Review Article

A comprehensive review on the effect of sugarcane trash ash on the sorption, degradation and leaching of atrazine and fipronil in agricultural soils

Abstract

Burning of surplus sugarcane trash for land clearing is a common practice followed by the farmers. The ashes generated from sugarcane trash burning will results in change in the physico-chemical properties of soils due to their alkaline nature. Ashes, due to presence of unburnt carbon, have exhibited potential to adsorb pesticides; therefore, might affect degradation, leaching and sorption of pesticides. Atrazine (Atz) and fipronil are commonly used pesticides in sugarcane. Due to their extensive application and their potential eco-toxicological effects, the global scientific interest focusing on the research of the environmental fate and behavior of pesticides after their entrance in the environmental matrices is undiminished. A comprehensive review on the effect of sugarcane trash ash on the sorption, degradation and leaching of atrazine (Atz) and fipronil in agricultural soils is so far not available. The objective of this review is thus to systematically summarize the impact of sugarcane trash ash on fate of atrazine (Atz) and fipronil in agricultural soils. Notably, the mechanisms and factors influencing were also extensively elucidated. This review helps better understand the effects of sugarcane trash ash on sorption, leaching, and degradation of atrazine (Atz) and fipronil in agricultural soils.

KEYWORDS: Atrazine (Atz) fate, Fipronil fate, Atrazine (Atz) and Fipronil Adsorption, Atrazine (Atz) and Fipronil Degradation, Atrazine (Atz) and Fipronil Leaching

Introduction

Soil acts as sink for the pesticides applied on crops as a greater part of pesticide sprayed on crops end-up in soil. Once present in soil, pesticides migrate from one compartment of the environment to another and can act as a source of contamination. The magnitude of extent a contaminated soil act as contaminant source depends on pesticide's persistence in the soil. Sorption is a key process that affects the availability of pesticide in soil solution for degradation, leaching and bioactivity. [1, 2] Intentional or unintentional addition of anything to the soil affects its physico-chemical properties that greatly affect availability of pesticides in soil by affecting the partitioning of pesticides in soil and water phase. Research on sorption of pesticides by agricultural soils, and subsequent bioavailability, has emphasized the roles of soil organic matter and clays. However, field burning of crop residues is practiced worldwide for immediate clearing land and their role as sorptive phase is largely ignored. Ashes arising from crop residue burns have shown significantly high adsorption capacity for pesticides. [3] Ash, which is alkaline in nature, can significantly alter soil properties and can affect pesticide fate. The ashes produced under different conditions from different source materials possess widely different chemical compositions and surface properties. [4] Ashes, which are directly incorporated into soils following burning, may play a significant role on pesticide fate as they contain charcoal-like materials, and that the presence of these materials as adsorbents for pesticides can alter soil sorptive properties and pesticide bio-availability. While, much attention in the past has been paid to the impact of burning on air quality, the environmental role of ash/chars in agricultural soils has not been understood.

Atrazine (Atz) is a selective, systemic, pre- and post-emergent herbicide used to control annual grasses and many broad-leaved weeds in sugarcane. [5] Studies suggest that atrazine (Atz) is an endocrine disruptor that can cause hormone imbalance. Fipronil is a broad-spectrum insecticide that belongs to the phenyl pyrazole group and is used for insect-pest control in sugarcane, corn, golf courses, and commercial turf. Fipronil is a WHO Class II moderately hazardous pesticide, and has a rat acute oral LD_{50} of 97 mg kg^{-1}.It is recommended for control of early shoot borer & root borer in sugarcane. (Table 1)

Pesticides have become an important tool as a plant protection agent for boosting food production. They renders enhanced crop/food productivity by drastic reduction of vector-borne diseases. [6] The industrialization of the Indian agricultural sector has increased the chemical burden on natural ecosystems. [7] Pesticides have a positive effect on plant health in terms of pest’s control, increased productivity and improved crop storage; but, their injudicious use have impacts on food safety negatively. Pesticide residues and corresponding metabolites may affect non-targeted organisms like fish, bees, butterflies, birds and other beneficial organisms. [8] Traces of pesticides can be detected in all components of the environment i.e. air, water and soil. [9] Pesticides are known to move from point of application to adjoining areas and may be transported long distances. [10] After application to crops, herbicide undergoes different physical, chemical and biochemical processes, for example, photolysis, hydrolysis, degradation, leaching, volatilization, adsorption etc. It is estimated that only 0.1% of the applied herbicides actually reaches to the target weeds, and the rest of it gets distributed in different ecosystems, leading to “herbicide loss”. [11, 12] (Figure 1)

Results and Discussion

Sorption of atrazine (Atz) and fipronil in soils

The soil has a major influence on the fate and behaviour of pesticides applied to crops. Pesticide molecules partition between the aqueous and solid phases of soil. There are following factors which influence the fate and behavior of pesticides in soil systems:

- Chemical Decomposition
- Photochemical Decomposition
- Microbial Decomposition
- Volatilization
- Movement
- Plant Or Oganism Uptake
- Sorption

The phenomenon of adsorption-desorption directly or indirectly influences the magnitude of the effect of the other factors. Adsorption is one of the major factors affecting the interactions occurring between pesticides and soil colloids. [13] Sorption is rate limiting to volatilization, bioavailability, and subsurface transport. The fate of a pesticide in soil is fundamental to the assessment of its behaviour in the environment and vital in ensuring the safe use of pesticide product. [14, 15] These workers explained the mechanism of the adsorption of pesticide molecules by soil colloidsand indicated that following facter affect the adsorption-desorption of pesticides in soils:

- Physical and chemical nature of the pesticide
- Soil colloid
- Soil reaction
- Soil temperature
- Soil moisture

- Nature of the saturating cation on the soil colloids
- Nature of the pesticide formulations

Atrazine (Atz) sorption

Atrazine (Atz) is an important triazine herbicide used as pre- or post-emergence control of broad leaf weeds. Atrazine (Atz) exhibited a weak adsorption capacity in soils, indicating it is highly mobile in the soil–water environment and can easily cause groundwater pollution. Therefore, much attention should be paid to the environmental behavior of pesticide. [16] Yu (2020)[16] studied batch sorption to determine the adsorption and desorption coefficients (K_d) of atrazine (Atz) and four degradation products in California sand, sandy loam, silty loam, and clay loam soils. The adsorption coefficients for atrazine (Atz) were found to be between 0.427 and 2.03. The K_{oc} for maximum and minimum K_d were calculated as 135 and 90.9. The K_d values for N-dealkylatedatrazine were found to be slightly lower (0.116 - 1.44) than for atrazine (Atz). Hydroxyatrazine showed a little higher adsorption to soil (K_d = 1.643 - 8.165) than atrazine (Atz) and N-dealkylated products. The K_d value for diaminochlorotriazine was determined to be 0.108 - 0.800. The results indicated that atrazine (Atz) and N-dealkylated metabolites were not strongly adsorbed onto soil, and they were easily desorbed. Hydroxyatrazine was, however, well adsorbed onto soil.

Weber (1993) studied atrazine (Atz) sorption in H^+- and Ca^{2+}- saturated soil organic matter(OM), Ca^{2+}-saturated montmorillonite clay, Norfolk sandy loam and Drummer silt loam at suspension pH values of 2.0 to 6.3. Sorption of atrazine (Atz) was high in organic matter sorbents; but, similar for montmorillonite clay and the two soils. Sorption of herbicide on the Drummer soil was much greater than on the Norfolk soil, due to the higher OM content of the former. Decreasing the pH greatly increased sorption of herbicide by all sorbents. Atrazine (Atz) sorption was attributed to ionic bonding at low pH and physical bonding at neutral pH. Mobility and bioavailability of the atrazine (Atz) in soils is expected to be lower at low pH than at high or neutral pH.

