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REVIEW

Toxicity, degradation and analysis of the herbicide atrazine

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Abstract Excessive use of pesticides and herbicides is a major environmental and health concern worldwide. Atrazine, a synthetic triazine herbicide commonly used to control grassy and broadleaf weeds in crops, is a major pollutant of soil and water ecosystems. Atrazine modifies the growth, enzymatic processes and photosynthesis in plants. Atrazine exerts mutagenicity, genotoxicity, defective cell division, erroneous lipid synthesis and hormonal imbalance in aquatic fauna and nontarget animals. It has threatened the sustainability of agricultural soils due to detrimental effects on resident soil microbial communities. The detection of atrazine in soil and reservoir sites is usually made by IR spectroscopy, ELISA, HPLC, UPLC, LC–MS and GC–MS techniques. HPLC/LC–MS and GC–MS techniques are considered the most effective tools, having detection limits up to ppb levels in different matrices. Biodegradation of atrazine by microbial species is increasingly being recognized as an eco-friendly, economically feasible and sustainable bioremediation strategy. This review presents the toxicity, analytical techniques, abiotic degradation and microbial metabolism of atrazine.

Keywords Atrazine · Herbicide · Toxicity · Microbial degradation · Monitoring

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Introduction

Atrazine (6-chloro-*N*-ethyl-*N*′-(1-methylethyl)-1,3,5-triazine-2,4-diamine is a synthetic triazine herbicide used to control grassy and broadleaf weeds in sugarcane, wheat, conifers, sorghum, nuts and corn crops (Iriel et al. 2014; Kumar et al. 2016; Zhao et al. 2017). It was first introduced in twentieth century and often used alone or in amalgamation with other herbicides for agricultural applications (Correia et al. 2007; Kadian et al. 2008; Lewis et al. 2009). It is the second most widely consumed pesticide in the world with annual consumption of about 70,000–90,000 tons (Kumar et al. 2013; Cheng et al. 2016). In India, about 340 tonnes of atrazine is consumed annually (Solomon et al. 2013a, b).

Due to its long half-life of 41–231 days (Karlsson et al. 2016), low adsorption in soils and moderate aqueous solubility, it has a sky-scraping potential to contaminate not only agricultural fields, but also ground and surface water with the highest concentration up to 30 µg/L (Table 1) (Cerejeira et al. 2003; Schwab et al. 2006; Kumar et al. 2013). It was banned in several countries like Italy (Huang et al. 2009), Denmark (Glæsner et al. 2014), Finland and Germany (Vonberg et al. 2014) in the year 1991 and European Union banned atrazine in the year 1992 (White 2016) because its metabolites/residues had the potential to persist in fields and surface water for several years (Bethsass and Colangelo 2013; Nousiainen et al. 2015) resulting

Table 1 Chemical and physical properties of atrazine and degradation products

General name	IUPAC name	Chemical formula	Mw (g/mol)	Solubility in water (mg/L)	Log P (at 25 °C)	Density (g/cm^3)	Henry's law constant (Pa m^3 mol^{-1})
Atrazine	2-Chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine	$C_8H_{14}ClN_5$	215.69	70	1.92	1.19	1.093291^{e-007}
Hydroxyatrazine	4-(Ethylamino)-2-hydroxy-6-(isopropylamino)-1,3,5-triazine	$C_8H_{15}N_5O$	197.24	5.9	2.09	1.3	6.36×10^{-08}
Deisopropylatrazine	6-chloro-*N*-ethyl-1,3,5-triazine-2,4-diamine	$C_5H_8ClN_5$	173.6	–	1.19320	1.455	–
Deethylatrazine	2-Amino-4-isopropylamino-6-chloro-s-triazine	$C_6H_{10}ClN_5$	187.63	2700	1.90	1.38	3.55×10^{-07}
N-Isopropylammelide	6-(Propan-2-ylamino)-1H-1,3,5-triazine-2,4-dione	$C_6H_{10}N_4O_2$	170.17	33	−0.47500	1.51	–
Biuret	Imidodicarbonic diamide	$C_2H_5N_3O_2$	103.08	20,000	0.52490	1.432	–
Allophanate	Urea-1-carboxylate	$C_2H_3N_2O_3^-$	103.06	Insoluble	0.23740	1.581	–
Ammelide	6-Amino-1,3,5-triazine-2	$C_3H_4N_4O_2$	128.09	Insoluble	−0.55380	1.573	–
2-Chloro-4-hydroxy-6-amino-1,3,5-triazine	2-Chloro-4-hydroxy-6-amino-1,3,5-triazine	$C_3H_3ClN_4O$	146.54	–	−0.01830	2.1	–
Cyanuric acid	1,3,5-Triazine-2,4,6(1H,3H,5H)-trione	$C_3H_3N_3O_3$	129.08	2000	−2.24850	2.5	8.7×10^{-15}

