Former Fruitgrowers Chemical
Company Site, Mapua: Assessment
of the Possible Releases to Air
During Soil Processing

Report to the Parliamentary Commissioner
for the Environment

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Executive Summary

This report provides an assessment of the contaminants that may have been released to air from the soil processing activities during the clean-up of the former Fruitgrowers Chemical Company pesticide manufacturing plant at Mapua, Nelson. An extensive air monitoring programme was undertaken during the site clean-up, but was directed at the following narrow range of contaminants:

> Aldrin, chlordane, dieldrin, DDT/DDE, Lindane (HCH), hexachlorobenzene, heptachlor
>
> Chromium, manganese, nickel
>
> Dioxins and furans (limited stack testing only)

This assessment considers other contaminants that may also have been released from the site.

A site assessment report produced in 1992 listed about 85 different pesticides and other agrichemicals that were believed to have been used on the Mapua site. At least nine other pesticides have been shown to be present through various site investigations undertaken since that time. Information on all of these pesticides is given in Appendix 1 of this report, including the properties relevant to the potential for persistence on the site, and information on the possible by-products of decomposition.

On the basis of their relative persistence and potential toxicities, the following pesticides were assessed as being of greatest concern and should have been included in the site monitoring and risk assessment programme:

endosulfan	pentachlorophenol	amitrole
atrazine	coumatetralyl	fenvalerate
PCBs	arsenic and organo-arsenicals	mercury compounds

It would have been prudent to test for a range of organophosphates as well, especially azinphosmethyl, chlorpyrifos, diazinon, fenitrothion, disulfoton, coumaphos, fenthion, iodophenfos and parathion.

The following breakdown products may also have been present on the site, and should have been included in the monitoring programme:

> Chlorinated aromatics, phenolics, aniline and other aromatic amines, nitroaromatics, chlorinated aromatic amines, and ethylene thiourea

The processing of contaminated soil through the dryer introduced the potential for additional risks due to pesticide volatilisation, the release of pesticide decomposition products, and substances formed as products of incomplete combustion. The pesticides of most concern for releases by volatilisation include chlorpyrifos, diazinon, disulfoton, fenitrothion, and malathion. The potential decomposition products of most concern would include chlorinated aromatic hydrocarbons, phenolics, aromatic amines and nitro-compounds, and nitrogen heterocyclics. While the most relevant products of incomplete combustion are the dioxins and furans, PAHs and nitro-PAHs.

We can not say with any certainty whether any of the above substances were discharged from the site and, if so, in what quantities. However, it is this lack of knowledge that raises the greatest concerns. The health risk assessments done for the site clean-up were based on the assumption that all chemical risks had been identified and assessed. The work presented here shows that this may not have been the case.

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List of Abbreviations

DDE	Dichlorodiphenyldichloroethylene (a breakdown product of DDT)
DDT	Dichlorodiphenyltrichloroethane
DDX	This term is used to represent the four isomers of DDT: p,p'-DDE, p,p'-TDE, o,p'-DDT and p,p'-DDT.
Dioxins	The term used in this report to refer to the mixture of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans; these highly toxic chemicals are formed at very low levels in most combustion processes, but especially from the burning of chlorinated organic compounds
FCC	Fruitgrowers Chemical Company
HCB	Hexachlorobenzene, which was used in the past as a pesticide but is more commonly found as a contaminant in other organochlorine pesticides
HCH	Hexachlorocyclohexanes, in this case the mixture of three isomers analysed in the air samples (alpha, beta and gamma-HCH)
IARC	International Agency for Research on Cancer
LD_{50}	Dose shown to be lethal to 50% of a test population
MCD	Mechanico-Chemical Destruction
MfE	Ministry for the Environment
PAHs	Polycyclic aromatic hydrocarbons, formed at trace levels during combustion
PCBs	Polychlorinated biphenyls
TDE	Tetrachlorodiphenylethylene (a breakdown product of DDT, also known as DDD)
TDI	Tolerable Daily Intake
THI	Total Hazard Index
VOCs	Volatile organic compounds

Former Fruitgrowers Chemical Company Site, Mapua: Assessment of the Possible Releases to Air During Soil Processing

1.   Introduction

1.1   Background

The Fruitgrowers Chemical Company operated a pesticide manufacturing plant at Mapua, Nelson from the 1930s to 1988. These activities caused extensive contamination at the site, which has now been cleaned up in an exercise funded by the Ministry for the Environment and the Tasman District Council. The clean-up operation started with the Proof of Performance trials in early 2004, and was completed in mid-2007.

The Parliamentary Commissioner for the Environment received a significant number of complaints from the public about the management of the site clean-up operation. It was therefore decided to undertake an investigation under section 16 of the Environment Act 1986. The objective of this investigation was as follows:

> To determine whether the clean-up of the Mapua contaminated site has been managed in accordance with the Resource Management Act 1991, and to ascertain whether there may be adverse effects on the environment as a result of the clean-up operations.

The current report forms part of the overall investigation, and is intended to provide an assessment of contaminants that may have been released to air from the soil processing activities. An extensive air monitoring programme was undertaken during the site clean-up, but was directed at a relatively narrow range of contaminants. This assessment considers other contaminants that may have also been released.

1.2   Methodology

The work was done in accordance with the following steps:

1. Collection and tabulation of relevant information on the pesticides known to have been used on the site, including their relative volatilities, thermal and chemical stabilities, and expected behaviour, including key decomposition products, at temperatures of 100 °C, 200-400 °C, and when directly exposed to flame conditions (>800 °C).

2. Discussion and analysis of the above information on the basis of other relevant factors, including the relative amounts of each material used on the site, the expected persistence, relative toxicities and other possible mitigating factors, such as the likelihood of removal by the scrubbing system used on the plant.

3. Development of an overall analysis as to the emissions of pesticides and/or other breakdown products of greatest potential concern.

4. Preparation of a written report on all of the above.

1.3   Report Content and Layout

Section 2 of the report provides a brief description of the processes used for the site remediation work. Information on the pesticides and other contaminants known to be present on the site is given in Section 3, while Section 4 provides the assessment of the potential for releases to air. An overall summary and discussion is given in Section 5.

Tables of pesticide properties relevant to the assessment are given in Appendix 1.

2 Discharges to Air from the Mapua Site

This section gives a brief outline of the clean-up operations used at the Mapua site. A more detailed description was given in a previous report prepared by the author[1], and in two earlier documents[2,3].

