used in Ireland, typical application rates for a tebuconazole based product is presented in Table 4.

| Source: China Shenghua rates for SEGARD |                  |
|---|------------------|
| Crop Name                               | Application rate |
| Rust species                            | 125-250 g/ha     |
| Powdery mildew at                       | 200-250 g/ha     |
| Scald in cereals                        | 200-312 g/ha     |
| Septoria spp in cereals                 | 200-250 g/ha     |
| Early blight in tomatoes and potatoes   | 150-200 g/ha     |

TABLE 4: CROP APPLICATION RATES FOR TEBUCONAZOLE

### 2.8.2 Analysis of tebuconazole

Gründlinger *et al.* (1990, 2) recommends the use of Gas Chromatography (GC) and High Performance Liquid Chromatography (HPLC) when assessing the concentration of tebuconazole in treated wood and wood preservatives. Walorczyk (2004) outlined techniques for detecting trace levels on plums can be identified with low pressure gas chromatography/mass spectrometry (LP-GC/MS) the detection limit is 0.017mg/kg.

### 2.8.3 Toxicology of tebuconazole

A summary of the toxicology information relating to tebuconazole is presented below in Table 5:

| Source: PAN Pesticides Database |                        |
|---------------------------------|------------------------|
| Male rats LD50                  | 4,000 mg/kg            |
| Female rats LD50                | 1,700 mg/kg            |
| Mice LD50                       | 3,000 mg/kg            |
| Toxicity class WHO (a.i.)       | III slightly hazardous |
| EC classification               | Xn; R22                |
| US EPA Carcinogens              | C possible             |

TABLE 5: SUMMARY OF TEBUCONAZOLE

## 2.8.4 Ecotoxicity of tebuconazole

A summary of the ecotoxicity information relating to tebuconazole is presented in Table 6:

| Source: PAN Pesticides Database       |                         |
|---------------------------------------|-------------------------|
| Male Japanese quail acute oral LD50   | LD50 4438 mg/kg         |
| Female Japanese quail acute oral LD50 | LD50 2912 mg/kg         |
| Bobwhite quail acute oral LD50        | LD50 1988 mg/kg b.w     |
| Mallard ducks Dietary LC50            | for >4816 mg/kg         |
| Bobwhite quail Dietary LC50           | >5000 mg/kg feed        |
| Fish LC50 (96 h) for rainbow trout    | 4.4 mg/kg               |
| Daphnia LC50 (48 h)                   | 4.2 mg/l (flow through) |

TABLE 6: SUMMARY OF ECOTOXICITY FOR TEBUCONAZOLE

## 2.8.5 Environmental fate of tebuconazole

Work by Strickland *et al.* (2004 cited in Potter *et al.*, 2005, 1) in the US on peanuts crops where 47% of crops are sprayed with tebuconazole indicates that in aerobic loamy soil a half life of 49 days the UNEP (2002) threshold for persistence is a half life of greater than 180 days, a summary of extracted data on persistence is outlined in Table 7:

| Source: PAN Pesticides Database |             |
|---------------------------------|-------------|
| Adsorption Coefficient          | 1,000 (Koc) |
| Hydrolysis Half life            | 28 days     |
| Aerobic soil                    | 597 days    |
| Anaerobic soil half life        | 1,260 days  |

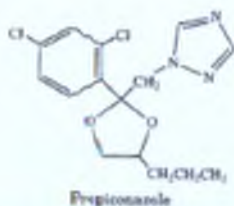
TABLE 7: TEBUCONAZOLE PERSISTENCE DATA

This data compares favourably to the persistent metals actives in CCA, according to Coover and Sims (1987) arsenic and chromium has a half life of  $10^8$  days in soil.

## 2.9 Propiconazole

The US EPA (2006, 2-4) gives an introduction to the second co-biocide in Tanalith<sup>®</sup> E, “propiconazole was first developed in 1979 by Janssen Pharmaceuticals of Belgium. It is now being marketed by Ciba-Geigy. The chemical name for propiconazole is: 1-((2-(2,4-Dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl)methyl)-1H-1,2,4-triazole”.

The fungicidal and antimicrobial properties of propiconazole are outlined in Ciba-Geigy (cited in Pesticide Information Profile 1997, 1) “in terms of mode of action it inhibits an enzyme involved in ergosterol biosynthesis which is critical to the formation of the cell walls in fungi”. The structure and properties of propiconazole is presented in Table 8.



| Source: PAN Pesticides Database |  |
|---------------------------------|--|
| Molecular weight                | 342.23   |
| Density                         | 400 g/l  |
| Solubility                      | In water 100mg/l   |
| Stability                       | Stable to elevated temperatures, and to photolysis and hydrolysis in pure water, under sterile conditions; hydrolysis          |
| Phytotoxicity                   | Good plant compatibility in most crops with any formulation, and achieved in more sensitive crops by appropriate formulations. |

TABLE 8: PROPICONAZOLE: PHYSICAL CHEMISTRY

Agricultural Trade Names: Tilt, Alamo<sup>®</sup>, Banner<sup>®</sup>, Orbit<sup>®</sup>, and Quilt<sup>™</sup> are listed in Crop Protection (2004) as being used in Ireland. Propiconazole is used as a fungicide on a number of agricultural crops, fruit and nut trees, ornamentals and turf. It is also used as a wood preservative and as an antimicrobial/material preservative in adhesives, paints, coatings, leather, paper, textiles, and specialty industrial products. Typical application rates are outlined in Table 9.

| Source: Ciba-Geigy        |   |
|---------------------------|---|
| Propiconazole application | Application rate                        |
| Cereals                   | 0.75 kg active ingredient (ai)/ hectare |
| Celery                    | 0.5 kg ai/hectare                       |
| Peanuts                   | 0.5 kg ai/hectare                       |
| Corn                      | 0.5 kg ai/hectare                       |
| Shade trees               | 8.06 kg ai/hectare                      |

TABLE 9: PROPICONAZOLE APPLICATION RATES

Application timings: All through-out the growing season when needed, Ciba-Geigy (1997, 1).

### 2.9.1 Toxicology of propiconazole

A summary of the toxicology information relating to propiconazole is presented below in Table 10:

| Source: PAN Pesticides Database        |                              |
|--|------------------------------|
| Male rats Oral acute LD50              | 1,517 mg/kg                  |
| Rabbit dermal toxicity Oral acute LD50 | 4,000 mg/kg                  |
| Toxicity class WHO (a.i.)              | II moderately hazardous      |
| EC classification                      | Xn, R22 harmful if swallowed |
| US EPA Carcinogens                     | C possible                   |

TABLE 10: SUMMARY FOR PROPICONAZOLE

When you look at the toxicity profile of the secondary biocides in copper azole they compare favourably to the earlier CCA formulation where oral acute LD50 rats for arsenic was 763mg/l, Oxford (2005) and for chromium trioxide 52 mg/l, Elementis (2001, 6).



## 2.9.2 Ecotoxicity of propiconazole

| Source: PAN Pesticides Database    |                      |
|------------------------------------|----------------------|
| <b>Birds generally non-toxic</b>   |                      |
| Bobwhite quail                     | LD50 2,825 mg/kg b.w |
| Bluegill Dietary LC50              | 1.3 – 10.2 mg/kg     |
| Brown trout Dietary LC50           | 3.3 mg/kg feed       |
| Fish LC50 (96 h) for rainbow trout | 0.9 – 13.2 mg/kg     |
| Water fea Dietary LC50             | 3.2 mg/l             |

TABLE 11: SUMMARY OF ECOTOXICITY FOR PROPICONAZOLE

## 2.9.3 Environmental fate of propiconazole

In terms of what happens to propiconazole in soils Chauhan *et al.* (2007) concluded that it can be safely used in paddy crops due to degradation properties and strong affinity for soil. A summary of these degradation properties is presented in Table 12, propiconazole appears to be less persistent than the other co-biocide in Tanalith® E which is tebuconazole.

| Source: PAN Pesticides Database |           |
|---------------------------------|-----------|
| Adsorption Coefficient          | 656 (Koc) |
| Hydrolysis Half life            | 442 days  |
| Aerobic soil                    | 71 days   |
| Anaerobic soil half life        | 211 days  |

TABLE 12: PROPICONAZOLE PERSISTENCE DATA

## 2.10 Use of triazoles in Irish Agriculture

The triazoles were invented primarily for an agricultural application and are widely used as fungicides in Ireland, primarily in cereals. McCabe (2005, 21) outlined the important role triazoles play in modern Irish agriculture particularly in “early season disease control in wheat is to get good control of *Septoria tritici*”. The Pesticides Forum (2007, 11) in the UK identified that “the resistance of *Septoria tritici* to the strobilurins contributed to a decline in usage on wheat and an increased use of chlorothalonil (Bravo®)”.

McCabe (2005, 21) notes that “the strobilurins fungicides (listed by Damicone 2003 as Quadris®, Flint®, Cabrio®) which were traditionally used in cereals are reported to have low level resistance problems and triazoles seem to be the way forward”.

According to Bayer in Courier (2006) triazole fungicides account for 25% of the world agricultural fungicide market”. A summary of commonly used triazole fungicides is presented in Table 13:

| Source: Crop Protection 2004 |                       |           |                          |
|------------------------------|-----------------------|-----------|--------------------------|
| Product                      | Actives               | Rate l/ha | Crops                    |
| Stereo®                      | Propiconazole 62.5g/l | 2 l/ha    | Barley                   |
| Bolt®                        | Propiconazole 250g/l  | 0.5l/ha   | Wheat, Barley, Oats      |
| Bumper®                      | Propiconazole 250g/l  | 0.5l/ha   | Wheat, Barley            |
| Menara®                      | Propiconazole 250g/l  | 0.5l/ha   | Wheat, oats, barley      |
| Beam®                        | Tebuconazole 133g/l   | 1.5l/ha   | Wheat, oats, barley      |
| Folicur®                     | Tebuconazole 250g/l   | 1l/ha     | Wheat, oats, barley, rye |

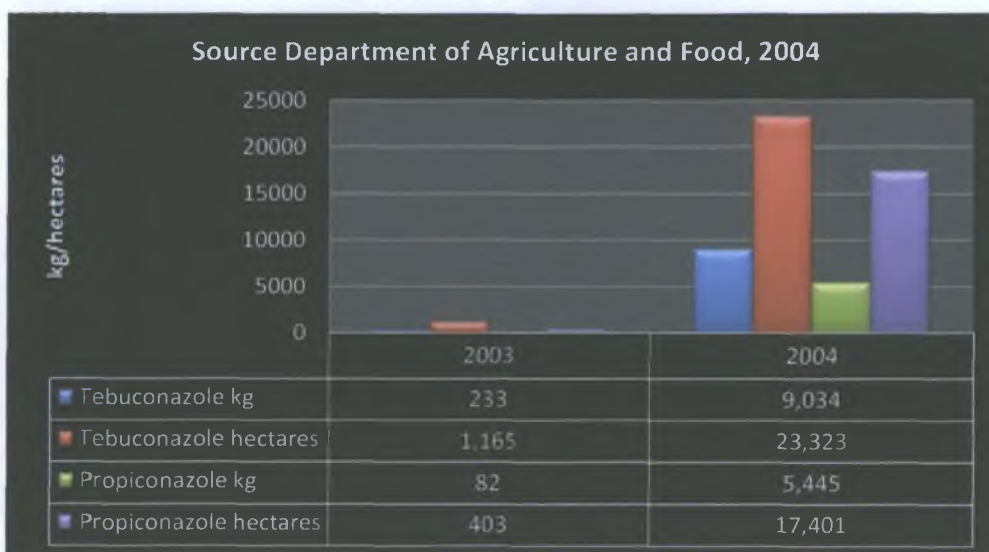
TABLE 13: CROP PROTECTION PRODUCTS USED IN IRELAND THAT CONTAIN TEBUCONAZOLE AND PROPICONAZOLE

In 2003 the Pesticide Control Service, PCS (2003) issued an alert about issues with winter wheat “products containing only strobilurin type active substances can no longer be relied on to give effective control of *Septoria tritici*” and recommended the use of triazole fungicides.

The trend in Irish agriculture is towards increased use of triazole fungicides for cereal crops. Pesticide data available from Department of Agriculture for usage in 2003

indicated that 1,165 acres, which were reported to be arable silage, was sprayed with tebuconazole. A year later there was a 20 fold increase in area sprayed however the reported crops sprayed was mainly wheat and barley in the 2004 report. The trend for propiconazole was even more dramatic with area sprayed increasing by 43 times in one year, the crops sprayed with propiconazole were reported to be mainly barley and wheat, Department of Agriculture and Food (2004). In terms of what the current situation in the intervening five years the data is not available yet.

The data presently available from the Department of Agriculture relating to application of tebuconazole and propiconazole is presented in Graph 1:



GRAPH 1: FUNGICIDE USE IN IRELAND

In terms of seasonality the general situation for application of fungicides according to the EPA (2008, 218) is that “use of pesticides is strongly seasonal with heaviest usage during April, May and June”.

When you look further down the supply chain at residues on food, a review of UK quarterly data, Pesticide Residues Committee (2007) indicates that traces (detection limits 0.02 mg/kg) of tebuconazole are being found in apples, cabbage, grapes, herbs, leeks, peaches (propiconazole detected) and nectarines. In Ireland, the Department of Agriculture, Food and Rural Development (2000, 9-15) did not detect tebuconazole or propiconazole residues in food sampled in 2000. In an updated 2006 report by the Department of Agriculture, Fisheries and Food of all pesticide residues detected in

food, 2.1% of residues were found to be tebuconazole, propiconazole was only detected in one peach sample from Chile.

Tebuconazole is the main pesticide detected in food analysed by the Department of Agriculture, Fisheries and Food, a summary is presented in Table 14:

Source: Department of Agriculture, Fisheries and Food, 2006 table 2 pp 11-31

| Food name   | Country of origin | Tebuconazole mg/kg |
|-------------|-------------------|--------------------|
| Pear        | Portugal          | 0.04               |
| Nectarines  | Canary Islands    | 0.31               |
| Nectarines  | Spain             | 0.02               |
| Peach       | Italy             | 0.02               |
| Plum        | Italy             | 0.05               |
| Grapes      | Chile             | 0.03               |
| Lettuce     | Spain             | 0.04               |
| Cabbage     | Ireland           | 0.03               |
| Carrots     | Israel            | 0.03               |
| Parsnips    | Ireland           | 0.02               |
| Onions      | Ireland           | 0.03               |
| Cauliflower | Ireland           | 0.03               |
| Tomato      | Spain             | 0.04               |

TABLE 14: SUMMARY OF PESTICIDES DETECTED

## ***2.11 Groundwater and surface water issues in Ireland***

Groundwater is a very important source of potable water in Ireland and is generally protected from contaminants by a layer of vegetation, soil and parent rock material. According to the United States Geological Survey (1993) “the effects of past and present land-use practices may take decades to become apparent in ground water. When weighing management decisions for protection of ground-water quality, it is important to consider the time lag between application of pesticides and fertilizers to the land and arrival of the chemicals at a well. This time lag generally decreases with increasing aquifer permeability and with decreasing depth to water”.

The UK Groundwater Forum (1998) outlined the situation in UK where they are finding organic pesticide residues in groundwater at levels reported to be below the Drinking Water Limits but the trend is a cause for concern.

Moe *et al.* (2007) quantified the groundwater resource “the total annual groundwater abstraction for public, group and industrial water supplies is almost 200 million m<sup>3</sup>”. Nationally, almost 30% of water supplies are obtained from groundwater according to ERBD (cited in Williams and Lee, 2007). Groundwater is usually abstracted by pumping from wells or boreholes, although spring water is also exploited. Well depths in bedrock aquifers typically range from 30-100m below ground. It is estimated that at least 100,000 wells and springs are in use nationally, ERBD (2007). Williams and Lee (2007, 6) describe the way water flows through bedrock “in most Irish bedrock aquifers, groundwater flows through fissures, fractures and faults. The amount of groundwater that can flow through fractured bedrock depends on the number, size and connectivity of fissures”.

Ryan (1998, 123) described the interaction between rainfall, soil and groundwater “in terms of leachability of soils a factor known as preferential flow needs to be considered, where flow of water during heavy rainfall can allow pollutants to by-pass the soil matrix and proceed rapidly to the groundwater” and Schulte *et al.* (2005, 125) produced some useful guidance on these soil associations which is outlined in Figure 2.

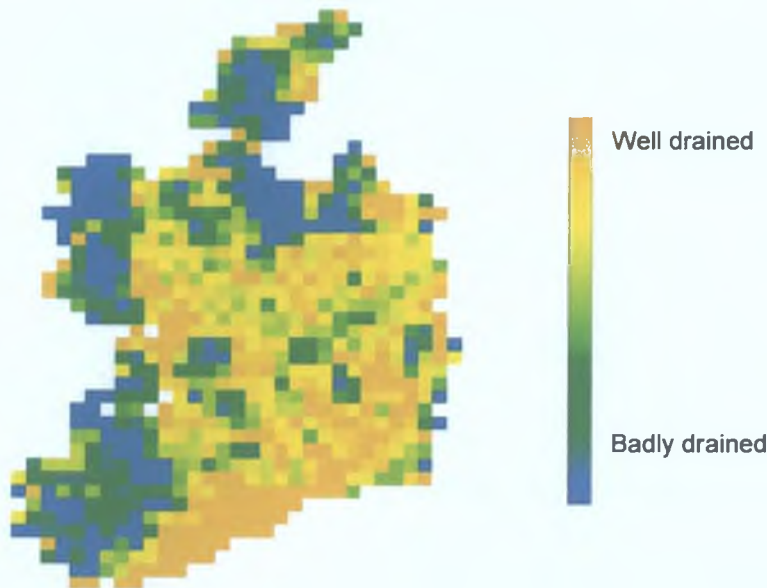


FIGURE 2: SOIL ASSOCIATIONS IN IRELAND

In the EPA document Guidance Note on Storage and Transfer of Materials for Scheduled Activities (2004) it was recognised that the environmental risk at a particular site is closely related to the ground conditions on-site, a facility located on impermeable soil over a non-productive aquifer is likely to have a lesser environmental risk than a site on free draining soil over a vulnerable aquifer, the interaction between soil and different wood preservative active ingredients is explored later in this review section.

The rainfall patterns in Ireland based on data collected by the Irish Meteorological Service (2009) are presented in Figure 3 and can be read alongside the soil association data in Figure 2.

Source: Irish Meteorological Service (2009)

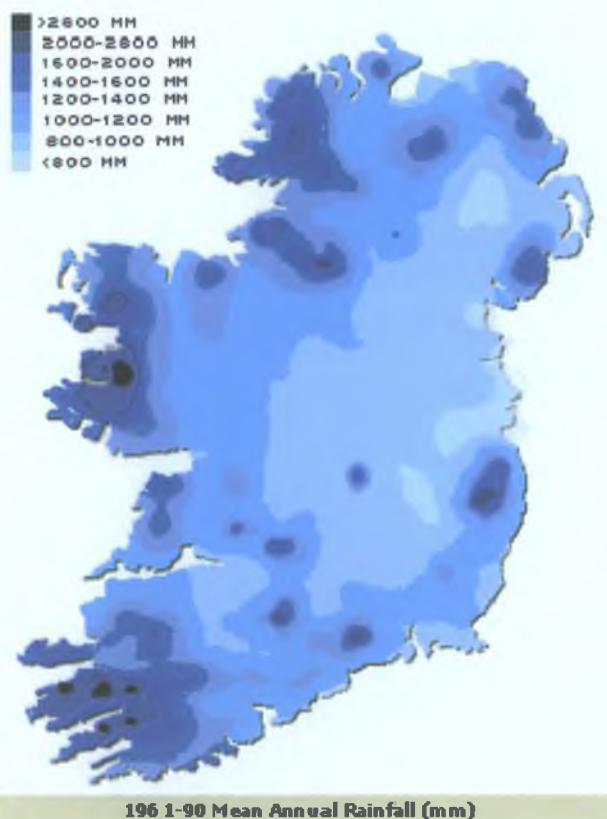


FIGURE 3 RAINFALL PATTERNS IN IRELAND

### 2.11.1 Determination of Groundwater Quality

The monitoring of groundwater is a very complex process however there are well established steps set down in BS 10175:2001 Investigation of potentially contaminated sites – Code of Practice, BSI (2001) in the process from setting objectives, developing a conceptual model (textual hypothesis of the nature and sources of contamination, potential migration pathways and potential receptors) to actual site investigation by way of sinking wells and analysis of groundwater. The US EPA (1992) developed a comprehensive guidance document for well design and construction and recommend well head diameters of 2 inch or 4 inch.