Laird et al. (1994) [17] determined the distribution coefficients for sorption and desorption of atrazine (Atz) for all combinations of 3 chemical treatments and 4 particle size fractions prepared from a soil clay. Organic and inorganic components were 11 and 89.5% of the mass and contributed 68 and 32% of the affinity of the soil clay for atrazine (Atz) sorption, respectively. Organic matter associated with the coarse clay had substantially greater affinity for atrazine (Atz) and showed greater sorption-desorption hysteresis as compared to organic matter associated with the fine clay. Silicate minerals had a moderate affinity for atrazine (Atz) and showed little sorption-desorption hysteresis. Free Fe compounds in soil interacted with silicate minerals to reduce affinity of the silicate minerals for atrazine (Atz). Atrazine (Atz) primarily retained on silicate clays by physi-sorption; but, both physi-sorption and chemical sorption leads to retention of atrazine (Atz) by soil organic matter (SOM).

Baskaran et al. (1996) [18] studied atrazine (Atz) sorption in an allophanic (Patua silt loam) and a non-allophanic (Tokomaru silt loam) soils. The Patua soil sorbed more atrazine (Atz) than the Tokomaru soil and was attributed to the higher organic matter and the presence of short-range order clays (allophane).

Moorman et al. (2001) [19] described sorption of atrazine (Atz) in surface soils, subsoils, and sediments. Average adsorption partition coefficients (K_f) were 0.43 ± 0.25 for oxidized till, 0.51 ± 0.02 for loess, and 0.55 ± 0.24 for alluvium. Adsorption of atrazine (Atz) is controlled mainly by organic C. Samples of unoxidized tills adsorbed atrazine (Atz) at levels is equivalent to surface soils. Subsurface sediments retained atrazine (Atz) during desorption to a greater relative extent than that predicted from adsorption isotherms. Although adsorption-desorption of atrazine (Atz) in subsurface sediments is generally low, but, there is sufficient retention to warrant consideration of sorption processes in the assessment of atrazine (Atz) transport in the subsurface environment. Magesan et al., (2003) [20] suggestted that atrazine (Atz) adsorption decreased with soil depth and was correlated with percentage clay content, total C, cation exchange capacityand surface area.

Ling et al. (2006) [21] investigated the influence of dissolved organic matter (DOM) on the sorption of atrazine (Atz) in ten soils. DOM at lower concentrations significantly increased the sorption of atrazine (Atz) in soil; while, it reduced sorption at higher concentrations. The distribution coefficient in the presence of DOM was negatively correlated with the OC content and positively correlated with the clay content.

Ahmad and Rahman (2009) [22] investigated sorption characteristics of atrazine (Atz) and imazethapyr, in 101 soils with allophanic and non-allophanic clays of New Zealand using the batch equilibration technique. The K_d values of atrazine (Atz) and imazethapyr ranged from 0.7 - 52.1 and from 0.1 - 11.3 L kg^{-1}, respectively. For atrazine (Atz), the sorption affinities for the allophanic set of soils (mean K_d of 8.5 L kg^{-1}) were greater than for the non-allophanic set of soils (mean K_d of 7.5 L kg^{-1}). None of the measured soil properties could alone explain adequately the sorption behavior of the herbicides. The variation in K_{oc} values was larger for atrazine (Atz) (mean K_{oc} of 126.9 L kg^{-1}) than for imazethapyr (mean K_{oc} of 13.2 L kg^{-1}). The prediction equations for atrazine (Atz) and imazethapyr developed overseas failed to provide the acceptable values of sorption coefficients for the soils of New Zealand. The study highlighted the danger of using sorption coefficient data from the literature for practical assessments of the herbicide leaching in New Zealand soils.

Lima et al. (2010) [23] studied the effect of different organic amendments on sorption of atrazine (Atz) and suggested higher sorption in compost amended soils. The highest K_{FOC} value was observed for the soil with the highest aromatic content. High aromatic content leads to more hydrophobicity of organic matter, and hydrophobic interactions play a main role in binding of atrazine (Atz).The soil mixed with FYM, having a high content of carboxylic units, was responsible for hydrogen bonding between atrazine (Atz) and organic matter. Dominance of hydrogen bonds than hydrophobic interactions may be responsible for the lower desorption in FYM mixed soil. The stronger hydrogen bonding reduces the leaching of atrazine (Atz) into drinking water and runoff.

The mechanism of atrazine (Atz) sorption by soil organic matter has been a topic of considerable controversy. Early work [24] showed that sorption was inhibited by the low pKa (1.68) of the herbicide molecule and proton transfer between it and carboxyl groups at low pH were proposed as the probable mechanism of retention by organic colloids. Gamble et al., 1994 [25] supported this mechanism as they observed sharp peaks in liquid chromatography at pH $\leq$ 3, which strongly correlated with the extent of carboxyl protonation and peak diminished in the presence of metal cations. Martin-Neto et al. (1994) [26] and Sposito et al. (1996) [27] provided additional experimental support through infrared spectra demonstrating an increased content of carboxylate species in atrazine (Atz)-humic acid adducts. Moreover, they also concluded, in agreement with theoretical studies, that the electron-donating capability of atrazine (Atz) usually was not sufficient to engage an electron-transfer complexation mechanism with humic acids. Senesi (1995), [28] on the other hand, had proposed electron transfer between the triazine ring (or the amino groups) in atrazine (Atz) and quinone-like moieties in humic acid as a principal mechanism of sorption, reasoning that such complexes would be stabilized as semiquinone species by the complex molecular structure of humic acid. Senesi et al., (1995), [28] and Sposito et al., (1996) [27] indeed found this mechanism (increase of semiquinone free radical content in atrazine (Atz)–humic acid adducts) to operate in some instances. Martin-Neto et al., 2001, [26] supported the important contribution of hydrophobic interactions to the pH-dependent sorption of atrazine (Atz) by humic substances. However, others indicated that atrazine (Atz) adsorption to clay mineral was significant.

Fipronil sorption

The sorption-desorption of fipronil is affected by soil properties and variables such as pH, ionic strength, temperature, etc. Bobé et al., (1997) [29] shown that the adsorption of fipronil on two Sahelian soils (Saguia and Banizoumbou) and a Mediterranean soil (Montpellier) was dependent on the amount of organic matter with respective K_f of 4.3, 7.3 and 45.5. Adsorption isotherms were S-type; but, in Montpellier soil, it changed quickly from S to C type. Temperature increase lead to increase in K_f and change of the mechanism of the fipronil−soil interaction. K_f decreased as the methanol quantity of the binary mixture increased. Doran et al. (2009) [30] predicted that fipronil was subject to rapid, immediate sorption to the soil. Fipronil sulphide accumulated and sorbed rapidly to the soil. Ying and Kookana (2001) [31] reported the sorption of fipronil and its metabolites, desulfynil and sulphide on a range of soils from South Australia. The K_f values for fipronil on the soils varied from 1.94 to 4.84. Its two metabolites have a higher sorption affinity for soils, with K_f values varied from 11.09 to 23.49 (sulphide) and 4.70 to 11.77 (desulfynil). Sorption coefficients were found to be better correlated to the soil organic carbon (SOC) than clay content. The average K_{oc} value for fipronil was 825 ± 214. Co-solvents in soil solutions have a significant influence on the sorption of fipronil. Methanol had less effect on the sorption of fipronil as compared to acetonitrile.

