CHAPTER-1

Tebuconazole- Physical-Chemical Properties, Environmental Fate and Methods of Analysis in different matrices

The agricultural sector dominates the economic scenario of our country. The increasing global population and higher demand of food led to intensive and advanced agricultural practices as well as proper utilization of natural resources. Among the key inputs used in agricultural technologies, pest management plays a vital role to get assured crop protection in order to achieve our increased demand for food grains. Nowadays, huge amounts of fungicides are used primarily to control spoilage of crops as a result of fungal attack to increase the quantity and quality of the agricultural products (Wada A.C., 2003; Li H., et al., 2008). However, the fungicides often contaminate the environment, as well as cause public health problems due to their high toxicity and long persistence (Ricardo C. et al., 2006; Canal-Raffin M., et al., 2008; Fai P. B., et al., 2009). Pesticide residue may constitute a significant source of contamination of air, soil and water which could thus become a threat to the plant and animal community of the ecosystem (Khan S.U., 1980). Consequently, there has been a great concern about the effects of pesticides on environment and humans by retention (sorption), transportation (dissipation/degradation) and leaching from surface to ground water. Pesticides reach the soil surface mainly when directly used on soil or sprayed on the crops.

Triazole fungicides are one of the top ten classes of currently used pesticides and have higher consumption as compared to other fungicides available worldwide (Fenner K.et al., 2013). Triazole fungicides exhibit their antifungal activity by inhibiting the biosynthesis of fungal ergosterol (Song, Z. et al., 2007).Tebuconazole (TEB) is a common triazole fungicide that has been extensively used in grains, vegetables and fruits for the control of plant pathogenic fungi (Zhou J.et al., 2016). Consequently, traces of this compound are present in plant tissues, as well as in soil. Tebuconazole was developed by Bayer AG, South Africa in 1988. It is also known by others names, such as fenetrazole, terbuconazole, terbutrazole and ethyltriazole. Tebuconazole is a systemic fungicide with protective, curative, and eradicant action. It is rapidly absorbed into the vegetative parts of the plant, with translocation principally acropetally (Tomlin CDS, 2009). The many types of commercial formulation are available in market. In these types of formulation, Folicur 25.9% EC and 250 EW were first time registered in India in 2007 by Bayer Crop Science for controlling soil-borne and foliar diseases in grave, groundnut, cereal crops and garlic (Bayer crop science, India).

1.1 General Information

Common name : Tebucomazole

Trade Name (Bayer-Crop Science): Folicur, Raxil, Elite, Horizon, Lynx, Matador

Uses (Pesticide types) : Fungicide, Plant growth regulatory

Chemical group : Triazole

Chemical Class : Hetrocyclic

CAS RN : 107534-96-3

CAS Name :

(±)-α-[2-(4-Chlorophenyl) ethyl]-α-(1,1-dimethylethyl)-1*H*, 1, 2, 4- triazole-1-ethanol

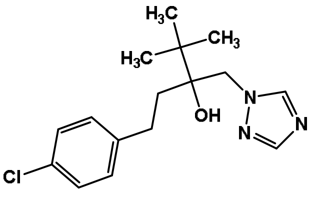
IUPAC Name :

(RS) - 1-p-Chlorophenyl- 4, 4-dimethyl-3-(1H, 1,2, 4-triazol-1-ylmethyl) pentan- 3-ol

Molecular Formula : $C_{16}H_{22}ClN_3O$

Molecular Weight : 307.82 g/mole

Structure :



1.2 Physical and chemical properties

Physical Sate : Colorless crystals powder

Colour : Colourless crystals

Odour : Odourless

Melting point : 105 ºC

Vapour pressure : 1.7 x 10^{-3} mPa (20 ºC as per OECD 104)

Henry's Law constant : 1 x 10^{-5} m^3/mole at 20 deg ºC

Specific gravity/ Density : 1.25 (26 ºC)

Partition coefficient : Kow logP = 3.7 (20 ºC)

Solubility : **In Water** 36 mg/l (pH 5-9, 20 ºC)

Dichloromethane > 200 g/l

Iso-propanol, toluene 50-100 g/l

Hexane < 0.1 g/l all at 20 ºC (Tomlin CDS, 2009)