In terms of providing confidence in data presented to regulatory authorities, the sampling equipment for taking ground-water samples, sampling procedures, storage of samples and recording of results should be carried out in accordance with a structured protocol or standard, BS 6068-6.11:1993 Water quality – Guidance on sampling of ground-waters offer a good base line for any monitoring work to be done at IPC licensed sites, BSI (1993).

### **2.11.2 Pesticide analysis procedures**

There are currently no laboratories in Ireland offering pesticide analysis service to the limits of detection required which are 0.02 to 0.01 µg/l. The surface-water and groundwater samples collected by OCM were analysed by Mountainheath Services Ltd, OCM Report (2007, 05664/1), the in-house methods were not documented but in-house methods at another UK laboratory (Source : discussion with Arch colleagues May 2009) outline the following protocol:

- Biocides are extracted into dichloromethane using a liquid/liquid technique. The extracts are then concentrated with transferral into iso-hexane.
- The extract is injected into a Gas Chromatograph interfaced to a Mass Selective detector operating in Electron Ionisation (EI) mode, using selected ion monitoring mode.
- The collected data is then compared with data obtained from a series of standard solutions, treated similarly, by PC based data handling software.

### ***2.12 Regulatory Framework for Wood Preservatives***

Chemical companies that market wood preservatives are subject to very strict and financially onerous regulation in terms of approval for use. The Biocidal Products Directive 98/8/EC (BPD) established a regulatory regime in which active substances like tebuconazole and propiconazole used in biocidal products, such as wood preservatives, that had successfully cleared a review process would be placed on Annex 1 for use in the particular biocidal product type. Wood preservative products are called Product Type 8, according to the Official Journal of European Communities Products (1998) these are used for the preservation of wood, from and including the



saw-mill stage, or wood products by the control of wood-destroying or wood-disfiguring organisms. Wood Protection Association (2008) explains the relevance of this process in environmental terms “the inclusion of a substance on Annex I means that the substance has an acceptable environmental and human risk profile in terms of its intended use. This includes a risk assessment of the application processes to be used, including wood impregnation plants”.

Connell (2004, 3-4) described the process for approval of “active substances will be assessed under the BPD, whilst other substances used in wood protection formulations or as additives will be subject to (Registration, Evaluation and Authorisation of Chemicals) REACH. The Marketing and Use Directive 76/769/EC has been used to regulate the marketing and use of dangerous substances and scope has extended to include wood preservatives and has resulted in major restrictions on wood treated with creosote and CCA”. In Ireland the Pesticide Control Service banned the use and marketing of CCA based wood preservatives in 2004, PCS (2004).

The Integrated Pollution Prevention and Control Directive (IPPC, 96/61/EC) was implemented in Ireland when the Environmental Protection Agency Act 1992 was introduced. In 1994 “all plants for the treatment or protection of wood, involving the use of preservatives, with a capacity exceeding 10 tonnes/day” was included in the IPC licensing schedule. To assist IPC licensed treaters the EPA published their BATNEEC Guidance Note for Wood Treatment and Preservation in 1997.

The Timber Quality Bureau of Ireland (TQBI) Code of Practice which was based on the British Wood Preserving and Damp Proofing Association (BWPDA) Code of Practice which takes Best Available Technique (BAT) into account was never formally published. In the UK the Environmental Agency has officially endorsed the Wood Preserving Association (WPA) 2003 Code of Practice which is accepted as best practice in the industry.

In Ireland when IPPC licensed treaters are considering design of containment facilities they are directed to the IPC Guidance Note on Storage and Transfer of Materials for Scheduled Activities 2004. The guidance in this document proved to be invaluable for

operators planning new installations however many of issues referred to in the EPA Office of Enforcement Report 2005 are likely to be related to pre 2004 installations which ran on CCA in the past.

At present the EU are proposing a new Directive “Industrial Emissions Directive” which will include a new IPPC category on preservation of wood products with a production capacity exceeding 75m<sup>3</sup> treated timber per day, if implemented in Ireland this should supersede the existing “10 tonnes per day rule”, this formal position was outlined in a letter from the Department of Environment, Heritage and Local Government in 2008 to the Wood Marketing Federation (WMF).

In the UK implementation of the Integrated Pollution Prevention and Control Directive (IPPC) was through the Pollution Prevention and Control Regulations (PPCR 2000) and under this regime only wood preservation plants using Tributyltin oxide (TBTO) were licensed by the Environment Agency, ATP (2008) and plants using water-based products are effectively exempt from the type of licensing regime that applies in the Republic of Ireland.

### ***2.13 IPPC Compliance Issues in Ireland***

According to the EPA Office of Enforcement (2005) 177 site inspections of 50 wood treatment operations were carried out in 2004-2005, resulting in a total of 369 non-compliances and the issuing of 103 notifications of non compliance, this compares unfavourably to the EPA report six years earlier, when 42 plants were licensed there were no reported non-compliances, EPA (1998). There was no detail on number of inspections carried out in 1998, on-site surface and groundwater monitoring was not up and running at that stage. The nature of non-compliances reported in 2004 pertained mainly to contamination of surface water and groundwater due to poor storage of treated wood, inadequate bunding or spillage and there were known surface water or groundwater contamination issues at 15 facilities.

Lebow (2004) identified that the key aspect of good site practice and pollution avoidance was allowing enough time for chemical fixation reactions to render the

toxic ingredients insoluble in water. In an EPA workshop on IPC Regulation of the Timber Preservation Sector in 2002 Dr Jonathan Derham identified this issue and issued guidance letters to IPPC licensees and wood preservative suppliers that for high pressure products a holding time of 48 hours post treatment is provided for, Derham (2002 & 2004).

With the move away from CCA, post 2004, where the fixation reaction was temperature dependent to the above neutral pH type, work by Hughes (1995) on formulations like copper azole found that the rate of fixation should be relatively constant during summer and winter months, combined with the EPA requirements for 48 hours post treatment holding times in IPPC site licensee conditions, one would have expected to see an improvement in terms of compliance.

In terms of the CCA legacy at wood preservation sites, work carried out in New Zealand by Armishaw *et al.* (1994, 44-48) indicates that in most cases the contaminants, arising from leaching of CCA treated timber, are quite firmly bound to the soil and should not leach significantly as rainwater percolates down through the ground. Copper and arsenic were very rapidly immobilised by the soil while chromium fixation occurred more slowly. In the event of soil getting contaminated with CCA wood preservatives the main issue is with the persistence of the metals in the soil, according to Coover and Sims (1987) arsenic and chromium have a half life of  $10^8$  days in soil.

In the most recent report by the EPA, in conjunction with data collected by OCM, Sexton (2007) reviewed surface-water and ground-waters analysis at IPPC licensed sites which indicated that the only pesticides detected above the comparative standard of  $0.1\mu\text{g/l}$  was tebuconazole and propiconazole, one site exceeded  $10\mu\text{g/l}$  for tebuconazole in ground-water and two sites exceeded  $10\mu\text{g/l}$  for tebuconazole and propiconazole. There was no information provided in this EPA assessment in relation to upstream levels and possible background levels of pesticides. In relation to persistent metals, three sites had copper concentrations above the interim guideline value, which is derived from drinking water standards (IGV) of  $2\text{mg/l}$ . Historical pollution from CCA, which was phased out in 2004, was also observed at three sites.

The 2007 EPA report did highlight the need for bund integrity testing every 3 years to prevent un-controlled losses to the environment. In order to reinforce the need for liquid tight bunds at wood preservation sites using Tanalith® E in Ireland Arch Timber Protection issued a Best Practice – Treatment Plant Design and Site Maintenance update to timber treaters in February 2008.

## ***2.14 Environmental Auditing***

In order for an operator to establish compliance and plan for improvement a management system needs to be implemented, in terms of environmental management an audit is a way to measure performance on-site. An audit compares an actual condition or situation to an identified standard, Meyers (1998). The seven principles of auditing as per ISO 14010 are:

- Objective and scope of audit needs to be known to plan the audit.
- Objectivity, independence and competence of auditor needs to be established to give the audit validity.
- Due professional care in the way audit is conducted in terms of interaction with personnel being audited.
- Systematic procedures should be followed to provide structure.
- Audit criteria established, evidence collected and findings reported.
- Reliability of audit findings and conclusions essential to make the process worthwhile.
- Audit report structure to follow ISO 14011 recommendations, this standard is part of the ISO 14010 auditing series which describes how to establish an audit program including planning, staffing and reporting, Pinero (2009, 2). The structure should have the following, Meyers (1998):
  - Site location map, facility plot plan, process flow diagram, organisation chart.
  - Reference to previous environmental reports, data and correspondence from the agency.

### 2.14.1 Structure of Environmental Audit

After a review of the publicly available information on wood preservation environmental standards the following documents appear to be the main benchmarks for auditing purposes in Ireland:

#### **BATNEEC Guidance Note for Wood Preservation EPA 1994.**

The main requirements in this EPA document are:

- Optimisation of impregnation process to ensure minimum wastage.
- Roofing and bunding of impregnation and immediate post-impregnation area.
- Bunding of tanks to contain 110% of the solution.
- Overground pipelines and transfer lines should be inspected by a competent person i.e. an engineer.
- Bunding of all stored materials with separate bunding for incompatibles.
- Site organisation to ensure segregation of potentially contaminated surface waters from uncontaminated area.
- Chemical off-loading to be carried out so as to avoid spillage.
- Technology for recovery and recycle.
- Waste Handling and Minimisation procedures to prevent hazard waste generation.

#### **Code of Practice for the Operation of Timber Treatment Plants in an Environmental Conscious Manner, TQBI, 1996.**

This draft code of practice was developed by a working party of relevant trade associations, the EPA were not formally involved and unfortunately the document was never formally published or launched. The document provides very useful advice for operators and refers to the following:

- Mixing tank overflow devices and siphon breaks. A majority of plants are using water-based products which require mixing on-site and overflow of mixing tanks is a potential risk if not controlled.
- Bunding 110% capacity of chemicals stored on-site.
- Chemical delivery via fixed coupling within bund, this is to ensure that product is pumped into bulk storage tanks in a controlled fashion.
- Annual inspection by competent person.

- Pre and post treatment handling to facilitate recovery of drippings.
- Training and emergency procedures i.e. plants should be operated by trained and competent personnel.

**IPC Regulation of the Timber Preservation Sector, Jonathan Derham, EPA, 2002.**

This workshop was attended by all the trade associations involved in wood preservation activities and helped to foster a new spirit of communication between operators and the regulators, main issues discussed were:

- Treatment of dry clean timber.
- Eliminate rainwater contamination of containment facilities.
- 48 hour post treatment holding times and undercover capacity.

**Environmental Issues at EPA Licensed Timber Treatment Facilities, Thomas Sexton, EPA, 2007 & OCM Report.**

This presentation was given at the Arch Timber Protection Training Course in December 2007 and a summary of the OCM survey on IPPC licensed plants was presented.

- Integrity testing of bunds.
- Bunds sealed with impermeable material.
- Drag out areas liquid tight and undercover.
- Storage of treated timber on hard standing areas.
- Tracking system for treated timber to demonstrate compliance with 48 hour rule.
- Surface water monitoring:
  - Copper mg/l vs. Dangerous Substances Regulations limits of 0.03 mg/l.
  - Pesticides µg/l vs. Drinking Water Regulations limits of 0.1 µg/l.
- Groundwater monitoring:
  - Copper mg/l vs. Drinking Water Regulations limits of 2 mg/l.
  - Pesticides µg/l vs. Drinking Water Regulations limits of 0.1 µg/l.
- Historical pollution from use of Chromated Copper Arsenate:
  - Chromium mg/l vs. Drinking Water Regulations limits of 0.05 mg/l.
  - Arsenic mg/l vs. Drinking Water Regulations limits of 0.01 mg/l.

## 3 METHODOLOGY

### 3.1 *Wood Preservation Process*

In order to get an good “snap shot” of the current status of IPPC licensed sites using Tanalith® E at high pressure preservation facilities in Ireland it was decided to carry out an on-site audit of the processes on-site, the basic preservation process is outlined in Figure 4:

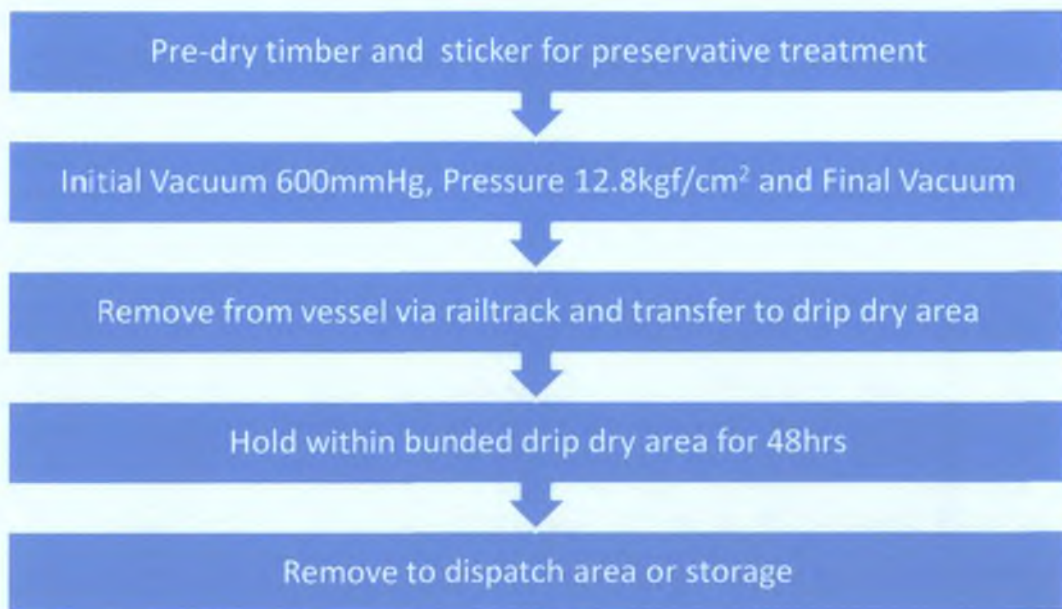


FIGURE 4: WOOD PRESERVATION PROCESS

### 3.2 *Quantitative and qualitative assessment basis for audit*

The methodology in terms of approaching the data collection phase of the audit was based on the preliminary investigation procedures outlined in BS 10175: 2001 Investigation of potentially contaminated sites – Code of Practice. BSI (2001) where a combination of documentary research and site reconnaissance is recommended.

The data collected was a combination of quantitative (usage rates, surface and groundwater analysis results) and qualitative data (soil and aquifer rating, condition of containment facilities based on visual assessment).

In terms of reporting this data collected during the on-site audit it was decided to use a similar structure to the existing Arch Planned Preventative Maintenance Scheme check-sheet which uses a traffic light system:

- Green: Complies with BATNEEC and Manufacturers Instructions.
- Amber: Minor non compliance and recorded as an observation.
- Red: Condition not acceptable and would be classified as non compliance requiring corrective action.
- Sites were identified by date of audit and initial.

### **3.2.1 Environmental Audit evaluation methods**

In terms of evaluating the importance of each item assessed during the audit the structure used in the Northern Ireland Environment and Heritage Technical Guidance Note IPPC H7 headings were used as a reference point when assessing the importance of each item in the audit checklist:

- Site Environmental Setting and Pollution History:
  - Evidence of previous pollution - CCA issues that might still persist on-site.
- Identify Pollution Prevention Measures:
  - Containment measures – bund integrity testing and drip dry facilities.
- Identify Potentially Polluting Substances:
  - Do active ingredients breach set limits? – surface and groundwater results at each IPPC site.
- Assess the effectiveness of the Pollution Prevention Measures:
  - Management systems in place i.e. training and on-site procedures.

With these criteria in mind the sites were rated using a numerical system which was based on the Hastam (1991) system which uses a scoring system. The scoring ranges from one to five (1 = non-compliant, 5 = fully compliant). To take account of the importance of surface-water, groundwater analysis and pollution history results a double rating was applied i.e. marked out of ten, an example of a completed audit is presented as Plate 6 in Appendix 2.



### ***3.3 Analysis of groundwater and surface results***

In terms of reporting the sampling results reviewed it was decided to review all data available for each site, the latest data for each parameter is presented, if results exceeded the limits significantly and showed no sign of improvement it was recorded as a red. In the case of minor non compliances where it was felt that later results showed improvement it was recorded as amber.

#### **3.3.1 Water sampling procedures**

There are established protocols for taking water samples i.e. BS 6068-6 Water quality – Part 6: Sampling – Section 6.11 Guidance on sampling of ground-waters. The protocol followed by OCM during their 2007 sampling programme refers to the following procedures that should be followed to ensure that sampling is representative (Source OCM Report 07-05664/1 for site PH260109):

- Purge three well volumes from the well before sampling, dispose of this water 50 metres from well.
- Bailer should be de-contaminated (follow scrubbing and rinsing protocol) prior to use, when bailer is lowered into well care should be taken to avoid contact with well sides or ground when removed from well.
- Groundwater samples should be transferred to 1,000 ml amber glass bottles with Teflon-lined cap, fill the bottle in a fashion to exclude air bubbles.
- Samples should be labelled with following information:
  - Client name, site name, date and time collected, analysis required, type of preservative and sample identification number.
- Bottles are placed in cooler with ice at 4<sup>0</sup>C and surround bottles with vermiculite.

In terms of volumes of water required if you are doing a full spectrum of analysis two litres minimum is required while for copper and propiconazole one litre is sufficient (communication with ATP Technical Centre colleagues, 2009).

### 3.4 Site Visits

During the 1<sup>st</sup> quarter of 2009 eleven IPPC licensed sites which used Tanalith® E were visited for the purposes of carrying out an environmental audit, this represented a 100% sample of IPPC licensed sites using copper azole wood preservatives in Republic of Ireland, geographical distribution of these plants is outlined in Table 15.

*Source: IPPC licence files*

| County     | No of IPPC licensed plants |
|------------|----------------------------|
| Co Laois   | 3                          |
| Co Carlow  | 1                          |
| Co Wicklow | 1                          |
| Co Galway  | 1                          |
| Co Donegal | 1                          |
| Co Cavan   | 1                          |
| Co Sligo   | 1                          |
| Co Cork    | 1                          |
| Co Mayo    | 1                          |

TABLE 15: DISTRIBUTION OF IPPC LICENSED TREATMENT PLANTS USING TANALITH® E

### 3.5 Geological and meteorological data

During the audit the geological information which might have an influence on surface-water and groundwater results at each site was recorded and assessed. In order to quantify the results a numerical rating system was adopted where the GSI (2006) aquifer classification was adopted and is presented in Table 16.