2.1 Process Description/Overview

The clean-up programme at Mapua involves excavation of contaminated soil and other materials, which are crushed and screened, and then processed through a treatment plant. There are two main components to the treatment plant; initial conditioning of the contaminated soil in a rotary drier; followed by treatment in a ball-mill reactor. The rotary drier is the primary source of discharges to air, which are controlled through the use of a gas clean-up system. Other potential discharges to air are fugitive emissions from the treatment plant, dust emissions from the site activities generally, and wind-blown dust.

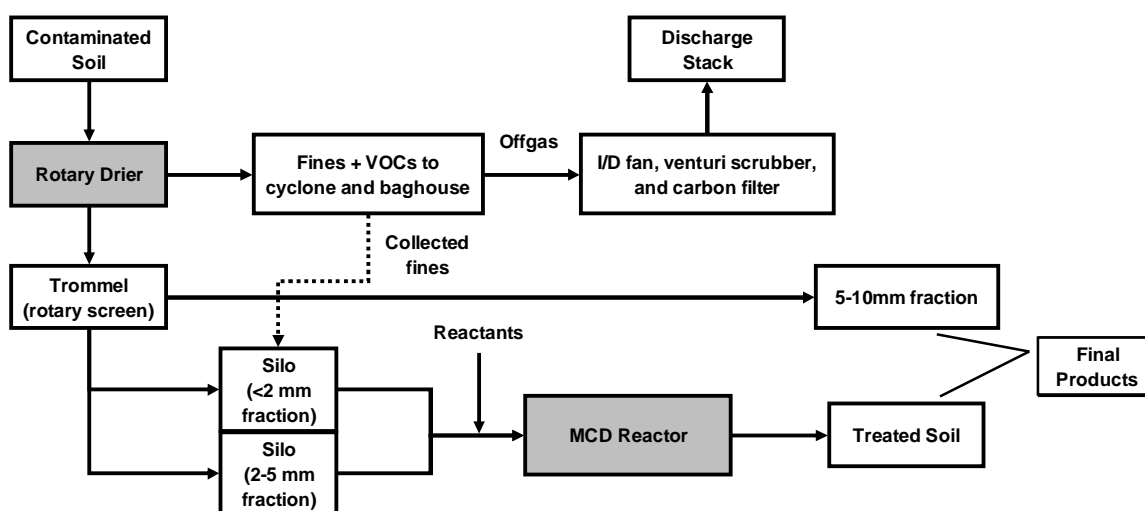The treatment processes at Mapua are summarised in the flow chart shown in Figure 2.1 below.

Figure 2.1: MCD Process Flow Diagram

The rotary drier is a direct-fired unit operated with diesel fuel. The term direct-firing indicates that the burner flame is directed into the centre of a horizontal rotating cylinder, while the soil is fed in at one end and discharged from the other. The temperature of the gases discharging from the burner is monitored to ensure a degree of control over the drying temperatures (120°C), although the temperatures within the drier will be higher than the exhaust. In addition, there is significant potential for any off-gases from the soil to interact directly with the hot flame.

The ball-mill reactor is referred to as a Mechanico-Chemical Destruction (MCD) process. The reactor is operated at a temperature of 70°C, which will tend to promote the release of volatile organics from the contaminated soil. However, there is also likely to be highly localised heating at the points of contact between the balls, and as a result of the exothermic nature of the chemical reactions. It is not clear whether the MCD reactor is fitted with any sort of vapour venting system. Even so, there will inevitably be vapour releases at any points of entry to, or exit from, the reactor, and around any equipment seals. It is not possible to say whether or not these releases were of any significance, because it appears they were never monitored.

2.2 Potential Emissions to Air

The soil at Mapua is contaminated with a range of organochlorine pesticides, including chlordane, DDT, dieldrin, and HCH. There are also measurable amounts of toxic metals, other types of pesticides, and a range of other organic contaminants. There is the potential for any and all of

these substances to be carried off-site as contaminants in the dust emissions. The organochlorine pesticides and other organic contaminants may also be released in the vapour phase, as part of the emissions from the treatment plant, or by volatilisation from the contaminated soil.

The assessment of these potential emissions to air is the main focus of this report, and is covered in detail in sections 3 and 4.

2.3   Air Monitoring Programme and Health Risk Assessment

The Air Discharge Consent for the Mapua site[4] included the following requirements for the monitoring of emissions to air and ambient air impacts:

- Emission testing at 3-monthly intervals from the discharge stack
- Daily monitoring for total suspended particulate and monthly monitoring for dust deposition at three sites in the vicinity, including one site which was to serve as an indicator of 'background' conditions

All of the stack emission and ambient samples collected in the above programme were analysed for the following contaminants:

- Chromium, manganese, nickel
- Aldrin, chlordane (2 isomers), dieldrin, DDX (4 isomers), hexachlorocyclohexanes (3 isomers), hexachlorobenzene, heptachlor (+ epoxide)
- Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (on only a limited number of samples)

Emissions of polychlorinated biphenyls were also tested during the Proof of Performance trials.

The monitoring results for the organochlorine pesticides and metals were assessed using a Total Hazard Index (THI). This index was calculated for each contaminant by dividing the estimated daily intake — based on the potential exposures to air and dust — by the tolerable daily intake (TDI). The THI was then calculated from the sum of the individual hazard index results for each substance.

The key advantage of the THI approach is that it allows the risks from multiple substances and multiple exposure routes to be summed up in a single, easily understood, number. However, such convenience must be exercised with caution. In particular, it is important that all of the possible exposures from all of the possible contaminants be properly assessed.

3.   Pesticides Used on the Site

3.1   Information on Pesticide Use

The FCC activities on the Mapua site ran from the 1930s through to 1988, and involved the processing, packaging and storage of a wide range of pesticides and other agrichemicals. A list of the pesticides believed to have been used on the site is given in Table 1 of a 1992 report by Woodward Clyde[5]. This table was developed on the basis of historical records and discussions with ex-employees. However, when compared against the substances identified in a 2005 report on site investigations[6] the list appears to be incomplete. The following additional substances were noted in the 2005 report:

Mecoprop	Picloram
Endosulphan	Pentachlorophenol
Hexachlorobenzene	Heptachlor
Bromopropylate	Bromacil
Metolachlor	

The 1992 list and the additional substances identified in the 2005 report have been used in developing the tables of pesticides and pesticide properties, which is given in Appendix 1. To assist in the subsequent analysis, the pesticides have been arranged in the following very broad groupings: organochlorines, organophosporous compounds, triazines and related substances, other nitrogen-containing pesticides, phenoxy herbicides, and other. In addition, the listings within each table have been ordered alphabetically, and also according to the estimated site usage.