As per U.S. EPA, cancer classification: Tebuconazole classified as group C category, that's possible to human carcinogen (U.S. EPA, Cancer annual report, 2015). Pesticide residues are now being detected in soils and waters in different areas around the world (Rabiet M., *et al.,* 2010; Herrero-Hernández E.*et al.,* 2011; Pose-Juan E. *et al.,* 2014). Consequently, soil and water contamination is a growing concern, as pesticide compounds are toxic and cause health and environmental problems. Legislations around the world advise to introduce specific measures to prevent soil contamination and limit the transport of contaminants through water resources, especially groundwater to reduce the risks and impacts of pesticide uses. Pesticide application and management in agriculture may cause the diffuse and point pollution of soil and water bodies. Diffuse sources of soil pollution include spray drift, run-off, leaching, etc., whereas point sources include farmyard activities, direct contamination, and overspray (EC, 2009; Carter, A., 2000; Balderacchi M.*et al.,* 2013).

1.3 Dissipation

The fate of fungicides in soil is governed by processes that affect their persistence, such as chemical and microbial degradation, and processes that affect mobility, which involve adsorption, diffusion, and absorption by plants, dissipation by runoff, wind erosion, volatilization, leaching and assimilation by microorganisms. The most common quantitative measurement of the sorption of organic pollutants from aqueous solution is the K_{OC}. Thus, compounds with higher K_{OC} values will be less mobile than those with lower values (Navarro S. et al., 2009).

The Henry's Law constant also indicates that tebuconazole is expected to nonvolatile from moist soil and water surfaces. Tebuconazole is not also expected to volatilize from dry soil surfaces based upon its vapor pressure (Lyman W.J., 1990).

The adsorption and degradation as well as understanding dissipation rate of the pesticides are the most important parameter in assessing their fate in the environment (Boesten J.J.T.I., et, al, 1991). Further, the adsorption-desorption studies are useful for generating essential information on the, transformation and uptake by organisms (Russell M.H., 1995 and Guth J.A., et al., 1977); leaching through the soil profile (Helling C.S., 1971); volatility from soil (Burkhard N. et at., 1981); and run-off from land surfaces into natural waters. Adsorption data can also be used for comparative and modelling purpose (Green R.E., et al., 1990).The distribution of a chemical between soil and aqueous phases is a complex process depending on different factors as the chemical nature of the substance (Sabljic A., 1984), the characteristics of the soil (Paya-Perez A., et al., 1989), and climatic factors such as rainfall, temperature, sunlight and wind.

Adsorption is the primary process of how the soil retains a pesticide and is defined as the accumulation of a pesticide on the soil particle surfaces. Pesticide adsorption on soil depends on both the chemical properties of the pesticide (i.e., water solubility, polarity) and properties of the soil (i.e., organic matter and clay contents, pH, surface charge characteristics, permeability etc.). The degree of adsorption is described by an adsorption distribution coefficient (K_d), which is mathematically defined as the amount of pesticide in soil solution divided by the amount adsorbed to the soil. For most pesticides, organic matter is the most important soil property controlling the degree of adsorption.

Tebuconazole is highly adsorbed by soils and mainly concentrated in the topsoil layer. Tebuconazole degraded slowly in soil in laboratory studies, but under field conditions the compound is degraded much more rapidly (EFSA, 2008). Its degradation is influenced by the soil organic carbon (OC) content because it has high affinity for soil organic matter (OM). Low OC content contributes to decreased adsorption and therefore encourages the microbial degradation of the fungicide. Several authors have studied the degradation of this fungicide in soils under laboratory conditions. (Bending G.D. et al., 2007; Potter T. L.et al., 2005; Strickland T.C., 2004; White P.M. et al., 2010). But the dissipation of tebuconazole under field conditions has scarcely been studied and no published data are currently available on the extent and rate at which this compound degrades in soil amended with organic residues (Guo X.L.et al., 2010; Laabs V. et al., 2000). Only few studies have examined the influence of different organic amendments on pesticide dissipation (Cabrera A. et al., 2009; Dolaptsoglou C. et al., 2009).