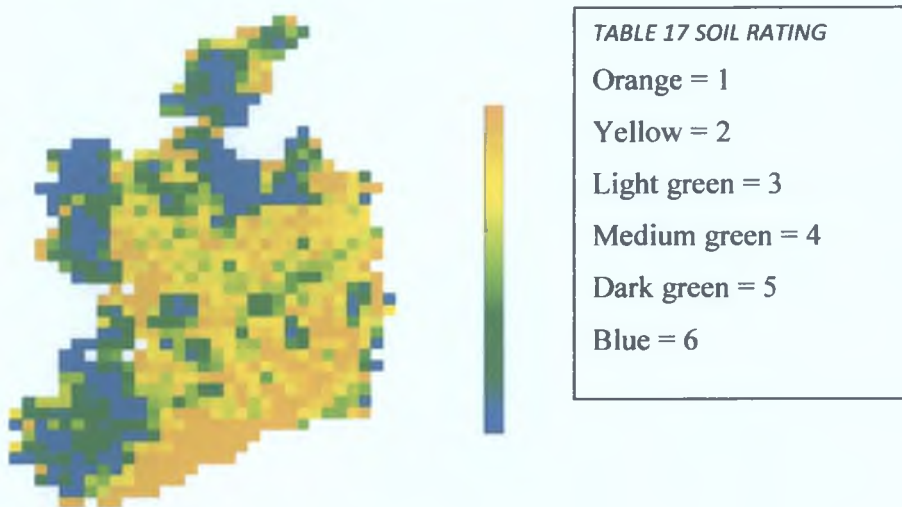
During the audit the aquifer rating was recorded based on available information from geological records available on-site or in the IPPC public file held by the EPA, the lower the rating number the greater the aquifer yield ie Rf (rating 1) has a yield of occasionally >500 m<sup>2</sup> per day while a Pu (rating 8) has yield <50 m<sup>2</sup> per day.

| Source: GSI (2006)         |        |
|----------------------------|--------|
| GSI Aquifer Classification | Rating |
| Rf                         | 1      |
| Rk <sub>d</sub>            | 2      |
| Rk <sub>c</sub>            | 3      |
| Lm                         | 4      |
| Lk                         | 5      |
| Ll                         | 6      |
| Pl                         | 7      |
| Pu                         | 8      |

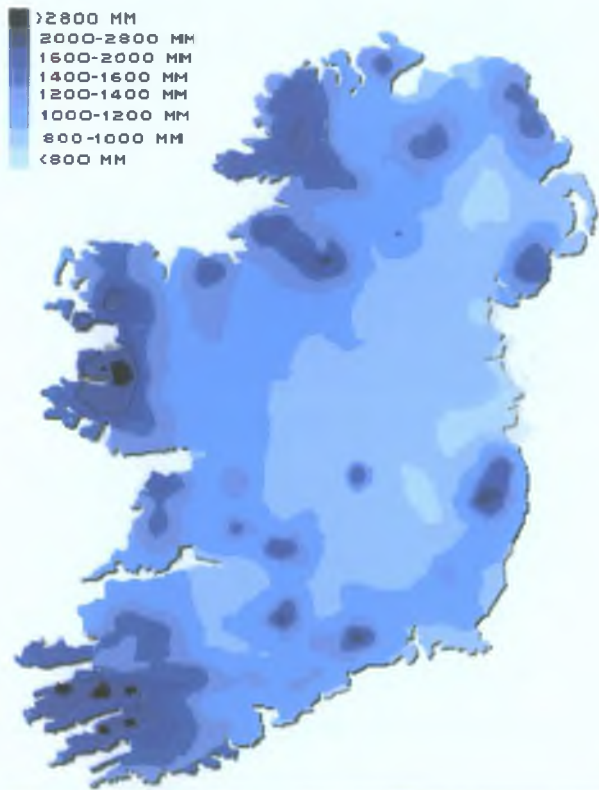
TABLE 16: AQUIFER RATING SYSTEM

In relation to soil and climate condition the classification referred to earlier in Figure 2 and was sourced in Schulte *et al.* (2005, p. 125) was adopted using a numerical rating system in Table 17.

The sites within category orange (rating 1) are 100% well drained while sites rated as blue (rating 6) are 100% poorly drained.



The rainfall patterns in Ireland based on data collected by the Irish Meteorological Service (2009) is rated in numerical terms in Table 18.



|                 |     |
|-----------------|-----|
| <1,000mm        | = 1 |
| 1,000 – 1,200mm | = 2 |
| 1,200 – 1,400mm | = 3 |
| 1,400 – 1,600mm | = 4 |

196 1-90 Mean Annual Rainfall (mm)

## 4 CASE STUDY OF SITE PH260109

The site Ref PH260109 was selected as a case study site to help illustrate the complex interaction between site geology, treatment plant history, range of surface-water and groundwater monitoring results.

### 4.1 Site layout

The site layout with location of surface-water and groundwater sample points, SW4 and BR1 in relation to the preservative treatment plant location is presented in Plate 2.

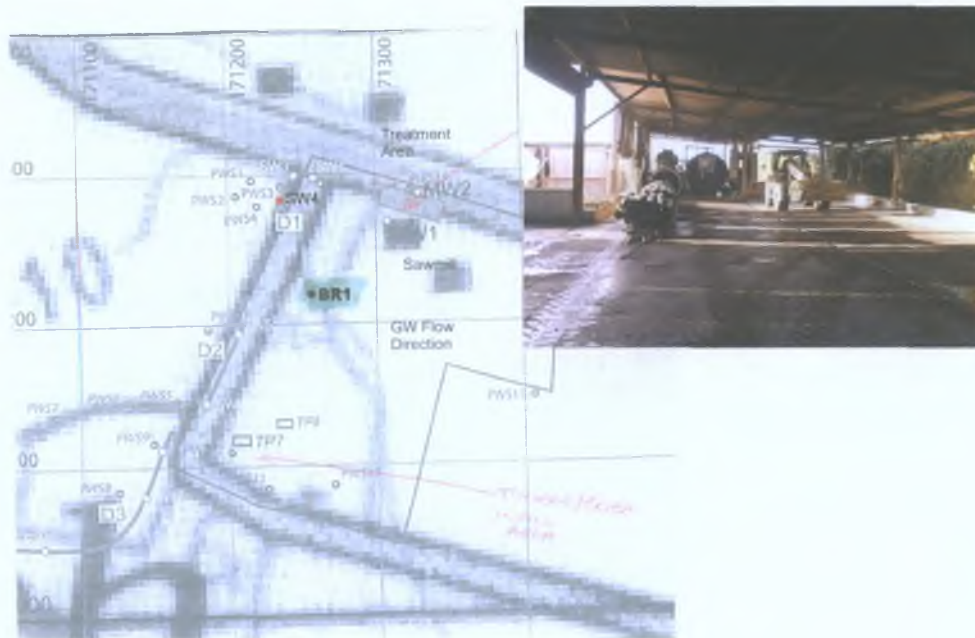


PLATE 2: MAP OF SITE SOURCE OCM (2007, 4)

### 4.2 Well design

The site is underlain by Dartry Limestone Formation which is a dark fine grained cherty limestone, OCM (2007, 9) and reported yield of groundwater is  $2.1\text{m}^3$  per day, Minerex (2007, 13). The borehole used for groundwater sampling was sunk in 2004 with the following dimensions: internal diameter 158mm, depth 48m, depth to water 1.2m and 1.17 in November, Minerex (2007, 1). The volume in the well is reported to be 921 litres, a diagram of the well is presented as Plate 7 in Appendix 3.

### 4.3 Chemical usage at site PH260109

The volume in tonnes of chemicals used at site PH260109 during the wood preservation process is outlined in Table 19.

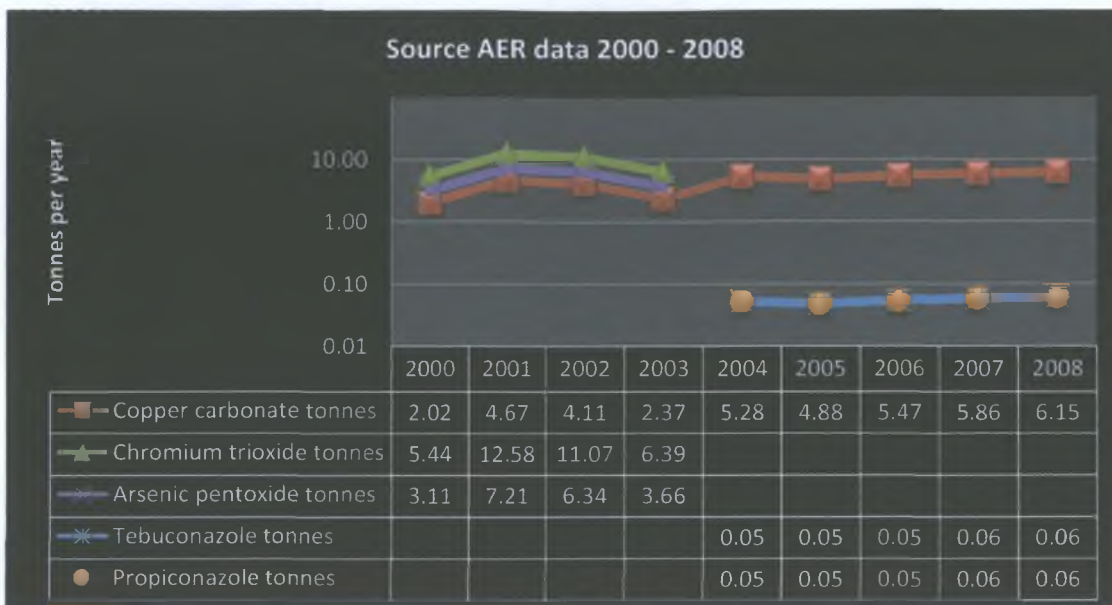


TABLE 19: PH260109 CHEMICAL USAGE

The volumes of CCA used were extrapolated from Annual Environmental Report (AER) data for 2000 to 2003 using the chemical ratio in the Material Safety Data Sheet for the CCA formulation, Tanalith C, Arch Timber Protection (2002, 1) which was used on site up until 2004, the ratio for the three actives was, chromium trioxide 30.2%, copper oxide 11.2% and arsenic pentoxide 17.3%, this CCA formulation used in Ireland was a 58.7% concentrate.

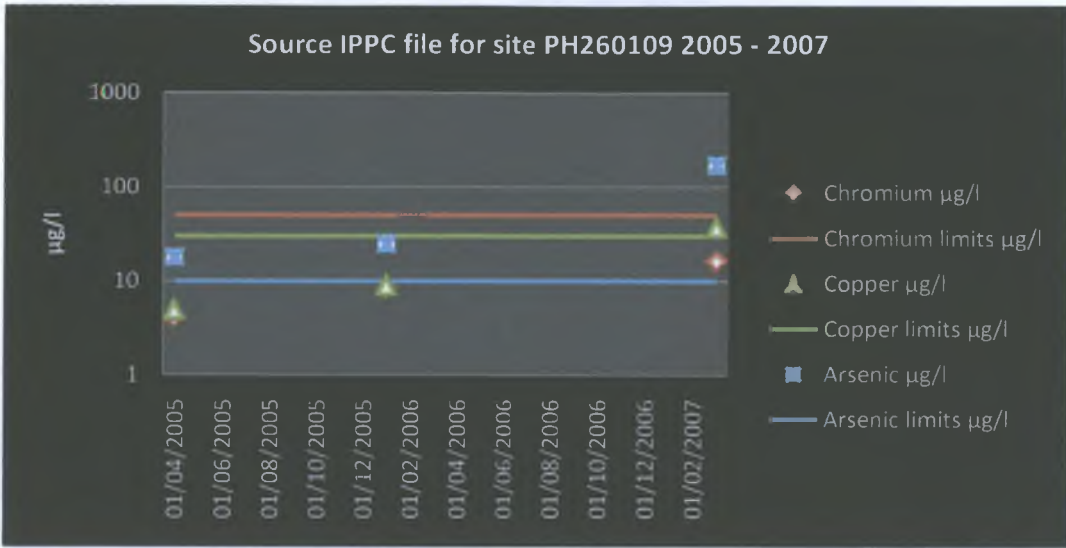
The volumes of copper azole used were extrapolated from AER data for 2004 to 2008 using the chemical ratio in the Material Safety Data Sheet for Tanalith E, Arch Timber Protection (2007, 1), the ratio for the three actives was, copper carbonate 20%, tebuconazole 0.2% and propiconazole 0.2%, the overall concentrate of the Tanalith E formulation based on extrapolation from the Material Safety Data Sheet is 65.4% concentrate.

The move from CCA to copper azole in 2004 was prompted by the implementation of Marketing and Use Directive 76/769/EC in Ireland by the Pesticide Control

Department. In chemical terms following the move to copper azole the usage of copper increased on average by 40% while the usage of secondary actives reduced by 77% with the move to organic secondary biocides.

#### 4.4 Surface-water results for site PH260109

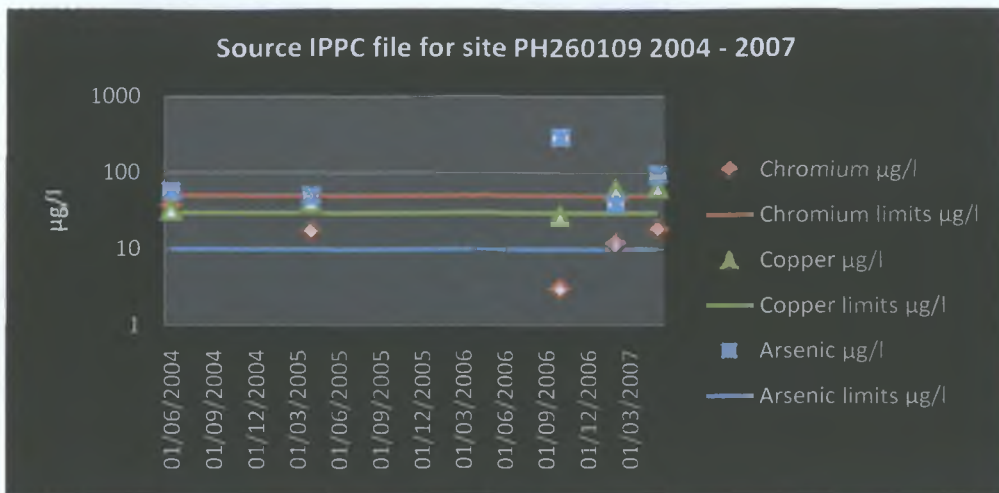
The surface water analysis carried out by the EPA is presented in Graph 2, the metal analysis was reported to be in accordance with APHA procedures using ICP-MS, water sample preservation was with HNO<sub>3</sub> (Source IPPC file for PH260109).



GRAPH 2 SURFACE-WATER MONITORING BY EPA

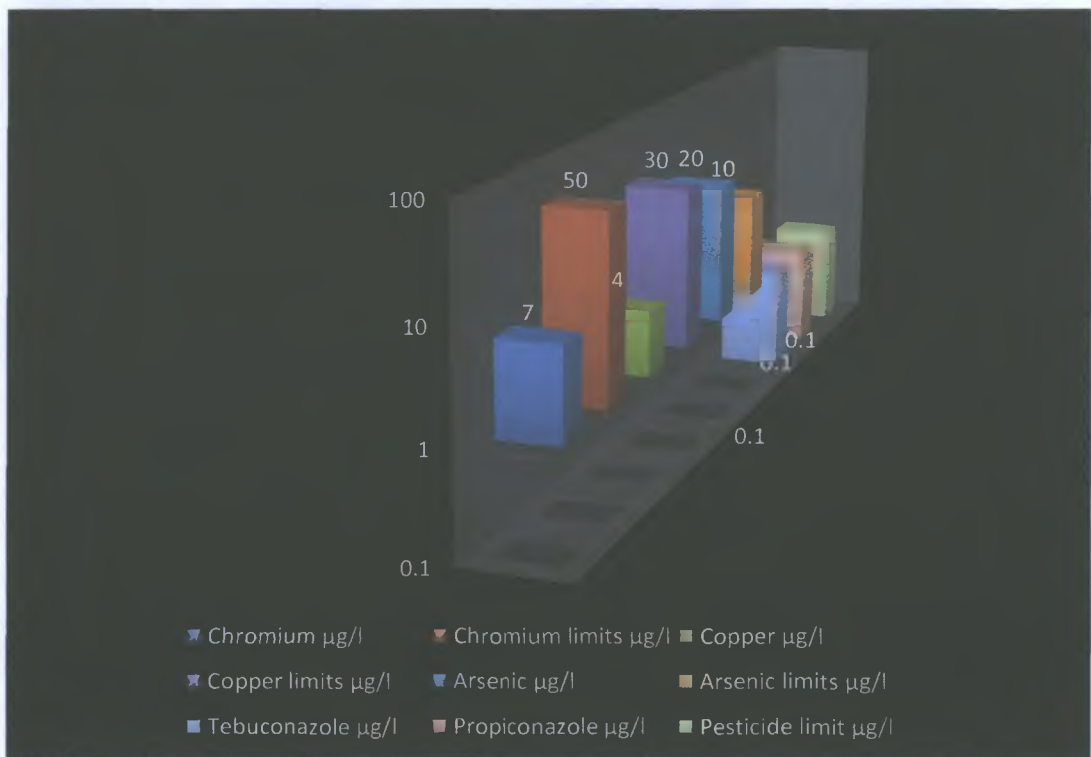
The main issue is elevated arsenic which is likely to originate from previous activities on site which used CCA for the last 35 years, OCM (2007, 3). The treatment plant operation preceded the containment facilities required in IPPC licence issued by the EPA in 1998, EPA (1998, 7), the licence did not give specific guidance on post-treatment holding times for CCA treated timber.

The monitoring by Minerex in Graph 3 shows a similar trend for arsenic in terms of non-compliance.



GRAPH 3 SURFACE-WATER MONITORING BY MINEREX

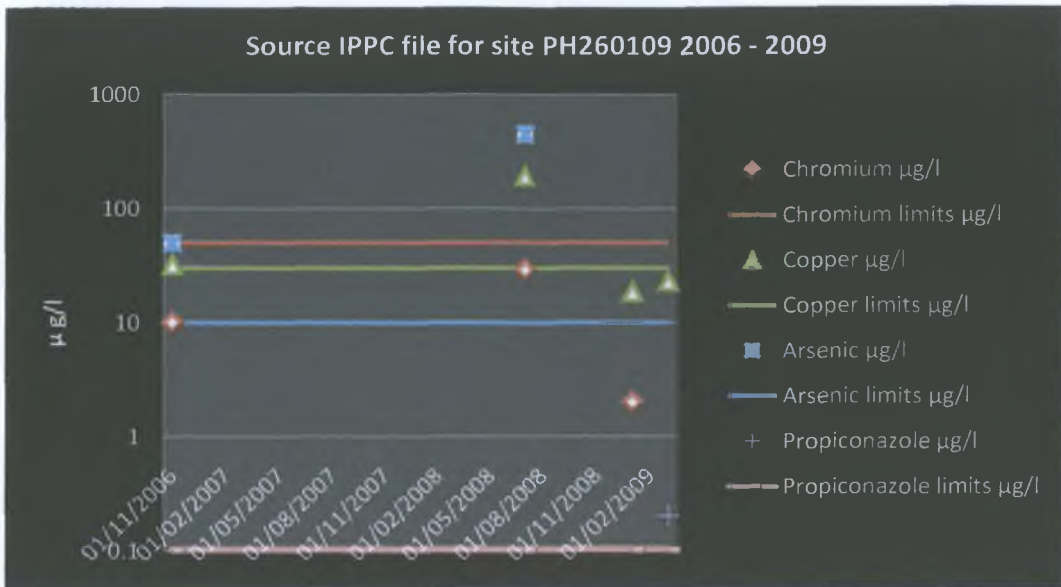
The OCM monitoring results, presented in Graph 4, for surface-water which was carried out as part of their assessment of 19 high-pressure treatment facilities, OCM (2007, 1) and assessed the presence of metals and pesticides.