3.2   Listing of Pesticide Properties

The tables in Appendix 1 include the following properties for each pesticide (where available):

Melting point, boiling point and vapour pressure

Octanol-water coefficient (Log P) and water solubility

Stability to heat, water (hydrolysis) and other factors such as air and light

Acute oral LD_{50} (rat) and Allowable Daily Intake (ADI), as indicators of toxicity

Soil half life, soil mobility, and half life under anaerobic conditions

Known or expected breakdown products from thermal decomposition and hydrolysis

Most of this information has been taken from The Pesticide Handbook[7], which is an internationally recognised reference in this field. Additional information on breakdown products was taken from a review by Lawless et al[8].

Some of the above properties (eg. melting and boiling point) are simply provided as basic indicators of the physical nature of each of the pesticides. The significance of others (eg. solubility and soil mobility) will be explained in the relevant parts of section 4. Additional comment is required here for the following properties:

The values for octanol-water coefficient give a measure of the tendency for substances to distribute between aqueous and organic phases. As such they indicate the potential for bioaccumulation through dissolution in fat. Highly non-polar substances, such as DDT, have a high coefficient (ca > 4) whereas highly polar substances have values less than 1 (eg. amitrole). The latter values are also reflected in high values for water solubilities (ca. >1000 mg/L).

The values for LD_{50} and ADI have been included as very rough indicators of relative toxicity. However, caution is required in their use. For example, the LD_{50} measurements based on rats may not be relevant to the effects on humans. Also, they do not allow for effects by other exposure routes (inhalation, skin contact and absorption), or for chronic effects such as cancer. Where relevant, the IARC cancer classifications have been noted in the tables.

3.3   Pesticide Persistence

An analysis of pesticide persistence was given in the 1992 Woodward Clyde report. However, this was simply based on published persistence data and is potentially misleading.   Most of the published data is taken from studies of decomposition in the field or under controlled laboratory conditions, at the expected field application rates. These rates are typically of the order of 0.5 to 5 kg/ha, whereas site spillages or disposal by dumping or burial would be equivalent to application rates several orders of magnitude higher than this. Under such conditions, the normal microbiological breakdown processes are rendered ineffective.   In addition, material buried under ground is not exposed to the effects of sunlight or oxygen.

The two most relevant properties for persistence in spillage or burial situations are water solubility and hydrolysis rates. Pesticides with moderate to high solubility (ca. >30 mg/L) will be leached into groundwater and gradually lost from the site by water movement and dispersion. And those that react readily with water, especially under neutral or mildly acidic conditions, will be converted into other substances. Even then, caution is required because some of these breakdown products can be more toxic than the parent compounds. Soil mobility also needs to be considered because some pesticides can be rendered non-leachable by adsorption to the soil. The published rates of breakdown in soil, field degradation, and reactivity towards sunlight are only relevant in relation to possible surface spillages.

The limitations of the Woodward Clyde analysis are demonstrated by the fact that some of the substances listed as being non-persistent (eg. carbaryl, chlorpyrifos, and hexazinone) were found in surface soil or groundwater samples collected from the site in 2004 (Tonkin and Taylor, 2005). These soil samples were all taken from the top 10cm of soil.   However, it appears that more extensive sub-surface testing was carried out in 1996 (report not sighted, but quoted in the Tonkin and Taylor report) and this showed elevated levels of mercury, sulphur, organophosphorous pesticides and phenoxy acid herbicides at several locations.

Another shortcoming with all of the site investigations is the spatial limitations of the sampling. Inevitably, the number of locations sampled and the number of samples collected is limited by the available funds. The sampling strategies adopted in the site investigations are quite consistent with common practice. However, the chances are high that significant areas of contamination were missed, especially with the sub-surface testing.

3.4   Breakdown Products

Pesticide decomposition in the field generally proceeds through a series of partial breakdown products, before being totally 'mineralised' by conversion to simple salts, and gases such as carbon dioxide.   In some cases the intermediate breakdown products can be more toxic and/or more persistent than the original pesticides. It is therefore important that these substances be included in any assessment of the potential risks from the site.

The intermediate products formed by hydrolysis have been noted in the tables because these are especially relevant to sites contaminated by spillages and dumping. The intermediate products formed as a result of microbial action are often quite similar to those due to hydrolysis, but of less relevance here (for the reasons noted above).

The potential products formed by thermal decomposition have also been noted, although the information available on this aspect is very limited. Many of the entries are simply based on a general understanding of thermal decomposition processes.

4.   Assessment of Possible Releases to Air

The starting point for this section is an assessment of which pesticides were most likely to be present on the Mapua site, and which of these are the most concern. The potential for releases to air as a result of the site activities will then be assessed, including the presence of contaminants in wind-blown dust, and possible emissions from the soil processing plant.

4.1   Which Pesticides Were Likely to be Present in the Site Soil?

The pesticides most likely to have been present on the site, at the time of remediation, are those with low water solubilities (<30mg/L), slow hydrolysis rates (DT50>~90d), and low soil mobility. Stability towards air and sunlight are also relevant. On this basis, there is a strong probability that the following substances would have still been present:

>   All of the organochlorines, including hexachlorobenzene, pentachlorophenol and endosulfan

>   Organophosphorous compounds: azinphosmethyl, chlorpyrifos, diazinon, fenitrothion, disulfoton, coumaphos, fenthion, iodophenfos and parathion.

>   Limited amounts of some of the triazines and related compounds, although these are mainly an issue for their potential for leaching into groundwater, and persistence therein.

>   Other nitrogen compounds: carboxin, diuron, linuron, chlorfensulphide, phenothiazine and picloram.   The rest should be expected to either break down (hydrolyse) and/or leach away.

>   Phenoxy herbicides: these are most likely to be present only in limited amounts because, while they are all quite stable to hydrolysis, they are also quite leachable. Note though, that some of the ester forms may be less mobile, and hence more persistent.

>   Other pesticides: chlorothalonil, coumatetralyl, fenvalerate and bromopropylate.

Of the above, the following would be of most concern:

>   All of the organochlorines because of their persistence coupled with potential health effects from long-term (chronic) exposures.

>   Amitrole and atrazine are a concern for potential carcinogenicity. Most others have low toxicity

>   Coumatetralyl and (possibly) fenvalerate.

The organophosphorous compounds would be of less concern. These are all acutely toxic but the effects are usually associated with exposures at relatively high concentrations, which are unlikely as a site emission.

There should be no significant concerns in regard to any of the 'other nitrogen' compounds or the phenoxy herbicides listed above, because of their generally low toxicities.

The following pesticide breakdown and/or hydrolysis products would also be of interest because of their significant potential toxicities:

>   Dioxins and furans (present as contaminants in phenoxy herbicides)

>   Chlorinated aromatics (eg. from dichlofenthion, penconazole, linuron and diuron)

>   Aniline and other aromatic amines (eg. from carboxin)

>   Nitro-aromatics (eg. nitrophenols from fenitrothion and dinocap)

>   Chlorinated aromatic amines (eg from diuron)

>   Ethylene thiourea (from dithiocarbamates)

4.2   Potential Fugitive Emissions from the Site

Most of the above could be released from the site as contaminants of wind-blown dust. This is probably the biggest potential source on a mass basis.