Spomer and Kamble (2010) [32] studied fipronil adsorption in 3 Nebraska soils with different organic matter content. Adsorption curves indicate constant partitioning of fipronil to the soil and K_d and K_f values increased with increasing OM content. Desorption hysteresis suggested that fipronil has a propensity to stay in the adsorbed state. Shuai et al. (2012) [33] reported that the K_{oc} value for fipronil was 1184 L kg^{-1}.

Almalike et al. (2016) [34] studied the adsorption-desorption behaviour of fipronil on eight agricultural soils. The kinetics study for adsorption-desorption processes followed first order rate law. The –ve value for each of ΔG^0, ΔH^0 and ΔS^0 confirmed that fipronil adsorption decreased with increase in temperature.

Singh et al. (2016) [35] suggested that fipronil sorption onto soils fitted to the Freundlich isotherm model. The sorption-desorption of fipronil changed with ionic strength of the soils. Sorption decreased, whereas desorption increased, with temperature while no effect of pH was observed. The cumulative desorption from soil was inversely related to soil organic carbon (SOC) content. IR spectra of sorbed fipronil indicated the participation of amino, nitrile, sulfone, chloro and fluoro groups and the pyrazole moiety of the fipronil. The sorption of fipronil on soils takes place by a physical process by the hydrogen bonding. Increase in soil organic carbon (SOC) help to reduce desorption of fipronil. Silva et al. (2016) [36] studied that organic residues from sugarcane crop and processing are commonly applied/left on the soil to increase its fertility. These residues influenced pesticide sorption. Straw and cake filter residues enhanced fipronil sorption.

Degradation of atrazine (Atz) and fipronil in soils

Intensive use of agrichemicals in natural environments are become a major concern and stimulate scientists to develop suitable methods to assess the potential for the degradations of these chemicals. The amount of degradability depends upon the chemical properties of the pesticides. Physico-chemical properties of soil affect the degradation of pesticides to a great extent. Soil microbial components mainly govern degradation of pesticide in soil. Soil micro-organisms are important attributes of soil quality. Judicious use of the pesticides does not adversely affect the soil biological parameters. At higher dose of pesticides, the suppressive effects are transitory. Studies showed that there is a positive correlation between pesticide degradation rates, physico-chemical and biological properties of soil. [37]

Atrazine (Atz) degradation

It is well known that atrazine (Atz), one of the most widely used herbicide, can be chemically and microbially degraded, and its chemical and microbial degradation products (Figure 2) are frequently detected in soils. Two soil factors that may affect the rate of atrazine (Atz) degradation are soil pH and OM. Atrazine (Atz) is a weak base, pKa 1.7, and its sorption decreased with increase in soil pH. Soil pH has a greater effect on the rate of degradation than OM or other soil properties. [38] Roeth et al., (1969) [39] reported that atrazine (Atz) degraded 2 to 3 times faster in the top soils as compared to sub soils. Increase in temperature at a rate of 10°C from 15 to 35°C leads to 2 to 3 times increase in degradation rate in these soils. Moisture content increase from 0.4 to 0.8 field capacity leads to up to 6 times increase in $^{14}CO_2$ release from chain-labelled ^{14}C-atrazine (Atz). Skipper and Volk (1972) [40] reported that atrazine (Atz) degradation was affected by soil type, atrazine (Atz) dose, and moisture content. The isopropyl side chain and triazine ring of atrazine (Atz) were less attacked. The hydroxyatrazine ring was affected quickly than the atrazine (Atz) ring.

Smith and Walker (1989) [41] showed that with increase in soil moisture content and temperature half-life of atrazine (Atz) decreased. Skipper et al., (1967) [42] determined significance of microbial vs. chemical degradation of atrazine (Atz) in greenhouse incubation. Bacterial isolates and *Aspergillus fumigates* released 0.4–0.7% and 4.0% of ethylamino chain-labelled atrazine (Atz) as $^{14}CO_2$, respectively in sterile soil; but, no detectable $^{14}CO_2$ was released from ring-labelled atrazine (Atz). Degradation of the hydroxyatrazine ring was three times greater than chloroatrazine in non-sterile soils. Hydroxyatrazine accounted for about 20% of the extracted ^{14}C-activity after two to four weeks both in non-sterile or sterile soils. Nearly 73% loss of atrazine (Atz) toxicity in 3–4 weeks after incubation in non-sterile soil was observed. This experiment showed chemical hydrolysis of chloroatrazine to hydroxyatrazine as the major pathway of degradation in soils.

Mueller et al. (2010) [43] reported that half-life of atrazine (Atz) was less than 4 days in soil of pH 5.5 under laboratory conditions and 8 d in the field.

Soil microbial community plays a significant role in atrazine (Atz) degradation. Several reports suggest that repeated use of atrazine (Atz) in crops leads to its enhanced degradation and it is attributed to acclimatization of soil microbes to atrazine (Atz). The $t_{1/2}$ of 41 to 231 days for atrazine (Atz), however, in soils with a history of atrazine (Atz) use, atrazine (Atz) degraded faster at 6.5 pH than in soil of pH 6. [44] Houot et al. (2000) [44] reported that soils, which has received atrazine (Atz), degrade atrazine (Atz) more rapidly than did soils which had never received atrazine (Atz). Soil pH was the most significant affecting degradation and atrazine (Atz) degraded faster at 6.5 pH than in soil of pH 6. Atrazine (Atz) accumulation in soil do not influence its mineralization rate, but large quantity of bound residues were accumulated in soils that degrade little atrazine (Atz). Similarly, Mueller et al., (2010) [43] examined the interaction of soil pH with differing levels of atrazine (Atz) application over four year in field. Soil from all plots, which was previously treated with atrazine (Atz), showed fast atrazine (Atz) dissipation. Slower atrazine (Atz) dissipation was observed in plots which has a pH 5.5 or less.

Abdelhafid et al. (2000) [45] suggested that atrazine (Atz) degradation is affected by microbial adaptation and C and N availability in soil. Repeated applications of atrazine (Atz) increased mineralization in a soil under continuous maize, while atrazine (Atz) mineralization was slow in an adjacent soil under wheat because atrazine (Atz) was not applied. In the adapted soil, organic amendment has little effects on atrazine (Atz) degradation, while in the non-adapted soil, it influence atrazine (Atz) dealkylation more than triazine ring mineralization. Mineral N in both soils, slowed triazine ring mineralization. The inhibitory effect of the organic N on atrazine (Atz) mineralization enhanced with their N mineralization rate. Despite its slow N mineralization rate, biuret addition greatly decreased atrazine (Atz) mineralization because it may be one of the last intermediates in atrazine (Atz) degradation. Rapid triazine ring mineralization is dependent on microbial adaptation after repeated atrazine (Atz) application. It is mainly govern by N availability in soil.

Radosevich and Tuovinen (2004) [46] found that the primary microbial degradation pathway was N-dealkylation of the side chains to produce deethylatrazine and deisopropylatrazine. The presence of atrazine (Atz) and its three metabolites, deethylatrazine (DEA, 2-amino-4-chloro-6-isopropylamino-s-triazine), deisopropylatrazine (DIA, 2-amino-4-chloro-6-ethylamino-striazine) and hydroxyatrazine (HA, 2-hydroxy-4-ethylamino- 6-isopropylamino-s-triazine), have also been detected in surface and ground water. [47]

Popov et al. (2005) [48] studied the degradation of atrazine (Atz) in flood plain soil in natural grasslands and cropped fields in the Liverpool Plains, NSW. Degradation rate in cropped soil was more rapid than in 2 grassland soils. The t-RFLP analysis confirmed the presence of *Rhodococcus*sp, *Pseudomonas aeruginosa*, *Clavibactermichiganense*, *Acinetobacter* sp., *Pseudomonas* sp., and *Streptomyces* sp., were responsible for the faster degradation of atrazine (Atz) in the cropped soil.