GRAPH 4 SURFACE-WATER ANALYSIS OCM



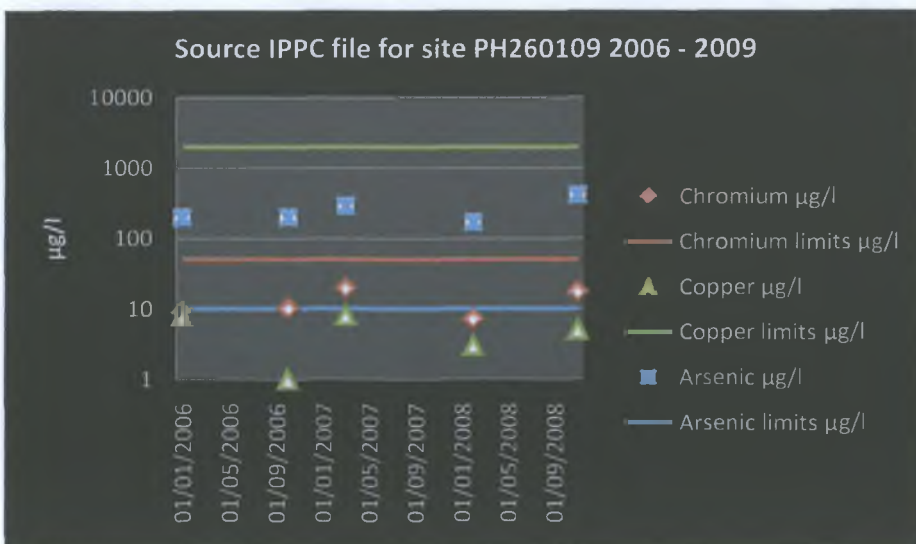
The OCM monitoring for surface-water point SW4 indicated that tebuconazole and propiconazole was below the limit for pesticides however surface-water analysis for 2009 carried out by Arch and outlined in Graph 5 indicates that propiconazole is elevated at 0.2µg/l at SW1 sample point.



GRAPH 5 SURFACEWATER ANALYSIS ARCH

#### 4.5 Groundwater results for site PH260109

The groundwater results for water sampled from BR1 are presented in Graph 6, 7 and 8.

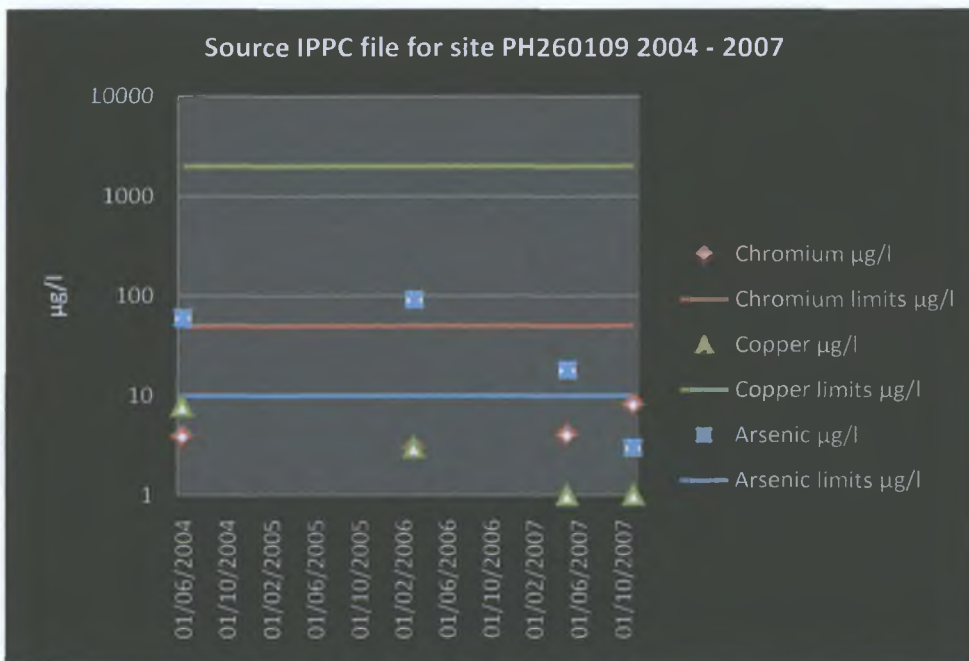


GRAPH 6 GROUNDWATER MONITORING BY EPA

These EPA and Minorex results indicate that historical CCA soil contamination is linked to the elevated arsenic levels in groundwater, it is worth commenting that the OCM analysis in July 2007 indicates arsenic level of 4µg/l to be below the limit. The weather conditions during the sampling period might have a bearing on results, during the winter months the likelihood of rainfall leaching un-fixed arsenic in the soil would be higher and the wet summers of 2007 and 2008 would not have helped the situation (Irish Meteorological Service, 2009).

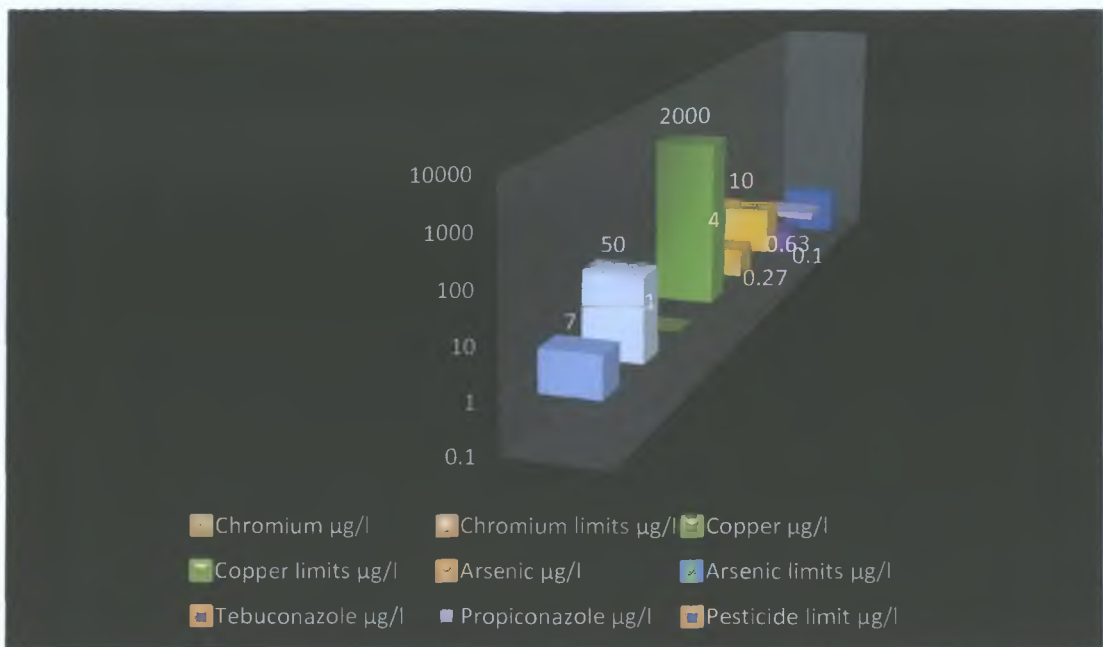
Soil analysis carried out by Minorex (2004, 14) indicated that from a sample size of 12 samples the average arsenic level was 16.4mg/kg, this is below the Dutch Intervention Level of 55mg/kg, Dutch Ministry of Housing (2000).

Groundwater results derived from Minorex and OCM files are presented in Graph 7 and 8.



GRAPH 7 GROUNDWATER MONITORING BY MINEREX

The OCM results derived from samples collected during the summer of 2007 are presented in Graph 8.



GRAPH 8 GROUNDWATER MONITORING BY OCM

This sampling period by OCM was during July 2007 and results indicated that the biocides, tebuconazole and propiconazole were above the drinking water limits.

OCM (2007, 20) reported that the layer of subsoil was shallow and permeable and this results in the groundwater being permeable to contamination, the aquifer beneath the site is classified as a regionally important karstified aquifer. The treatment plant and post treatment handling area is up slope from the rest of the site so attention should focus on any un-capped area in the vicinity of the treatment plant. The audit indicated that treatment plant containment facilities were bund tested in 2009 and was certified as compliant. A copy of the site audit result is presented in Appendix 2.

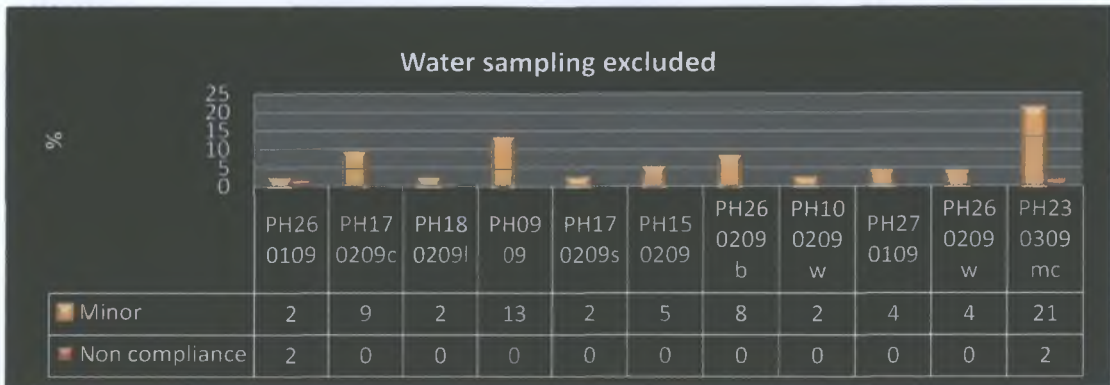
*This case study has been prepared solely by the author and does not necessarily reflect the views of Arch Timber Protection.*

## 5 RESULTS AND DISCUSSION

### 5.1 Results of Environmental Audits

#### 5.1.1 General compliance

A summary of general compliance as reported during the site audits is presented in Graph 9, the results of water analysis are excluded from this graph and included in Graph 10.



GRAPH 9: ENVIRONMENTAL AUDIT EXCLUDING SAMPLING

The major non-compliances noted related to an engineering issue at one plant where pressure exceeded the safe working limit of  $12.8\text{kgf/m}^2$ , this was adjusted back to safe level during the audit. The other major non-compliance related to the vulnerability of a surface water drain to an accidental contamination. Graph 10 takes account of surface and groundwater analysis results for copper and pesticides which will be described in more detail later in this document, the weighted score for each site as described in section 3.1.2 is also presented for each site.



GRAPH 10: ENVIRONMENTAL AUDIT - % TOTAL COMPLIANCE

A summary of general compliance as determined using criteria outlined in 3.2.1 is presented in Graph 11, when you compare the water monitoring results to the OCM results reported by Sexton (2007, 8-9) the situation has improved slightly for pesticides based on the assumption that tebuconazole and propiconazole levels reported by Sexton related to high pressure sites using copper azole. The surface-water analysis for tebuconazole had four non-compliances and five for propiconazole, groundwater results for tebuconazole had seven non-compliances and five for propiconazole.

The situation in relation to copper levels reported in groundwater is positive with 100% compliant while copper levels in surface-water, where limits are lower, is 60% compliant.



GRAPH 11 SUMMARY OF AUDIT COMPLIANCE

### 5.1.2 Sites with tracking system for 48 hours post holding times

The EPA identified the need for a post treatment tracking system in 2007, eight sites out of eleven had introduced a tracking system to help verify that freshly treated timber is held within a contained bunded area for a period of 48 hours to facilitate fixation of chemicals and drying of the wood preservative solution.



PLATE 3 : LABELS USED TO INDICATE TIME AND DATE OF TREATMENT TO FACILITATE TRACKING OF TREATED TIMBER.

### 5.1.3 Bund tested in last three years

Containment facilities were highlighted in 2007 as a key issue, nine sites had independent bund tests in last three years. One site which has had compliant bund testing results was in the process of relocating and re-engineering the plant due to on-going groundwater contamination issues.



PLATE 4: TYPICAL BUND OBSERVED DURING AUDIT.

#### 5.1.4 Covering removed from packs

During the audit only two of the sites had plastic covering on timber packs prior to treatment, this issue was identified as a possible source of pesticide contamination where un-fixed preservative could be present on the surface of pack and can be mobilised when exposed to rainfall, ATP (2008 G1/08).



PLATE 5: PLASTIC COVERING IS A POTENTIAL SOURCE OF CONTAMINATION

#### 5.1.5 Treatment plants exposed to rainfall

When IPC licensing was introduced in 1997 protection of facilities from rainfall was identified as an issue to be addressed, eight sites had treatment plant facilities which complied with the BATNEEC requirements for total containment i.e. cover of storage tanks, vessel, bunded area, drag out area and 48 hour post treatment holding area. The non-compliant plants were old plants with small throughputs and in the current economic climate of 2009 are unlikely to have the financial resources to become compliant in the short term. During the audit guidance was given to make interim improvements which are financially viable i.e. kerbed area around exposed rail-tracks and post treatment holding area to recover contaminated surface-water in a controlled fashion.

### **5.1.6 Previous CCA contamination issues**

45% of sites had historical CCA contamination issues which they were trying to deal with on a site by site basis. Two sites had elevated levels of chromium in groundwater (0.134mg/l & 4.2mg/l) while three sites had issues with arsenic (groundwater 0.4mg/l & 0.038mg/l, surface-water 0.05mg/l). When you consider that the persistence of arsenic and chromium with a half life of  $10^8$  days in soil, Coover and Sims (1987), measures should be taken to prevent leaching through the soil profile, these complex issues was expanded upon in the case study presented in Chapter 4 on site PH260109.

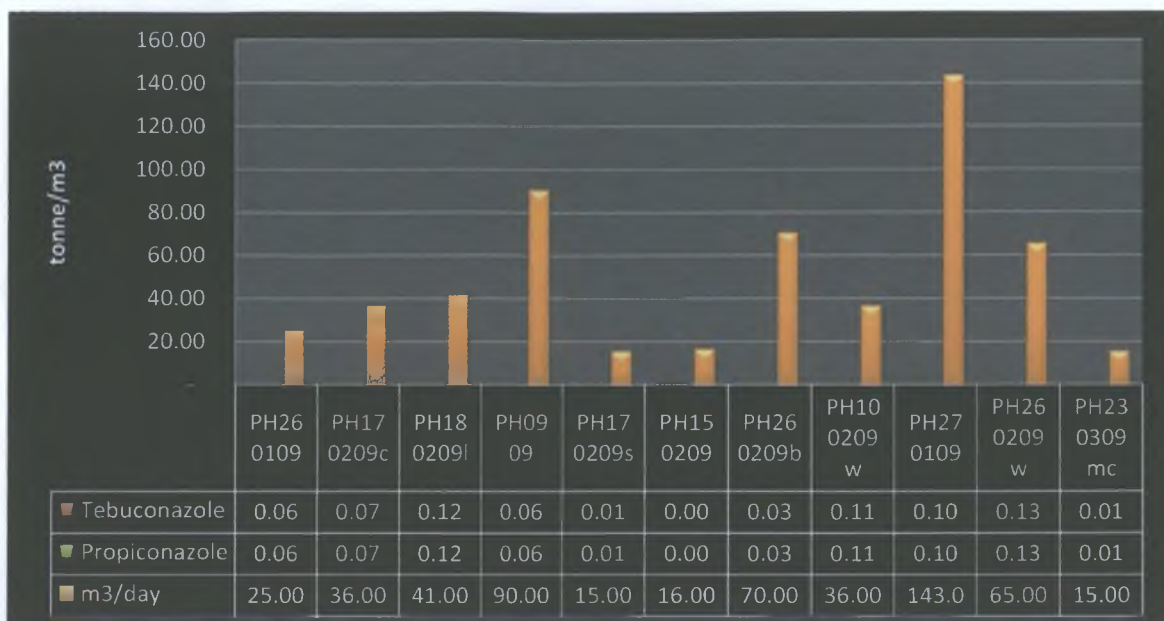
### **5.1.7 Treatment plant capacity and usage**

It was considered important to benchmark the IPPC licensed plants against the current IPPC licence threshold of “10 tonnes of treated timber per day” and the new proposed EU Directive which will set a threshold of  $75\text{m}^3$  per day, based on data presented in Graph 12 only two sites would be above this new threshold if the directive is implemented in Ireland.

The current 10 tonne limit relates to the treatment capacity of the plant in terms of weight of timber. This is difficult to quantify since moisture content of timber prior to treatment can affect the weight to volume ratio, the new proposal for  $75\text{m}^3$  per day is more measurable since processing records detail actual throughput in  $\text{m}^3$  terms. This move to computer controlled plants should make this estimation more quantifiable and accurate.



Graph 12 summaries the quantities of azole biocides used at IPPC sites in 2008, the m<sup>3</sup> per day capacity for each site is extrapolated from available information at each site.



GRAPH 12: 2008 TEBUCONAZOLE AND PROPICONAZOLE USEAGE IN TONNES

In terms of active ingredients impregnated into the timber during the timber preservation process it is estimated that 0.7 tonnes of tebuconazole and 0.7 tonnes of propiconazole was used during the impregnation process at IPPC licensed sites in 2008. In terms of what is considered a worst case scenario for losses from bunded treatment plants a figure of 0.1% has been used according to Atkin (2009).

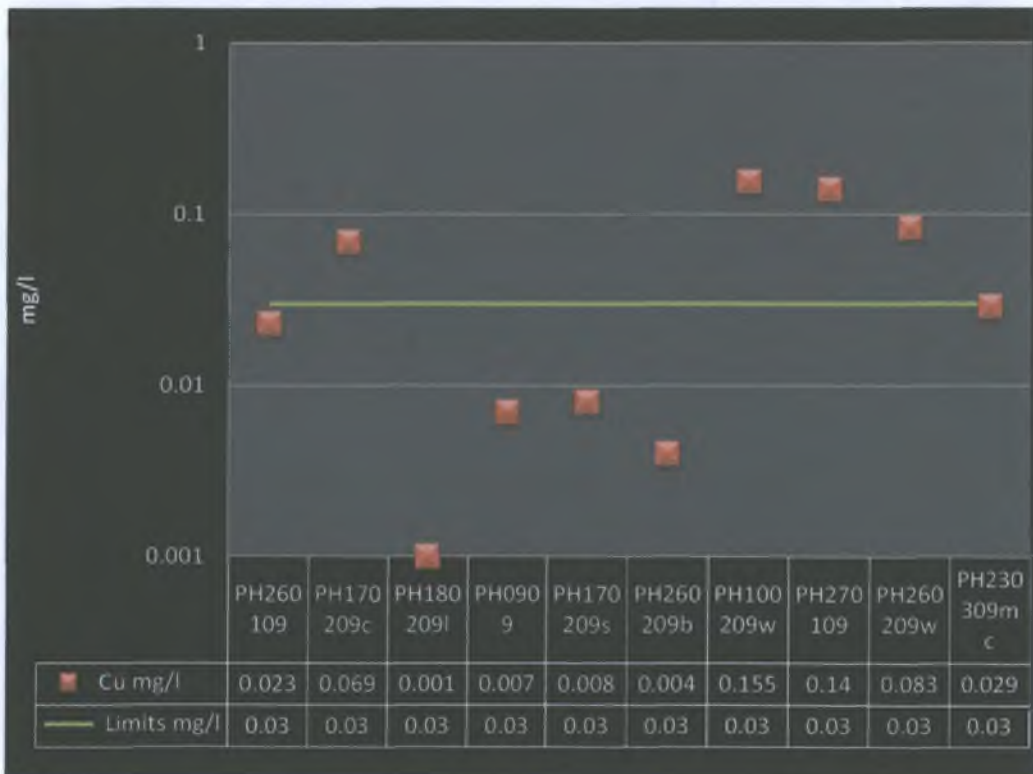
These figures should be considered in the context of earlier reported situation in Irish agriculture i.e. 9 tonnes of tebuconazole and 5.4 tonnes of propiconazole applied to the land as part of crop protection processes in Ireland during a single year in 2004 Department of Agriculture and Food (2004, 18), unfortunately figures for 2008 are not available from the Department.

