Environmental Fate and Toxicology of Chlorothalonil

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1 Introduction

The fungicide chlorothalonil (2,4,5,6-tetrachloro-1,3-benzenedicarbonitrile; CAS 1897-45-6; Fig. 1) was introduced in 1965 by Diamond Shamrock Corp. and was first registered in 1966 for use on turfgrass within the United States. An additional registration was granted 4 years later for use on potatoes, marking it the first approved food crop for application (US EPA 1999). It is formulated as concentrates,

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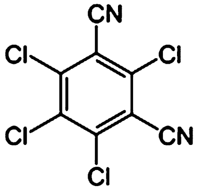

Fig. 1 Chlorothalonil structure

powders, and granules, among other registered formulations. Some of the prominent products containing chlorothalonil as the active ingredient include Bravo®, Daconil® and Sweep® (US EPA 1999). These or other chlorothalonil formulations have been applied to crops such as celery, beans, peanuts, and peaches, among others. Within the USA, approximately 34% of the total chlorothalonil applied is used on peanuts, 12% on potatoes and 10% on golf courses (US EPA 1999).

Chlorothalonil is a broad spectrum, non-systemic, organochlorine fungicide and mildewicide It is principally used to control fungal foliar diseases on various fruits, vegetables, ornamentals and turf (US EPA 1999). Chlorothalonil's success as an antifouling paint additive and wood protectant qualified it to replace organotin biocides such as tributyltin; however, once applied, it is slowly released into waterways and potentially contaminates surface water bodies (Sakkas et al. 2002). Although surface waters near marinas in San Diego, CA were monitored for such antifouling residues, none were detected above a detection limit of 10 ng/L (Sapozhnikova et al. 2007). In California, surface and groundwater were monitored for chlorothalonil residues from 1993 to 2000. Of the samples collected (705 total) from USGS water monitoring stations, only one surface water sample contained chlorothalonil at a concentration of 0.29 μg/L (USGS NAWQA; US EPA 2007).

Chlorothalonil has a low water solubility and is moderately persistent in soils, having half-lives ($t_{1/2}$s) up to 19 days. Because of its water solubility, the potential for chlorothalonil to impact groundwater is low; however, it has been found to highly impact aquatic organisms (US EPA 1999). The environmental fate of chlorothalonil was last reviewed in the mid 1990s (Caux et al. 1996). The goal of this paper is to review the relevant literature that has appeared since 1996, focusing on chlorothalonil's chemistry, environmental fate and toxicity.

2 Chemistry

Chlorothalonil is a chloronitrile fungicide (Tomlin 2000), and specifically is a polychlorinated aromatic (US EPA 1999). Technical grade chlorothalonil is an odorless or slightly pungent, colorless crystalline solid. Chlorothalonil is insoluble in water (at 25 °C), but is slightly soluble in kerosene, acetone and xylene, and this compound strongly adsorbs to soil and sediment. Chlorothalonil is denser than water, potentially susceptible to hydrolysis under alkaline conditions, stable against photolysis and is degraded by both aerobic and anaerobic microbes. Additional physiochemical properties of chlorothalonil are presented in Table 1.

Table 1 Physiochemical properties of chlorothalonil

Chemical Abstracts Service registry number (CAS#)[a]	1897-45-6
Molecular Formula[a]	$C_8Cl_4N_2$
Molecular weight (g/mol)[a]	265.9
Density at 20 °C (g/mL)[a]	2.0
Melting point (°C)[a]	252.1
Octanol-water partition coefficient (log K_{ow})[b]	2.88
Organic carbon normalized partition coefficient (K_{oc})[c]	5,000
Vapor pressure at 25 °C (torr)[b]	5.72×10^{-7}
Henry's law constant atm m^{-3} mol[b]	1.4×10^{-7}
Solubility (g/kg)[a]	0.81
Water (mg/L)	<10
Kerosene	20
Acetone	80
Xylene	

[a] Data from Tomlin (2000)
[b] CA DPR Risk Characterization Document (2005)
[c] Data from Waltz et al. (2002)

3 Chemodynamics

3.1 Soil

Chlorothalonil has the potential to strongly adsorb to soil and sediment, as indicated by its high K_{oc} constant. Adsorption isotherms on five clay minerals (montmorillonite, Na-bentonite, Ca-bentonite, allophone and kaolinate) and three soils, having an organic carbon content of 1.1, 1.4 and 5.2%, respectively, were investigated by Fushiwaki and Urano (2001). Based on the Freundlich isotherm equation, chlorothalonil had a lower adsorption capacity (k_f values ranged from 70 to 2,000) than did pentachlorothioanisole ($k_{f\,\mathrm{values}}$ ranged from 4,400 to 30,000). In addition, n-values ranged from 1.3 to 1.8 for each of the soils and clays (Fushiwaki and Urano 2001). Furthermore, the adsorption rate was not linked to organic carbon content; however, it may be influenced by inorganic matter.