in the contamination of surface and water bodies. Some studies reveal the surpass levels of atrazine 3 and 0.1 μgL^{-1} found in drinking water of the USA and Europe (Mahía et al. 2007). The maximum acceptable concentration (MAC) for atrazine in drinking water is 5 µg/L (Cerejeira et al. 2003). The acceptable daily intake (ADI) is derived on the basis of division of a NOAEL by appropriate uncertainty factors. It is one of the most widely used herbicide, and several times it has been reported to be at levels above the limits in water bodies (Graymore et al. 2001).

The production of atrazine increased from 0.26 metric tonnes to 0.67 metric tonnes from the year 2009 to 2012 (Ministry of fertilizers and chemicals, Govt. of India). Environment protection agency classifies atrazine in toxicity class III on a scale of I to IV (I being the most toxic). It is registered for only two crops (apple and sugar) by the central insecticides board and registration committee in India (Bhushan et al. 2013). Atrazine has been classified as an endocrine disrupting pesticide by the US Environmental Protection Agency (Morales-Pérez et al. 2016). The International Agency for Research on Cancer (IARC) has categorized atrazine in the list of carcinogenic pesticides (Mahler et al. 2017). This review covers the toxicity, analytical monitoring by using recent techniques and degradation (chemical, photochemical and microbial) aspects of atrazine.

Toxicity of atrazine

Agricultural chemicals have potential to alter species composition, decrease diversity, interfere with normal succession patterns and alter food webs as a whole (Lin et al. 2016a, b, c). The intensification of industrial and agricultural practices chiefly the utilization of pesticides has in almost every way made our natural resources miserable (Dutta et al. 2016). Various toxic effects of atrazine on humans, plants, animals and microorganisms are displayed in Fig. 1.

Effect on nontarget plants

One of the most unintentional exposures of pesticides is to the nontarget plants. Atrazine has shown to manifest complete death or stunted growth, translocation, root or shoot uptake, phenotype alteration, mutation and resistance (Burken and Schnoor 1997; Szigeti and Lehoczki 2003; Hassan and Nemat 2005; Nemat and Hassan 2006; Su and Zhu 2006). The different results of atrazine accumulation could be due to the use of different plant species, since distinct mechanisms control the accumulation of atrazine in target and nontarget plants. Concentration- and time-dependent effects of atrazine exposure have been noticed. Atrazine is absorbed by shoots and roots and transported