Solomon et al. (2013) [49] reported that the persistence of atrazine (Atz) in soil was affected by the metabolic action of habituated native microbes. Different microbes degrade atrazine (Atz) by different mechanism. Neutral pH favour atrazine (Atz) degradation by microbes. Yale et al., (2017) [50] reported that repeated application of atrazine (Atz) accelerated degradation rate which has impact on the environmental fate of atrazine (Atz). Soils with a range of physicochemical properties and cultivated histories confirmed similar degradation kinetics. The half-life of atrazine (Atz) decreased from an average of 25 days to <2 days from first and second application respectively.

Barrios et al. (2019) [51] assessed the persistence and transport of atrazine (Atz) at high infiltration rates expected from higher intensity precipitation due to climate change scenarios in the Midwestern U.S. Higher infiltration promote maximum distribution of hydroxyatrazine in the soil profile for sandy loam soil as compared to loam soil. The mean half-life of atrazine (Atz) was lower at high soil moisture level. This study is relevant to climate change where more intense precipitation are expected, which cause higher infiltration and increased soil moisture.

Fipronil degradation

Fipronil is relatively persistent insecticide and degrade by photo, chemical and biological means in soils. (Figure 3) Bobé et al., (1998) [52] studied the abiotic degradation of fipronil in aqueous solution and on the surface of two soils from Niger (Saguia and Banizoumbou) and one Mediterranean soil (Montpellier). The pH influenced hydrolysis of fipronil and the half-life being 770 h (pH 9.0), 114 h (pH 10.0), 11 h (pH 11.0), and 2.4 h (pH 12.0). Fipronil was stable at pH 5.5 and under neutral conditions. 5-Amino-3-carbamoyl-1-(2,6-dichloro-4-(trifluoromethyl)phenyl)-4-[(trifluoromethyl)sulfinyl]pyrazole was the only one hydrolysis product found. Fipronil hydrolysis in aqueous solution (pH 5.5) followed first-order kinetics with concomitant formation of 5-amino-3-cyano-1-(2,6-dichloro-4-(trifluoromethyl)phenyl)-4-(trifluoromethyl)pyrazole and 5-amino-3-cyano-1-(2,6-dichloro-4-(trifluoromethyl)phenyl)pyrazole-4-sulfonic acid. The degree of photo-transformation is inversely proportional to fipronil adsorption.

Ying and Kookana (2002) [53] studied degradation of fipronil in soil under laboratory and field conditions. Laboratory studies revealed that soil moisture content had a great effect on the degradation rate of fipronil. High soil moisture contents (>50%) favored the formation of a sulfide metabolite of fipronil by reduction; while, low soil moisture (<50%) conditions favored the formation of fipronilsulfone metabolite by oxidation. Microorganisms in soil enhanced the degradation of fipronil to sulfide and sulfone metabolites. Desulfinyl metabolite was formed by photodecomposition of fipronil in water and on the soil surface. The desulfinyl derivative degraded rapidly in field soils compared with fipronil. The average half-life of fipronil and its metabolites in field soil was 188 days.

Zhu et al. (2004) [54] studied the microbial degradation of fipronil in the soil environment. The $t_{1/2}$ in non-sterile clay loam soil was very less as compared to the sterile soil, suggesting microbial participation in its degradation. Pei et al., (2004) [55] evaluated the fate of fipronil in Pakchoi and soil. The results revealed that degradation of fipronil was faster in Pakchoi than in soil. Photo-degradation and oxidization govern the degradation reaction in soil while reduction followed in pakchoi. Reduction and hydrolyzation have little influence on the degradation process in soil.

Gunasekara et al. (2007) [56] studied degradation of fipronil and reported that exposure to sunlight at the surface formed fipronil-desulfinyl, oxidation near the surface produced fipronil-sulfone, hydrolysis throughout the upper layer formed fipronil-amide and reduction below the surface produced fipronil-sulfide. The $t_{1/2}$ of fipronil and its metabolites varied from 111-3503 d, based on soil conditions.

Masutti and Mermut (2007) [57] assessed the degradation of fipronil in sugarcane soil of North Eastern Brazil. The biodegradation was dependent on the bioavailability of the fipronil and degradation rate is found to be biphasic. Degradation of fipronil varied from 83 days (initial concentration = 978 ng g^{-1}, short-term experiment) to 200 days (initial concentration = 689 ng g^{-1}, long-term experiment). The sulfone metabolite was the major product, but the sulphide and amide derivatives were also formed in non-sterile soil. Redox potential played important role as aerobic sites favoring the formation of the sulfone than the sulfide metabolite.

Guo et al. (2008) [58] studied the degradation of fipronil in rice soils. The observed $t_{1/2}$ of fipronil in aerobic condition were 165 d, 267 d and 42 d in black soil, red soil and rice soil, respectively; while respective $t_{1/2}$ in anaerobic condition was 31 d, 173 d and 32 d. It was thought that anaerobic bacteria in soil may be the key factor in fast fipronil under anaerobic condition.

The transformation of fipronil in urban stream sediments from California, under facultative and anaerobic conditions. Degradation of fipronil in sediments generally followed exponential decay kinetics, and the first order half-lives of fipronil were 4.6-18.5 days in anaerobic sediments. The persistence of fipronil under facultative conditions were considerably longer, with half-life from 25-91 days. Sterilization decreased the dissipation of fipronil, indicating that microbial activity was an important factor in fipronil transformation in sediment. Under facultative conditions, fipronil sulfide and sulfone were observed while only fipronil sulfide was detected in anaerobic samples.

Silva et al. (2016) [36] determined the effect of organic residues on the degradation of fipronil and atrazine (Atz) in two soils. The degradation study was carried out with laboratory-incubated soils. Fipronil showed to be more persistent than atrazine (Atz). Vinasse amendment to the soil increase fipronil and atrazine (Atz) degradation; but, cake filter addition decreased the degradation rates for both pesticides.

Atrazine (Atz) and fipronil leaching in Soils

Pesticides, that enter the unsaturated soil profile, are transported vertical by the water flux and this process is called leaching. The pesticides are sorbed, desorbed, and degraded as they move through the soil. The rate of movement of a pesticide through the soil profile affected by the pesticide properties, soil properties and environmental conditions. Persistence (DT_{50}) and sorption/desorption (Koc) are parameters that most affect pesticide movement in soil.