Patakioutas and Albanis (2002) investigated the trend between adsorption and organic matter (OM) content. Soils of varying OM content and varying concentrations of chlorothalonil (0.1–0.5 mg/L) produced three adsorption isotherm shapes. As soil OM content increased, the shape of the isotherm changed from S- to L- to C-shape and k_f values respectively ranged from 96.3 to 1,356.9 (Patakioutas and Albanis 2002). The results of this study illustrated the strength of OM in immobilizing pesticides.

Chlorothalonil adsorbs most strongly to soils that have high organic matter, silt and clay. It has a low affinity to bind to sand, thus it is moderately to highly mobile in sandy soils (US EPA 1999). To investigate this, Gamble et al. (2000), analyzed the distribution of chlorothalonil among a quartz sand soil. The soil (Simcoe: 90–95% quartz sand) was placed in solution microcosms. After 14 days, 43.3% of the chlorothalonil remained in solution, 26.2% resided in the labile sorbed state and 30.5% existed as a bound residue. It is thought that the 5–10% non-quartz material was responsible for sorbing the measured bound residues (Gamble et al. 2000).

The half-life of chlorothalonil that had been applied to a low-humic sandy soil was 12 days; 45% of the parent compound had been transformed into one major metabolite hydroxychlorothalonil (van der Pas et al. 1999). Furthermore, movement of this metabolite through the soil was decreased from adsorption, although low concentrations were measured in groundwater (van der Pas et al. 1999). Wang et al. (2009) determined the half-lives for chlorthalonil on both non-sterilized and sterilized non-amended soil (containing sandy loam, sand and clay) to be 8.8 and 19 days, respectively.

To address the possibility of soil runoff, Potter et al. (2001) investigated degradation rates and soil surface residues from peanut plots (Tifton loamy sand) treated with seven successive chlorothalonil applications (1.25 kg/ha; 2-week intervals). Soil residues were highest following the second application, however concentrations decreased as plant canopies obstructed disposition. Half-lives were determined for both chlorothalonil ($t_{1/2}$ = <1–3.5 days) and its primary product 4-hydroxychlorothalonil ($t_{1/2}$ = 10–22 days); further breakdown products had half-lives 10–20 times longer than chlorothalonil (Potter et al. 2001). Waltz et al. (2002) also confirmed that the known metabolite hydroxychlorothalonil (HC) is more persistent in soil compared to its parent. In summary, chlorothalonil is regarded to remain bound to soil, primarily because it has low water solubility and a high Koc constant.

3.2 Water

Pesticides that are used on turf grasses and other vegetation pose a potential risk of leaching into groundwater. Wu et al. (2002) evaluated chlorthalonil's potential to leach and the distance it travels in soil. Because of its low water solubility, chlorothalonil displayed a negligible tendency to leach in soil, as evidenced by its retention in the upper 0.2 cm thatch layer in soil samples collected before, and 0, 2, 7, 15, 30, 61, 83, and 120 days following treatment (Wu et al. 2002). Armbrust (2001) measured leachate for both chlorothalonil and its degradate, hydroxylchlorothalonil (HC). Of 130 samples analyzed, HC was found in 87% of the samples, but chlorothalonil was detected in only one. Although HC is persistent in soil, the evidence indicates that it is rapidly photodegraded under aqueous conditions and has a half-life of 35 min; hence, HC should not pose a potential risk to surface water (Armbrust 2001).

The potential for chlorothalonil to run off of application sites was simulated by Haith and Rossi (2003). Mean annual runoff concentrations for golf course greens, in three U.S. cities (Boston, Philadelphia and Rochester) were determined to be 0.477, 0.699 and 0.372 mg/L, respectively, whereas for fairways, concentrations were 0.296, 0.450 and 0.256 mg/L, respectively (Haith and Rossi 2003). For both greens and fairways, these measured concentrations exceeded the aquatic 96-h LC_{50} values for both the rainbow trout and water flea. The use of chlorothalonil on peanut fields, particularly in U.S. regions that have increased rainfall, increases the potential to contaminate local streams and ponds. However, the presence of increased plant foliage may decrease leaching of this chemical, although the degree of foliar wash-off for chlorothalonil has not been determined (Potter et al. 2001).

3.3 Air

The rate of volatilization of chlorothalonil from water, dry and moist soil is low, as predicted by its having low vapor pressure and Henry's law constant values (Table 1). Because of the low vapor pressure, initial volatilization is slow and volatility loss continues over a longer time period (Leistra and Van den Berg 2007). In general, the volatilization of chlorothalonil can be regarded as negligible and does not represent a significant dissipation route.