## 5.2 Copper analysis results

The copper results for surface and groundwater obtained during the audit are presented in Graph 13, 14 and 15. The main source of the data obtained was independent water analysis carried out by OCM in 2007, routine analysis by the EPA and analysis carried out by the licensees as part of their licence conditions, a record of full data obtained during the audit is recorded in the individual audit sheet.

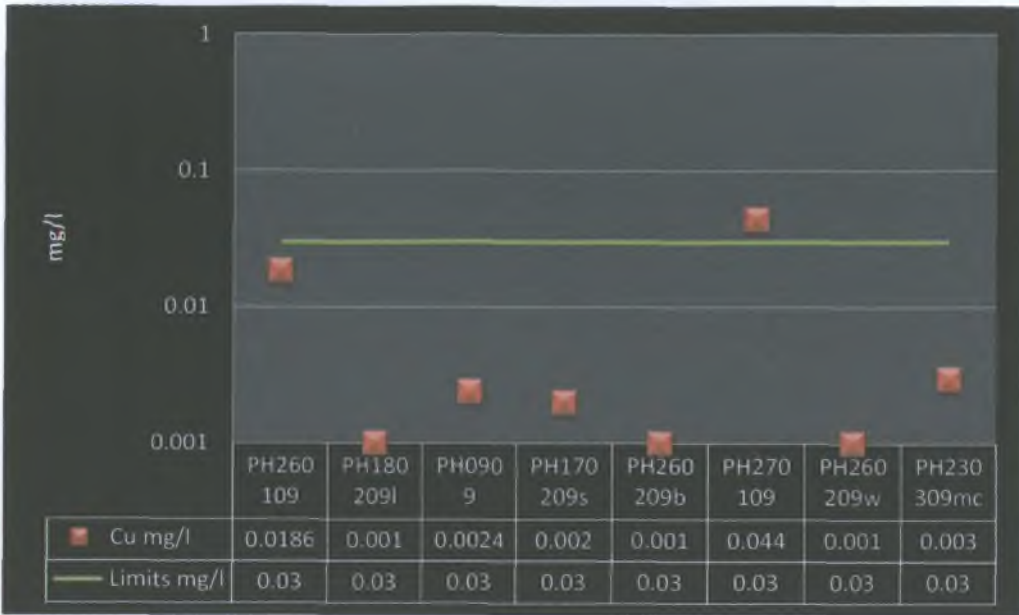
### 5.2.1 Surface water downstream results for copper

Data obtained from ten sites indicates that there are four sites with elevated levels of copper in surface water emissions from site. When you look at the data presented in Graph 16 and 17 (surface-water downstream results for azole pesticides) the three sites PH100209w, PH270109 and PH260209w have corresponding elevated pesticide (propiconazole and tebuconazole) levels which suggests that there is an issue relating to post-treatment holding of treated timber and protection of surface water drains.



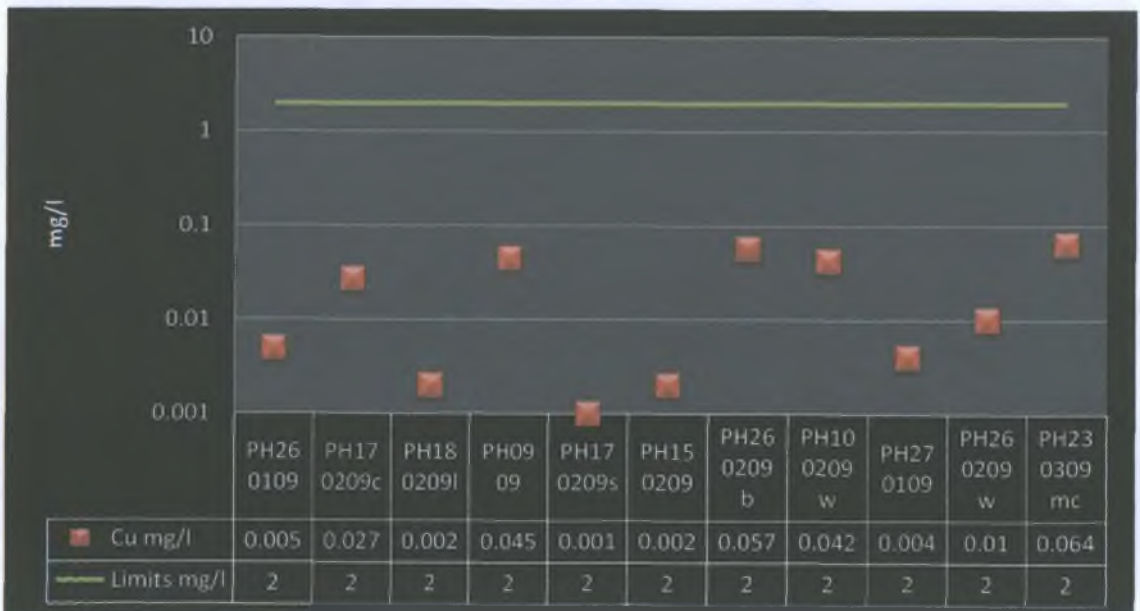
GRAPH 13: SURFACE WATER FOR COPPER DOWNSTREAM

Surface water results for copper upstream is presented in Graph 14, only one site PH270109 has elevated levels of copper in upstream and downstream sampling, this sampling was carried out by the EPA 9/10/07, OCM independent analysis 6/7/07 was 0.001mg/l for upstream and 0.002mg/l downstream sampling during the same year.



GRAPH 14: SURFACE WATER FOR COPPER UPSTREAM

The results for copper detected in groundwater are presented in Table 15, all of the sites audited were compliant with groundwater limits.



GRAPH 15: GROUNDWATER COPPER

### 5.3 Pesticides results from IPPC sites audited

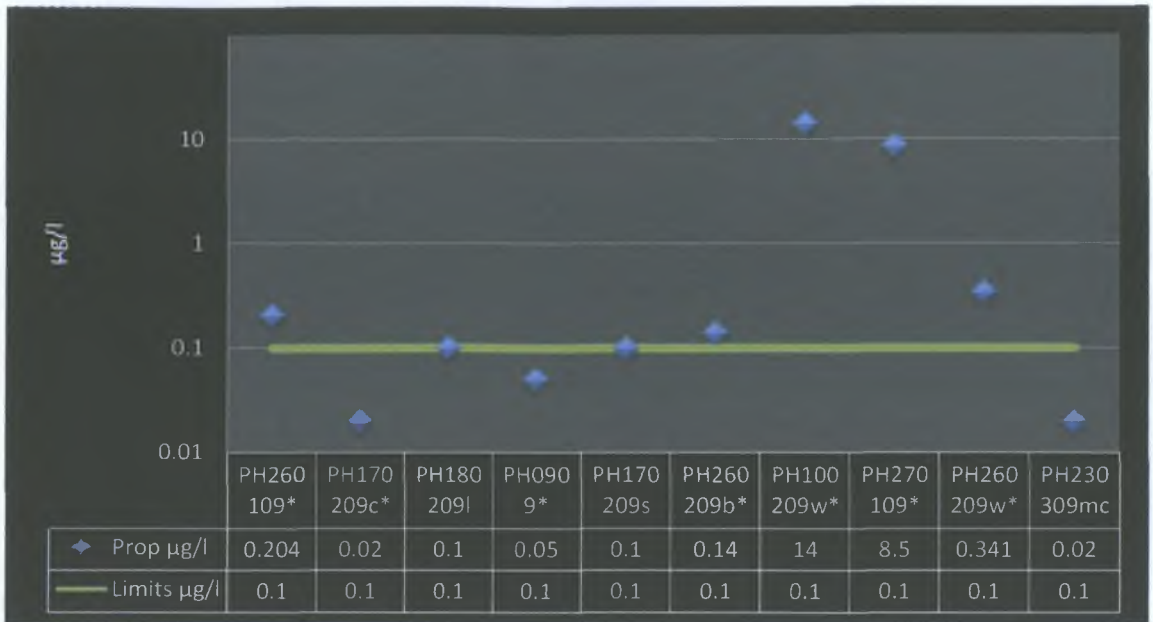
The data collected in relation to levels of propiconazole and tebuconazole in surface water is presented in Graph 16, 17 and 18, five of these sites had elevated levels in downstream samples. The site 260209b with elevated levels of propiconazole and tebuconazole did not have corresponding elevated levels of copper but showed elevated pesticide levels in upstream samples, this site is in a cereal growing region. The environmental audit noted the presence of agricultural activity (cereals, ploughed areas, set aside pasture) on the site boundaries, these sites were identified with an \* in water analysis graphs 16 - 20. The site audits were carried out during the winter which was before the growing season so it was not possible to identify the crops during the audit.

Results for PH270109 were from EPA sampling in 9/10/07, OCM sampling 6/7/07 indicated 0.42µg/l for tebuconazole and 0.59µg/l for propiconazole. The data presented in Graph 16 refers to tebuconazole and is more historical than for propiconazole levels in Graph 17.



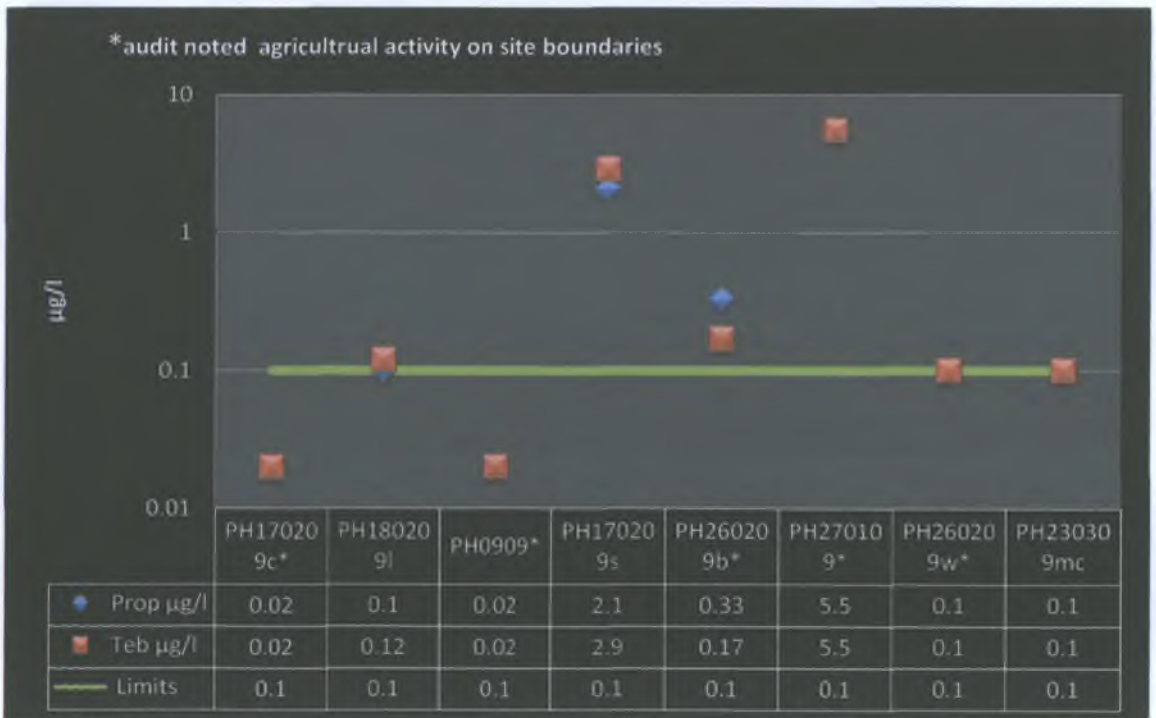
GRAPH 16: SURFACE WATER DOWNSTREAM TEBUCONAZOLE

The data for propiconazole is presented in Graph 17, the trend is similar to tebuconazole, data for sites PH260109 and PH230309mc is 2009 data.



GRAPH 17: SURFACE WATER DOWNSTREAM PROPICONAZOLE

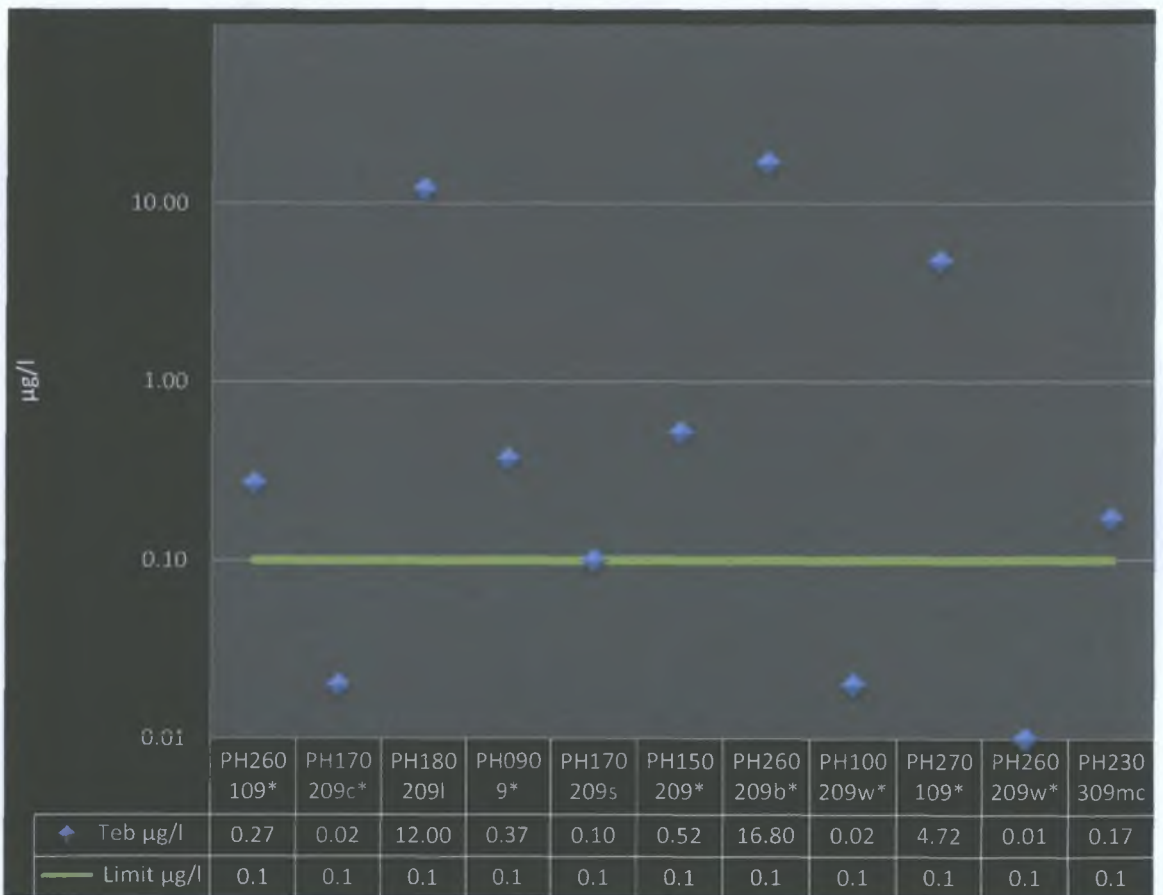
Surface-water samples taken upstream, mainly OCM data from 2007 is presented in Graph 18, 50% of sites had elevated levels based on audit data presented.



GRAPH 18: SURFACE WATER UPSTREAM TEBUCONAZOLE AND PROPICONAZOLE

During the audit at site PH170209s the licensee was somewhat sceptical of the upstream results since downstream and groundwater analysis by OCM for the same site in 2007 did not indicate elevated levels of pesticides, more up to date data on pesticides was not available on-site. Results for PH270109 were from EPA sampling in 9/10/07, OCM sampling 6/7/07 indicated <0.1µg/l for both pesticides.

Groundwater analysis, which represents down gradient sample points, for tebuconazole and propiconazole is presented in Graphs 19 and 20, seven of the sites had elevated levels with the most serious issues at sites PH270109, PH260209b and PH180209l remediation and investigation work has been on-going at these sites at time of audit.



GRAPH 19: GROUNDWATER ANALYSIS TEBUCONAZOLE

Propiconazole data available during the audit is presented in Graph 20, the data for site PH180209I is 2009 and data for tebuconazole in Graph 19 is more historic (OCM 2007). During the audit off-site groundwater sample points was not available at all sites.



GRAPH 20: GROUNDWATER ANALYSIS PROPICONAZOLE

## 6 STATISTICAL ANALYSIS OF AUDIT RESULTS

Correlation measures the strength of a linear relationship and gives added weight to a relationship, Owen and Jones (1994, 470). The correlation coefficient output from the comparison analysis is presented in Table 20 for all the sites audited and to be statistically significant, the Pearson P Value must be less than 0.05 as indicated in Table 20, Prism (2009), a sample of the data is presented in Appendix 1.

| Data compared  | MS Excel correlation | Pearson Correlation | Pearson Correlation |
|--|----------------------|---------------------|---------------------|
| Data set compared                                      | Coefficient          | Coefficient         | P Value             |
| Teb µg/l Downstream vs. teb kg/year                    | 0.418                | 0.440               | 0.175               |
| Prop µg/l Downstream vs. prop kg/year                  | 0.446                | 0.464               | 0.151               |
| Teb µg/l Groundwater vs. teb kg/year                   | 0.085                | 0.085               | 0.803               |
| Prop µg/l Groundwater vs. prop kg/year                 | -0.259               | -0.251              | 0.456               |
| Teb µg/l upstream vs. teb µg/l groundwater             | 0.081                | 0.021               | 0.951               |
| Prop µg/l upstream vs. prop µg/l groundwater           | -0.132               | -0.033              | 0.923               |
| Prop µg/l upstream agri vs. prop µg/l groundwater agri | -0.025               |                     |                     |
| Teb µg/l Downstream vs. copper downstream              | 0.842                | 0.848               | 0.001               |
| Prop µg/l Downstream vs. copper downstream             | 0.862                | 0.862               | 0.001               |
| Teb µg/l groundwater vs. copper groundwater            | 0.149                | 0.147               | 0.667               |
| Prop µg/l groundwater vs. copper groundwater           | 0.500                | 0.439               | 0.177               |
| Cu mg/l downstream vs. cu tonnes/year                  | 0.574                | 0.617               | 0.043               |
| Cu mg/l groundwater vs. cu tonnes/year                 | -0.246               | -0.246              | 0.466               |
| Prop downstream vs. prop upstream                      | 0.930                | 0.373               | 0.259               |
| Prop downstream agri vs. prop upstream agri            | 0.9984               | 0.998               | 0.002               |
| Copper upstream vs. copper groundwater                 | -0.373               | -0.329              | 0.323               |
| Copper downstream vs. copper groundwater               | -0.082               | 0.005               | 0.989               |
| Copper downstream vs. copper upstream                  | 0.775                | 0.437               | 0.179               |
| Teb µg/l Downstream vs. teb groundwater                | 0.077                | -0.107              | 0.755               |
| Teb µg/l Downstream vs. teb upstream                   | 0.867                | 0.307               | 0.358               |
| Teb µg/l Downstream agri vs. teb upstream agri         | 0.997                | 1.000               | 0.000               |
| Teb µg/l Downstream vs. prop downstream                | 0.998                | 0.998               | 0.000               |
| Prop µg/l Downstream vs. prop groundwater              | -0.089               | -0.120              | 0.725               |
| Copper upstream vs. copper groundwater                 | -0.373               | -0.329              | 0.323               |
| Prop groundwater vs. teb groundwater                   | 0.781                | 0.784               | 0.004               |

TABLE 20 STATISTICAL ANALYSES



### 6.1.1 Spearman rank correlation

The Spearman rank correlation is the non-parametric alternative to correlation which was used via Minitab to compare the data that derived by the rating system adopted during the audit process.

| <i>Rank correlation</i>                  | Pearson Correlation |
|--|---------------------|
| Data set compared                        | Coefficient         |
| Teb µg/l Downstream vs. ranked rainfall  | 0.236               |
| Prop µg/l Downstream vs. ranked rainfall | 0.048               |
| Copper downstream vs. ranked rainfall    | 0.271               |
| Copper downstream vs. ranked soil        | 0.633               |
| Copper groundwater vs. ranked soil       | 0.416               |
| Tebuconazole downstream vs. ranked soil  | 0.214               |
| Teb groundwater vs. ranked soil          | 0.014               |
| Copper downstream vs. ranked aquifer     | 0.605               |
| Copper downstream vs. ranked score       | 0.633               |

TABLE 21 STATISTICAL ANALYSES

The Paired T test analysis carried out via Minitab is presented in Table 22 and Appendix 1.

| Paired T-Test and CI                                  | Correlation<br>T value | P value     |
|---|------------------------|-------------|
| Data set compared                                     | Coefficient            | Coefficient |
| Teb downstream vs. Teb µg/l Upstream                  | 0.82                   | 0.430       |
| Teb downstream agri vs. Teb µg/l Upstream agri        | 1.35                   | 0.250       |
| Teb µg/l downstream vs. Teb µg/l groundwater          | -0.70                  | 0.501       |
| Teb µg/l Upstream, Teb µg/l groundwater               | -1.3                   | 0.223       |
| Prop µg/l Downstream vs. Prop µg/l Upstream           | 1.06                   | 0.315       |
| Prop µg/l Downstream agri vs. Prop µg/l Upstream agri | 1.02                   | 0.385       |
| Prop µg/l Downstream vs. Prop µg/l groundwater        | -0.54                  | 0.6         |
| Prop µg/l Upstream vs. Prop µg/l groundwater          | -0.90                  | 0.389       |
| Cu downstream mg/l vs. Cu mg/l upstream               | 2.57                   | 0.028       |
| Cu downstream mg/l, Cu mg/l groundwater               | 1.27                   | 0.233       |
| Cu mg/l upstream vs. Cu mg/l groundwater              | -1.78                  | 0.105       |

TABLE 22 STATISTICAL ANALYSES

## 6.2 Discussion of statistical results

The data analysed was derived from information gathered during the environmental audit, it is accepted that the ideal scenario for the methodology would be that all surface-water and groundwater analysis was carried out on the same day and that all analysis was by the same ILAB approved laboratory which included a full set of downstream and upstream results for all IPPC licensed sites, however the work has shown some useful trends which will be described.