The air monitoring programme showed significant concentrations of organochlorine pesticides in airborne particulate matter and dust deposition. It would have been appropriate for these samples to have been analysed for a wider range of pesticides, including those listed in 4.1 above.

4.3   Effect of Heating to 100°C

The following pesticides have significant volatility (vapour pressure > 1mPa @ 20/25°C), although those marked with a star are not expected to be present in significant quantities, either because of low site usage and/or the assessment given above:

Most of the organochlorines, but especially aldrin, heptachlor and lindane

chlorpyrifos	ciodrin*	dialifos*
diazinon	dichlofenthion*	dichlorvos*
disulfoton	ethopropohos*	fenchlorvos*
fenitrothion	isazofos*	malathion
phorate*	terbufos*	

This volatility would be beneficial in terms of speeding up losses from the site soon after any spillages or dumping took place. However, it would also lead to increased vapour emissions during the soil drying process, if any of the pesticides were still present in significant amounts. The potential for releases of the organochlorine pesticides by this route was clearly demonstrated by the ambient air monitoring results (although the vapour/particulate distribution may also have been due to a post sampling effect).

4.4   Effect of Heating to 200 to 400°C

There is the potential for heating at temperatures significantly above 100°C during soil processing in the dryer, either as a result of poor temperature control, the development of localised hot-spots, or the movement of particles and gases into the vicinity of the burner flame. As shown in the appendix, many pesticides are thermally unstable and will begin to break down at these temperatures. Some may also start to burn.

Information on the specific chemicals likely to be formed under these conditions is very limited. However, if we adopt a fairly generalised approach, it would be reasonable to expect them to consist of the chemicals caused by simple fragmentation of the pesticide molecules. The number of different chemicals that could possibly be formed in this way is enormous. However, those of most interest or concern would include the chlorinated aromatic hydrocarbons, phenolics, aromatic amines and nitro-compounds, and nitrogen heterocyclics (ie a mixture similar to the breakdown products listed in 4.1 above).

It is not really possible to be more specific than this, given the paucity of detailed information. It should also be noted that the actual quantities of these chemicals produced at any instant would be relatively limited, except when batches of highly contaminated soil were being processed.

4.5   Effect of Direct Exposure to Flame Conditions

If any of the contaminated soil particles or pesticide vapours came into direct contact with the flame zone of the dryer, they would be exposed to temperatures of about 800°C or higher, coupled with a strongly oxidising environment. Under these conditions the pesticides would start to burn, or combust. If this process was allowed to go to completion, it would reduce the pesticides to very

simple combustion by-products, such as carbon dioxide, and water. There would also be a variety of acidic gases formed, such as sulphur dioxide, hydrogen chloride, hydrogen cyanide and the oxides of nitrogen, and possibly arsenic oxide (see section 4.7 below), depending on the elements present in the individual pesticides.

However, incomplete combustion is of more concern, and more likely, in this situation because dryers are usually not designed to ensure complete combustion of any substances passing through the flame zone. The by-products formed will consist of similar decomposition products to those noted in section 4.4 above, along with substances formed by partial oxidation of the pesticides or their breakdown products. There is also the potential for new chemicals to be formed by recombination of the various molecular fragments. This latter group includes the polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (dioxins and furans for short), along with polycyclic aromatic hydrocarbons (PAHs). Some pesticides also provide the potential for nitro-PAHs and nitrogen heterocyclics to be formed, from the nitrogen/aromatic precursors.

There is a significant potential for dioxins and furans to be formed from the mixture of pesticides present at Mapua, because many of the substances include chlorinated and/or aromatic components. These chemicals are a particular concern because of their very high toxicities, environmental persistence and potential for bioaccumulation. The PAHs and nitro-PAHs are of similar concern because some have been shown to cause cancer in humans.

Dioxins and furans were shown to be present in the emissions from the soil treatment plant on several occasions – albeit at moderately low levels - and they were also found in the activated carbon filters used for gas clean-up. No tests were carried out for PAHs or nitro-PAHs, although the PAHs were found in some soil samples during the early site investigations.

4.6   Polychlorinated Biphenyls (PCBs)

It is surprising that no routine monitoring was done for PCB emissions, because these were found in a significant number of the soil samples collected from the site (eg. just over 50% of the samples reported in Tonkin and Taylor, 2005). PCBs are classified as semi-volatile organics and can be expected to behave in a similar way to the organochlorine pesticides. They can also be a significant cause of dioxin emissions when burned.

PCBs are persistent in the environment, bioaccumulative and toxic. Some have been classified as human carcinogens.

4.7   Metallo-Organic Pesticides and Sulphur

The Woodward Clyde report (1992) indicated that a range of metallo-organic pesticides had been used on the site, including those based on arsenic, mercury, tin and lead. The potential environmental and health hazards of these metals are well known, and they should have all been included in the monitoring programme. In addition, the following specific risks should have also been assessed:

> Arsenic trioxide and some of the organo-arsenicals (eg. Cacodylic acid) have significant volatility and can therefore present a vapour hazard, especially when heated.

> Mercuric chloride and some of the organo-mercury compounds (eg. ethylmercury chloride and phenylmercuric acetate) also have significant volatility and can present a vapour hazard, especially when heated.

Elemental sulphur was also used on the site, apparently in large quantities. The main hazard associated with this substance would be the formation of sulphur dioxide if burned.

4.8   Effectiveness of the Emission Control Equipment

The soil dryer was fitted with an emission control system that was intended to remove most of the particulate emissions, and also volatile organics. However, the overall effectiveness of this system has been questioned because there is clear evidence that it may have sometimes been overloaded (especially the carbon filter).

Regardless of the above, it would be reasonable to expect that most of the acid gases noted in 4.5 above would have been effectively removed by the water scrubber. However, the same can not be said for most of the potential organic emissions discussed in sections 4.3 to 4.6, and in very broad terms, it can be expected that the releases of most of these would parallel what was found with the organochlorine pesticides.