Bedos et al. (2010) measured chlorothalonil levels in air shortly after the fungicide was applied to wheat (theoretical application dose of 880 g/ha; application volume of 150 L/ha) in May of 2006. Measurable air concentrations were recorded in the human breathing zone (0.68 m above the soil) following the application. A cumulated volatilization flux, after 31 h, was determined to be 5 g/ha, respectively, which represents an approx. loss of 0.6% of the theoretical application dose. Air concentrations decreased slightly over 6 days (from 28 $\mu g/m^3$ to 64 ng/m^3), and a volatilization flux of 17.5 g/ha was estimated for this compound (Bedos et al. 2010).

4 Environmental Degradation

4.1 Abiotic Processes

4.1.1 Hydrolysis

Chlorothalonil is stable to hydrolysis at pH 5 and 7 (Szalkowski and Stallard 1977; US EPA 1999). However, under basic conditions (pH 9), the compound degrades to form two products: 3-cyano-2,4,5,6-tetrachlorobenzamide and 4-hydroxyl-2,5,6-trichloroisophthalonitrile (Szalkowski and Stallard 1977). Kwon and Armbrust (2006) proposed that the pathway for chlorothalonil degradation in aquatic systems would proceed by reductive dechlorination, oxidative dechlorination/hydrolysis and base hydrolysis (Fig. 2). The US EPA (1999) reported a hydrolysis half-life value for chlorothalonil of 30–60 days.

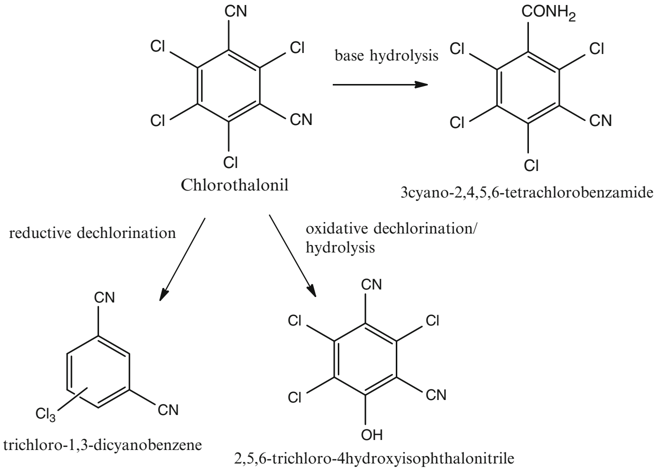

Fig. 2 Proposed aquatic degradation pathway for chlorothalonil (Adapted from Kwon and Armbrust 2006)

4.1.2 Photolysis

Aqueous dissolved concentrations of chlorothalonil absorb sunlight within the wavelength range of 300–340 nm, and direct photolysis represents a major degradation pathway for this fungicide (Leistra and Van Den Berg 2007). Chlorothalonil, exposed directly to light (300–400 nm) photolytically degraded more rapidly in natural waters ($DT_{50}=0.21$–0.76 days) than in a buffered aqueous system (pH 7; $DT_{50}=1.1$ days; Wallace et al. 2010). Monadjemi et al. (2011) investigated the photodegradation of chlorothalonil on a simulated plant surface, specifically using paraffin wax (irradiated at wavelengths between 300 and 800 nm). A field-extrapolated half-life of 5.3 days resulted, and suggested that chlorothalonil is susceptible to direct photolysis, in addition to surface penetration. In addition, these authors found the main degradation route was via reductive dechlorination (Monadjemi et al. 2011). Waltz et al. (2002) studied the photodegradation of hydroxychlorothalonil (HC), chlorothalonil's major hydrolytic metabolite. Results were that HC in the water samples exposed to simulated sunlight (via use of lamps) absorbed radiation, and this substance was photolyzed with a $t_{1/2}$ of 33–37 min).

Degradation of chlorothalonil via the Fenton reaction (Fe^{3+}/H_2O_2; Fig. 3) was effectively archived by Park et al. (2002). Half-lives were determined under dark ($t_{1/2}=77$ min) and UV irradiated conditions ($t_{1/2}=49.5$ min), and results indicate that breakdown was enhanced by increased ferric ion concentrations (dark $t_{1/2}=31.7$ min and UV $t_{1/2}=16.9$ min). This reaction proceeds by dechlorination of chlorothalonil.

