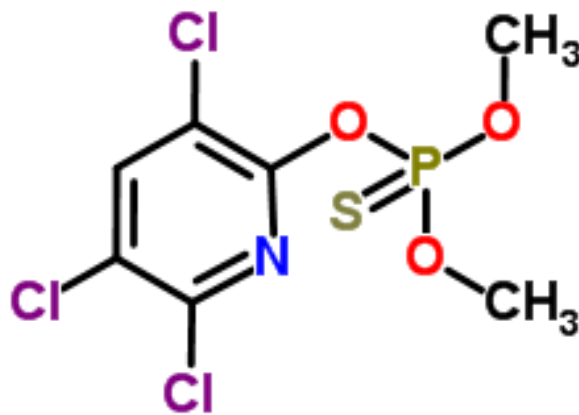


REPORT

ENVIRONMENTAL FATE OF CORNUBIA SPILL RELATED PESTICIDES AND THEIR DEGRADATION PRODUCTS THAT ENTER THE LITHOSPHERE, AQUASPHERE, ATMOSPHERE AND BIOSPHERE



Terbufos

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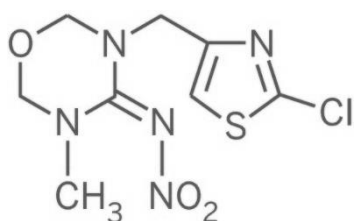
1. Introduction.

- a. Classification of pesticides. Pesticides (referred to as agricultural remedies in South Africa in terms of Section 1: Definitions of the Fertilizers, Farm Feeds, Agricultural Remedies and Stock Remedies, 1947 (Act No. 36 of 1947) are divided into:
 - i. Chemical based pesticides that may be natural of origin (extracted mainly from plants or yeasts), synthetic of origin (man-made) or semi-synthetic (natural chemicals that are transformed into man-made analogues by a few synthetic interventions).
 - ii. Biological pesticides that are divided into:
 1. Macro-biological organism such as (but not limited to) parasitic wasps, beetles and nematodes that predate on plant pest species, and
 2. Micro-biological organisms such as fungi, viruses and bacteria that are used to control undesired plant pests, plant pathogens and undesired plant species.
- b. Two endpoints of importance that must be considered for pesticides that enter the lithosphere, atmosphere, aquasphere and biosphere (including foodstuffs produced for human and animal consumption):
 - i. Being transformed in or on living biota either by enzymatic action, oxidation, reduction, hydrolysis and forming complexes with enzymes or smaller organic molecules into either molecules that resemble the parent molecules or part of the parent molecules, or molecules that are vastly different from the parent molecule or any parts of the parent molecule. These processes are collectively called metabolism. The FAO/WHO definition of a metabolite is captured in the REVISED DRAFT GUIDELINES ON PERFORMANCE CRITERIA FOR METHODS OF ANALYSIS FOR THE DETERMINATION OF PESTICIDE RESIDUES IN FOOD AND FEED (2017) as “**Metabolite:** Component of a pesticide residue occurring in a commodity as a result of biotic transformation (metabolism) of a pesticide in a biological system (e.g. plant, animal)”.
 - ii. Being transformed in the abiotic spheres by oxidation, reduction, hydrolysis, saponification, UV degradation (*via* solar radiation or photolysis) or heat (not only solar but other natural sources of heat such as geophysical heat). These processes are collectively referred to as physical degradation of break-down of pesticides.
- c. Selection of substances for the purpose of demonstrating the reasons for focusing on only certain physical degradation products of pesticides and not on metabolites.
 - i. The substances selected at the very start of the monitoring process (July and August 2021), were selected for a number of reasons, including but not limited to human toxicity, environmental toxicity, persistence and resistance to degradation, and volume that was originally in the Cornubia warehouse. The purpose of sampling by

the UPL appointed specialist teams for air, fresh water, ground water, marine and estuary water, sediments, soils and bivalves, was to assess whether substances would behave as described for their physical chemistry and to predict an end point (time frame) when the concentration of substances in the various affected areas would be at a point that would not negatively affect natural repatriation and recolonisation of biota or biota that might be re-introduced by the various specialist teams.