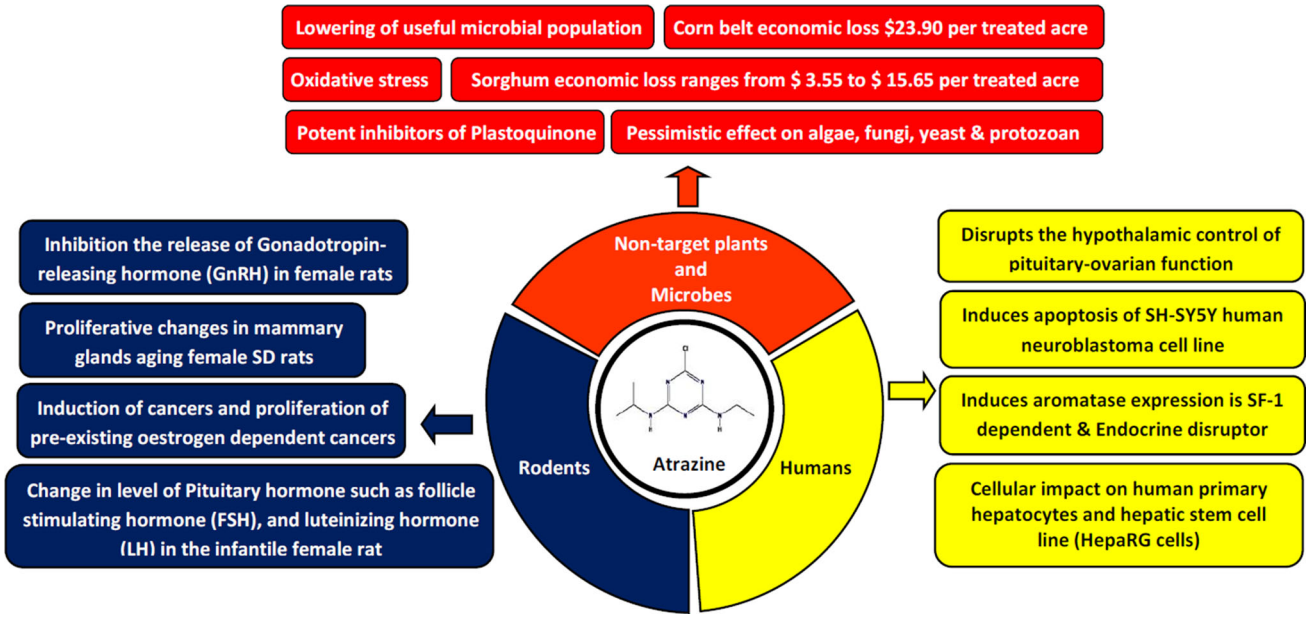

Fig. 1 Toxicity and detrimental effects of atrazine on humans, plants, animals and microorganisms

solely by xylem (Francisco 2001; Szigeti and Lehoczki 2003). Pre-emergence herbicides are used to stop the germination of plant seeds. Atrazine is absorbed by leaves as well as roots and has postemergence as well as pre-emergence activity on weeds (Ahrens and Newton 2008). The negative effects of postemergence atrazine treatment upon peroxidase, ascorbate peroxidase and lipid peroxidation were determined in a 15-day experiment (Akbulut and Yigit 2010). Target and nontarget plants exposed to atrazine usually suffer oxidative stress caused by the generation of reactive oxygen species such as superoxide anion radical, hydroxyl radical, singlet oxygen and hydrogen peroxide. Generation of H_2O_2 in roots of maize exposed to atrazine was also assayed after chemical extraction in a previous study. The most important mechanism used by plants to prevent oxidative stress is through reactive oxygen species scavenging (Burken and Schnoor 1997; Hassan and Nemat 2005; Nemat and Hassan 2006; Szigeti and Lehoczki 2003; Su and Zhu 2006). It has been noticed that the exposure and accumulation of atrazine cause oxidative toxicity and antioxidant response in Zea mays (Li et al. 2012). Gao et al. (2011) indicated atrazine to be a potential threat to seagrass seedling function, and the impact is much higher for adult plants. Exposure to 10 μg/L atrazine significantly lowers the plant fresh weight and total chlorophyll concentration, and up to 86.67% mortality was recorded at the 100 μg/L concentration.

Basically plants have detoxification ability against various pesticides. Enzymes detected in plants responsible for detoxification of various pesticides are cytochrome 450, peroxidases, aryl acylamidases, esterases, lipases, proteases, amidases, oxygenases and reductases (Jiang et al. 2016). It has been noticed that the increasing antioxidant enzyme activities enable *Pennisetum americanum* seedlings to cope with the oxidative stress induced by moderate concentrations (20 mg kg^{-1} or below) of atrazine. Cytochrome P450 monooxygenase genes are known to be involved in modification and detoxification of herbicide atrazine in Oryza sativa (McGregor et al. 2008; Tana et al. 2015). Exposure to atrazine can trigger specific GT genes and enzyme activities in Oryza sativa (Lua et al. 2013). Another major detoxification mechanism in leaf tissue of maize is through glutathione conjugation (GS-atrazine). It is considered to be an important biotransformation mechanism of a atrzine in plants. The recovery of atrazine-inhibited photosynthesis is accompanied by a rapid conversation of atrazine to GS-atrazine when atrazine was directly introduced into the leaf tissue. This pathway is relatively inactive in roots and shoots (Shimabukuro et al. 1970). Another detoxification pathway for atrazine in corn corresponds to a chemical hydroxylation process. The mechanism was also described under invitro conditions. Benzoxazinones mixture (DIMBOA, DIBOA, 2-monoglucosyl DIMBOA + 2-monoglucosyl DIBOA) extracted from corn plantlets were able to transform 91% of atrazine into 2-hydroxyatrazine in 24 h. The natural concentration of benzoxazinones in the vacuolar sap of corn seedlings and the pH play a major role in high rate of atrazine chemical hydroxylation in vivo (Raveton et al. 1997). Occurrence of atrazine in water bodies can have serious