Penuela and Barcelo (1998) investigated the influence of water quality and photosensitizers (TiO_2 and $FeCl_3$) on the degradation of chlorothalonil, by using a xenon arc lamp and natural sunlight. They found that the $t_{1/2}$ of chlorothalonil in deionized

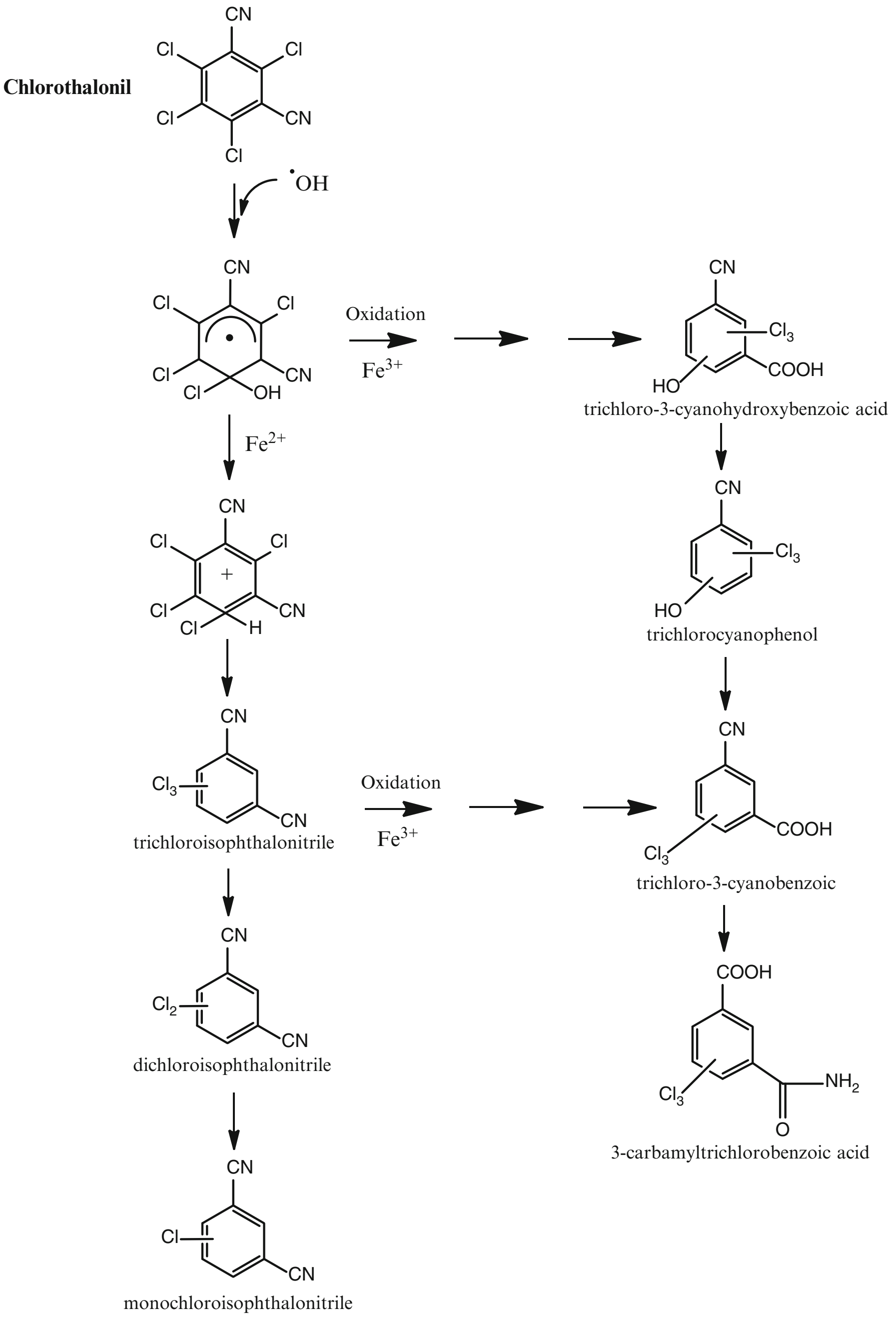

Fig. 3 Proposed breakdown pathway of chlorothalonil treated with Fenton reagent (Fe^{3+}/H_2O_2). (Adapted from Park et al. 2002)

water (101.17 h; sunlight) was longer than deionized water irradiated under a xenon lamp (36.86 h); groundwater irradiated with the lamp had a half-life of 0.71 h. Moreover, addition of the photosensitizers decreased half-lives as well; $FeCl_3$ was a better catalyst under lamp irradiated water ($t_{1/2} = 1.37$ h) than water irradiated by sunlight ($t_{1/2} = 4.24$ h). The results of this study demonstrated that degradation follows first-order kinetics in the presence of catalysts (Penuela and Barcelo 1998).