The pesticide analysis required as part of the IPPC licence requirements is a very expensive process where testing for individual parameters can cost approximately £110 per sample, Environment Agency (2007, pg 3) requires volumes of water (1 litre) which need to be stored and transported to an approved laboratory in the UK. When you look at the results for surface-water downstream there is a strong, statistically significant linear relationship between copper downstream and tebuconazole downstream [Pearson P value 0.001], copper downstream and propiconazole downstream show a similar significant relationship [Pearson P value 0.001]. The situation with groundwater trends for copper and the pesticides appears more complicated with less evidence of correlation (Pearson P values 0.667 & 0.177).

The surface-water downstream results for tebuconazole and propiconazole are significantly correlated [Pearson P value 0.000] which suggests that surface-water analysis for either parameter will give a good indication of compliance. The relationship for groundwater analysis for tebuconazole and propiconazole is also significant [Pearson P value 0.004].

When you look at the surface-water downstream results versus usage data there is a good correlation between copper downstream and copper used [Pearson P value 0.043, T test 2.57 & P value 0.028]. The relationship between pesticides (propiconazole, tebuconazole) and usage is weaker and not statistically significant (Pearson P value 0.151 and 0.175 respectively). The groundwater data for copper and pesticides versus usage does not indicate that there is a significant correlation.

The data for pesticides upstream shows weak correlation between pesticide analysis downstream and upstream for all sites. The results for propiconazole surface-water downstream versus upstream (Pearson P value 0.259, T value 1.06 & P value 0.315) and tebuconazole surface-water (Pearson P value 0.358, T value 0.82 & P value 0.43) do not indicate that there is a linear relationship based on available data compared however the presence of pesticides in upstream analysis could indicate an underlying issue at some sites. There was no data available for upstream groundwater analysis.

When the sites identified during the environmental audit as being in agricultural areas are assessed separately the relationship between pesticides downstream and upstream is statistically significant for both tebuconazole and propiconazole, the results for propiconazole surface-water downstream versus upstream [Pearson P value 0.002, T value 1.02 & P value 0.385] and tebuconazole surface-water [Pearson P value 0.000, T value 1.35 & P value 0.250] indicate that a strong linear relationship exists and external sources appear to be making a contribution to surface-water emissions.

The surface-water limits for these biocides are low and these external contributions at certain sites is going to make compliance challenging. When pesticides upstream was compared with groundwater for sites in agricultural areas the relationship was not significant however if up-gradient/off-site results for pesticides in groundwater was available it would help to create a better picture of the situation with groundwater inputs at certain sites and should be part of the scope of any further site investigation work.

## 7 CONCLUSION AND RECOMMENDATIONS

### 7.1 Introduction

This section documents the key findings of the literature review and methodology (environmental audit and case study). It makes recommendations based on information gathered, evaluates areas where further research is required and highlights any difficulties that were encountered while researching the subject.

### 7.2 Key findings from the literature review and environmental audit

- Based on surface-water and groundwater data reviewed during the on-site audit of IPPC licensed sites using copper azole based wood preservatives, it is evident that there are on-going issues with tebuconazole and propiconazole, 64% of sites have groundwater compliance issues. Statistical analysis of the results indicate that tebuconazole and propiconazole are being detected at levels consistent with the ratio of the actives in the wood preservative Tanalith<sup>®</sup> E which was being used at the sites audited.
- The review of available literature indicates that these secondary biocides, used in conjunction with copper, are very effective in terms of performance from a wood preservation perspective and are widely used in Irish agriculture and horticulture. These secondary biocides compare favourably with its predecessor CCA in terms of potential environmental impact and occupational health and safety risk factors.
- Copper, which is the main active in copper azole, is not being detected at elevated levels in groundwater at sites assessed however 40% sites have surface-water compliance issues, a key issue here is that the copper limits for surface-water are 66% lower than what is required for groundwater.
- On-site activities at IPPC licensed sites appear to be the main source of surface-water and groundwater non-compliance issues and in general can be controlled by improved on-site management, in particular improved pre and post treatment practice, the way timber is presented prior to treatment and then subsequently stored after the impregnation process can help reduce losses of preservative.

- The condition of the containment facilities has improved since licensing was introduced in 1997 and some of the issues at some sites relate to historical issues with CCA. In terms of the soundness of the containment facilities 82% have been tested in the last three years and certified as liquid tight.
- The literature indicates that propiconazole and tebuconazole are widely used in agriculture, 73% of IPPC licensed sites that are being monitored for presence of these biocides are in areas where agricultural activities which might use these pesticides were noted during the audit.
- The statistical analysis for all sites included in the audit does not indicate that there is a significant relationship between upstream levels of these biocides and downstream results however when you look at specific sites in agricultural areas, where 50% of these sites had elevated levels in upstream sampling, the correlation for tebuconazole and propiconazole downstream is statistically significant when compared with upstream analysis results.
- Statistical analysis of the results indicates that monitoring for copper in surface-water is a sound indicator of compliance on-site and correlates well with pesticide analysis, background levels of copper in Ireland are well established.
- Groundwater situations on-site are more complex than surface-water and copper and pesticide analysis is required to indicate and verify compliance.
- The case study illustrated the difficulty in dealing with historical contamination from CCA in particular persistent metals like arsenic and chromium, measures to prevent leaching of these metals through the soil profile need to be introduced as a first step.
- There does not appear to be a strong relationship between quantities of azole biocides used and surface-water/groundwater results while for copper there is a significant correlation between quantity used and surface-water results i.e. the greater the volume used the higher the likelihood of elevated levels of copper in surface-water which need to be dealt with.
- If the “10 tonne per day threshold” is replaced by the proposed “75 m<sup>3</sup> per day threshold” then approximately 82% of current IPPC licensed copper azole sites would be below the new threshold and would revert to control by local authorities assuming the EU Directive is implemented in Ireland as drafted.

### ***7.3 Recommendations***

The following recommendations are being made following review of the findings:

- This environmental audit is a worthwhile exercise and should help operators with their continuous improvement planning and benchmark their performance from year to year. The audit should be carried out during the growing season to facilitate identification of crops in agricultural areas.
- The draft version of the Code of Practice for the Operation of Timber Environmental Conscious Manner, TQBI, should be revisited by the following stakeholders: EPA, Department of Environment, Pesticide Control Service, Irish Timber Council, Wood Marketing Federation, NSAI, Health and Safety Authority, Enterprise Ireland and wood preservative suppliers.
- The pre and post treatment holding recommendations in the Arch Timber Protection document G1/08 should be followed to help minimise any potential losses of preservatives in particular ensuring that timber is presented in a fashion prior to treatment to facilitate access of the liquid solution and post treatment drying. The importance of holding the treated timber for 48 hours after treatment in a contained area cannot be over-stated.
- Monitoring for copper and pesticides should have upstream/off site sample points included for surface-water and groundwater to help give a more complete picture of what is happening on and off-site.
- In areas where agricultural inputs of pesticides is likely surface-water monitoring for copper may be more robust and less prone to external influences.

### ***7.4 Scope for further research***

There is certainly more scope to investigate the background levels of pesticides in surface-water and groundwater at IPPC licensed sites and project could be extended to include all wood preservative sites using high and low pressure systems and wood preservatives.

## 8 BIBLIOGRAPHY

ALcontrol Laboratories Ireland, 2007. *Detection Methods*. Available at:  
<http://www.alcontrol.co.uk>

*American Wood Protection Association Standard*, 2008. U1-08, p. 25.

Anon, 2008. *Frequently asked questions*. Available at:  
<http://www.faqs.org/patents/app/20080293793>.

Anon., 2006. *Strainer Treatment Test*, Wood Technology Centre, University of Limerick, p. 8.

Anon., 2004. Emission factors programme Task 1 – Summary of simple deck studies (2003/4). AEAT/ENV/R/1715/Issue 1 March 2004, p. 6.

Arch Timber Protection, 2001. *Plant Operation Training Manual*, Chp. 3.

Arch Timber Protection, 2002. *Material Safety Data Sheet for Tanalith C3310*, Data Sheet No 3310 1.1.2, p. 1.

Arch Timber Protection, 2004. *Tanalith® E International Dossier*, p.6.

Arch Timber Protection, 2007. *Material Safety Data Sheet for Tanalith® E 3494*, Data Sheet No 3494 3.0, p. 1.

Arch Timber Protection, 2007. *Material Safety Data Sheet for Tanalith® E 3494*, Data Sheet No 3494 3.0, p. 6.

Arch Timber Protection, 2008. *Plant Operator and Site Management Training Manual*.

Arch Timber Protection, 2008. *Specifiers Guide to Vacsol Aqua and Vacsol Azure Treated Timber*. Available at: <http://www.archtp.com/>

Arch Timber Protection, 2008. *Best Practice – Treatment Plant Design and Site Maintenance*. Technical, Environmental & regulatory Affairs, Ref G1/08.

Archer, K. and Preston A., 2006, *An Overview of Copper Based Wood Preservatives*. CSI. Available at: <http://www.forestprod.org/woodprotection06archer.pdf>

Armishaw, R.F., Fricker, A.G. and Fenton G.A., 1994. *Soil and Groundwater Studies at Some CCA Timber Treatment Sites*, Industrial Research Limited, Wellington, New Zealand, pp. 44-48.

Aston David, 2004. *Environmental Risk Assessment – Progress so far*, Final Workshop COST ActionE22 ‘Environmental Optimisation of Wood Protection’ Lisbon – Portugal, p. 4.

Atkin, C., 2009. Personal communication in relation worst case scenario for losses from banded treatment sites.

BAM EW, 1990. *Testing results for tebuconazole*. The Federal Office for Materials Research and Testing, Berlin, West Germany,

Bergfald & Co. 2005. *A Study of the priority substance of the Water Framework Directive*, Report on behalf of the Norwegian Pollution Control Authority, TA-2140/2005, ISBN 82-7655-276-5, p.80.

Bravery, A.F., Berry, R.W. Carey, J.K. and Cooper D.E., 2007. *Recognising wood rot and insect damage in buildings*. Published by BRE Press, Garston, Watford, ISBN 1 86081 603 7, p.25.

British Standards Institution, 1993. *Water quality – Guidance on sampling of groundwaters*, BS 6068-6.11:1993. BSI, London.



British Standards Institution, 2001. BS 10175:2001 *Investigation of potentially contaminated sites* – Code of Practice. BSI London.

British Standards Institution, 2003. B.S. 8417:2003. *Preservation of timber-Recommendations*. BSI, London.

Brooks, K., M., 2004. *The affects of dissolved copper on salmon and the environmental effects associated with the use of wood preservatives in aquatic environments*. Western Wood Preservers Institute, Vancouver, p. 2.

Chauhan, R., Chopra I., Madan V.K. and Kumari B., 2007. *Laboratory Degradation Studies of Propiconazole in Clay Loam Soil*, Medicinal and Aromatic Plants Section, Department of Plant Breeding Department of Entomology, CCS Haryana Agricultural University Hisar-125004, Haryana, India, p. 144.

China Shenghua Group Agrochemical Group, *Application Rate for SEGARD*. Available at: <http://www.diytrade.com/china/tebuconazole/>

Ciba-Geigy, 1997. *Technical Information Bulletin for Propiconazole Fungicide*. Greensboro, NC. 15 pp. (cited in Pesticide Information Profile , 1997. Extranet Extension Network, Propiconazole, p. 1.).

Clenaghan, C., O'Neill, N. & Page, D., 2005. *Dangerous Substances Regulations National Implementation Report*, Environmental Protection Agency, PO Box 3000, Johnstown Castle, Co Wexford, p. 34.

Connell, M., 2004. *Issues facing preservative suppliers in a changing market for treated wood*. Final Workshop COST Action, Portugal, pp. 3-4.

Cooper, PA., D.L. Alexander, and T. Ung, 1993. *What is chemical fixation? Chromium –containing waterborne wood preservatives: Fixation and environmental issues*. Forest Products Society, Madison, WI, pp. 7-13.

Cooper, P., Ung T., Edlund, M-L. and Jermer, J., 2005. *Inorganic preservative levels in soil under treated wood decks after 8 years natural exposure in Boras, Sweden*. Paper prepared for the 36<sup>th</sup> Annual Meeting Bangalore, India IRG/WP 05-50233, p. 6.

Coover, M.P. and Sims, R.C.C., 1987. *The effects of temperature on polycyclic aromatic hydrocarbon persistence in an unacclimated agricultural soil*. *Hazardous Waste and Hazardous Materials*, 4:69-82, cited in Technical Support Document for Exposure Assessment and Stochastic Analysis, Chemical Specific Soil Half lives 2000.

Courier, 2006. *The Bayer Crop Science Magazine for Modern Agriculture* 2/06, p. 3 Available at: <http://www.bayercropscience.com/bayer/cropscience/cscms.nsf/id/>

Crop Protection, 2004. *Fungicides*, Irish Farmers Journal 17<sup>th</sup> April 2004, p. 48.

Damicone, J., 2003 *Potential for Cucurbit Downy Mildew in 2003*. Plant Disease and Insect Advisory. Oklahoma State University.

Department of Agriculture and Food. 2003. *Pesticide Usage Survey, Grassland and Fodder Crops*. Available at: <http://www.pcs.agriculture.gov.ie>

Department of Agriculture and Food. 2004. *Pesticide Usage Survey, Arable Crops Report No 2*. Government of Ireland 2007, Available at: <http://www.pcs.agriculture.gov.ie> Table 11, p. 18.

Department of Agriculture, Food and Rural Development, 2000. *Pesticide residues in Food 2000*, table 2, Available at: <http://www.pcs.agriculture.gov.ie>, pp 9 -15.

Department of Agriculture Fisheries and Food, 2006. *Pesticide residues in Food 2006*, table 2, Available at: <http://www.pcs.agriculture.gov.ie> pp 11-31.

Derham, J., 2002. *IPC Regulation of the Timber Preservation Sector*. EPA Workshop, Dublin, June 2002.

Derham, J., 2004. EPA letter in relation to holding times for treated timber.

Dutch Ministry of Housing, 2000. *Dutch guidance for soil chemistry*, Department of Soil Chemistry.

Dutzmann, S. and Suty-Heinze, A., 2004. *Prothioconazole: a broad spectrum demethylation-inhibitor (DMI) for arable crops*, Bayer 249-264, p. 1.

EC Drinking Water No 2 Regulations, 2007 (Statutory Instruments SI No 278 of 2007).

Edlund, M-L., and Jermer, J., 2002. *IRG/WP 02-30297 Evaluation of wood preservatives for Nordic wood preservation class AB*. SP Swedish Testing and Research Institute, table 5, pg. 9.

Edlund, M-L. 1998, *Why field tests are needed*, Scandinavian Wood Preservation Conference. Stockholm, Sweden.

Elementis, 2001. *Material Safety Data Sheet for Chromium Trioxide*. Available at <http://www.Elementischromium.com/pdf/pesticide.pdf>

Environment Agency, 2007. Quote Reference No 2762.1, 3. National Laboratory Service, Leeds.

Enterprise Ireland Directory of Timber Preservation Plants 1996. National Timber Centre, Enterprise Ireland, Glasnevin, Dublin 9.

Environment, Heritage and Local Government, 2008. Letter from Ian Keating to Wood Marketing Federation, 12<sup>th</sup> May 2008.

Enviros Consulting Ltd, 2003. *Assessment of File on Classification of Treated Timber Waste*, Final Report prepared for the Environmental Protection Agency, Manchester, pp. 8-10.

EPA Report on IPC Licensing and Control 1998. Environmental Protection Agency, PO Box 3000, Johnstown Castle, Co Wexford.

EPA, 1998. *Integrated Pollution Control Licence No 353*, p. 7. Environmental Protection Agency, PO Box 3000, Johnstown Castle, Co Wexford.

EPA, 2003. *Towards Setting Guideline Values for Protection of Groundwater in Ireland*. Environmental Protection Agency, PO Box 3000, Johnstown Castle, Co Wexford.

EPA Office of Enforcement Report 2005. *Focus on Environmental Enforcement*. Environmental Protection Agency, PO Box 3000, Johnstown Castle, Co Wexford.

EPA Register of Quality Approved Laboratories submitting data to EPA 2007. Environmental Protection Agency, PO Box 3000, Johnstown Castle, Co Wexford.

EPA, 2008. *Chemicals and other Environmental Issues*, p 218. Environmental Protection Agency, PO Box 3000, Johnstown Castle, Co Wexford.

ERBD (in preparation) National Abstraction Pressure Assessment Study, carried out by the ERBD project. Available at: <http://www.erbd.ie> (cited in Williams N. H. and Lee, M. 2007. *Ireland at risk – Possible implications for groundwater*).

Fay, D., McGrath, D., Zhang, C., Carrig, C., O Flaherty, V., Kramers, G., Carton, O.T. and Grennan, E., 2006. *Towards A National Soil Database*, RTDI Programme 2000-2006

Freeman M. H., Shupe T. F., Vlosky R. P. and Barnes H. M., 2003. *Past, Present and Future of the Wood Preservation Industry*. Forest Products Journal, Vol. 53, No. 10, p11.

Gray, S.M. and Dickinson, D. J., 1998. *The role of copper in fixed waterborne systems*. Record of the 1988 Annual Convention of the British Wood Preserving Association, pp. 65-79.