detrimental effects on nontarget living organisms such as freshwater algae (Baxter et al. 2015, 2016; Bai et al. 2015; Andrus et al. 2013). Atrazine inhibited the growth of *Chlamydomonas mexicana* and also leads to an increase in carbohydrate content and chlorophyll a accumulation (Kabra et al. 2014). The toxicity of atrazine along with its metabolites desethylatrazine and deisopropylatrazine was evaluated on the amphipods *Hyalella azteca* and *Diporeia* sp., and the unicellular algae *Pseudokirchneriella subcapitata*. It was found to be the most toxic followed by desethylatrazine and deisopropylatrazine and algae being the most sensitive of all. In case of chronic exposure, *Diporeia* sp. was found to be sensitive as compared to H. azteca by a large magnitude (Ralston-Hooper et al. 2009). Photosynthetic process, cell division, lipid synthesis were majorly affected in green alga, *Raphidocelis subcapitata* on exposure to atrazine (Ma et al. 2006). According to Solomon et al. (2013a, b), atrazine was not found to cause any lethality or permanent cell damage, but it acts to inhibit photo-phosphorylation.

Effects on aquatic fauna

Atrazine exhibited significant rate of micronuclei and nuclear abnormalities in Channa punctatus (Nwani et al. 2011). Atrazine showed acute toxicity to leopard frog (*Rana pipiens*), American toad (*Bufo americanus*), rainbow trout (*Onchorhynchus mykiss*) and channel catfish (*Ictalurus punctatus*) (Orton et al. 2006). Chironomus tentans was also studied for the effect of atrazine and binary combination of atrazine with chlorpyriphos. The result depicted atrazine not acutely toxic at even higher levels but when used in combination with chlorpyriphos, methyl parathion and malathion decreases the EC50 (effective concentration) values (Belden and Lydy 2001).

Also the toxicity of active ingredients to pesticide formulations with regard to atrazine, chlorpyriphos and permethrin in glochidia and juvenile life stages of a freshwater mussel (*Lampsilis siliquoidea*) were compared. The atrazine formulation (Aatrez) was more toxic than technical grade atrazine in chronic tests with juvenile L. siliquoidea. For other pesticides, acute and chronic toxicity of technical grade pesticides were similar to the toxicity of pesticide formulations. Atrazine and formulations did not cause any significant acute toxicity in glochidia and juveniles (Bringolf et al. 2007). In case of freshwater fish, *Rhamdia quelen*, histopathological changes in liver revealed leukocyte infiltration, hepatocyte vacuolization like steatosis and necrosis areas, leading to raised lesion index levels in all tested concentrations; process of osmoregulation was disturbed and gills showed changes in pavement cells and chloride cells (Mela et al. 2013). The effect of atrazine was also evaluated on some immune parameters of red-eared slider (*Trachemys scripta*). Lowered serum complement and lysozyme activities, reduced leukocyte number as well as their phagocytic activity and increased neutrophil/lymphocyte ratio depicted a positive correlation between atrazine (high dose) concentration and immunosuppressive effects (Soltanian 2016). The expression of carp HSP70 and 70-kDa heat shock cognate protein (HSC70) with atrazine and chloropyriphos treatment alone or in combination was significantly up-regulated in common carp (*Cyprinus carpio* L.) providing new insights into the mechanisms used by fish to adapt to stressful environment (Xing et al. 2013). Increased lipid peroxidation and decline in cholesterol and total proteins in liver and muscles were observed for atrazine, glyphosate and quinclorac in tadpoles of *Lithobates catesbeianus* (Dornelles and Oliveira 2014).