Studies by Sakkas et al. (2002) also showed that photolysis of chlorothalonil follows pseudo-first order kinetics. The photolytic degradation in waters from a river and a lake was determined to be more rapid (99% loss within 60 h) than in distilled or seawater (67 and 72% loss, respectively), when irradiated under both natural and simulated conditions. Major photoproducts (viz., chloro-1,3-dichlorobenzene, dichloro-1,3-dicyanobenzene, trichloro-1,3-dicyanobenzene and benzamide) were identified in this study (Sakkas et al. 2002). It is thought that the presence of dissolved organic matter (DOM) and other photosensitizers may have enhanced the rate of photodegradation. To investigation, studies which included photosensitizers indicated that increased concentrations of bicarbonate promoted degradation rates, whereas, degradation via carbonate radicals ($\cdot CO_3^-$) dominated under situations, in which degradation via the hydroxyl radical ($\cdot OH$) was minimal (Wallace et al. 2010). In summary, direct photolysis of chlorothalonil proceeds rapidly and is enhanced by the presence of photosensitizers.

4.2 Biotic Processes

Microbial digestion is thought to be the primary pathway by which chlorothalonil is degraded (US EPA 1999). Chen et al. (2001) studied the effects of microbes on fungicides in three soil types (Canfield silt-loam Luvisol; pH 6.3; unamended and amended with alfalfa leaves and wheat straw). They found chlorothalonil inhibits microbial activity in the treated soils. In unamended soil, enhanced mineralization and decreased nitrification rates occurred. Mori et al. (1996) evaluated the microbial degradation of chlorothalonil in unfertilized and fertilized (farmyard manure) soil. Microbial activity was enhanced in soil treated with a combination of chemical and farmyard fertilizer and degradation increased as soil pH reached neutrality. Incorporating manure in the soil stimulated the microbes, although they required additional carbon sources (Mori et al. 1996). Wang et al. (2011) studied chlorthalonil's anaerobic degradation in four paddy soils. In these studies, soil pH and total carbon content both highly affected the rate of biodegradation. Results indicate that chlorothalonil was more efficiently degraded under neutral pH (6.3–6.6) conditions and in soil containing 3–4% total carbon (Wang et al. 2011).

Motonaga et al. (1996) identified the gram-negative rod bacterium, TB 1, from chlorothalonil-treated soil. This bacterium transformed more than 75% of chlorothalonil present in the soil into 4-hydroxy-2,5,6-trichloroisophthalonitrile and chloride anion via hydrolysis, rather than via mineralization. Out of 50 identified chlorothalonil degrading bacteria, the TB 1 strain was the only one to produce the

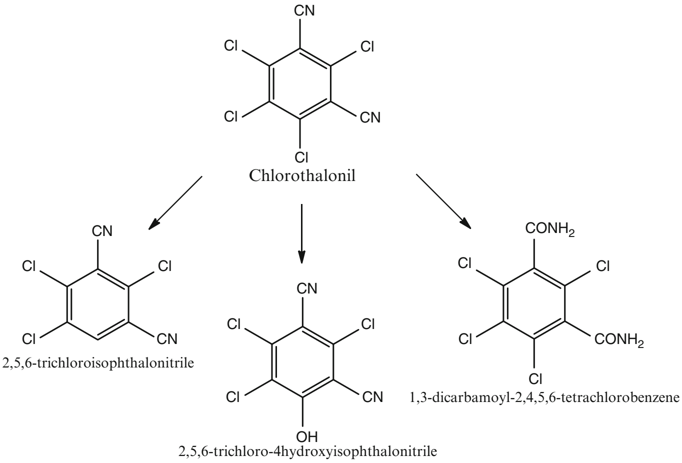

Fig. 4 Proposed microbial degradation pathways for chlorothalonil via dechlorination and hydroxylation (Adapted from Ukai et al. 2003)

hydroxylated metabolite (Motonaga et al. 1996). Zhang et al. (2007) observed the NS1 strain of *Bacillus cereus* to degrade chlorothalonil as a result of cometabolism, and carbon sources enhanced its degradation. Liang et al. (2010) isolated the bacterial strain CTN-11 (identified as an *Ochrobactrum* sp.) from chlorothalonil-contaminated soil. This strain degraded chlorothalonil to undetectable levels within 48 h when exposed to a temperature range of 20–40 °C and a pH from 6 to 9. Under anaerobic conditions, hydrolytic dechlorination occurred, producing the more stable hydroxy metabolite (Liang et al. 2010).

The influence of the chlorothalonil chlorine atoms on degradation was examined by Ukai et al. (2003). They found that chlorothalonil degradates appear to contain 3–4 chlorine atoms, and these degradates suppress soil degradation of the parent compound. The two major degradate products (Fig. 4) were 2,5,6-trichloro-4-hydroxyisophthalonitrile and 2,5,6-trichloroisophthalonitrile. Other degradation products were identified by Sato and Tanaka (1987). They also concluded that degradation occurred via dechlorination and partial substitution (Fig. 5). The possible degradation products for chlorthalonil are listed in Table 2.

