QUALITY OF 2,4,5-T AVAILABLE IN NEW ZEALAND

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Summary

Evidence is produced which defines the extremely low levels of TCDD ("dioxin") contamination in 2,4,5-T manufactured or imported into New Zealand since 1973. The TCDD contamination has been established to be well within the maximum official standard of 0.1 ppm on a 2,4,5-T basis. The 2,4,5-T used by New Zealand farmers can be stated as equal to the highest quality available in the world. The destruction of TCDD containing residues from the production of 2,4,5-trichlorophenol as an intermediate for 2,4,5-T manufacture is achieved by high temperature, high oxygen incineration in a specially designed furnace. Under The Clean Air Act this incineration process has received New Zealand Department of Health approval based on non detection of TCDD in the flue gases.

A great deal of public concern has developed in recent years about the quality of our environment and particularly as it could be affected by widespread use of pesticides. Because of our relatively intensive pastoral and cropping agriculture, New Zealand farmers have been frequent users of pesticides, particularly for the control of weeds and insect pests. Since the withdrawal of DDT as a pastoral insecticide, few chemicals have aroused as much public attention over the past few years as 2,4,5-T. Since its introduction in 1948 as a brushkiller for controlling introduced and indigenous scrub weeds, 2,4,5-T has become the most widely used herbicide in New Zealand.

Real public interest in 2,4,5-T did not develop until it was used as a defoliant in the politically controversial war in Vietnam. Further concern in New Zealand in 1971 was aroused with the report of two cases of human foetal deformities near Te Awamutu (Sare and Forbes 1971). As a result of this, the Agricultural Chemicals Board appointed a specialist sub-committee in 1972 to investigate the Te Awamutu incidents and also the need for possible restrictions on the use of 2,4,5-T (Allingham 1972). Although no conclusive evidence could be established that the 2,4,5-T could have caused the birth deformities, they did recommend further restrictions on the use of 2,4,5-T. Apart from the withdrawal of registrations for use of 2,4,5-T directly on food crops and around the home environment, normal farm use of 2,4,5-T containing products was permitted with the addition of the following label warnings:

- women of child bearing age should avoid exposure to 2,4,5-T
- avoid contamination of any public, domestic or private water supply.

Although the sub-committee recommended restrictions on aerial application of 2,4,5-T, these were not accepted by the Agricultural Chemicals Board. However, the most important recommendation adopted

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was that from April 1 1973, 2,4,5-T made available for use in New Zealand should contain not more than 0.1 ppm TCDD (2, 3, 7, 8-tetrachloro-dibenzo-dioxin) on a 2,4,5-T basis. This was a significant reduction in TCDD contamination from the previous maximum level of 1 ppm for 2,4,5-T products sold in New Zealand.

This TCDD contaminant in 2,4,5-T was first reported in 1957 as causing chloracne, a persistent severe skin disorder (Kimmig and Schulz 1957). In fact, the first assays established for TCDD in 2,4,5-T were based on skin response to the compound applied to the inner surface of a rabbit's ear. This was sensitive for detecting TCDD in the range of 1 to 10 ppm.

In 1969 TCDD was identified as a potent teratogen giving rise to foetal deformities in offspring of laboratory animals exposed to TCDD during pregnancy. The teratological significance of 2,4,5-T has been reviewed by Goldberg (1971) and Wilson (1972). Presumably this evidence was considered in the decision to relax the restrictions placed on the use of 2,4,5-T in Canada. Since 1972, 2,4,5-T products sold in Canada which contain less than 0.5 ppm TCDD do not require label warnings referring to their possible teratogenic toxicity hazards to pregnant women.

Since 1968 when Ivon Watkins-Dow Limited commenced manufacture of 2,4,5-trichlorophenol in New Zealand, our company has been well aware of the possible presence of the highly toxic TCDD impurity being formed in a side reaction. In this process, symmetrical 1, 2, 4, 5-tetrachlorobenzene is hydrolysed in a solution of methanol and sodium hydroxide in water to form sodium trichlorophenate under conditions of high temperature and pressure. 2,4,5-trichloroanisole is an intermediate in this reaction and unfortunately, a minor contaminant formed is TCDD, by the combination of two molecules of 2,4,5-trichlorophenol.

By 1965, analytical techniques had been developed to the stage where TCDD could be detected by gas chromatography to the level of 1 ppm in 2,4,5-trichlorophenol and in 2,4,5-T. Since 1966, world scale plants such as those developed by Boehringer, Germany and Dow Chemical USA, have produced 2,4,5-trichlorophenol containing less than 1 ppm. Similar technology has been used in the closely monitored operation of the Ivon Watkins-Dow plant in New Zealand since 1968.