The rate at which a chemical dissipates is expressed as the half-life. The half-life of a pesticide depends on soil types, its formulation, and environmental conditions (e.g., temperature, moisture). Therefore, to assess of its behavior in environment, the dissipation study is performed in a range of soils (Bromilow R., 2003). Other processes that influence the fate of the chemical include plant uptake, soil sorption, leaching, and volatilization. If pesticides move off-site (e.g., wind drift, runoff, leaching), they are considered to be pollutants. The potential for pesticides to move off-site depends on the properties of the pesticide, soil properties, rate and method of application, frequency and timing of rainfall or irrigation, and depth to ground water. Hence it is prudent to study the fate of pesticides in soils where pesticides are to be applied on crops. Organic residues are commonly added to soil through agricultural practices. Pesticides are frequently applied jointly with organic amendments or sequentially during the crop growing season. This practice may give rise to a potential interaction between pesticide and amendment, and the environmental fate and behavior of pesticides in soil can be modified (Bricen˜o G. et al., 2007). Amendments may increase pesticide persistence in the soil, which has the potential to increase runoff and leaching risks (Herrero-Hernández, E. et al. 2011). Some studies have suggested that the addition of amendments to soil might also lead to an increase in pesticide adsorption (Dolaptsoglou C. et al., 2009). Most of the laboratory research studies investigated the effects of organic amendments on the adsorption, mobility and degradation of pesticides in soils (Kandian N. et al., 2008; Marı´n-Benito J.M. et al., 2009a; Marı´n-Benito J.M., 2009b; Wang H., et al., 2009). Beulke S. et al. studied whether the degradation of pesticides in simple laboratory system differed from that in the field, and how some of the simplifications inherent to laboratory studies present serious shortcomings (Beulke S. et al., 2005). Some authors have indicated that the extension of laboratory-derived kinetic data to field settings should be addressed with caution (Potter T. L.et al., 2005).

Physicochemical methods to immobilize pesticides in vulnerable soils are currently being developed to prevent water contamination. Some of these methods include the use of different organic residues to modify soils, as their high organic matter (OM) content could limit the transport of pesticides from soil to groundwater and/or facilitate their dissipation, avoiding the diffuse or point pollution of waters due to the intensive use of these compounds (Rodríguez-Cruz M.S. et al., 2012; Álvarez-Martín A. et al., 2016).

1.4 Pesticides transport in aqueous systems

Since tebuconazole is persistent in soils and presents low to moderate mobility, it poses a low risk of groundwater contamination (EFSA, 2008). However, tebuconazole has been detected in streams, wastewaters and lakes at concentrations of up to 9.1 mg $L^{-1.}$ (Berenzen N., et al., 2005; Kahle M. et al., 2008). Which exceeds the EU's limit of 0.1 mg L^{-1}, and hence the fungicide poses a risk of runoff into river basins and streams. The result of adsorption-desorption studies of tebuconazole indicates a low mobility of the compound. Lack of leaching and a strong sorptivity to soil particles makes groundwater contamination unlikely, except in accidental spill or direct overspray situations. However, precaution must be taken to avoid contamination of water or drainage system (Jamet P. et al., 1992, Kordell W. et al, 1993a, Xu F. et al, 1999) with tebuconazole.

As a result of massive global consumption (Sabik H.et al., 2000) of pesticides, the pesticides and their degradation products spread through the environment and can contaminate water resources (Caracciolo A. B., et al., 2010). Poorly managed agricultural operations can lead to contamination of surface and ground waters by these agrochemical molecules (Kolpin D. W., et al., 1998; Gunningham N.et al., 2005). Pesticide residues may reach the aquatic environment through nonpoint and point pollution sources by direct run-off or leaching of these compounds or by careless disposal of empty containers or the washing of equipment after their application. Proximity of crop fields to surface waters, water body characteristics (surface area, depth and flow), and climatic conditions (temperature, humidity, wind and precipitation) of each particular region are factors that affecting surface water contamination (Kreuger J., 1998; Neumann M. et al., 2002; Tesfamichael A.A. and Kaluarachchi J.J., 2006). The mobility of pesticides in soil and hence their transfer to other environmental compartments, depends on variety of complex dynamic physical, chemical and biological processes, including sorption–desorption, volatilization, chemical and biological degradation, uptake by plants, runoff and leaching (Vryzas Z., et al., 2009). It is also governed by the physicochemical characteristics of the compounds (solubility in water, their capacity to be retained by soil components and their degradation rate), the properties of the medium in which they are applied, their abiotic and biotic degradation (Caracciolo A. B., et al., 2010) and other external factors, such as local rainfall and wind patterns or the topology of the area (Martínez R. C., et al., 2000; Arias-Estévez M. et al., 2008).