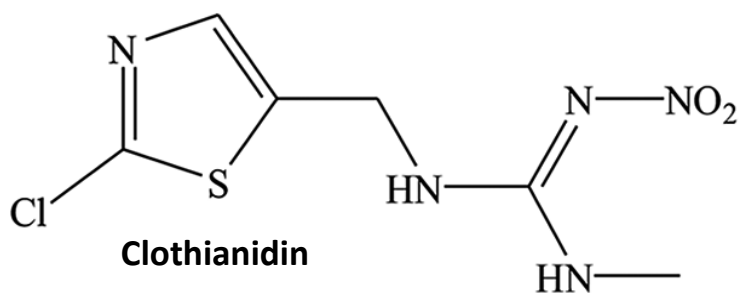
- ii. Substances selected for this report. Not all substances of concern are covered in this report because many were never detected and many were detected at miniscule quantities. The substances reported on in this report demonstrate that not every substance degrades into a degradation product of concern while some produce degradation compounds of concern.

- d. Pesticide metabolites and degradation products of human health concern. When pesticides are applied to edible crops, there is a strong possibility that the substances may undergo either metabolism inside plant tissue, or on plant surfaces, or undergo physical degradation



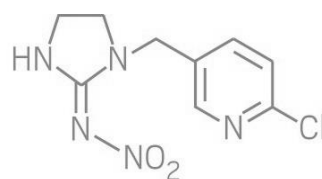
Thiamethoxam

due to natural effects described above. Health authorities all over the world determine the maximum residue limits (MRLs) for



Clothianidin

pesticides and their metabolites and/or degradation products of toxicological concern. These MRLs are contested between health regulators of different nations but do take into account that certain pesticides are metabolised or degraded to substances of concern and if so, such substances are added to the parent compounds of which the total residues must be determined as the MRL values. Examples of such pesticides are thiamethoxam which metabolises rapidly to clothianidin and when residues of thiamethoxam are measured the corresponding residues for clothianidin must be added to those of thiamethoxam as the final residue. An example of a molecule with at least five possible metabolites and/or degradation products, and for which ONLY the parent compound residue concentration is required for residue analysis, is imidacloprid. The referenced South African Government Gazette Notices for MRLs in foodstuffs bear testimony to the fact that only a small percentage of pesticides are regarded as producing metabolites or degradation products of toxicological concern. Many pesticides form complexes with the naturally occurring glutathione in the body which accelerates detoxification and breakdown of toxins such as pesticides, which means that pesticides that are prone to glutathione complex formation are of less toxicological concern than those that are resistant to glutathione complex formation.

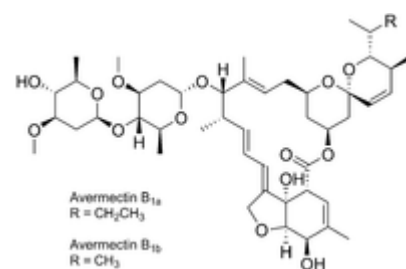


Imidacloprid

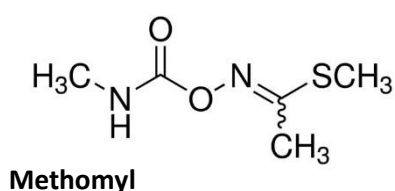
- e. Irreversible soil particle binding. Pesticide molecules are adsorbed onto soil particles (not absorbed) to a greater or lesser extent. A few pesticides such as paraquat are irreversibly adsorbed onto soil particles and makes it virtually impossible to be extracted from soils for analysis, especially from clay mineral particles. Diquat is very similar to paraquat in this behaviour. Such molecules are only detectable as ions in water bodies (both paraquat and diquat are bipolar cations). If liberated from soils, the ions are rapidly degraded by soil microbes in less than one week.
- f. All pesticides (including biological pesticides) are prone to metabolism and physical degradation to a greater or lesser extent. There is no golden rule that can be applied to all pesticides. Each pesticide (substance molecule or organism in the case of biological pesticides) has its own unique physical chemistry characteristics or biological characteristics (in the case of biological pesticides) that afford it its own susceptibility criteria in terms of metabolism or physical degradation. To offer examples of the vast differences in molecular degradation and metabolism:

- i. Brodifacoum is a second generation coumatryl anti-coagulant rodenticide that undergoes slow metabolism to the glucuronide complex in the intestines of a target animal (such as a rat), while coumatetralyl which is a first generation coumatryl anti-coagulant rodenticide undergoes rapid metabolism by oxidation in a target animal's intestines. Its elimination half-life in target animal plasma is $DT_{50} = 0.52$ days while that of brodifacoum is 91.7 days. This demonstrates that two molecules synthesised on the same carbon frame are vastly different in their metabolism and half-life in an organism.