5 Toxicology

5.1 *Mode of Action*

The fungicidal activity exhibited by chlorothalonil is attributed to the inactivation of cell sulfhydryl enzymes (Vincent and Sisler 1968; Sherrard et al. 2003). Gallagher et al. (1992) recorded a depletion of glutathione, resulting in the inhibition of

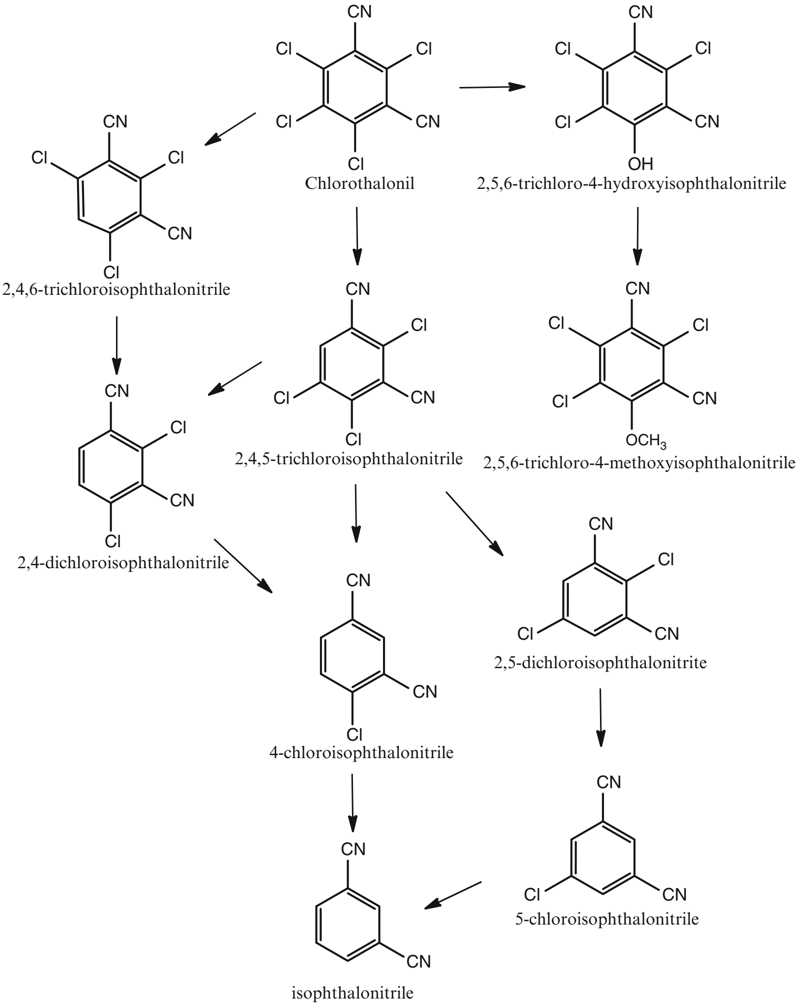

Fig. 5 Proposed soil degradation pathway for chlorothalonil (Adapted from Sato and Tanaka 1987)

Table 2 Possible microbial degradation products[a]

Compound name	Soil conditions	Metabolite
4-hydroxychlorothalonil	Aerobic	Major
Metylthiotrichloroisophtalonitrile	Aerobic	Major
3-carbamyl-2,4,5-trichlorobenzoic acid	Aerobic acidic	Major
3-cyano-2,3,4,5,6-tetrachlorobenzoamide	Aerobic acidic	Major
Trichloroisophtalonitrile	Aerobic	Minor
m-phthalonitrile	NA	Breakdown product

[a] Data from Carlo-Rojas et al. (2004)

Table 3 Toxicity (expressed as 48-h or 96-h LC_{50} values) of technical grade chlorothalonil to aquatic organisms

Aquatic organism	Scientific name	Concentration (μg/L)
Rainbow trout[a]	*Lepomis macrochirus*	10.5–76
Fathead minnow[a]	*Pimephales promelas*	23
Bluegill[a]	*Lepomis macrochirus*	51–84
Waterflea[a]	*Daphnia magna*	54–68
Pink Shrimp[b]	*Penaeus duorarum*	154

[a] Data from US EPA (2007)
[b] Data from US EPA (1999)

glucose oxidation in exposed channel catfish. A study, in which *Saccharomyces pastorianus* and *Neurospora crassa* were exposed to chlorothalonil confirmed that glucose oxidation was impaired and soluble thiol content was reduced from chlorothalonil treatment (Vincent and Sisler 1968). Tillman et al. (1973) concluded that the mechanism of chlorothalonil's toxic action resembles that of the trichoromethylsulfenyl fungicides. Although many studies have examined chlorothalonil's mode of action, chlorothalonil and other chloronitriles have been categorized as having multiple sites of action; resistance to the fungicide does not develop (FRAC 2013).