Grundlinger, R and Exner, O., 1990. *Tebuconazole – A new triazole fungicide for wood preservation*, Bayer AG, paper prepared for 21<sup>st</sup> Annual Meeting in Rotonia, p. 2.

Gründlinger, Roland and Exner, O., 1990. *Tebuconazole, a new wood preserving fungicide*. IRG/WP/3634, paper prepared for the 21<sup>st</sup> Annual Meeting Rotorua, New Zealand May 1990, p. 3.

GSI, 2006. *Aquifer classification*. Available at:  
[http://www.gsi.ie/NR/rdonlyres/01C4199F-A257-48A0-A963-5CB65A779F6E/0/aquifer\\_classification\\_Oct06.pdf](http://www.gsi.ie/NR/rdonlyres/01C4199F-A257-48A0-A963-5CB65A779F6E/0/aquifer_classification_Oct06.pdf)

Homebond Issue No 33, 2005. *Timber Preservative Pre-treatment in Domestic Buildings*, January 2005.

Hughes, A. S., 1995. *Reaction Mechanisms and fixation properties of copper based timber preservatives*, Hickson Timber Products Ltd. BWPDA Annual Convention 1995, p.7.

IFIC., 2001. *Irish Forest Industry Chain Submission on CCA*, IBEC, Dublin.

International Programme on Chemical Safety, 1998. *Environmental Health Criteria 200, Copper*. Section 1.3.

Irish Meteorological Service, 2009. Rainfall patterns in Ireland. Available at:  
<http://www.met.ie>

Kennedy, M. J. and Collins, P. A., 2001. *Leaching of preservative components from pine decking treated with CCA and copper azole and interaction of leachates with soils*. IRG/WP 01, Queensland Forestry Research Institute, p. 13.

Kugler, M., Bruns, R., Jaetsch, T., and Spetmann, P., 2008. *Fungicidal Mixtures for Wood Preservation*. Lanxess Corp, Pittsburg, US.

Leblow, S., 1996. *Leaching of Wood Preservative Components and their mobility in the Environment*. Summary of Pertinent Literature. US Forest Service, General Technical Report FPL-GTR-93, p. 2 – 8.

Lebow, S., 2004. *Alternatives to Chromated Copper Arsenate (CCA) for Residential Construction*, USDA Forest Service, Forest Products Laboratory Madison, Wisconsin Prepared for Proceedings of the Environmental Impacts of Preservative-Treated Wood Conference Orlando, Florida February 8–10, p. 3.

Magner, D., 2009. *Forestry & Timber Yearbook 2009*, p. 90, Irish Timber Growers Association, ISBN 0953481000.

McCabe, T., 2005. *Fungicide use strategies should remain in the new era.*, UCD, Crop Protection , Farmers Journal, p. 21.

McDonald J.H, 2008. Statistics. Available at:  
<http://udel.edu/~mcdonald/statspearman.html>. It may be cited as pp. 202-204 in:  
McDonald, J.H. 2008. Handbook of Biological Statistics. Sparky House Publishing, Baltimore, Maryland

McGrath, D. and McCormack, R.J., 1999. *The Significance of Heavy Metal and Organic Micro-pollutants in Soils*, Teagasc Report ARMIS 4268, Johnstown Castle Research Centre, Wexford, p.13.

Meyers, R., A., 1998. *Environmental Analysis and Remediation*, Vol 4. Wiley Encyclopaedia Series in Environmental Science, p. 2423.

Minerex, 2004. *Risk Assessment Study of Contamination to Water and Soils*. Report No. 1672-087, p. 13.

Minerex, 2007. *Biannual Monitoring*. Report No. 1672-511, p. 1.

Mitsuhahi, G., J., M., 2007. *Limiting Copper Loss from Treated Wood in or Near Aquatic Environments*, A THESIS.

<http://ir.library.oregonstate.edu/dspace/bitstream/1957/6358/1/Thesis%20Final%20Jul30.pdf> p. 19.

Moe, H., Daly, D., Hunter Williams, N., Mills, P. and Gaston, L. 2007. *A National Assessment of Groundwater Abstraction Pressures*. Proceedings of IAH (Irish group) 27th Annual Groundwater Conference, Groundwater: Pressures and Opportunities. pp. 5-25 - 5-32.

National Standards Authority of Ireland, 2005. IS 435-1:2005 Table 10 Penetration and retention recommendations. NSAI, Glasnevin, Dublin 9.

National Standards Authority of Ireland, 2007. I.S. 436:2007 *Farm Fencing – Timber. Post and Wire*. NSAI, Glasnevin Dublin 9, Table C6, p.23.

Nordic Wood Preservation Council, 2008. *Wood Preservatives approved by the Nordic Wood Preservation Council*, January 1st 2008 List No 78, Norsk Treteknisk Institutt, Sweden.

Nordic Wood Project, 2008. Report No. 98056, 2008.

Northern Ireland Environment and Heritage Technical Guidance Note IPPC H7.  
*Guidance on the Protection of Land under the PPC Regime: Application Site Report and Site Protections and Monitoring Programme*, p5.

OCM (2007) *Establishing Natural Background Levels for Groundwater in Ireland*, O'Callaghan Moran & Associates, on behalf of the South Eastern River Basin District Project Team.

Office of Environmental Enforcement, 2006. *Focus on Environmental Enforcement*, 2004 – 2005, Environmental Protection Agency, PO Box 3000, Johnstown Castle, Co Wexford, p. 7.

Official Journal of the European Communities, L 123/48.

Osiose Sweden AB. (2002). *Material Safety Data Sheet for Celcure AC-800*.

Owen, F., and Jones, O., 1994. *Statistics*, 4<sup>th</sup> Edition, Pitman Publishing, p. 470.

Oxford University, 2005. *Safety datasheet for arsenic*. Available at <http://msds.chem.ox.ac.uk/>

Page, D., Burke, D., Wall, B. and O'Leary G., 2007. *The Provision and Quality of Drinking Water in Ireland*, EPA Report 2006-2007, Environmental Protection Agency, PO Box 3000, Johnstown Castle, Co Wexford. p. 23.

PAN Pesticides Database. Available at [http://www.pesticideinfo.org/Detail\\_Chemical.jsp?Rec\\_Id=PC35028](http://www.pesticideinfo.org/Detail_Chemical.jsp?Rec_Id=PC35028).

Pesticide Control Service, 2000. *Pesticide Residues in Food*, Department of Agriculture. Available at: <http://www.pcs.agriculture.gov.ie>



Pesticide Control Service, 2004. *Restrictions on marketing and use of CCA- (Copper, Chrome and Arsenic) treated timber*. Available at: <http://www.pcs.agriculture.gov.ie>

Pesticide Residues Committee, 2007. *Pesticides Residues Monitoring Report, 4<sup>th</sup> Qtr Report*. Pesticide Residues Committee, York.

Pesticides Forum, 2007. *Report of indicators reflecting the impacts of pesticide use*, p. 11.

Pesticides in Ground Water, 2003. Available at: <http://ga.water.usgs.gov/edu/pesticidesgw.html>.

Pinero, E., 2009. *Introduction to EMS auditing concepts and ISO 14000*. Office of the Federation Environment Executive.

Prism, 2009. *Analyzing Data with Graph Pad Prism. Interpreting P values*.

Rand, G., M. and Petrocelli, S. R., 1985. *Fundamentals of Aquatic Toxicology*, p. 4.

Report for EPA, 2007. Available at: <http://www.epa.ie/downloads/pubs/research/land/ertdi>, p. 4.

Reregistration Eligibility Decision, 2006. *(Red) for Propiconazole*, EPA, Case No 3125, 2006.

Ryan, Richard, 1998. *Water movement in a structured soil in the south east of Ireland: preliminary evidence for preferential flow*, Michael Ryan, Teagasc, Johnstown Castle, Wexford, p. 124.

Schulte, R.P.O., Diamond, J., Finkle, K., Holden, N.M. and Brereton, A.J. 2005 *Predicting the soil moisture conditions of Irish grasslands*. Irish Journal of Agricultural and Food Research 44, p 125.

Sexton, T., 2007. *Environmental Issues at EPA Licensed Timber Treatment Facilities*, Environmental Protection Agency Presentation, ATP Training Course.

Strickland, T.C., T.L. Potter and H. Joo. 2004. *Tebuconazole dissipation and metabolism in Tifton loamy sand during laboratory incubation* and Pest Manage. Sci. 60:703–709 (cited in Potter T. L et al, 2005. Accelerated Soil Dissipation of Tebuconazole following Multiple Applications to Peanut, p. 1).

Suttie, E. D., Bravery A. F., & T B Dearling, T. B., 2002. *IRG 02-30289, Alternatives to CCA for ground contact protection of timber: a perspective from UK on performance and service life expectations*. Paper prepared for the 33rd Annual Meeting Cardiff, Wales, UK.

Suttie, E. D., 2009. *Letter to Dr A. S. Hughes, Ref. 254-114, 23<sup>rd</sup> January 2009*. BRE Garston, Watford.

TQBI 1997. *Advisory Note and Code of Practice for the Operation of Timber Treatments Plants in a safe and Environmental Conscious Manner*. Forbairt, Glasnevin, Dublin 9.

UK Groundwater Forum, 1998. *Groundwater: a valuable resource*. Available at: <http://www.nwl.ac.uk/gwf>.

UNEP-GEF, 2002. *Regionally based assessment of Persistent Toxic Substances*.

US Department of Transportation, 2004. *Initial Preservative Treatment of Wood in Covered Bridges*. [www.tfhr.gov/structur/pubs/04098/19.htm](http://www.tfhr.gov/structur/pubs/04098/19.htm), chapter 19.

US EPA, 1992. *RCRA Ground water monitoring*. Draft Technical Guidance, Office of Solid Waste, ch. 6.

United States Geological Survey, 1993. *Pesticides in Groundwater*. Available at: <http://ga.water.usgs.gov/edu/pesticidesgw.html>

US EPA, 2006. *Reregistration Eligibility Decision (RED) for Propiconazole, Prevention Pesticides and Toxic Substances (7508P)*, p. 2 – 4.

Waldron, L. and Cooper, P., 2002. *Modelling of wood preservative leaching in service*, Faculty of Forestry, University of Toronto. Available at <http://www.ccaresearch.org/Pre-Conference/pdf/Waldron.pdf>.

Walorczyk, S., 2004. *Fast Identification of trace level Pesticide residues*, Journal of Plant Protection Vol. 44 No 2.

Water Quality (Dangerous Substances) Regulations, 2001 (Statutory Instruments SI No 12 of 2001).

Wilkinson J.G., 1979. *Industrial Timber Preservation*, Rentokil Library, 1979. Published by Associated Business Press, London, ISBN 085227 1034.

Williams, N. H. and Lee, M., 2007. *Ireland at risk – Possible implications for groundwater resources of climate change*, Groundwater Section, Geological Survey of Ireland.

Wood Marketing Federation, 2008. Submission on the proposed Directive on Industrial Emissions (COM (2007) 844 final) to the Department of the Environment, Heritage and Local Government.

Wood Protection Association, 2003. *Timber Treatment Installations 2003 Code of Practice for Safe Design and Operation*. Published by Environment Agency, Bristol.

Wood Protection Association 2008. *Reasons why wood impregnation plants should not be an added activity in the Proposed Directive on Industrial Emissions COM (2007) 844 Final*.

Woodspec 2007, *A Guide to designing, detailing and specifying timber in Ireland*.  
Wood Marketing Federation, table A.4.3, p 66. Published by Wood Marketing  
Federation, Wicklow, Ireland, ISBN 978-0-9539976-1-9.

Woodspec 2007, *A Guide to designing, detailing and specifying timber in Ireland*.  
Wood Marketing Federation, section E, p 321. Published by Wood Marketing  
Federation, Wicklow, Ireland, ISBN 978-0-9539976-1-9.

Wüstenhöfer, B., Wegen, H-W. and Metzner, W., 1990. *Tebuconazole, a new wood  
preserving fungicide*. IRG/WP/3634. Paper prepared for the 21<sup>st</sup> Annual Meeting  
Rotorua, New Zealand.

## 9 APPENDICES

### 9.1 Appendix 1

| Site       | Prop µg/l Upstream | Prop µg/l groundwater |
|------------|--------------------|-----------------------|
| PH170209c* | 0.02               | 0.02                  |
| PH170209s  | 2.1                | 0.1                   |
| PH260209b* | 0.33               | 47.8                  |
| PH270109*  | 5.5                | 2.66                  |
| PH260209w* | 0.1                | 0.02                  |

Prop upstream µg/l vs. prop groundwater -0.258035745

| Site       | Teb µg/l Downstream | Teb µg/l Upstream |
|------------|---------------------|-------------------|
| PH170209c* | 0.02                | 0.02              |
| PH0909*    | 0.05                | 0.02              |
| PH260209b* | 0.34                | 0.17              |
| PH270109*  | 6.2                 | 5.5               |
| PH260209w* | 0.1                 | 0.1               |

Teb µg/l Downstream agri vs. teb upstream agri 0.999718152

| Site       | Prop µg/l Downstream | Cu downstream mg/l |
|------------|----------------------|--------------------|
| PH260109*  | 0.204                | 0.0192             |
| PH170209c* | 0.02                 | 0.069              |
| PH180209l  | 0.039                | 0.001              |
| PH0909*    | 0.05                 | 0.007              |
| PH170209s  | 0.1                  | 0.008              |
| PH260209b* | 0.14                 | 0.004              |
| PH100209w* | 14                   | 0.155              |
| PH270109*  | 8.5                  | 0.14               |
| PH260209w* | 0.341                | 0.083              |
| PH230309mc | 0.02                 | 0.002              |

Prop µg/l Downstream vs. cu downstream 0.862214082

| Site       | Teb µg/l Downstream | Prop µg/l Downstream |
|------------|---------------------|----------------------|
| PH260109*  | 0.1                 | 0.204                |
| PH170209c* | 0.02                | 0.02                 |
| PH180209l  | 0.1                 | 0.1                  |
| PH0909*    | 0.05                | 0.05                 |
| PH170209s  | 0.1                 | 0.1                  |

|            |      |       |
|------------|------|-------|
| PH260209b* | 0.34 | 0.14  |
| PH100209w* | 11   | 14    |
| PH270109*  | 6.2  | 8.5   |
| PH260209w* | 0.1  | 0.341 |
| PH230309mc | 0.41 | 0.02  |

Teb µg/l Downstream vs. prop downstream 0.99843358

| Site       | Copper carbonate tonnes<br>/year | Cu downstream mg/l |
|------------|----------------------------------|--------------------|
| PH260109*  | 5.6                              | 0.023              |
| PH170209c* | 6.82                             | 0.069              |
| PH180209l  | 12.3                             | 0.001              |
| PH0909*    | 5.6                              | 0.007              |
| PH170209s  | 0.96                             | 0.008              |
| PH260209b* | 2.68                             | 0.004              |
| PH100209w* | 11.05                            | 0.155              |
| PH270109*  | 10.42                            | 0.14               |
| PH260209w* | 12.8                             | 0.083              |
| PH230309mc | 1.49                             | 0.029              |

Cu mg/l Downstream vs. cu T/year 0.574162134

| Site       | Teb µg/l Downstream | Tebuconazole<br>kg/year |
|------------|---------------------|-------------------------|
| PH260109*  | 0.1                 | 56                      |
| PH170209c* | 0.02                | 68.2                    |
| PH180209l  | 0.1                 | 123                     |
| PH0909*    | 0.05                | 56                      |
| PH170209s  | 0.1                 | 9.6                     |
| PH260209b* | 0.34                | 26.8                    |
| PH100209w* | 11                  | 110.54                  |
| PH270109*  | 6.2                 | 104.2                   |
| PH260209w* | 0.1                 | 128                     |
| PH230309mc | 0.41                | 14.9                    |

Teb µg/l Downstream vs. teb kg/year 0.418545828

### Paired T-Test and CI: Teb µg/l downstream\_1, Teb µg/l Upstream

Paired T for Teb µg/l downstream\_1 - Teb µg/l Upstream

|                       | N  | Mean | StDev | SE Mean |
|-----------------------|----|------|-------|---------|
| Teb µg/l downstream_1 | 11 | 1.67 | 3.59  | 1.08    |
| Teb µg/l Upstream     | 11 | 0.81 | 1.77  | 0.53    |
| Difference            | 11 | 0.86 | 3.48  | 1.05    |

95% CI for mean difference: (-1.48, 3.20)

T-Test of mean difference = 0 (vs. not = 0): T-Value = 0.82 P-Value = 0.430

### Paired T-Test and CI: Teb µg/l downstream\_1, Teb µg/l groundwater

Paired T for Teb µg/l downstream\_1 - Teb µg/l groundwater

|                       | N  | Mean  | StDev | SE Mean |
|-----------------------|----|-------|-------|---------|
| Teb µg/l downstream_1 | 11 | 1.67  | 3.59  | 1.08    |
| Teb µg/l groundwater  | 11 | 3.18  | 5.81  | 1.75    |
| Difference            | 11 | -1.51 | 7.15  | 2.16    |

95% CI for mean difference: (-6.31, 3.30)

T-Test of mean difference = 0 (vs. not = 0): T-Value = -0.70 P-Value = 0.501

### Paired T-Test and CI: Teb µg/l Upstream, Teb µg/l groundwater

Paired T for Teb µg/l Upstream - Teb µg/l groundwater

|                      | N  | Mean  | StDev | SE Mean |
|----------------------|----|-------|-------|---------|
| Teb µg/l Upstream    | 11 | 0.81  | 1.77  | 0.53    |
| Teb µg/l groundwater | 11 | 3.18  | 5.81  | 1.75    |
| Difference           | 11 | -2.37 | 6.04  | 1.82    |

95% CI for mean difference: (-6.43, 1.69)

T-Test of mean difference = 0 (vs. not = 0): T-Value = -1.30 P-Value = 0.223

### Paired T-Test and CI: Prop µg/l Downstream, Prop µg/l Upstream

Paired T for Prop µg/l Downstream - Prop µg/l Upstream

|                      | N  | Mean | StDev | SE Mean |
|----------------------|----|------|-------|---------|
| Prop µg/l Downstream | 11 | 2.13 | 4.67  | 1.41    |
| Prop µg/l Upstream   | 11 | 0.75 | 1.69  | 0.51    |
| Difference           | 11 | 1.38 | 4.34  | 1.31    |

95% CI for mean difference: (-1.53, 4.30)

T-Test of mean difference = 0 (vs. not = 0): T-Value = 1.06 P-Value = 0.315

### Paired T-Test and CI: Prop µg/l Downstream, Prop µg/l groundwater

Paired T for Prop µg/l Downstream - Prop µg/l groundwater

|                       | N  | Mean  | StDev | SE Mean |
|-----------------------|----|-------|-------|---------|
| Prop µg/l Downstream  | 11 | 2.13  | 4.67  | 1.41    |
| Prop µg/l groundwater | 11 | 4.68  | 14.32 | 4.32    |
| Difference            | 11 | -2.55 | 15.59 | 4.70    |

95% CI for mean difference: (-13.02, 7.93)

T-Test of mean difference = 0 (vs. not = 0): T-Value = -0.54 P-Value = 0.600

### Paired T-Test and CI: Prop µg/l Upstream, Prop µg/l groundwater

Paired T for Prop µg/l Upstream - Prop µg/l groundwater

|                       | N  | Mean  | StDev | SE Mean |
|-----------------------|----|-------|-------|---------|
| Prop µg/l Upstream    | 11 | 0.75  | 1.69  | 0.51    |
| Prop µg/l groundwater | 11 | 4.68  | 14.32 | 4.32    |
| Difference            | 11 | -3.93 | 14.48 | 4.37    |

95% CI for mean difference: (-13.66, 5.79)  
 T-Test of mean difference = 0 (vs. not = 0): T-Value = -0.90 P-Value = 0.389