- ii. The natural insecticide abamectin (an avermectin class substance isolated from an actinomycete) is very stable in the pH range from 4 to 7, even though it is a substance of natural origin. Abamectin is rapidly excreted unmetabolized by animals while it is photolytically covered to an isomer on plant surfaces (the latter is physical transformation and not metabolism). It is photolytically unstable in water with a half-life (DT_{50}) of only 2 days while in non-photolytic conditions the DT_{50} is 213 days at pH = 9. This is an example of a natural pesticide that is not metabolized and behaves very differently in photolytic versus a-photolytic conditions in terms of degradation.



- iii. Methomyl (a carbamate substance) is not susceptible to aqueous photolysis, while being unstable in a-photolytic slightly acidic to neutral water (in a pH range from 4 to 7) for slightly more than 30 days ($DT_{50} > 30$ days). It becomes very labile (subject to physical transformation) at alkaline pH levels. It is very rapidly metabolised in animals and excreted as volatile substances such as carbon dioxide (CO₂) and acetonitrile (CH₃CN) and polar metabolites in urine. Glutathione plays a role in its metabolism by displacing the thiomethyl group and subsequent transformation of



the thiomethyl group to a mercapturic acid derivative. Once applied to plant surfaces it rapidly degrades (mineralises) to carbon dioxide (CO₂) and acetonitrile (CH₃CN). In soil and groundwater it was determined to be unstable and degraded in less than 0.2 days in groundwater and 4 to 8 days in soils in the slightly acidic to neutral pH range.

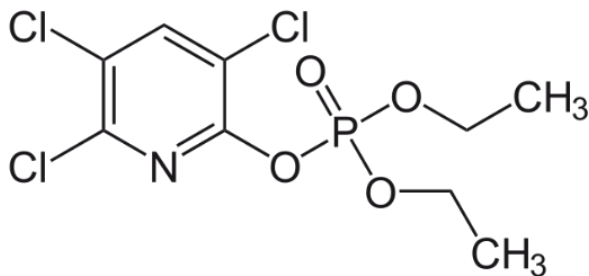
2. Degradation products of pesticides.

- a. During development of synthetic and natural pesticide molecules, organic chemists synthesise literally thousands of molecules annually. It is estimated that 20,000 new molecules are synthesised for every molecule that eventually becomes a commercial pesticide. A number of studies are required by regulatory authorities around the world such as the US Environmental Protection Agency (USEPA), the European Food Safety Authority (EFSA) and in the case of South Africa, the Directorate of Agriculture Inputs Control of the Department of Agriculture, Land Reform and Rural Development. In the context of safety, the following data must be provided by manufacturers/originators of pesticides to the regulatory authorities for consideration before such new substances will be registered as pesticides:
 - i. All the standard physical chemistry characteristics of the substances such as (but not limited to) physical state (liquid, solid or gas), colour, melting point, boiling point, sublimation point (if applicable), density, solubility in water and organic solvents, K_{oc}, K_{ow}, pK_a, Henry constant, hydrolytic stability, pH sensitivity, thermal stability and aqueous photolytic stability (Turner, A.J., 2021).
 - ii. Human health and environmental health toxicological data. This includes acute and chronic toxicology for human beings (derived and extrapolated from animal studies (rat, dogs, pigs, mice, guinea pigs), wild animals (birds, mammals (referenced mostly to human toxicology as mentioned earlier), fish, aquatic invertebrates, honeybees, crustaceans, earthworms, algae, monocotyledon and dicotyledon plants.
 - iii. Chemical degradation (break-down curves) of substances on target surfaces, as well as in soil and water under aerobic, anaerobic, photolytic and non-photolytic, acid and alkaline conditions. If any degradation products (substances that are often erroneously referred to as metabolites) are found, their toxicology must also be revealed as it may or may not have an influence on human health and environmental health. Some degradation products of substances may have toxicology that is considered by regulatory authorities as similar to that of the parent compounds while others may be significantly more toxic or benign in toxicological characteristics.
 - iv. Metabolism in edible commodities or on their surfaces. If pesticides undergo significant metabolism in or on edible commodities, such as in the case of terbufos and produce metabolites of toxicological concern, the toxicological studies must be conducted for such metabolites and declared by the originator of the substances.
 - v. Human health risk assessment of pesticide substances and their metabolites and degradation products. Due to the extremely individualistic physical chemistry and toxicological characteristics of pesticide molecules, it is required to take metabolites and degradation products of pesticide molecules into account when conducting human and environmental health risk assessments because of the possibility that