5.2 Aquatic Organisms

The potential for chlorothalonil to bioaccumulate in aquatic species is relatively low because it aggressively binds to soils. Yet, exposure from sediment-bound residues is possible. Although it is assumed that bioaccumulation will be minimal, chlorothalonil has been found to be highly toxic to many aquatic species. For example, it is highly toxic to fathead minnow (*Pimephales promelas*) and somewhat less toxic to *Daphnia magna* and pink shrimp (*Penaeus duorarum*; Table 3).

Early life-stages of the freshwater mussel, *L. siliquoidea*, were exposed to selected technical-grade pesticides. Chlorothalonil was more toxic to glochidia (48-h $EC_{50} = 0.04$ mg/L) than to juvenile mussels (96-h $EC_{50} = 0.28$ mg/L), and had higher toxicity than other pesticides such as atrazine and fipronil (Bringolf et al. 2007).

Larval and adult stages of the grass shrimp, *Palaemonetes pugio*, were exposed to a range of chlorothalonil concentrations, and thereafter exhibited increased toxicity with increasing temperature (25° vs. 35 °C) and salinity (20 ppt vs. 30 ppt; DeLorenzo et al. 2009). Furthermore, 96-h LC_{50} values for larvae were more variable among exposure conditions. Under standard and high salinity conditions 96-h LC_{50} values were 49.1 and 39.4 μg/L, respectively. In addition, 96-h LC_{50}s for adult shrimp were 156 and 116 μg/L, respectively, under the same conditions. Generally, results show that toxicity increased as exposure length increased from 24 to 96 h (DeLorenzo et al. 2009).

Laboratory and field bioassays were conducted to determine the potential hazard chlorothalonil poses towards aquatic fauna. Rainbow trout (96-h $LC_{50}=69$ µg/L) was more sensitive than blue mussels (96-h $LC_{50}=5.94$ mg/L) and the water flea (48-h $EC_{50}=97$ µg/L), when exposed under laboratory conditions (Ernst et al. 1991). However, caged organisms, exposed under field conditions (aerially treated pond), were less sensitive, and exposed rainbow trout did not suffer any mortality. Ernst et al. (1991) concluded that environmental factors such as, microbial degradation, dilution and adsorption to suspended matter reduced chlorothalonil's toxicity.

The toxicity and site of chlorothalonil accumulation was investigated by Davies and White (1985). Four fish species (*Salmo gairdneri*, *Galaxias maculates*, *G. truttaceus and G. auratus*) were exposed under flow-through conditions (≤0.6 mg/L, 13–16 °C, $[O_2]=8$ mg/L), and exhibited increased toxicity; 96-h LC_{50} values ranged from 16.3 to 29.2 µg/L. In addition, using radiotracers (10 µg/L; 96-h) Davies and White (1985) found that ^{14}C-CN labelled chlorothalonil to be highly accumulated within the gall bladder and hind gut of each species.

5.3 Mammals

Groups of pregnant female mice were orally administered chlorothalonil at doses ranging from 0 to 600 mg/kg/day. Although the treatments produced no mortality, signs of toxicity, such as weakness and reduced activity did occur at the 400 and 600 mg/kg/day dose levels (Farag et al. 2006). Also observed at these concentrations was significant embryo lethality and a reduction in live fetuses (Farag et al. 2006). According to the US EPA (1999), chlorothalonil is considered to be practically non-toxic to small mammals, based on having a measured rat LD_{50} of >10,000 mg/kg. However, a known degradate, SDS-3701 is much more acutely toxic than the parent compound (viz., possessing an acute female rat LD_{50} of 242 mg/kg). This degradate possesses high chronic oral toxicity towards pregnant rabbits and has a developmental no observable effect level (NOEL) of 33 mg/L, compared to chlorothalonil itself (NOEL = 330 mg/L; US EPA 1999).

Mozzachio et al. (2008) investigated the incidence of pesticide applicators that were both exposed to chlorothalonil and were diagnosed with cancer. They found no direct link to applicators with colon, lung or prostate cancers; approximately 3,600 applicators used chlorothalonil an average of 3.5 days per year. Although animal studies have provided sufficient evidence to classify chlorthalonil as a probable carcinogen, it is not known if it is a human carcinogen or not (Mozzachio et al. 2008).

5.4 Birds

Chlorothalonil is acutely non-toxic to birds when administered orally; LD_{50} values range from >2,000 mg/kg-bwt for Japanese quail to >10,000 mg/kg-bwt for both mallard and northern bobwhite quail (US EPA 2007). Reproductive effects caused by dietary exposure have been investigated in bobwhite quail. At the highest dose of 10,000 mg/kg, reproductive impairment occurred and caused effects on general health and hatching survival. Additional studies with Mallard ducks were conducted and decreased egg production was observed (WHO 1996). Although chlorothalonil's toxicity is low to birds, similar to what occurs in mammals, its degradate SDS-3701 is much more toxic. Avian studies have shown that Mallard ducks are the most sensitive bird species to the toxicity of SDS-3701, which has an acute LD_{50} of 158 mg/kg (US EPA 2007).