5.   Summary and Discussion

The emission testing, ambient air monitoring and health risk assessment for the Mapua site clean-up was directed at the following relatively narrow range of potential contaminants:

Aldrin, chlordane, dieldrin, DDT/DDE, Lindane (HCH), hexachlorobenzene, heptachlor

Chromium, manganese, nickel

Dioxins and furans (limited stack testing only)

Previous testing of soil and groundwater showed that a variety of other pesticides and other contaminants were also present on the site. This is consistent with the analysis presented in section 4.1 which indicates that a much wider range of pesticides could also be present. The following were assessed as being of greatest potential concern and should have been included in the site monitoring and risk assessment programme:

endosulfan	pentachlorophenol	amitrole
atrazine	coumatetralyl	fenvalerate
PCBs	arsenic and organo-arsenicals	mercury compounds

It would have been prudent to test for a range of organophosphates as well, especially azinphosmethyl, chlorpyrifos, diazinon, fenitrothion, disulfoton, coumaphos, fenthion, iodophenfos and parathion.

The following breakdown products may have also been present on the site, and should have been included in the monitoring programme:

Chlorinated aromatics, phenolics, aniline and other aromatic amines, nitroaromatics, chlorinated aromatic amines, and ethylene thiourea.

The processing of contaminated soil through the dryer introduced the potential for additional risks due to pesticide volatilisation, the release of pesticide decomposition products, and substances formed as products of incomplete combustion. The pesticides of most concern for releases by volatilisation include chlorpyrifos, diazinon, disulfoton, fenitrothion, and malathion. The potential decomposition products of most concern would include chlorinated aromatic hydrocarbons, phenolics, aromatic amines and nitro-compounds, and nitrogen heterocyclics. While the most relevant products of incomplete combustion are the dioxins and furans, PAHs and nitro-PAHs.

We can not say with any certainty whether any of the above substances were discharged from the site and, if so, in what quantities. However, it is this lack of knowledge that raises the greatest concerns. The health risk assessments done for the site clean-up were based on the assumption that all chemical risks had been identified and assessed. The work presented here shows that this may not have been the case.

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Appendix 1: Tables of Pesticide Properties

The tables given on the following pages provide lists of properties for all of the pesticides believed to have been used on the Mapua site. The pesticides have been arranged in the following very broad groupings: organochlorines, organophosporous compounds, triazines and related substances, other nitrogen-containing pesticides, phenoxy herbicides, and other. In addition, the listings within each table have been ordered alphabetically, and also according to the estimated site usage.

Guide to Column Headings

Site Usage	(taken from the Woodward Clyde 1992 report)	
	I = < 100 kg or 100 litres/yr	
	II = < 1 tonne or 1000 litres/yr	
	III = 1-10 tonnes or 1000-10,000 litres/yr	
	IV = 10-50 tonnes or 10,000-50,00 litres/yr	
	V = 50 tonnes or 50,000 litres/yr,	
	U = unknown usage but present in site soil or groundwater	
M Pt	melting point	
B Pt	boiling point	
VP	vapour pressure	
K_{ow}	octanol-water coefficient (values shown are the log of the coefficient)	
Water sol	water solubility, in mg/litre	
Heat stability	stability of the pesticide at elevated temperatures	
Hydrolysis	rate of hydrolysis (values quoted are the times for 50% decomposition – DT50)	
Other Stability	other relevant stability information, where available	
Acute Oral LD50	an indicator of toxicity, based on the 50% lethal dose (LD_{50}) for oral exposure in male rats, in mg/kg of body weight	
ADI	allowable daily intake (for human exposure, in mg/kg per day)	
Soil half life	time, in days, for 50% loss in soil	
Soil mobility	the ease with which the substance is leached from soil	
Anaerobic half life	time for 50% loss in soil under oxygen-free conditions	
Thermal products	expected products from thermal decomposition	
Hydrolysis products	expected products from hydrolysis	
Other comments	other relevant information, including the cancer classification by the International Agency for Research on Cancer (IARC)	

Codes Used in the Tables

3d (or similar)	3 days		hyd	hydrolysed
alk	alkali		insol	insoluble
d	decomposes		mod	moderate(ly)
dec or decomp	decomposed		neg	negligible solubility
de-HCL	dehydrochlorinated		oxidn	oxidation
dil	dilute		photol	photolysis
DT50	time for 50% decomposition		prod	products

Table A1: Organochlorine Pesticides
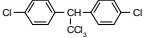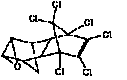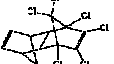
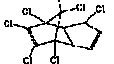| Name	Formula/Structure	Site Usage	M Pt, C	B Pt, C	VP, mPa (@20/25C)	Kow (logP)	Water sol (mg/L)	heat stability	Hydrolysis (DT50)	Other stability	Acute Oral, rat LD50 (mg/kg)	ADI (mg/kg/day)	soil half life (days)	soil mobility	anaerobic half life	thermal products	hydrolysis products	other comments
DDT/DDE		V	109	185-187, 0.05mmHg	0.025	6.1	insol	stable to 300C		persistent	113-118	0.01	4-30yrs (temperate)			dioxins	converted to DDE in soil, etc	IARC Class 2B, bioaccumulative
dieldrin		V	175-176		0.4		0.186	stable to >250C	stable to acid & alkali	persistent	37-87	0.0001	persistent			dioxins		bioaccumulative
lindane (γ-HCH)		V	113		4.4	3.5	8.52	stable to 180C	stable to acid		88-270	0.005	mod persistent			dioxin potential	de-HCL by strong alkali	IARC Class 2B
aldrin		III	104	145, 2mmHg	8.6		0.027	stable to 200C	stable pH 4 to 8	persistent	38-67	0.0001	persistent			dioxins	converted to deildrin in soil	bioaccumulative
endrin		I	d >200		0.00002		neg	d >200		persistent	7.5-17.5	0.0002	persistent			dioxins		bioaccumulative
endosulfan		U	>80		0.83	-4.74	0.32		slowly hyd in dilute acid & alk	stable in sunlight	70-110	0.006	30-70 (but 150-240 for the sulphate)	non-leacher		dioxins	diol + SO2	endosulfan sulphate is the initial decomp product
heptachlor		U	95-96	135-145	53	4.4-5.5	0.056	stable to 160	4.3d, pH5, 4.5d, pH6, 3d, pH8	persistent	147-220	0.0001	9-10 mths			dioxins	epoxides	IARC Class 2B, bioaccumulative
hexachlorobenzene		U	226	323-326	1.45		insol	stable	stable		10,000							IARC Class 2B, bioaccumulative
pentachlorophenol		U	191	d 310	16 @ 100	5.1	80 (but Na salt - 330)	d 310	stable	persistent	210		persistent					IARC Class 2A