some metabolites and degradation products may be of greater toxicological concern than their parent compounds. It is standard practice amongst regulatory authorities (that include a broad-spectrum environmental health and food safety agencies) to publish requirements for the analysis of pesticides, and if they produce metabolites or degradation products of concern, to list such products as substances that must be measured when conducting food safety. The metabolites or degradation products of concern are listed in the MRL regulations that are published by health authorities such as the SA Department of Health (2012, 2020).

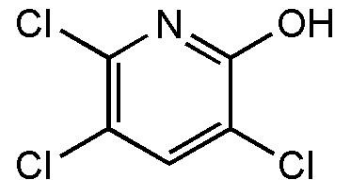
3. Degradation products of pesticides of toxicological concern in environmental health.

a. Organophosphate molecules. It is well known that organophosphate molecules that contain



Chlorpyrifos

sulfur atoms in the phosphate substructure of the substances either linked by single or double bonds to the phosphorus atom, readily undergo desulfuration (sulfur that is double bonded to the



phosphorus atom is replaced by oxygen), or oxidation (sulfur atom

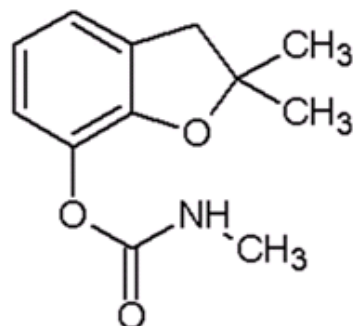
that is single bonded or double bonded to the phosphorus atom) to the sulfoxide (-SO-) and then to the sulfone (-SO₂-). Some molecules such as

fenthion sulfoxide and fenthion sulfone are more toxic than the parent compound, while others such as the sulfoxide and sulfone of terbufos are less toxic than the parent compound. Choud *et al.* (2011) demonstrated that the 96 hr LC₅₀ values for terbufos, terbufos sulfoxide and terbufos sulfone against *Ceriodaphnia cf dubia* were found to be 0.08 ug/L, 0.36 ug/L and 0.19 ug/L. This is not always the case. Chlorpyrifos degrades differently by separation of the phosphate moiety from the parent compound to produce a benign phosphate ester and the well-known 2,4,5-trichloropyridinol (TCP or TCPY), the latter which is recognised of equal toxicity to the parent compound depending on the test media. Cacéres *et al.* (2000) found that TCPY was more toxic to *Daphnia carinata* in cladoceran culture medium but in natural water its toxicity was less than that of chlorpyrifos. The LC₅₀ values in cladocerna culture medium against *D. carinata* were reported as: chlorpyrifos 0.24 ug/L and 0.2 ug/L while in natural water no toxicity of TCPY against the organism was found at 2.0 ug/L. The authors hypothesised that the combination of the parent compound and TCPY's toxicity of LC₅₀ = 0.08 ug/L in cladoceran culture medium suggest that in fresh water the same phenomenon may be found. Once again, is it important to point out the complexity of toxicology and how it can vary or be contradictory based on a multitude of parameters.