5.5 Plants

Chlorothalonil residues that appear on foliar surfaces after application to various crops have been investigated. Putman et al. (2003) used cranberries to evaluate dislodgeable foliar and fruit residues following application of chlorothalonil with and without an adjuvant. Two applications were made: one at 20% cranberry blossom bloom and another at 80% bloom (14 days later). Measured dislodgeable foliar residue concentrations were found to increase with the use of an adjuvant; the estimated half-life for chlorothalonil with and without adjuvant was determined to be 12 and 13 days, respectively. Furthermore, the cranberries were harvested 76 days post-application, and showed fruit residues of chlorothalonil and its metabolites 4-hydroxy-2,5,6-trichloroisophthalonitrile and 1,3-dicarbamoyl-2,4,5,6-tetrachlorobenzene (Putnam et al. 2003).

Not only is chlorothalonil present on foliar surfaces, but it can also cause oxidative stress if taken up by plants. An experiment on upland rice (*Oryza sativa*) was conducted to determine the impact of chlorothalonil application on the plant with or without the presence of arbuscular mycorrhizal fungus (AMF; *Glomus mosseae*). Under both conditions, plant growth was significantly inhibited and the presence of fungi decreased phosphorous concentrations within plant shoots (Zhang et al. 2006). Further investigation showed chlorothalonil to induce oxidative stress, and affect catalase, ascorbic peroxidase, and peroxidase activity (Zhang et al. 2006).

5.6 Fungi

The effectiveness of chlorothalonil as a fungicide has been studied on vesicular arbuscular mycorrhizal (VAM) *Glomus aggregatum* fungi. Chlorothalonil was mixed into Wahiawa silty clay soil (at concentrations ranging from 0 to 200 mg ai/kg soil), and the applied levels decreased VAM colonization with increasing concentrations (Habte et al. 1992). In addition, Habte et al. (1992) noted that chlorothalonil toxicity persisted for 12.5 weeks after initial soil application. Exposure of the VAM *G. intraradices* fungi, at 0.13 mg/L, reduced overall VAM formation

(Wan et al. 1998). They also found the concentration at which growth and development was inhibited by 50% to be 0.05 ± 0.01 mg/L for extraradical mycelial growth and 0.04 ± 0.009 mg/L, respectively, following a 14 days inoculation.

Latteur and Jansen (2002) investigated the ability of 20 fungicides to affect the infectivity of conidia of the fungus *E. neoaphidis*- an insect pathogen. Chlorothalonil (1,250 g ai/ha dose), and four other fungicides inhibited infectivity and prevented mortality to aphids, following their exposure to the fungus. Mueller et al. (2005) observed that chlorothalonil, and 12 other fungicides eliminated the germination of 6 rust fungi (*Puccinia hemerocallidis*, *P. iridis*, *P. menthae*, *P. oxalis*, *P. pelargonii-zonalis*, *and Pucciniastrum vaccinii*) within 24 h, when they were exposed during and after fungicide application; chlorothalonil completely inhibited spore germination within 8 h.

6 Summary

Chlorothalonil is a broad spectrum, non systemic, organochlorine pesticide that was first registered in 1966 for turfgrasses, and later for several food crops. Chlorthalonil has both a low Henry's law constant and vapor pressure, and hence, volatilization losses are limited. Although, chlorothalonil's water solubility is low, studies have shown it to be highly toxic to aquatic species. Mammalian toxicity (to rats and mice) is moderate, and produces adverse effects such as, tumors, eye irritation and weakness. Although, there is no indication that chlorothalonil is a human carcinogen, there is sufficient evidence from animal studies to classify it as a probable carcinogen.

Chlorothalonil has a relatively low water solubility and is stable to hydrolysis. However, hydrolysis under basic conditions may occur and is considered to be a minor dissipation pathway. As a result of its high soil adsorption coefficient this fungicide strongly sorbs to soil and sediment. Therefore, groundwater contamination is minimal. Degradation via direct aqueous or foliar photolysis represents a major dissipation pathway for this molecule, and the photolysis rate is enhanced by natural photosensitizers such as dissolved organic matter or nitrate. In addition to photolysis, transformation by aerobic and anaerobic microbes is also a major degradation pathway. Under anaerobic conditions, hydrolytic dechlorination produces the stable metabolite 4-hydroxy-2,5,6-trichloroisophthalonitrile. Chlorothalonil is more efficiently degraded under neutral pH conditions and in soil containing a low carbon content.

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