Sorption as already dicussed plays a fundamental role in the advective–dispersive transport dynamics, persistence, transformation and bioaccumulation of pesticides (De Jonge R.J. et al., 1996). Furthermore, many pesticides can persist for long periods in an ecosystem. Organochlorine insecticides, for instance, were detectable in surface waters 20 years after their use and hence have been banned (Larson S. J. et al., 1997). Further once a persistent pesticide has entered the food chain, it can undergo ‘‘biomagnification’’, i.e., accumulation in the body tissues of organisms, where it may reach concentrations many times higher than in the surrounding environment. Information on the actual levels of pesticides into the environment is fundamental for proper risk assessment and the rational design of risk reduction measures. An estimated bioconcentration factor (BCF) of 140 was calculated for tebuconazole (TOXNET, Tebuconazole) using a log Kow of 3.7. According to a classification scheme (Franke C. et al, 1994), this BCF suggests that the potential of tebuconazole for bioconcentration in aquatic organisms is high (TOXNET, Tebuconazole) provided the compound is not metabolized by the organism**.** Tebuconazole is not expected to undergo hydrolysis in the environment due to the lack of functional groups that hydrolyze under environmental conditions (Meylan W. M. et al, 1999) and it has been shown to be stable to hydrolysis (Tomlin CDS, 2009).

This uptake of pesticides into watercourses is now a topic of considerable environmental interest due to the increasing number of compounds detected in water and it has required establishing of strict directives (Palma P., et al., 2009). Surface water contamination may have ecotoxicological effects for aquatic flora and fauna. The presence of pesticides in water intended for human consumption is linked to high treatment costs, possible toxicological incidences and prohibition of water use (Quintana J. et al., 2001; Claver A., et al., 2006; Donald D. B. et al., 2007).

Based on a classification scheme (Swann R.L. et al, 1983), the K_{oc} values of tebuconazole is ranging from 470-6000 (Kordell W. et al, 1993a, Xu F. *et al.*, 1999 and Jamet P. *et al.*, 1992) and it indicates moderate to no mobility in soil and expected to adsorb to suspended solids and sediment (TOXNET, Tebuconazole). Volatilization from water surfaces is not expected (Tomlin CDS, 2009) based upon Henry's Law constant of 1×10^{-5} m^3/mole at 20 deg °C.

1.5 Methods of Analysis

The most widely used detection techniques for the determination of pesticides residues from soil, water, vegetables, fruits and many others biological matrices are mass spectrometry combined with gas and/or liquid chromatography. A variety of extraction techniques have been employed over the years to determine pesticides and their degradation products in the matrices, including liquid–liquid extraction (LLE) (Sabik H., et al., 1997), solid-phase extraction (SPE) (Sabik H., et al., 1995 and Sabik, H., 1998), solid-phase microextraction (SPME) (Choudhury T. K., et al., 1996 and. Boyd-Boland A.A., et al., 1996), semi-permeable membrane device (SPMD) (Ellis G.S. et al., 1995 and Huckins J.N. et al., 1993), supercritical fluid extraction (Papilloud S. et al., 1996), QuEChERS and ultrasound assisted extraction (UAE). The most commonly used solvents for extraction are ethyl acetate, acetonitrile, methanol, acetone, n-hexane and dichloromethane. The UAE is an alternative extraction technique for common Soxhlet, QuEChERS (quick, easy, cheap, effective, rugged and safe), SPE and shaking flask extraction (Aydin M. E. et al., 2006, Tor A. et al., 2006 and Tor A. et al., 2006a) for pesticides residues from different matrices.