**Paired T-Test and CI: Cu downstream mg/l, Cu mg/l upstream**

Paired T for Cu downstream mg/l - Cu mg/l upstream

|                    | N  | Mean   | StDev  | SE Mean |
|--------------------|----|--------|--------|---------|
| Cu downstream mg/l | 11 | 0.0472 | 0.0568 | 0.0171  |
| Cu mg/l upstream   | 11 | 0.0066 | 0.0135 | 0.0041  |
| Difference         | 11 | 0.0405 | 0.0523 | 0.0158  |

95% CI for mean difference: (0.0054, 0.0757)  
 T-Test of mean difference = 0 (vs. not = 0): T-Value = 2.57 P-Value = 0.028

**Paired T-Test and CI: Cu downstream mg/l, Cu mg/l groundwater**

Paired T for Cu downstream mg/l - Cu mg/l groundwater

|                     | N  | Mean   | StDev  | SE Mean |
|---------------------|----|--------|--------|---------|
| Cu downstream mg/l  | 11 | 0.0472 | 0.0568 | 0.0171  |
| Cu mg/l groundwater | 11 | 0.0235 | 0.0243 | 0.0073  |
| Difference          | 11 | 0.0236 | 0.0617 | 0.0186  |

95% CI for mean difference: (-0.0178, 0.0651)  
 T-Test of mean difference = 0 (vs. not = 0): T-Value = 1.27 P-Value = 0.233

**Paired T-Test and CI: Cu mg/l upstream, Cu mg/l groundwater**

Paired T for Cu mg/l upstream - Cu mg/l groundwater

|                     | N  | Mean     | StDev   | SE Mean |
|---------------------|----|----------|---------|---------|
| Cu mg/l upstream    | 11 | 0.00664  | 0.01349 | 0.00407 |
| Cu mg/l groundwater | 11 | 0.02355  | 0.02432 | 0.00733 |
| Difference          | 11 | -0.01691 | 0.03145 | 0.00948 |

95% CI for mean difference: (-0.03804, 0.00422)  
 T-Test of mean difference = 0 (vs. not = 0): T-Value = -1.78 P-Value = 0.105

**Paired T-Test and CI: Prop µg/l Downstream, Prop µg/l Upstream (Agri areas)**

Paired T for Prop µg/l Downstream - Prop µg/l Upstream

|                      | N | Mean  | StDev | SE Mean |
|----------------------|---|-------|-------|---------|
| Prop µg/l Downstream | 4 | 2.25  | 4.17  | 2.08    |
| Prop µg/l Upstream   | 4 | 1.49  | 2.68  | 1.34    |
| Difference           | 4 | 0.763 | 1.502 | 0.751   |

95% CI for mean difference: (-1.627, 3.153)  
 T-Test of mean difference = 0 (vs. not = 0): T-Value = 1.02 P-Value = 0.385

**Paired T-Test and CI: Teb µg/l downstream, Teb µg/l Upstream (Agri areas)**

Paired T for Teb µg/l downstream - Teb µg/l Upstream

|                     | N | Mean | StDev | SE Mean |
|---------------------|---|------|-------|---------|
| Teb µg/l downstream | 5 | 1.34 | 2.72  | 1.22    |
| Teb µg/l Upstream   | 5 | 1.16 | 2.43  | 1.08    |





Difference                    5   0.180   0.299   0.134

95% CI for mean difference: (-0.191, 0.551)

T-Test of mean difference = 0 (vs. not = 0): T-Value = 1.35   P-Value = 0.250

## 9.2 Appendix 2

### Environmental Audit

enchmark for Audit is BATNEEC Guidance Note for Wood Preservation EPA 1994, Code of Practice For the Operation of Timber Environmental Conscious

anner, TQBI, 1996. IPC Regulation Of the Timber Preservation Sector, Jonathan Dereham, EPA, 2002.

Audit Reference No. PH260109

28th January 2009

Date of audit

PD353

Site ID Number

Treatment Vessel

Manufacturer

Manufacturer's I.D. No.

Type of door

Year of manufacture

|          |
|----------|
| IPV      |
|          |
| 5' x 40' |
|          |

Return to Cover Sheet

Bottom of Report

The Red, Amber, Green Traffic Light System indicates the condition of the equipment at the time of audit.

#### KEY

|   |
|---|
| ● |
| ● |
| ● |

Green - complies with BATNEEC and Manufacturers Instructions.

Amber - minor non compliance and raised as an observation

Red - condition not acceptable and would be classified as non compliance requiring corrective action.

#### Technologies for load minimisation

Inventory control

Use of processing records

Total chemical usage per annum

Optimisation of impregnation process to ensure minimum wastage

Use of retention cycles

Initial and final vacuum

Tilting of packs

Presentation of pack to facilitate post treatment drying

Roofing and bunding of impregnation and immediate post-impregnation area

Size of treatment vessel and capacity per day assuming normal production

Is vessel fitted with pressure relief valve and pressure gauge?

Is vessel banded and undercover?

Storage tank capacity and dimensions

Are storage tanks banded and undercover, give dimensions?

Are storage tanks fitted with overflow alarms?

Mixing tank capacity and dimensions

Is system designed to prevent siphoning ie 150mm gap?

Is Mixing tank banded and fitted with overflow devices?

Only treatment certs issued

28 tonnes in 08

Treat to Arch spec - PLC control

Pressure of 17 kgfm<sup>2</sup> venting through Sherlock valve, reduce

Stakes mainly - sloped on skids

Good, no plastic

5 x 40 IPV 25m<sup>3</sup> per day based on 3 per day

Pressure gauge working ie 17 kgfm<sup>2</sup> and safely fitted

Yes

2.8m dia x 7.8m long = 48,000 litres

Yes 67,000 litre capacity

Yes audible alarms

1.8 x 1.2 x 1.2 = 2590 litres

Balcock fitted and 150mm gap

Yes

#### Comments

| Condition/Action Required | Weighted |   |   | Total | Score |
|---------------------------|----------|---|---|-------|-------|
|                           | ●        | ● | ● |       |       |
|                           |          |   |   |       |       |
|                           |          |   | X |       |       |
|                           |          |   | X |       |       |
|                           |          |   | X |       |       |
| X                         |          |   |   | 5     | 5     |
|                           |          |   | X | 4     | 4     |
|                           |          |   | X |       |       |
|                           |          |   | X | 4     | 4     |
|                           |          |   | X | 4     | 4     |
|                           |          |   | X | 5     | 5     |
|                           |          |   | X | 5     | 5     |

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Page 1

|  |  |  |   |   |   |    |   |
|--|--|--|---|---|---|----|---|
| Storage tank capacity  | Use of ibcs - mild steel tank recommended                                |  | x |   | 2 | 5  | 2 |
| Is bulk storage tank banded and undercover, give dimensions?   |  |  |   |   |   |    |   |
| <b>Bunding of tanks</b>  |  |  |   |   |   |    |   |
| Does banded area for storage tanks appear liquid tight?  | Bund test indicates liquid tightness                                     |  |   | x | 4 | 5  | 4 |
| Has bund been tested in last 3 years?  | Yes JS O Hara Engineering tested 8/1/09                                  |  |   | x | 5 | 5  | 5 |
| Is bund sealed with substance resistant to the preservative?   | Bund wall re-sealed recently   |  |   | x | 3 | 5  | 3 |
| Size of tank   | 7.26 x 5.2 x 1.772 = 67,000 litres                                       |  |   | x | 5 | 5  | 5 |
| Is post treatment drying area capacity sufficient for 48hrs production?  | Yes 33 x 11 + 6 x 6 + 13 x 9 = 516m <sup>2</sup>                         |  |   | x |   |    |   |
| Does holding area appear liquid tight?   | Yes  |  |   | x | 5 | 5  | 5 |
| Is there a tracking system in place to demonstrate >48hrs status?  | Pack label used to indicate time and date of treatment                   |  |   | x | 5 | 5  | 5 |
| Is holding area designed to facilitate recovery of dripping solution?  | Yes slopes back to railtrack and sump for collection                     |  |   | x | 5 | 5  | 5 |
| <b>Overground pipelines and transfer lines</b>   |  |  |   |   |   |    |   |
| Are inspection records available ie PPMS Report?   | last visit 8th May 06, next visit due June 09                            |  |   | x | 4 | 5  | 4 |
| Are there any obvious leaks present that require attention?  | No major leaks observed, door sealed on pressure                         |  |   | x | 4 | 5  | 4 |
| <b>Bunding of all stored materials with separate bunding for incompatibles</b>                                     |  |  |   |   |   |    |   |
| Are concentrate ibcs stored within banded area in safe manner?   | 1 ibc on top of mix tank, 2 in drip dry area                             |  |   | x | 3 | 5  | 3 |
| Is banded area suitable for materials stored?  | Stored within bund   |  |   | x | 5 | 5  | 5 |
| <b>Site organisation to ensure segregation of potentially contaminated surface waters from uncontaminated area</b> |  |  |   |   |   |    |   |
| Is treatment plant area potentially exposed to excess rainfall?  | Yes  |  |   | x | 3 | 5  | 3 |
| Is there a potential risk of surface waters entering bund under normal conditions?                                 | No, kerbed area and good drainage system                                 |  |   | x | 5 | 5  | 5 |
| Are surface water drains suitably designed/situated to prevent contamination?                                      | Surface drains not at risk based on observation                          |  |   | x | 4 | 5  | 4 |
| <b>Chemical off-loading to be carried out so as to avoid spillage</b>  |  |  |   |   |   |    |   |
| Are bulk storage tanks suitably banded?  | Use of ibcs  |  |   | x | 4 | 5  | 4 |
| Is product delivery via lockable fixed coupling within bund?   | Filled by tanker within bund, gravily feed                               |  |   | x | 2 | 5  | 2 |
| Is tanker connection point within banded area?   | Yes  |  |   | x | 3 | 5  | 3 |
| Is there an overflow alarm/device present to prevent/indicate overflow?  | No overflow device, just visual and supervision                          |  |   | x | 3 | 5  | 3 |
| Is system for dispensing preservative into operational tanks fail safe?  | Delivery into steel bulk tank recommended                                |  |   | x | 3 | 5  | 3 |
| <b>Technology for recovery and recycle</b>   |  |  |   |   |   |    |   |
| Is treatment site organised to recover preservative from dripping packs?   | Supershore site is banded  |  |   | x | 4 | 5  | 4 |
| Is there pooling of preservative in drip dry area  | No   |  |   | x | 4 | 5  | 4 |
| Is a rainwater harvesting system operated?   | Not at present, could use well water to flush out aquifer                |  |   | x | 2 | 5  | 2 |
| Estimate of water usage per day in litres  | 3000 litres per day  |  |   | x |   |    |   |
| <b>Waste Handling and Minimisation</b>   |  |  |   |   |   |    |   |
| Is banded area and storage tank free of debris?  | Banding around Tanagard ibc needs removing                               |  |   | x | 4 | 5  | 4 |
| Are measures taken to prevent build up of sawdust in plant area?   | Yes stakes given a good shake  |  |   | x | 4 | 5  | 4 |
| Is plastic removed from packs before treatment? If present quantify  | No plastic present   |  |   | x | 5 | 5  | 5 |
| Is there a dedicated forklift for the plant area or measures to prevent drag in?                                   | No dedicated forklift, potential for drag out                            |  |   | x |   |    |   |
| <b>Training and Emergency Procedures</b>   |  |  |   |   |   |    |   |
| Are plant operators trained and competent?   | Noel McHale and Sean McHale, present operator need training              |  |   | x | 2 | 5  | 2 |
| Is Plant Operation Manual/working instructions available on-site?  | No, 06 Manual needs updating and re-issue                                |  |   | x | 4 | 5  | 4 |
| Is there evidence of an Emergency Procedure plan in event of spillage?   | Plan in office, emergency poster at plant                                |  |   | x | 4 | 5  | 4 |
| <b>General site details</b>  |  |  |   |   |   |    |   |
| <b>Soil conditions</b>   |  |  |   |   |   |    |   |
| Is soil classified as free draining with reference to soil associations?   | Tills from namurain sandstones and shales, free draining                 |  |   | x |   |    |   |
| Does treatment plant pre-date containment facilities?  | Yes, historical issues with CCA  |  |   | x | 1 | 5  | 1 |
| Is there evidence of historical pollution on-site?   | Yes, arsenic detected in groundwater 0.4mg/l 08, drinking limit 0.01mg/l |  |   | x | 1 | 10 | 1 |
| <b>Aquifer status</b>  |  |  |   |   |   |    |   |
| Is aquifer status known?   | Regionally important R1c Extremely vulnerable                            |  |   | x |   |    |   |
| Is groundwater used for local abstraction for drinking water?  | No wells within 1 km   |  |   | x |   |    |   |
| Has a formal groundwater survey been carried out?  | Yes, O Callaghan, Moran and Associates Oct 07                            |  |   | x |   |    |   |
| <b>Activities on and off site</b>  |  |  |   |   |   |    |   |
| Are there any other activities on-site that might impact on groundwater/surface water                              | No other activities on-site using actives detected                       |  |   | x |   |    |   |

|  |   |  |  |  |  |  |  |  |  |  |  |  |         |
|--|---|--|--|--|--|--|--|--|--|--|--|--|---------|
| Are there any other activities off-site that might impact on groundwater/surface water | Mainly grassland on boundaries                                  |  |  |  |  |  |  |  |  |  |  |  |         |
| <b>Surface waters</b>  |   |  |  |  |  |  |  |  |  |  |  |  |         |
| Do surface water drains discharge directly to a water course?                          | Not directly  |  |  |  |  |  |  |  |  |  |  |  | 5 3     |
| Is water course used for local abstraction for drinking water?                         | Lough Gill used for water abstraction                           |  |  |  |  |  |  |  |  |  |  |  | 5 1     |
| <b>Surface water monitoring</b>  |   |  |  |  |  |  |  |  |  |  |  |  |         |
| Has independent downstream copper mg/l analysis in 2008 exceeded 0.03mg/l              | Yes 0.192mg/l in 03/07/08 was at 0.027 in 07.26/1/09 0.0186mg/l |  |  |  |  |  |  |  |  |  |  |  | 10 2    |
| Has independent upstream copper mg/l analysis in 2008 exceeded 0.03mg/l                | 26/1/09 0.094mg/l   |  |  |  |  |  |  |  |  |  |  |  | 10 3    |
| Has independent downstream tebuconazole µg/l analysis in 2008 exceeded 0.1µg/l         | No samples, <0.1 in 07  |  |  |  |  |  |  |  |  |  |  |  | 10 3    |
| Has independent upstream tebuconazole µg/l analysis in 2008 exceeded 0.1µg/l           | No samples, <0.1 in 07  |  |  |  |  |  |  |  |  |  |  |  | 10 3    |
| Has independent downstream propiconazole µg/l analysis in 2008 exceeded 0.1µg/l        | No samples, <0.1 in 07  |  |  |  |  |  |  |  |  |  |  |  | 10 10   |
| <b>Ground water monitoring</b>   |   |  |  |  |  |  |  |  |  |  |  |  |         |
| Has independent downstream copper mg/l analysis in 2008 exceeded 2mg/l                 | No 0.005mg/l in 08,   |  |  |  |  |  |  |  |  |  |  |  | 10 2    |
| Has independent upstream copper mg/l analysis in 2008 exceeded 2mg/l                   | No samples in 08, 0.27ug/l in 07                                |  |  |  |  |  |  |  |  |  |  |  | 10 1    |
| Has independent downstream tebuconazole µg/l analysis in 2008 exceeded 0.1µg/l         | No samples in 08, 0.63ug/l in 07                                |  |  |  |  |  |  |  |  |  |  |  | 260 163 |
| Has independent upstream tebuconazole µg/l analysis in 2008 exceeded 0.1µg/l           | No samples in 08, 0.63ug/l in 07                                |  |  |  |  |  |  |  |  |  |  |  | 191     |
| Has independent downstream propiconazole µg/l analysis in 2008 exceeded 0.1µg/l        |   |  |  |  |  |  |  |  |  |  |  |  |         |

63%

|  |   |
|--|---|
| <b>Summary of inspection results total</b> | <b>Summary of inspection results without sampling</b> |
| ● 2, 3%                                    | ● 1, 2%   |
| ● 12, 19%                                  | ● 10, 17%   |
| ● 49, 78%                                  | ● 49, 81%   |

### 9.3 Appendix 3

Source: Minerex (2004)

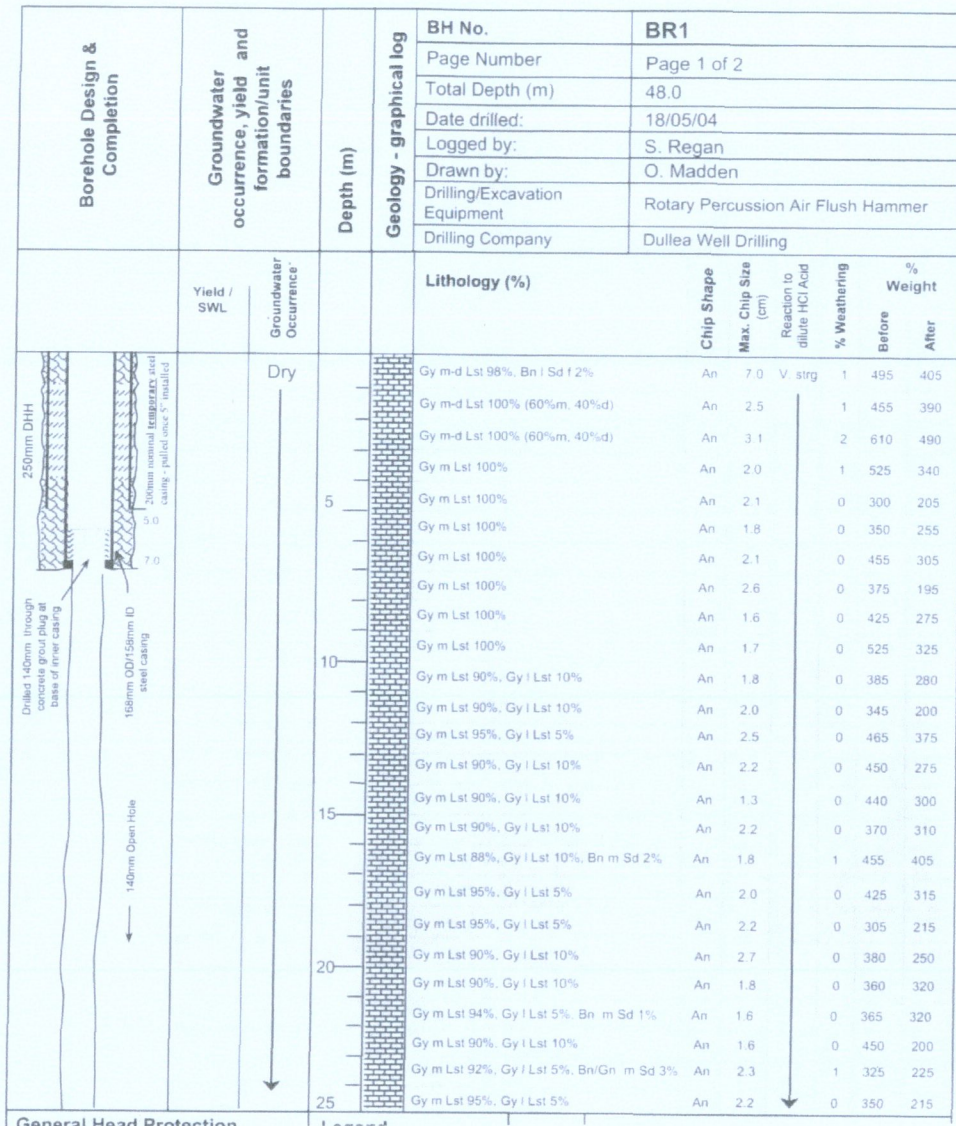


PLATE 7: WELL PROFILE OF BR1