Table A2: Phenoxy Herbicides

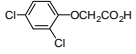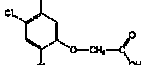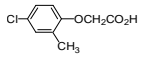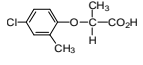| Name	Formula/Structure	Site Usage	M Pt, C	B Pt, C	VP, mPa (@20/25C)	Kow (logP)	Water sol (mg/L)	heat stability	Hydrolysis (DT50)	Other stability	Acute Oral, rat LD50 (mg/kg)	ADI (mg/kg/day)	soil half life (days)	soil mobility	anaerobic half life	thermal products	hydrolysis products	other comments
2,4-D		U	140.5		0.0186	0.04-0.33	23,180		stable	photol DT50 ~5d	639-764	0.01	<7	low-moderate		dioxin potential	2,4-dichlorophenol	IARC Class 2B. Strong acid, forms water-soluble salts. Properties vary depending on salt/ester
2,4,5-T		U	154-155		0.0007	2.0	150		stable		300-1700	0.03	slower than 2,4-D			dioxin potential	2,4,5-trichlorophenol	IARC Class 2B. Strong acid, forms water-soluble salts. Properties vary depending on salt/ester
MCPA		U	119-129	d 290	0.023	-0.7	294	d 290	stable	photol DT50 ~24d	962-1470		7			dioxin potential	4-chloro-2-methylphenol	Strong acid, forms water-soluble salts. Properties vary depending on salt/ester
MCPP (mecoprop)		U	93-95		1.6	0.1	880	stable	stable		930-1166	0.05	7-13			dioxin potential		IARC Class 2B. Strong acid, forms water-soluble salts. Properties vary depending on salt/ester

Table A3: Organophosphates

Name	Formula/Structure	Site Usage	M Pt, C	B Pt, C	VP, mPa (@20/25C)	Kow (logP)	Water sol (mg/L)	heat stability	Hydrolysis (DT50)	Other stability	Acute Oral, rat LD50 (mg/kg)	ADI (mg/kg/day)	soil half life (days)	soil mobility	anaerobic half life	thermal products	hydrolysis products	other comments
azinphosmethyl		V	73		0.001	2.96	28	d 200C	87d,pH4, 4d, pH9	photo, rapid	9	0.005	~21	low	?		anthranilic acid	initial oxdn prods more toxic
chlorpyrifos		V	42-43.5	>400	2.7	4.7	1.4	stable	1.5d, pH 8, 100d, pH7		135-163	0.01	7-15 (sur), 33-56 (sub)	low		dioxin potential	3,5,6-trichloro-pyridin-2-ol	breaks down to O'Cs
diazinon		V		125, 1mmHg	12	3.3	60	d 120C	12h, pH3, 185d, pH7, 6d, pH10	suscept. oxidn >100C	1250	0.002	3-54	low			diazoxon	fairly strongly adsorbed to soil
fenitrothion		V	0.3	140-145, 0.1mmHg	18	3.43	14	d 140-145	109d, pH4, 75d, pH9		1700	0.005	12-28 (surf), 4-20 (sub)				3-methy-4-nitrophenol, CO2	aminofenonitrothion forms in submerged state
fensulfothion		V	<25	138-141, 0.01mmHg	4	2.23	1540		readily in alk	readily oxidised	4.7-10.5	0.0003						readily isomerises to S-ethyl isomer
malathion		V	2.85	156-157, 0.1mmHg	3	2.75	145	reactive	107d, pH5, 6d, Ph7, 0.5d, pH9		1375-5550	0.3	99% degrad in 7d			explosive rearrangement @ 150C	(CH3O)2PS(S)Na or (CH3)2P(S)OH	readily rearranges to POR and P=S groups
phosmet		V	72-73		0.065	2.95	25	rapid decomp >100	13d, pH4.5, <4h, pH8.3	decomp sunlight	113	0.01	rapid breakdown					
disulfoton (thiodementon)		V	<-25	128, 1mmHg	13	3.95	25		133d, pH4, 169d, pH7, 131, pH9	photolysis DT50 1-4d	2-12	0.0003	rapid breakdown	low-moderate				
ethoprophos		IV		86-91, 0.2mmHg	46.5	3.59	700	stable 8hrs @ 150C	stable-acid, rapid hyd-alkali		62	0.0004	14-28d sandy loam					soil breakdown slower for higher organic content
coumaphos		III	95		0.013	4.13	1.5		stable	decomp by strong alkali + heat	41		23.8d on soil surface			dioxin potential		
phorate		III	<-15	118-120 (0.8mmHg)	85	3.92	50		3.2d, pH7, 3.9d, pH9	degraded by light + H20	3.7	0.0007	7-10				sulfoxide & sulfone	sulfone may persist in soil

Table A3: Organophosphates (continued)

Name	Formula/Structure	Site Usage	M Pt, C	B Pt, C	VP, mPa (@20/25C)	Kow (logP)	Water sol (mg/L)	heat stability	Hydrolysis (DT50)	Other stability	Acute Oral, rat LD50 (mg/kg)	ADI (mg/kg/day)	soil half life (days)	soil mobility	anaerobic half life	thermal products	hydrolysis products	other comments
carbophenothion		II		82 (0.01 mmHg)	1.07	4.75	<1	stable up to 80	mod stable, esp in alkaline	rapidly dec by NaOCl	79.4	0.0005	oxidised in soil & on plants				sulfone, sulfoxide, etc	
dichlofenthion		II	liquid		12.7	5.27	0.85				247					dioxin potential		
dichlorvos (DDVP)		II	<-80	(234)	210	1.9	18	d 185-280	32d, pH4, 2.9d, pH7, 2.0d, pH9	rapid dec in air	50	0.004	10h - 1d				dimethyl hydrogen phosphate, dichloroacetaldehyde then H3PO4	IARC Class 2B
fenthion		II	<-80	90 (1 Pa)	0.74	4.84	4.2	stable up to 210	223d, pH4, 200d, pH7, 151d, pH9	stable to light	250	0.007	rapid in aerobic conditions				sulfoxide & sulfone, then to xylenol	1.5d (sediment + water)
iodofenphos		II	76		0.106		<2	stable to 160	stable, except to strong acid & alk		2100					dioxin potential		
isazofos		II		120 (36Pa)	7.45	2.99	168	d >200	85d, pH5, 48d, pH7, 19d, pH9		40-60		10 (lab)					
methidathion		II	39-40		0.25	2.2	200		stable pH5-7, rapid hyd alkali & strong acid		25-54	0.001	3-18	low				
nankor (fenchlorphos)		II	40-42		110		40	stable below 60	stable pH5-7, hyd by dil alkali		1740					dioxin potential		
parathion		II	6.1	150 (80Pa)	0.89	3.83	11	isomerises ~130	272d, pH4, 260d, pH7, 130d, pH9		2	0.004	rapid	low			paraoxon, aminoparathion, 4-nitrophenol	
ciodrin (crotoxyphos)		I	liquid	135, 0.03 mmHg	1.9		1000		87h, pH1, 35h, pH9		52.8							
dialifos		I	67-69		133 @35		<1		2.5h, pH8		43-53							
terbufos		I	-29.2	69, 0.01mmHg	34.6		4.5	d >120	2-3d, pH4-9	stable 2+yrs @ ambient	1.6	0.0006	9-27					