A number of analytical methods have been published for extraction, clean up and determination of fungicides tebuconazole and its metabolites from different matrices. The tebuconazole residues in plant material, water and soil samples were analyzed using GC-MS method by Lee P. W. et al. The recoveries of tebuconazole in plant materials at fortified range from 0.01–7.0 mg kg^{-1} were 78 - 116%. The limit of detection (LOD) based on control interferences in matrices were ranged from 0.001 - 0.01 mg kg^{-1}. The limit of quantification (LOQ) based on recoveries was 0.01 mg kg^{-1}. The averaged recoveries in the soil were 96% at 0.1 mg kg^{-1} and 99% at 0.01 mg kg^{-1} spiked concentration levels. The instrumental response was linear over the range of concentration 0.01–1 mg kg^{-1}. The LOD and LOQ were established at 0.01 mg kg^{-1}. The recoveries in water at fortification levels 0.5 and 5 µg L^{-1} ranged from 92 - 113% and the LOQ of the method was 0.5 µg L^{-1} (Lee P. W., 2003). Ionara R. *et al.* analysed the tebuconazole residues in soya products. The residues were extracted by acetonitrile and acetone. The residues were analysed by LC-MS/MS. The determination limit of tebuconazole was 100 µg kg^{-1} (Ionara R. *et al.*, 2009). Caldas S. S.et al. applied microextraction technique using acetonitrile as the dispersive solvent and carbon tetrachloride as the extraction solvent to extract and pre-concentrate different classes of pesticides (carbofuran, clomazone and tebuconazole) in aqueous samples. The recoveries of the pesticides in the spiked water ranged from 62.7 - 120.0% and the LOQ of the method was reported to be 0.02 µgL^{-1} (Caldas S. S. et al., 2010). Jyot G. et al used gas chromatography with nitrogen phosphorous detector (GC-NPD) for quantification of trifloxystrobin and tebuconazole residues in grapes. The limit of quantification for trifloxystrobin and tebuconazole by aoptingthe method was 0.01 and 0.02 mg/kg respectively (Jyot G., et al., 2010). Ultrasonic extraction (UAE), followed by solid-phase extraction (SPE) was used to remove co-extractives. SPE procedures were performed on PSA (primary-secondary amine) cartridges (500 mg, 3 ml), the analytes being eluted with n-hexane–acetone (9:1 v/v, 2 ml). Finally the capillary gas chromatography coupled with nitrogen phosphorus detection (GC–NPD) was used for determination of hexaconazole, myclobutanil, and tebuconazole, in apples and soil. Recovery of method in apple and soil samples were ranged from 94.5 - 107.3% with relative standard deviations (RSDs) < 9.7% at the three spike levels (0.01, 0.1, and 0.5 mgkg^{-1}). Limits of quantification of the method for apple and soil were 0.01mgkg^{-1} (Deng Z., et al., 2010). Tebuconazole, trifloxystrobin and its metabolite trifloxystrobin acid were extracted with acetonitrile from five fruit and vegetable using QuEChERS procedure and subsequently cleaned up using primary secondary amine (PSA) or octadecylsilane (C18) as sorbent prior to GC analysis. The residues were analyzed using gas chromatography coupled with nitrogen-phosphorus selective detector (GC-NPD) and ion trap mass spectrometry (GC-IT-MS). The limit of detection (LOD) and limit of quantification (LOQ) of the methods were 0.4-7 and 1.2-20 µg/kg with GC-IT-MS/MS and GC-NPD respectively (Liu X. et al., 2011). Chiranjit K. et al developed Liquid Chromatography-Mass Spectrometry (LC-MS/MS) technique for quantitative analysis of the fungicide residue in groundnut and paddy. The average recovery of tebuconazole in different species of groundnut was between 86.33 - 91.87%. But in case of paddy, the average recovery ranged between 86.40 - 90.86% (Chiranjit K. et al., 2011). Li J et al. also analyzed eleven triazole fungicides from fruits. The samples were extracted from fruits with acetonitrile and cleaned-up using solid phase extraction (SPE) on a Carbon/NH_2 cartridge. The GC-MS/MS in the multiple reaction monitoring (MRM) modes was used for analysis of residues from matrices. The calibration curves showed good linearity in the range of concentration 10 - 500 µg/l. The correlation coefficients were > 0. 994. The average recoveries of the eleven fungicides in fruits at spiked levels of 10, 50, 100 and 250 µg/kg were between 82.6 - 117.1% and the relative standard deviations (RSD) was less than 10%. The limits of quantification (S/N = 10) were 0.8 µg/kg and 3.4 µg/kg (Li J. et al., 2012). Rao N. et al. used matrix solid-phase dispersion (MSPD), together with high performance liquid chromatographic method for determination of triazole fungicide residues (Tetraconazole, Tebuconazole, Hexaconazole and Difenconazole) in papaya. Average recoveries (using each concentration six replicates) of the method were in the ranged 90-98%, with RSD less than 2% at concentration levels 0.03 and 0.3 µg/mL. The limit of detection (LOD) and limit of quantification (LOQ) of the method was 0.01 µg/mL and 0.03 µg/mL respectively (Rao N., et al., 2012). Matisová E. et al. used capillary GC coupled with mass spectrometry for determination of tebuconazole residues in waters samples. The residues of tebuconazole in ground water were determined at concentration levels of 0.0258–0.8947 µg/L using this method (Matisová E., et al., 2012). Yunrui H. et al. reported a micro-solid phase extraction (µSPE) method by utilizing TiO_2 nanotube array for determination of fungicides thiram, metalaxyl, diethofencarb, myclobutanil and tebuconazole residues in environmental water samples prior to high performance liquid chromatography (HPLC). The experimental results indicated that TiO_2 nanotube arrays demonstrated excellent merits on the preconcentration of fungicides, and excellent linear relationship between peak area and the concentration of fungicides were obtained in the range of 0.1–50 µg L^{-1}. The detection limits for the fungicides were in the range of 0.016–0.086 µg L^{-1}($\boldsymbol{S}/\boldsymbol{N} = 3$). The spiked recoveries were in the range of 73.9–114% (Yunrui H. et al., 2013). Zhang Q. et al. used gas chromatography-tandem mass spectrometry (GC-MS/MS) for determination of propargite, tebuconazole and bromopropylate residues in green jujubes. The sample was extracted with acetonitrile and the organic phase was separated from water phase by adding NaCl. The extract was further purified on a carbon/ NH_2 cartridge with elution solvents of acetonitrile/toluene (3:1, v/v). Finally, the target analytes were analyzed by capillary gas chromatographic [column, 5MS (30 m x 0. 25 mm x 0. 25 µm)] combined with tandem mass spectrometry (GC-MS/MS). The average recoveries of the pesticides ranged from 75.8 - 103.6% with RSD 1.7 - 9.3% at spiking levels 0.01- 0.50 mg/kg (n= 5). The calibration curves showed good linearity in the range of 0.01-0.50 mg/kg, with a correlation coefficient of 0.99. The limits of quantification (LOQs) were 0.01 mg/kg for propargite, tebuconazole and bromopropylate in Taiwan green jujubes (Zhang Q. et al., 2014). Mercadante R. et al. determined tebuconazole in alcohol (TEC-OH) and tebuconazole acid (TEB-COOH) metabolites in human urine using liquid chromatography coupled with a triple quadrupole mass spectrometer equipped with an electron spray source. The accuracy and the limit of quantification (LOQ) of the method for the tebuconazole metabolites were 98-103%, and 0.3µg/L (Mercadante R. et al., 2014).