These parameters can vary for same pesticide from geographic site-to-site and soil depth. Dissolved organic matter (DOM) or WDC are other parameters that may complicate pesticide leaching behavior. Soil is chemically and physically heterogenous so different pesticide tests may produce different DT_{50} and Koc values. [59] Pesticide leaching is more for weakly sorbing and persistent compounds, climates with high precipitation and low temperatures, and soils with low organic matter (OM) and sandy texture. On the contrary, pesticides with a low persistence that degrade quickly, the risk of groundwater pollution decreases. Physico-chemical properties of the pesticide, soil permeability, texture and organic matter (OM) content of the soil, volatilization, crop-root uptake, and method and amount of pesticide application are key factors that affect the leaching rate of the pesticides. Soils with high clays and organic matter will hinder the movement of water, attach easily to many pesticides, and generally have a higher diversity and population of soil microbes that can degrade the pesticides. (Figure 4)

Atrazine (Atz) leaching in soils

Atrazine (Atz), a triazine herbicide, has been detected in ground water samples collected from agricultural lands. Though atrazine (Atz) concentration levels in the groundwater tend to be low, its long persistence in soil ($t_{1/2}$- 41 to 231 days) and moderate solubility in water (33 mg L^{-1}), suggested that it reached the water table. [60] Atrazine (Atz), an USEPA class C, “possible human carcinogen”, has the maximum contaminant level (MCL) in drinking water 3.0 μg L^{-1} by USEPA and below 0.1 μg L^{-1} for the European Union drinking water. Schiavon (1988) [61] evaluated the migration of ^{14}C atrazine (Atz) into water over a 1-year period using unperturbed-structure soil column under field conditions. Analysis of the leached pesticide residues showed the predominant presence of deethylatrazine. Southwick et al. (1992) [62] in Southern Louisiana soils reported effluent outflow atrazine (Atz) concentrations of 82 to 403 μg L^{-1} in subsurface drains within 5 to 11 d after application on a

Sharkey clay soil. Atrazine (Atz) concentrations in the surface Sharkey soil of 1432, 503, 208, 93, and 49 μg L^{-1} were found 2, 14, 35, 73, and 84 d after application, respectively. Southwick et al. (1995) [63] suggested that preferential or macropore flow was a significant process in this Sharkey clay soil. Graymore et al. (2001) [64] reported summary of atrazine (Atz) concentrations in aquatic systems (water/sediments) worldwide and atrazine (Atz) concentrations ranged between <0.001 to 1,000 µg L^{-1}.

Dousset et al. (1995) [65] studied the movement of ^{14}C-atrazine (Atz) in lysimeters in field conditions in loamy clay, calcareous clay and a high clay soils. After 10 months of application and a cumulative rainfall of 502 mm, the leachates from the calcareous clay soil contained more concentration (3.3%) of applied atrazine (Atz) as compared to loamy clay (0.9%) and high clay soils (1.1%). There was no correlation between the atrazine (Atz) residues and distribution of organic carbon content with depth. The amount of extractable residues in the upper levels of the lysimeters was found to be lower for the calcareous clay soil (19.2%) than loamy clay (30.0 %) and high clay soils (28.6%).The extractable residues increased (62.8%) with depth in the calcareous clay soil; while, it decreased in both loamy clay (16.3%) and high clay soils (17.6%).

Tasli et al. (1996) [66] studied leaching of atrazine (Atz) in corn field. Atrazine (Atz) and its metabolites deethylatrazine and deisopropylatrazine were found throughout the year in soil samples and soil-water samples. Atrazine (Atz) quantity differs from 0.2 to 14.7 µg L^{-1} in soil-water samples. The total amount of atrazine (Atz) and its metabolites (deethylatrazine, deisopropylatrazine soluble in the soil water of the 1m thick upper soil layer ranged throughout the year from 33 to 94 g ha^{-1}. Atrazine (Atz), initially exclusively found on the soil surface, found progressively at all levels of the 1m layer studied. One year after the application of 1 kg/ha atrazine (Atz), only 15% of the initial deposit was still present in the 1m thick upper layer. Through metabolization, early leaching, and volatilization the main part of the atrazine (Atz) deposit (80–85%) was dissipated essentially, while plant absorption and formation of non-extractable residues remained low.

Liu et al. (1995) [67] showed that ammonia fertilizers like anhydrous ammonia, aqua ammonia, and urea, first enhance soil pH, reduce atrazine (Atz) sorption and increases atrazine (Atz) desorption. Increased concentration of atrazine (Atz) in soil solution increased atrazine (Atz) leaching. Ammonia treatment resulted in 30-60% increase in atrazine (Atz) concentration in the leachate from different soil columns.

Highest run-off losses for the broadcast treatment (2.8–11% of that applied) and lowest for the 0.6-m band treatment (1.9–7.6%). The maximum effluent concentrations of atrazine (Atz) were measured from the broadcast treatment ranged from 600 to 1100 µg L-1. Sanchez-Camazano et al. (2005) [68] reported 0.04–25.3 µg L^{-1} in the surface waters and 0.04–3.45 µg L^{-1} in the ground waters for atrazine (Atz) from irrigated areas dedicated to corn cultivation in the Castilla-Le´on region, Spain. Du Preez et al. (2005) [69] reported the presence of atrazine (Atz) and its three metabolites, deethylatrazine, deisopropylatrazine and hydroxyatrazine in field-monitoring studies of surface and ground waters of a corn-production area of the Western Highveld region (North-West Province) of South Africa. Langenbach et al. (2008) [70] reported that, 53% of the ^{14}C-atrazine (Atz) remained within the upper 1 cm of surface soil, while in the subsurface microcosms the atrazine (Atz) was more evenly distributed. The results of miscible displacement experiments of Kulluru et al. (2010) [71] revealed that atrazine (Atz) could leach up to 65 cm depth in three test soils of India.

Delwiche et al. (2014) [72] shown that the biochar strongly sorb organic compounds and could be used to control atrazine (Atz) leaching. Use of pine chip biochar slowdown cumulative atrazine (Atz) leaching by 52% in homogenized soil columns. Biochar amendment in undisturbed soil columns do not significantly reduce atrazine (Atz) leaching. Atrazine (Atz) concentrations in ground water were found to be 53% lower in a field experiment after application of 10 t ha^{-1} acidified biochar as compared to control. Equal amount of peat applications by dry mass has no effect on atrazine (Atz) leaching. Peat-biochar mixture addition in plots showed no reduction; it may be due to peat organic matter competition with atrazine (Atz) for biochar sorption sites.

Fipronil leaching in soils

Bobé et al. (1998) [73] reported that fipronil and its metabolites, except amide metabolite; do not move beyond 10 cm depth. Amide metabolite is not considered as toxicologically significant; suggesting that insecticide do not poses leaching threat. Ling et al. (2006) [21] reported that sorption coefficient K_d values for fipronil in sediment-water system consistently increased with organic carbon contents of sediments. The K_d usually increased with contact time, suggesting decreased availability of aged residues.

Huang et al. (2010) [74] revealed the leaching properties of fipronil in Jiaxing rice soil and Jiangxi red soil in the continuous flooding situation. While 50% of used fipronil was leached through column in Jiaxing red soil, leaching losses were not significant in the Jiaxing rice soil. Fipronil may have potential risk, when it is used in Jiangxi red soil.

Chatterjee and Gupta (2010) [75] studied the leaching of fipronil and its two toxic metabolites (sulfone and desulfinyl) in undisturbed soil columns. Results showed that although majority of the fipronil present in top 0–5 cm layer, subtantial amount moved to 5–10 cm depth. Nearly, 90% residues of sulfone and desulfinyl metabolites remained in 0–5 cm core showing low movement of these metabolites as compared to fipronil. Granular formulation showed less fipronil movement than the SC formulations showed low movement in granular formulation.

Amount of fipronil and its metabolites in leachate and runoff decreased with time. The quantity of fipronil in the leachate from the all 3 soils correlated inversely with soil organic carbon (SOC) content. Fipronil losses mainly takes place through leaching as compared to losses via runoff due to low volumes of runoff water generated and less particle facilitated movement of fipronil.

Zhang et al. (2013) [76] reported that after 14 days leaching fipronil moved into lower layer of soil, although amount detected was relatively less than that retained in the surface layer. Leachate, which has collected at 1 h was toxic to duck weeds. This experiment proved that fipronil was sorbed on organic matter (OM) in surface soil, not easily degraded in field and will affect the succeeding crop. Similar were the observations of Keefer and Gold (2014) [77] and Rashid et al. (2018) [78] who proved that fipronil is bound to the soil and little movement takes place in soil profile.