Table A4: Triazines, Triazoles and Related Compounds

Name	Formula/Structure	Site Usage	M Pt, C	B Pt, C	VP, mPa (@20/25C)	Kow (logP)	Water sol (mg/L)	heat stability	Hydrolysis (DT50)	Other stability	Acute Oral, rat LD50 (mg/kg)	ADI (mg/kg/day)	soil half life (days)	soil mobility	anaerobic half life	thermal products	hydrolysis products	other comments
aminotriazole (amitrole)		V	157-159		0.00003	-0.97	264,000		35d	photol DT50 >30d	>10,000	0.002	<5		<56d	burns readily, but forms HCN & NOx		IARC Class 2A, powerful chelating agent
atrazine		V	176	205, 101kPa	0.0385	2.5	33	stable	9.5d, pH1, 86d, pH5, 5d, pH13	hyd strong acid & alk @ 70C	1869-3090	0.005	13-402	low-mod leaching	105->200d groundwater	burns readily but forms HCl, NOx	desethylatrazine, hydroxyatrazine	IARC Class 2A, v weak base, triazine ring is chemically stable
simazine		V	225-227(d)		0.0029	2.1	6.2	decomp @ MPt	8.8d, pH1, 96d, pH5, 3.7d, pH13	90% decmp in 96hr by uv	500-10,000	0.005	26-186	low leaching	persists in groundwater	burns readily but forms HCl, NOx	desethylsimazine, hydroxysimazine	v weak base, triazine ring is chemically stable
cyanazine		IV	167-169		0.0002	2.1	171	stable 1.8% d, 100h,75C	stable pH5 to 9	hyd strong acid & alk	182-334		14	leachable	persists in groundwater	burns readily but forms HCl, NOx		v weak base, triazine ring is chemically stable
aziprotryne		III	95		0.267		55		stable pH5-7, hyd in alkaline		3600-5833			leachable		burns readily but forms HCN, NOx		triazine ring is chemically stable
hexazinone		III	113.5	d	0.03	1.2	29,800	decomp	decomp str acid & alk	stable to light	1100	0.05	30-180	mobile		burns readily but forms HCN, NOx		triazine ring more readily broken in this cpd
prometryn		III	118-120	>300 @ 100kPa	0.165	3.1	33	stable	stable pH 5 -9, hydr by warm acid/alk	decomp by uv	>2000	0.01	14-158	low (absorbs to sediment)		burns readily but forms HCN, NOx		weak base, triazine ring is chemically stable
propazine		III	212-214		0.0039	3.01	5		stable pH 5 -9, hydr by warm acid/alk		>7000		80-100	mobile		burns readily but forms HCl, NOx	hyrdoxypropazine	v weak base, triazine ring is chemically stable
oxadiazon		I	87		0.1	4.91	1		stable acid & neutral, 38d, pH9		>5000		90-180	strongly adsorbed		dioxin potential		
penconazole		I	60-61	>360	0.17	3.72	73	stable to 350	stable (pH1-13)									weak base, traizine ring is chemically stable
terbacil		I	175-177	sublimes	0.06	1.9	710	stable to 175	stable in neutral and alkali	stable to light	934		150-210 (topsoil)			burns readily		breaks down more readily in moist biologically active soil
terbuthylazine		I	177-179		0.15	3.21	8.5		stable except strong acid/alk: 8d, pH1, 12d, pH13	mod stable to light (DT50 >40d)	1590-2000	0.0022	30-60	strongly absorbed, only slightly mobile				
bromacil		U	158-159		0.04	1.88	807	stable to 160	stable except in strong acid		2000	0.13	30-60					weak acid

Table A5: Other Nitrogen-Containing Pesticides

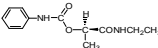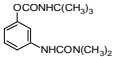| Name	Formula/Structure	Site Usage	M Pt, C	B Pt, C	VP, mPa (@20/25C)	Kow (logP)	Water sol (mg/L)	heat stability	Hydrolysis (DT50)	Other stability	Acute Oral, rat LD50 (mg/kg)	ADI (mg/kg/day)	soil half life (days)	soil mobility	anaerobic half life	thermal products	hydrolysis products	other comments
Amides																		
chlorthiamid		V	151-152		0.13		950	stable to 90C	stable to acid, hyd by alk		757		35 (dry), 14 (wet)			dioxin potential	2,6-dichlorobenzamide and 2,6-dichlorobenzoic acid	initial decomp to dichlobenil
metalxyl		II	63.5-72.3	295.9, 101kPa	0.75	1.75	8400	stable to 300C	>200d, pH1, 115d, pH 9, 12d, pH10	photolytically stable in soil and water	633	0.08	10-40					
Imides																		
captan		V	178		<1.3	2.8	3.3	d @ 180	32.4h, pH5, 8.3h, pH7, <2min, pH10		9000	0.1	~1d					
captafol (difolatan)		IV	160-161		neg	3.9	1.4	d @ 160	rapid in acid or alk		5000-6200							IARC Class 2A
folpet		III	178-179		0.021	3.11	0.8		rapid in conc alkali	slow hyd by moisture at ambient	>9000	0.01	4.3	immobile		burns readily, dioxin potential		DT50 <0.7h in water
iprodione		II	134		0.0005	3.0	13		stable in acid, 1-7d, pH7, <1h, pH9	degraded by uv light in soln	>2000	0.06	20-80 (lab), 919 (field)					
folpet		III	178-179		0.021	3.11	0.8		rapid in conc alkali	slow hyd by moisture at ambient	>9000	0.01	4.3	immobile		burns readily, dioxin potential		DT50 <0.7h in water
Aniline and Urea derivatives																		
carboxin		III	91-92		0.02	2.3	0.147		stable	photol in H2O,DT50 1.54h	2864	0.01	<1d				aniline	decomp prods are more toxic
chloroxuron		III	151-152		0.00024	3.2	3.7		stable at pH1 & 13	decomp by uv	3700		10-100			dioxin potential		decomp to (4-chlorphenoxy)aniline
dichloran (DCNA)		III	195		0.26	2.8	6.3	stable	stable up to 300C in water	uv photol DT50 41h	4040	0.01	39-78 but <3 in sediment			burns readily, dioxin potential		decomp to 4-amino-2,6-dichloroaniline
linuron		III	93-95		0.051	3.0	63.8	stable @ 90C	>1000 (pH5, 7, 9)	hyd in strong acid/alk	1500-5000	0.008	38-67	mobile		burns readily, dioxin potential	demethyl & demethoxyl derivs	derivs more toxic
diuron		I	158-159		0.0011	2.85	37.4	d 180-190	hydrolysed by acid & alkali		>2000	0.002	90-180			burns readily, dioxin potential	dimethylamine, dichloraniline	hydrolysis products more toxic