Based on the above discussion and in the absence of in-depth studies, particularly in tropical soil region as Gujarat state, the plan of present research work has been designed to evaluate the adsorption/desorption pattern of a triazole group fungicide tebuconazole in five different types of tropical region agricultural soil taken from Gujarat and Maharastra states in India. In these soils, one soil was amended with dead plats leaves to increase the soil organic carbon contents. All soils were having varying range of organic carbon, clay, texture, and pH. Simultaneously the research work was also carried out for understanding the degradation behavior of tebuconazole in three types of soil under biotic and abiotic laboratory condition**.** It is most important process used to predict the fate of pesticides in soils (Boesten, J.J.T.I. et al., 1991; Hasan S. and Ahmed G.A., 2014). Therefore, the present study has also been designed to investigate the biotic and abiotic degradation behavior of tebuconazole in three types of Indian soil and water at pH 4, 7 and 9 under sterile condition.

The objectives of the thesis are

1. Adsorption/desorption study of tebuconazole in soil using batch equilibration method.

2. Development and validation the Ultrasound-assisted extraction coupled with GC-NPD method and the use of the method for trace level determination of tebuconazole residue in soil, water and a model crop (Garlic).

3. Dissipation study of tebuconazole in soil under biotic and abiotic condition

4. Abiotic degradation/hydrolysis study of tebuconazole in aqueous medium at pH 4, 7 and 9.

1.6 References

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