However, not till specifications were set by the Agricultural Chemicals Board in 1971 was gas liquid chromatographic analyses for TCDD undertaken by our analytical laboratory. Unfortunately, the methods established are not suitable for analysis of TCDD in formulated products due to interference from solvents and emulsifiers. In the hands of trained technicians, TCDD, after suitable cleanup, can be fairly readily analysed in either 2,4,5-trichlorophenol, 2,4,5-T acid or in the final 2,4,5-T esters. In New Zealand, the standard method approved by the Agricultural Chemicals Board determines TCDD in 2,4,5-T esters down to 0.01 ppm with an accuracy of ± 0.002 ppm confidence limits.

Since April 1 1973, some hundreds of batches of all locally manufactured 2,4,5-T butyl and isooctyl esters have been monitored for TCDD by both the Chemistry Division of DSIR and by the analytical laboratory of Ivon Watkins-Dow Limited. The results have yielded a mean value of 0.033 ppm with a range of values from a minimum of 0.015 ppm to a maximum of 0.060 ppm TCDD. Every production batch of ester is analysed before it is released for further formulation in the plant. The 1975 established standard is now set by Ivon Watkins-Dow Limited at a maximum of 0.05 ppm, or half the legal limit allowed by the present Agricultural Chemicals Board requirements.

Any 2,4,5-T brought into New Zealand requires the importer to submit a Certificate of Analysis to confirm that it contains less than

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0.1 ppm TCDD. Check analyses which have been made on these shipments have shown that all have been safely within the legal limit.

It can therefore be concluded that all 2,4,5-T manufactured or imported in New Zealand since the gazetting of the Notice in April 1973 establishing new standards of quality for 2,4,5-T have been well below the legal limit of 0.1 ppm TCDD on the 2,4,5-T content. On this basis it can be accepted that commercially available 2,4,5-T products in New Zealand should not present a hazard to health or to the environment when they are used according to product label directions.

DEGRADATION OF TCDD IN MANUFACTURING WASTES

Because the manufacturing process at present used in New Zealand results in the production of more than 0.1 ppm TCDD in the sodium trichlorophenolate intermediate, a solvent extraction process has been developed for the removal of this excess TCDD contaminant. The xylene solvent extractant used also removes the main reaction by-product, 2,4,5-trichloroanisole. This extraction provides sufficient volume of solvent to maintain the by-products in solution during storage in a specially constructed tank where they are held for later incineration.

The destruction of TCDD and of the associated 2,4,5-trichloroanisole has necessitated the design and construction of a specialised high temperature incinerator. Both the design and its safe operation were required to meet the standards set by the New Zealand Health Department based on The Clean Air Act 1974. The parameters set for the operation of the plant were based on total destruction of TCDD and at the same time, a maximum emission of 2.3 kg per hour of the resulting hydrogen chloride in the effluent stream. Furthermore, it was desirable that the operating conditions yielded no highly visible smoke plume. These conditions were met by an incinerator capable of exposing the contaminated solvent diluted with fuel oil to a temperature of 1000°C under high oxygen input and for sufficient time in the combustion chamber to totally destroy the TCDD and 2,4,5-trichloroanisole. The initial operation of the plant under the supervision of Health Department analytical chemists and chemical engineers established the correct operating conditions of the plant. By sampling of the effluent stream in an aspirator solvent extraction system over an extended period of operation of the plant, the method of analysis developed was established to an accuracy down to 1 ppb $\pm$ 0.2 ppb for detecting both the TCDD and the 2,4,5-trichloroanisole. At these very low levels of detection using specialised gas liquid chromatographic methods, it was not possible to detect TCDD in the combustion gases. This is equivalent to greater than 98.5% proven destruction of TCDD.

On this basis it can be confidently stated that the TCDD contaminant in 2,4,5-T in the New Zealand environment is at an absolute minimum level. Biomagnification of TCDD has not been established under field conditions because it is broken down by sunlight and also adsorbed and slowly inactivated in soil (Kearney *et al.* 1973).

A new continuous recycling process is now being developed such that the operating conditions in the 2,4,5-trichlorophenol plant will directly yield less than the legal limit of 0.1 ppm of TCDD in the final 2,4,5-T. As no 2,4,5-trichloroanisole residue will be produced in this new process, the need for combustion of wastes from our plant will be eliminated. As a result, the New Zealand environment will potentially be exposed to still less contamination of TCDD without impairing the likely continuing high demand by the New Zealand farmer for 2,4,5-T brush-killer herbicide.

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