i. Degradation products. The organophosphates that were detected throughout the course of the monitoring after the Cornubia arson attack, fire and subsequent mass chemical spill, were chlorpyrifos (very regularly but tailing off strongly to the present where it is rarely detected, and terbufos (less than five positive detections found for terbufos at very low concentrations <5 ug/L)). As mentioned earlier, the two oxidation breakdown products of terbufos are much less toxic than the parent

compound and were regarded as not significant in the overall situation. It is extremely unlikely that they would have been detected given the very low concentration of the terbufos that was detected in a few samples. Chlorpyrifos offered a much better barometer for the organophosphates than terbufos because it was present in a large volume and offered better traceability than terbufos. The principal degradation of chlorpyrifos namely TCPY has been tracked throughout the monitoring but note that it is also the principal breakdown product of the herbicide triclopyr and are as such not solely attributed to triclopyr. TPCY can be traced throughout the monitoring at varying levels but is much stronger correlated with triclopyr than with chlorpyrifos. The volume of triclopyr in the Cornubia warehouse was also much larger than the chlorpyrifos volume.

- b. Carbamates. Carbamates are generally much less stable than organophosphates and break down more readily in the environment especially in conditions exceeding pH of 7. Note that large quantities of lime were used to finally extinguish the fire and that would have raised



Carbofuran

the pH of run-off water sufficiently to break down carbamates. The American Society for Testing and materials (ASTM) records that the USEPA does not recognise breakdown products of carbamates for all of this group of substances apart from aldicarb which is known to oxidise to its sulfoxide and sulfone. It is thus not scientifically valid to claim that carbamate pesticides all produce breakdown products or metabolites of toxicological concern. The carbamates present in the Cornubia were carbofuran, methomyl and oxamyl.

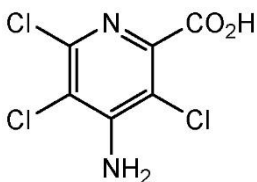
- i. Degradation products. No oxamyl or methomyl was detected in any samples throughout the monitoring process. The only carbamate being detected shortly after the spill, was carbofuran but subsequent to that, no samples ever tested positive for carbofuran. The only degradation product of carbofuran that is considered of toxicological significance is 3-hydroxycarbofuran of which the toxicity is acute oral mammalian virtually identical to that of carbofuran. It is, however, not a breakdown product but an oxidised analogue of carbofuran that is formed by metabolism in plants.

- c. Neonicotinoids are also known as chloronicotinyl substances. These substances are divided into two groups namely the cyano group such imidacloprid, thiamethoxam and clothianidin, and the nitro group of which acetamiprid is the most representative. Imidacloprid is known to break down to six substances of which two were found to be approaching toxicity levels close that of the parent compound for honeybees while 5-hydroxyimidacloprid was four to six times less toxic than the parent substance and three others showed no significant toxicity to honeybees (Suchail, *et al.*, 2001). Thiamethoxam is an interesting substance because it degrades very rapidly to another neonicotinoid clothianidin with a slightly less toxic profile for lower order animals, much less toxic profile for higher order animals but a much longer

soil half-life than that of thiamethoxam. Clothianidin undergoes limited metabolism in living biota to five metabolites but remains largely unchanged as a substance from a chemical breakdown point of view. It is scientifically invalid to refer to metabolites that are not produced in the aquasphere or lithosphere.

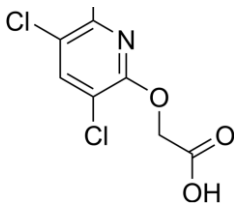
- i. Degradation products. Imidacloprid and clothianidin were chosen as substances to trace during the sampling period because of their long to very long term (clothianidin) half-lives while none of their degradation products were selected because these are either as toxic, less toxic or of no toxicity concern. Thiamethoxam was also targeted for tracking in the beginning but was replaced by clothianidin because thiamethoxam degrades to clothianidin fairly rapidly.

d. Herbicides that were chosen as substances of concern for environmental fate.



- i. Pyridyloxycarboxylic acid and pyridinecarboxylic acid. Two substances of this fairly similar chemical grouping namely triclopyr and picloram were selected because of their respective large volumes that were in the Cornubia warehouse. Both these herbicides are auxin mimics and have a profound effect on dicotyledon plants while their effect on established grass species is virtually nil. Seedling grasses may be affected but not necessarily killed. The ecotoxicology of both products is not of grave concern but algae may be stunted by the substances when concentrations in water exceed 50 mg/L.