Scorza and Franco (2014) [79] evaluated environmental behaviour of fipronil in Brazilian sugarcane fields. Pesticide quickly dissipates at soil surface within 15 days after treatment and no leaching was observed beyond 30 cm depth. Joshi et al., (2016) [80] reported that press mud compost and cereal straw were found to be most efficient in decreasing leaching of the fipronil by enhancing its degradation.

Pesticides have played a major role in enhancing crop production and crop productivity by controlling diseases and pests. But, presence of these toxic chemicals in the environmental components have raised concern about the safety of the environment both, point and nonpoint sources of contamination are responsible for the presence of these chemicals in the soil, air, water and biota. Soil acts as sink for the pesticides applied on crops as a greater part of pesticide spayed on crops end-up in soil. Further, runoff losses during heavy rainfall and drift during pesticide application too greatly contribute to environmental contamination. Once present in soil, pesticides migrate from one compartment of the environment to another and can act as a source of contamination. The magnitude of extent a contaminated soil act as contaminant source depends on pesticide's persistence in the soil. Sorption is a key process that affects the availability of pesticide in soil solution for degradation, leaching and bioactivity. [2, 81] Intentional or unintentional addition of anything to the soil affects its physico-chemical properties that greatly affect availability of pesticides in soil by affecting the partitioning of pesticides in soil and water phase. Greater retention of pesticide on soil particles might reduce its availability for degradation and bio-efficacy for pest control. Thus, there are chances that soil applied pesticide may persist for longer period in soils and less effective in controlling pests and weeds.

India is an agrarian country and generates a large quantity of agricultural wastes. Farmers opt for *in situ* burning of crop residues because it is a quick and easy way to manage the large quantities of residues and prepare the field for the next crop well in time. Mainly, the rice, wheat, sugarcane, fibre and oil seed crop residues contribute to on farm burning. Sugarcane is third most important crop that contributes to on farm burning of residues. Estimated 16.8-28.2 Mt per year sugarcane trashes is burnt in India. [1] Uttar Pradesh contributed maximum to the burning of sugarcane trash followed by Karnataka. These ashes generated in the field, as a post-harvest cleaning technique of land, may significantly affect the behavior of the pesticides that are applied to the crops grown in fields following burning of crop residues. Present study reports the effect of the sugarcane trash ash (S.T.A.) on sorption, leaching and degradation behavior of atrazine (Atz) and fipronil, two sugarcane pesticides, in three sugarcane growing soils.

Conclusions

Understanding the fate and behavior of atrazine (Atz) and fipronil in soil is essential to evaluate their potential environmental risks in environment. After application, a greater part of atrazine (Atz) and fipronil ends up in soil where it is acted upon by physical, chemical and biological forces. Adsorption-desorption of atrazine (Atz) and fipronil on soil components greatly affect the availability of atrazine (Atz) and fipronil for degradation, leaching and bioactivity. Physico-chemical properties of soils as well as environmental factors play an important role in deciding fate of atrazine (Atz) and fipronil. Thus, proper understanding of each process affecting atrazine (Atz) and fipronil fate is must to understand risks associated with atrazine (Atz) and fipronil use. On farm burning of surplus sugarcane trash by the farmers is generally followed as a quick, cheap and an easy way to dispose large quantities of sugarcane trash to prepare fields for sowing the next crop. [1] The ash generated from the burning of sugarcane trash is mixed in the soil. This will results in change in physico-chemical properties of soils. Ashe contain considerable portion of unburnt carbon, have exhibited high potential to adsorb pesticides.[82, 83, 84] therefore, might affect chemical and biological degradation and bio-efficacy. [85, 86, 87]

Fipronil and atrazine (Atz) are two commonly used pesticides in sugarcane cultivation. Atrazine (Atz) is used to control grassy and broad leaved weeds while fipronil is used to control shoot borer. Sugarcane trash ash is a carbon-rich material derived from on form burning of sugarcane trash ash. Sugarcane trash ash with high surface area and porosity generally increases atrazine (Atz) and fipronil sorption in soils as compared to the non amended soil. Moreover, Sugarcane trash ash decreases the fipronil and atrazine (Atz) degradation in soils due to sorption effect. However, the addition of Sugarcane trash ash may cause high microbial stimulation, which results in higher microbial degradation of fipronil and atrazine (Atz). Therefore, how Sugarcane trash ash affects the degradation of fipronil and atrazine (Atz) in soils depends on which action is dominant. The sorption/desorption of fipronil and atrazine (Atz) on sugarcane trash ash surfaces depend on the physicochemical characteristics of sugarcane trash ash: (i) chemical structure and composition, (ii) porosity, surface area, (iii) pH and elemental ratios and (iv) surface functional groups. It has been also observed that all these physicochemical characteristics of sugarcane trash ash rely on the feedstock type and production conditions. The degradation of fipronil and atrazine (Atz) in soil occurs via various reactions such as hydrolysis, photolysis, oxidation and biodegradation. Addition of sugarcane trash ash could directly or indirectly influence all these reactions, thereby altering the degradation of fipronil and atrazine (Atz) in soil.

Fipronil and atrazine (Atz) run off from agricultural soils to surface waters when water exceeds the soil's infiltration capacity and move to groundwater by leaching or vertical movement in the soil profile. Large macropores act as preferential flow pathways in leaching, prompting the rapid movement of the pollutants through the unsaturated zone. The physicochemical properties of the fipronil and atrazine (Atz) and soil properties (texture, clay content, OM, and permeability) play a critical role in the leaching process. Minor leaching is reported in soils with high sugarcane trash ash content because of their greater adsorption. The application of sugarcane trash ash to soils increases the soil OM content and hence decreases leaching. Nevertheless, the greater or lesser leaching of fipronil and atrazine (Atz) in sugarcane trash ash amended soils may not be due solely to the presence of additional sugarcane trash ash in amended soil, but also to structural changes in soil porosity induced by the higher soil sugarcane trash ash content

Consent for publication

All the authors agreed to submit the manuscript.

Data availability statement

All data will available from corresponding author, with reasonable request.

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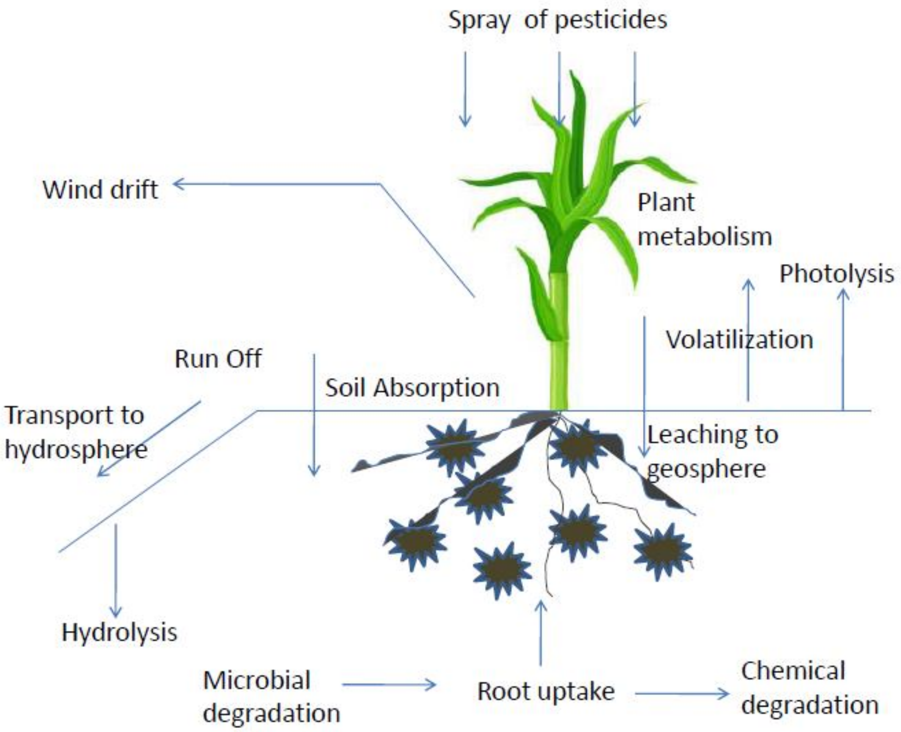