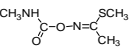## Table A5: Other Nitrogen-Containing Pesticides (continued)
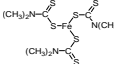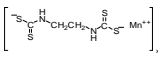
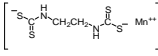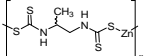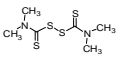| Name	Formula/Structure	Site Usage	M Pt, C	B Pt, C	VP, mPa (@20/25C)	Kow (logP)	Water sol (mg/L)	heat stability	Hydrolysis (DT50)	Other stability	Acute Oral, rat LD50 (mg/kg)	ADI (mg/kg/day)	soil half life (days)	soil mobility	anaerobic half life	thermal products	hydrolysis products	other comments
Carbamates																		
carbaryl (sevin)		IV	142		0.04	1.85	120	stable	12d, pH7, 3.2h, pH9	stable to light	264	0.008	7-14 (sandy) 14-28 (clay)					1-naphthol
carbetamide		III	119		neg	-1.58	3500			stable under normal storage	>2000		~30	mobile				
karbutilate		II	168		<0.026	1.64	94.4			stable in acid, 4.6d, pH8	3000		20-120					the coresponding phenol
methomyl		III	78-79		0.72	0.093	57,900	stable to 140C	30d, pH9, stable pH5,7	stable to sunlight	34	0.02	4-8d	mobile	<0.2d in groundwater	burns readily		
Dithiocarbamates																		
ferbam		III	d >180		neg	-1.6	130	d >180	decomp	decomp in storage	>4000	0.003	4.9					
mancozeb		(Zn),III	d >172		0.013	0.26	6.2	d >172	20h, pH5, 21h, pH7, 27h, pH9	slowly decomp by heat + moisture	>5000	0.03	<1					ethylenethiourea
maneb		III	d ~200		neg		insol	d ~200	<24h, pH 5, 7 & 9	slowly decomp by heat + moisture	>5000	0.03	25					ethylenethiourea
propineb		III	d150		neg	-0.26	10		1d, pH4,7, >2-5d, pH9	stable when dry	>5000	0.007	degrades rapidly	immobile				propylenethiourea
thiram		III	155-156		2.3	1.73	18	slowly degrades	128d, pH4, 18d, pH7, 9h, pH9		2600	0.01	0.5d (sandy soil)					
zineb		III	d 157		<0.01	<1.3	10	d 157		slowly decomp by heat + moisture	>5200	0.03						ethylenethiourea

Table A5: Other Nitrogen-Containing Pesticides (continued)
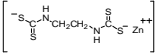
Name	Formula/Structure	Site Usage	M Pt, C	B Pt, C	VP, mPa (@20/25C)	Kow (logP)	Water sol (mg/L)	heat stability	Hydrolysis (DT50)	Other stability	Acute Oral, rat LD50 (mg/kg)	ADI (mg/kg/day)	soil half life (days)	soil mobility	anaerobic half life	thermal products	hydrolysis products	other comments
Other																		
chlorfensulphide		III	123.5		v low		insol		stable to acid & alk							dioxin potential		decomp to 2,4,4',5-tetrachlorodiphenylsulfide
dinocap		III	-22.5	138-140, 0.05mmHg	0.0033	4.54	0.151	d >200	stable in acid, 56h, pH7, 17h pH9	rapid decomp by light	990	0.008	4-24d	immobile	8d	burns readily	2,4- & 2,6-dinitrophenol	rapidly photolysed in water, but stable in dark
fenarimol		III	117-119		0.065	3.69	13.7		12h	rapid decomp by light	2500	0.01	14-130			burns readily, dioxin potential		hydrolytically stable, but rapidly photolysed (DT50 4-12h)
phenothiazine		III	185	371	neg		insol	stable								burns readily		
dodine		II	136		<0.01	1.65	630		stable		>1000	0.2	17.5-22.3	immobile	stable			
ethidimuron		II	156	d	0.00008	0.43	3000	d 217	stable acid, neutral, not alkali		>5000		90-120					
metolachlor		U	-62	100, @0.001 mmHg	4.2	2.9	488	stable to 275	>200d, pH 2 to 10		1936	0.1	20			burns readily		
picloram		U	d ~190		neg	1.9	0.56	d ~190	stable	decomp by uv in water, DT50 2.6d	>5000	0.2	30-90 (field)			burns readily, dioxin potential		moderately acidic, decomp strongly dependant on exposure to light

Table A6: Other Pesticides

Name	Formula/Structure	Site Usage	M Pt, C	B Pt, C	VP, mPa (@20/25C)	Kow (logP)	Water sol (mg/L)	heat stability	Hydrolysis (DT50)	Other stability	Acute Oral, rat LD50 (mg/kg)	ADI (mg/kg/day)	soil half life (days)	soil mobility	anaerobic half life	thermal products	hydrolysis products	other comments
chlorothalonil		III	252	350	0.076	2.92	0.81	stable	38d, pH9, stable pH5 & 7	stable to uv	>5000	0.02, 0.03	0.3-28d	low-immobile	0.3-28d	dioxin potential		IARC Class 2B, degradation faster in biotic/aquatic systems
dalapon	CH₃CCl₂CO₂H	III		185-190	0.01		sol		readily hydrolysed	dechlorinated by alkali >100C	9330		completely degraded in 3-4mths				dechlorinated	
dicamba		III	114-116	>200	1.67	-0.55	6600 (pH2), more at high pH	d ~200C	stable	photol DT50 14-50d	1707		<14			burns readily, dioxin potential		decomp to 3,6-dichlorosalicylic acid
coumatetralyl		II	172-176		neg	3.46	4	stable to >150	>1 yr	solns rapidly degraded by sunlight	16.5		51% mineralisation in 90d			burns readily		
fenvalerate (sumicidin)		II	40-54	d	0.019	5.01	neg	d	stable acid, neutral, not alkali		451	0.02				burns readily		pyrethroid
benzoximate		I	73		0.45	2.4	30		stable acid, not alkali		>15,000							
chlorthal-dimethyl		I	156		0.21	4.28	0.5	d 360										
bromopropylate		U	77		0.007	5.4	<0.5		34d, pH9, stable acid & neutral		>5000	0.03	40-70	low				