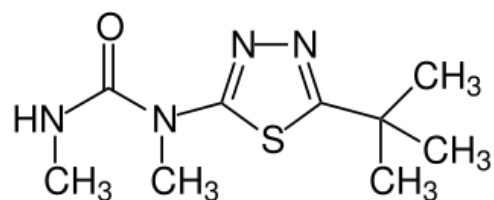
Triclopyr



Picloram

- 1. Degradation products. Triclopyr is susceptible to physical degradation and produces mainly TCPY (as in the case of chlorpyrifos) and small amount of 3,5,6-trichloro-2-methoxypyridine. The carboxylic acid moiety that is cleaved from the parent molecule is acetic acid that will mineralise over time. TCPY has been monitored in all samples that were submitted for analysis. Although it is a degradation product of both chlorpyrifos and triclopyr, is the chemical nature of triclopyr such that the bulk of the TCPY is believed to be the degradation of triclopyr. This understanding also correlates with the large quantity of triclopyr that was in the warehouse compared to a much smaller quantity of chlorpyrifos. Picloram is not readily degraded and according the USEPA evaluation (1995); the substance remains unchanged in soils for extended periods of time 167 – 513 days. It does, however, respond to photolysis in water and on top of soils rapidly by losing two chlorine atoms and by cleavage of the pyridine ring, which leaves the degradation products ineffective as toxins compared to the parent compound. The stability of picloram was sufficiently convincing to monitor and analyse for its presence in soil and water in its unchanged form.

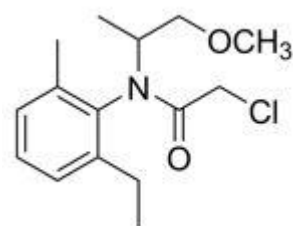
- ii. Thiadiazolylurea herbicides. Only one substance of this chemical class of herbicides that was present in the warehouse, is tebuthiuron. Tebuthiuron is moderately toxic to mammals and birds, of low toxic concern for fish and *Daphnia* but toxic to algae (EC₅₀ 0.05 mg/L – 4.06 mg/L). Tebuthiuron is used in high dosage rates



Tebuthiuron

to control broadleaf plants such as invasive trees and can also be used in much higher dosage rates to control grass species in certain crops. It is interesting that the substance is quite selective and does not attack all woody plants as would be the case for picloram, triclopyr and bromacil, and if used correctly can selective remove problematic tree species in savannah and grasslands. It is a very stable substance that is highly tolerant to photodegradation and is very stable over a pH range of pH = 3 to pH = 9. The only possible, but unlikely, degradation product is the *N*-demethylated substance and it is not worthwhile analysing for a substance's degradation products if the substance is not prone to natural degradation. Microbial breakdown in soil is possible, but very limited. It tends to survive in low moisture soils for very long periods of time (>1 year) and normally dissipate from soils by slow leaching and to a small extent microbial degradation (*N*-demethylation). The substance is even resistant to metabolism in plants and it is therefore senseless to try and analyse for degradation products of a substance that is not prone the degradation or metabolism.

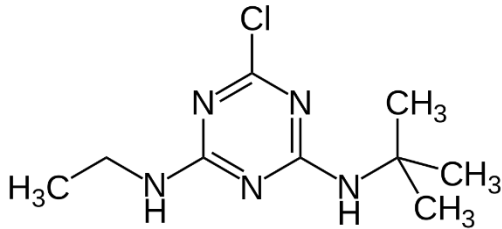
- iii. Chloroacetamide herbicides. Metolachlor (*R,S* racemic mixture) and *S*-metolachlor (88% *S*-enantiomer, 12% *R*-enantiomer) were chosen as substances of concern because of large quantities that were in the Cornubia depot, and because it is likely to pose a risk to fish and benthic organisms. Normal analysis does not differentiate between the two enantiomers, hence for all practical purposes, analysis was conducted for the racemic mixture. Other herbicides in this class of substances that are monitored are alachlor and acetochlor.