Spray of pesticides
Wind drift
Plant
metabolism
Photolysis
Volatilization
Run Off
Soil Absorption
Transport to
hydrosphere
Leaching to
geosphere
Hydrolysis
Microbial
degradation
Root uptake
Chemical
degradation

Figure 1. The environmental fate of atrazine and fipronil

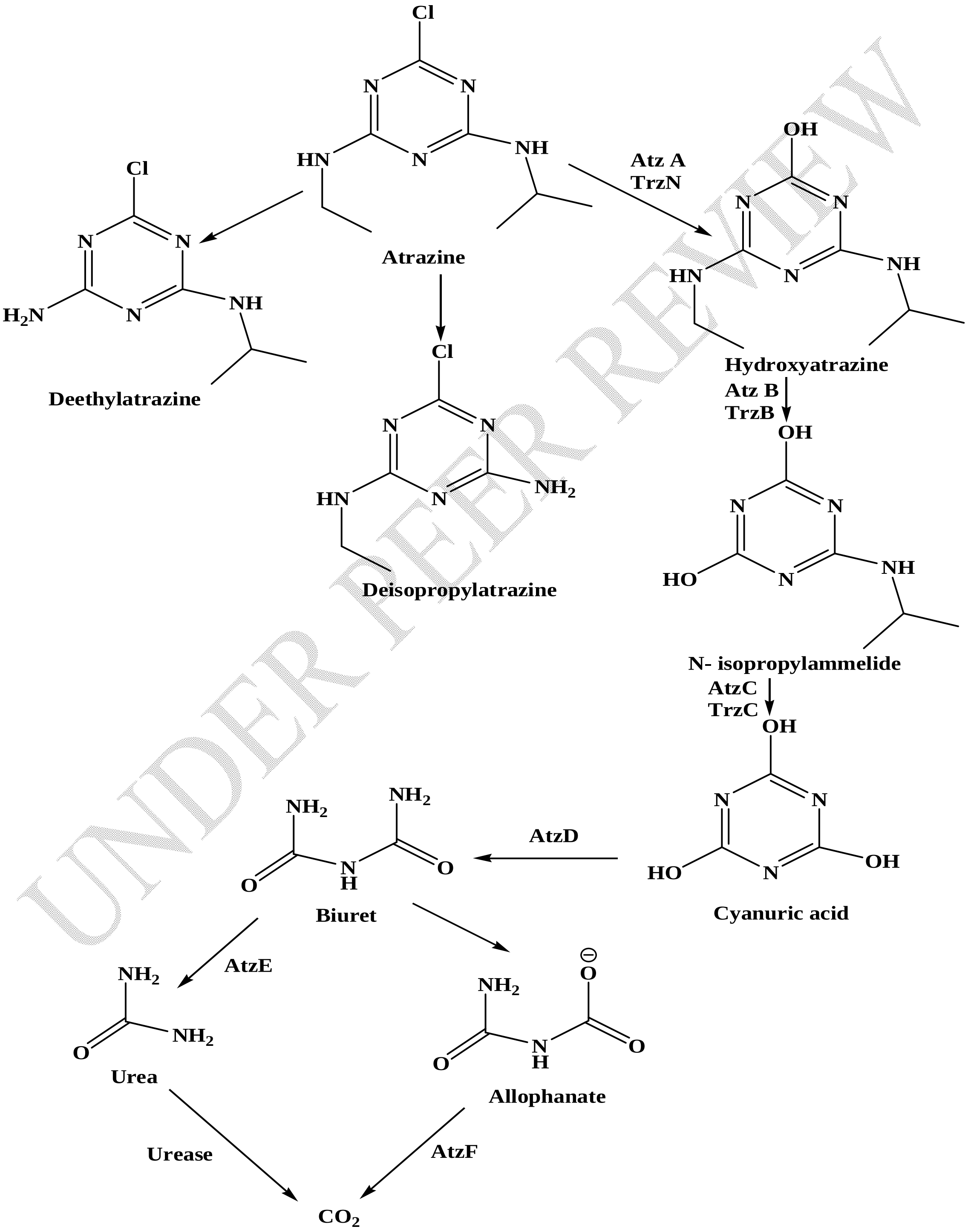


Figure 2. Atrazine (Atz) degradation pathways in bacteria

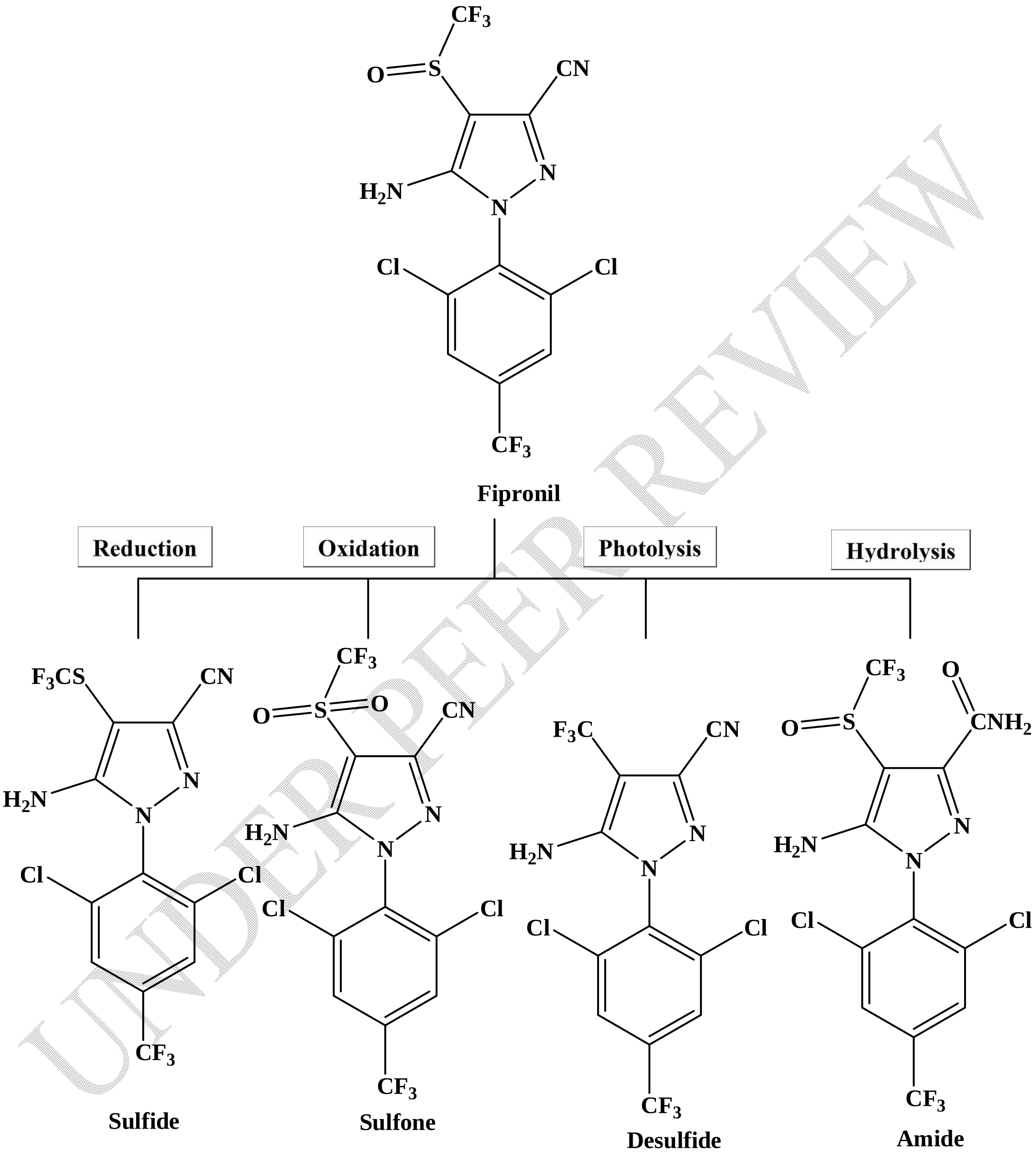


Figure 3. Degradation pathways of fipronil

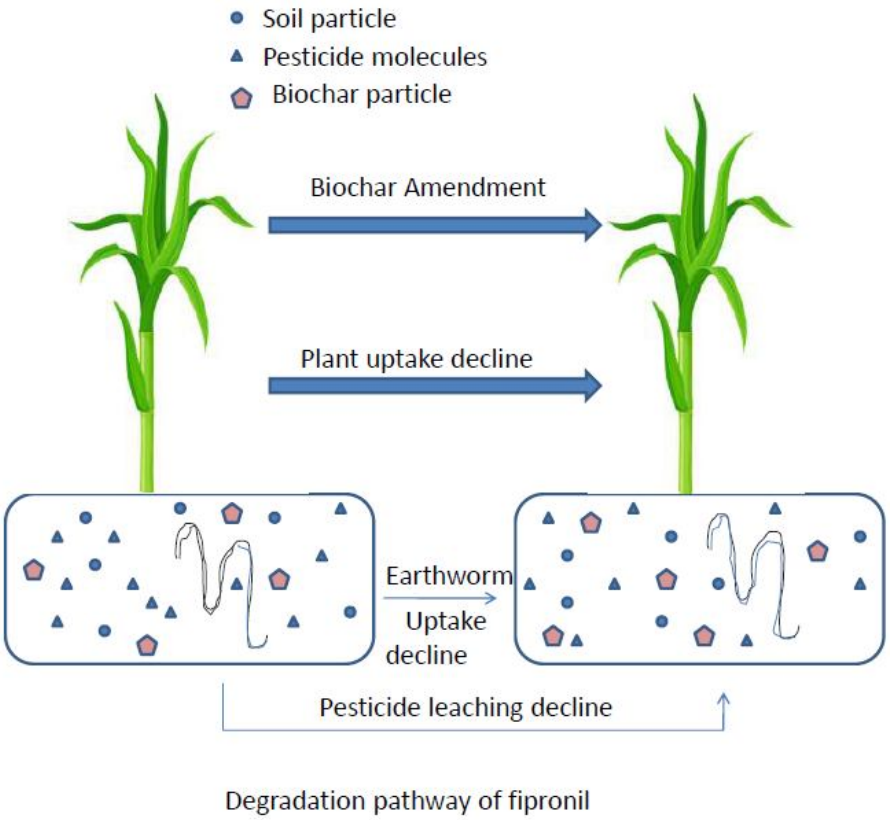
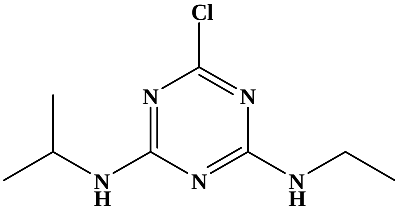
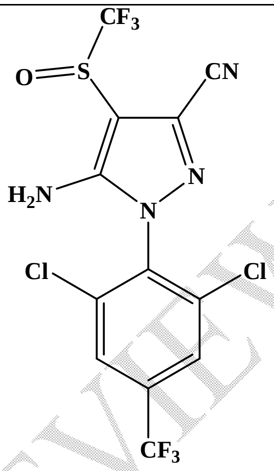


Figure 4. A schematic diagram of biochar amendment effects on the environmental Behavior of pesticides in soil

Table 1. Profile of Pesticide

Parameter	**Atrazine (Atz)**	**Fipronil**
Structure		
Chemical Name	6-chloro-N-ethyl-N (propan-2-yl)-1,3,5 triazine-2,4-diamine	(RS)-5-Amino-1-[2,6-dichloro-4 (trifluoromethyl)phenyl]-4(trifluoromethylsulfinyl) pyrazole-3-carbonitrile
Molecular formula	$C_8H_{14}ClN_5$	$C_{12}H_4Cl_2F_6N_4OS$
Introduced by	Geigy laboratories	BASF
Trade Name	Aatrex, Paraguat, Atrakal, Atragold, Atrazine (Atz) 50, Atlas	Fiprofort, Shrigent, Fiprocap 0.3 GR
Vapour Pressure	3.0×10^{-7} mm Hg at 20 °C	$2.78X10^{-9}$ mm Hg at 25 °C
Molar mass	215.69 g/mol	437.14 g/mol
Density	1.19 g/cm^3	1.55 g/cm^3
Physical S.T.A.te	White CryS.T.A.lline Solid	White Powder

Melting point	175 °C	200.5 °C
Boiling point	200 °C	510.1 ºC at 760 mmHg