Metolachlor

1. Degradation. Metolachlor is stable for over 200 days at ambient temperature (20 Centigrade) at pH 1 – 9 in water but is susceptible to alkaline degradation at pH 13 (DT₅₀ = 97 days) which dechlorinates the substance and at pH < 1, it undergoes *O*-demethylation. Since the extreme alkaline and acidic conditions required to produce these first-order degradation products did not materialise anywhere in the area that was affected by the Cornubia spill is it extremely unlikely, if not impossible, for metolachlor to have produced these two first order degradation products. Alachlor and acetochlor are also known to be resilient against hydrolysis and that is why is all cases the parent substances were chosen to be tracked during the monitoring process. This is the same for residue analysis in edible commodities.

- iv. Triazine herbicides. Terbutylazine is a stable molecule that is a systemic grass herbicide. The substance is susceptible to degradation in water pH = 1 (strongly acidic) and very strong alkaline (pH >13) conditions while in at pH = 5 – 9, its half-life is DT₅₀ 86 to >200 days. It is thus extremely unlikely that the conditions that prevailed from the onset of the spill to the present that water pH would have catalysed degradation of terbutylazine. It is one of

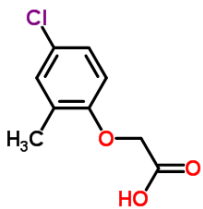


Terbutylazine

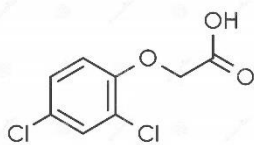
the substances that is still detected in some samples albeit in very low concentrations (excluding the “hot spots” under the Cornubia warehouse platform and in the deep horizons of the lower wetland).

1. Degradation. Terbutylazine is not readily prone to physical; degradation in water or soils, but there is one metabolite (not a degradation product) namely de-ethylterbutylazine (loss of the ethyl moiety on the N⁴ nitrogen atom). This metabolite was only found to represent <5% of the soil applied terbutylazine, hence is it not sensible to consider it as a substance of concern.

- v. Phenoxyacetic acid herbicides. MCPA is a typical phenoxyacetic acid herbicide with a residual activity of 3 to 4 months in soil when applied as a dicotyledon herbicide. 2,4-D is another widely used phenoxyacetic acid herbicide; the only difference between the two molecules is that MCPA has a methyl group at ring position 2 compared to chlorine atom in the case of 2,4-D.



MCPA

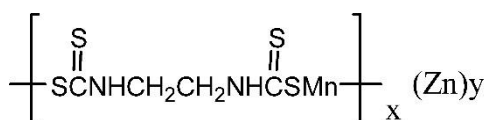


2,4-D

1. Degradation. The two molecules have very similar degradation and metabolic pathways in soil and water. Photolysis plays a role in physical degradation of phenoxyacetic acid, and depending on wavelength, are the degradation products aldehydes in water or de-acetylated by-products that are transformed further into phenolic analogues or cyclohexadienedione's. Breugemann and Trapp reported in 1989 that no degradation products of MCPA were found in the absence of organic materials in sediment. This explains why in some zone of the affected area, MCPA and 2,4-D still show a presence albeit in very low concentration.

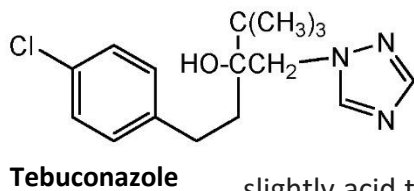
- e. Fungicides that were selected for monitoring. Only a few fungicides were detected at concentrations that warranted further monitoring.

- i. Alkylenebis(thiocarbamate). Mancozeb is a combination of maneb and zineb. Both substances have the same organic substance and differ only in the metals, namely

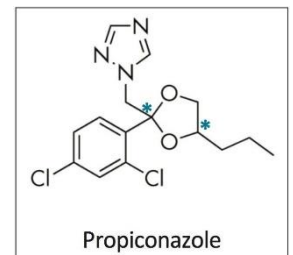


manganese and zinc that are used to produce the two complexes maneb and zineb. Both substances are labile to hydrolysis in aqueous solution at pH 5 to 9 in less than 24 hours. In soils maneb and zineb remain captured in the top 1 cm of soil with a half-life of DT₅₀ = 3 to 5 weeks.

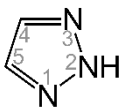
1. Degradation. As mentioned, are both substances labile in aqueous medium in the alkaline range to hydrolysis to release the metal ions and rearrangement of the organic substrate to form 5,6-dihydro-3H-imidazo(2,1-c)-1,2,4-dithiazole-3-thione which over time degrades to 2-imidazoline and oxidates thereof. The residue tested for on edible crops is the parent organic compound ethylenebis(dithiocarbamate) as the only substance of toxicological concern. The metal ions zinc(II) and manganese(II) will remain present and mobile in soils and water unless reduced to elemental compounds. Note, however, that both zinc and manganese are present in all soils and water bodies are measurable levels and presence of either of these metals or their cations cannot necessarily be attributed to the mancozeb that was in the Cornubia warehouse.



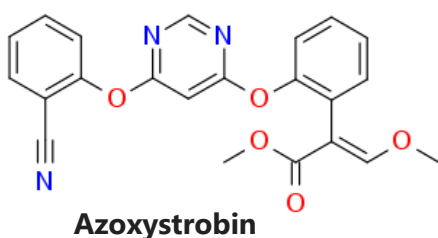
- ii. Triazole fungicides. Tebuconazole was detected in many of the fresh and estuary water, sediment and soil samples throughout the monitoring process, while propiconazole was detected from time to time but at very low concentrations. Both substances are systemic fungicides that are resilient to photolytic degradation but are labile to slightly acid to slightly alkaline water solutions (pH range 5 to 9). Tebuconazole is stable at elevated temperatures while propiconazole is much more sensitive to heat with a $DT_{50} = 12$ days in solar radiated soil. Tebuconazole does not accumulate in soils even though it is not degraded rapidly.



1. Degradation. The main degradation products that are analysed for in foodstuffs are the parent compounds tebuconazole and propiconazole. It was therefore decided to track the presence of the parent compound throughout the monitoring process because 1,2,4-triazole is also the break-down products of other triazole substances and cannot be attributed to tebuconazole and propiconazole alone. The toxicity of this degradation product is $LD_{50} > 1,600$ mg/kg and thus not of toxicological concern.



- iii. Strobilurin fungicides. Azoxystrobin was detected in some of the water samples in very low concentrations. It is stable to hydrolysis in the pH range 5 to 9 in aqueous environment but labile to photodegradation in water with a short half-life of $DT_{50} = 8.7 - 13.9$ days. In natural soil is it also susceptible to photodegradation with a half-life of $DT_{50} = 11$ days. Natural degradation in total field condition is rapid with $DT_{50} = 14$ days. It is generally of least toxicity concern for higher order animals but it is considered toxic for aquatic organisms (fish, *Daphnia*, algae, shrimps, oysters).



1. Degradation. For foodstuffs, only the parent compound is analysed as a substance of toxicological concern. The main degradation product in field conditions is the free acid after degradation of the methoxyacrylate moiety. This substance and other degradation products mineralise to carbon dioxide

4. Unique substances of concern. There was one unique substance namely MSMA (monosodiummethylarsonate) which is a widely used herbicide for the control of grasses in sugarcane and invasive *Cactus* species. MSMA was the one substance that required the focussed attention of the UPL specialists team due to the possibility of it transforming into lower oxidation states of arsenic of which the acute and chronic toxicity increases to the level of elemental arsenic which is a known carcinogen. It must also be put on record that elemental arsenic, its cations and oxides are ubiquitous (always present) in the natural environment.
 - a. Degradation. Due to the potential for MSMA to degrade to lower oxidation states of arsenic, including elemental arsenic, the decision was taken by the UPL appointed specialists to analyse all samples for elemental arsenic and not for any of the higher oxidised species of this element as a precautionary principle. Calculations for beach sediments, estuary sediments, seawater and bivalve were retro-calculated to determine acute and short-term chronic toxicity risks of MSMA but human health risk assessments were conducted as if all the arsenic was in elemental form which the form of long-term carcinogenic concern.

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