Solubility	In water 33.0 mg/L at 25 °C, 183 g/kg DMSO, 52 g/kg chloroform, 28 g/kg ethyl acetate, 18 g/kg methanol, 12 g/kg diethyl ether and 0.36 g/kg pentane.	In water 1.9 mg/L (pH 5), 2.4 mg/L (pH 9), 1.9 mg/L (distilled), all at 20 ºC. In organic solvents (g/L at 20 °C): acetone 545.9, dichloromethane 22.3, hexane 0.028, toluene 3.0
Stability	Stable under recommended storage conditions. Stable in slightly acidic or basic media; hydrolyzed to inactive hydroxy derivative by alkali or mineral acids.	Stable under recommended storage conditions
Log P	2.61	4.0
Log Kow	2.61	4.0
P^{Ka}	1.60, very weak base	-
CAS Reg. No.	1912-24-9	120068-37-3
Types of Formulations	WP	SC, EC, GR, WG
Rate of Applications	2 kg ha^{-1}	75.0-100.0 g ha^{-1}
Usual Carrier	Water	Water
Mode of action	Bind to the plastoquinone	Fipronil disrupts the insect central

	binding protein in photosystem II. Plant death results from Starvation and oxidative damage caused by breakdown in the electron transport process.	nervous system. It acts by blocking GABA-gated chloride channels and glutamate-gated chloride (GluCl) channels. This causes hyperexcitation of insect's nerves and muscles.
Use	It is used to prevent pre and post-emergence broadleaf weeds in crops such as maize (corn) and sugarcane and on turf, such as golf courses and residential lawns.	Fipronil is a broad-spectrum insecticide. It is used for insect-pest control in sugarcane, corn, golf courses, and commercial turf.