Freshwater clam, *Corbicula fluminea*, was also studied to evaluate the biochemical and genotoxic effects of the herbicides atrazine and Roundup. Atrazine interfered mostly in biotransformation, while Roundup interfered mainly in antioxidant defenses leading to lipid peroxidation. Herbicides mixture caused a significant increase in the occurrence of DNA damage (Dos-Santos and Martinez 2014). Atrazine shows profound influence on the oxidative stress markers and detoxifying enzyme of the exposed zebra fish (Blahova et al. 2013). Atrazine also causes changes in the glutathione S-transferase isoenzymes (GSTs) activity and their transcription varied within each organ and among organs of common carp (Xing et al. 2012). Atrazine behaves as enzyme inhibitor, impairing hepatic metabolism, and produces genotoxic damage to different cell types as studied in *Plotosus lineatus* (Santos and Martinez 2012). Various concentrations of atrazine also lead to continuous decline in levels of total protein and serum albumin in grass carp, *Ctenopharyngodon idella* (Khan et al. 2016a, b). Atrazine is also known to show detrimental effects on the digestive gland of *Crassostrea gigas*, pacific oyster by modulating important molecular and biochemical parameters within relatively short time period (Lee et al. 2017). Exposure to atrazine may be associated with decreased birth weight and preterm delivery. According to Zadeh et al. (2016), hematological parameters like hemoglobin, hematocrit and RBCs were significantly decreased by chronic toxicity of atrazine in fish, Tor grypus exposed to different levels of atrazine. The increase in concentrations of lactate dehydrogenase (LDH) and decrease in concentrations of creatinine phosphokinases (CPK), serum glutamic-pyruvic transaminase (SGPT) and alkaline phosphatase indicate an adverse effect of atrazine on grass carp, Ctenopharyngodon Idella (Khan et al. 2016a, b). In *Channa punctatus*, the biochemical parameters such as serum total protein, glucose and cholesterol values were found to decrease, while level of

urea significantly increased in all treatments suggesting anemia and hepatic damage. In a risk assessment study of atrazine in American surface waters, it was found that phytoplankton were the most sensitive organisms followed by macrophytes, benthic invertebrates, zooplanktons and fish. In estuarine crab, *Neohelice granulata* significant decrease in glycogen content and significant diminished content of vitellogenin proteins in ovary was detected after atrazine toxicity (Silveyra et al. 2017). In zebrafish, *Danio rerio* decrease in glutathione S-transferase and catalase and an increase in superoxide dismutase, glutathione peroxidase and reductase were observed indicating profound influence of atrazine on the oxidative stress markers and detoxifying enzymes (Blahova et al. 2013). Atrazine also affects gill respiration and ion regulation function of fingerlings (*Caspian kutum*) by damaging tissue, pavement cells and ionocytes (Khoshnood et al. 2015).

Effects on other invertebrates and vertebrates

Oluah et al. (2016) studied the toxicity and the histopathological effects of Atrazine on earthworms, *Nsukkadrilus mbae,* and reported significant adverse effects. Xu et al. (2006) compared atrazine and chlorotoluron toxicity on *Eisenia fetida* and found atrazine as more toxic to earthworms; combination showed synergistic effect. Superoxide dismutase (SOD) activity showed an increase. The exposure of chlorpyrifos to *E. fetida* in combination with atrazine or cyanazine was evaluated, in which the resultant toxicity was greater than the additive (Lydy and Linck 2003). Previous studies suggest that the pessimistic effects of atrazine on neuro-endocrine system occur by changing pituitary hormone levels, such as follicle-stimulating hormone (FSH) and luteinizing hormone (LH) (Cox 2001; Yang et al. 2014). Altered LH leads to prolonged prolactin secretion and subsequent stimulation of the mammary gland proliferative changes and increased incidence of mammary adenocarcinomas and fibroadenomas (Jowa and Howd 2011; Simpkins et al. 2011). Atrazine inhibits the release of gonadotropin-releasing hormone (GnRH), which decreases the secretion of LH that may lead to increased abortions in male Wistar rats (Stoker et al. 2002). Exposure to atrazine affects both germ cells as reduced motility and sperm counts in male rats (Victor-Costa et al. 2010: Pogrmic et al. 2009). Effects of atrazine were also observed as a decrease in levels of serum lipids and liver enzymes in adult mammals (Suzawa and Ingraham 2008: Hayes et al. 2002). Atrazine supposedly increases aromatase enzyme activity via inhibition of phosphodiesterase, which increases the aromatization of testosterone to estrogen (Hayes et al. 2006; Cooper et al. 2007). An increased estrogenic environment may favor altered relative sex hormone levels may affect reproduction and/or development and induction of cancers and proliferation of preexisting estrogen-dependent cancers (Oka et al. 2008). Other effects of metabolites of atrazine on the immune system, central nervous system and cardiovascular function have also been reported (Jin et al. 2010; Christin et al. 2003). In adult humans, non-Hodgkin's lymphoma associates with the exposure of the compound (Schroeder et al. 2001). According to Gely-Pernot et al. (2015), atrazine exposure interferes with normal meiosis, which affects spermatozoa production in male mice. Oxidative stress and disruptions in calcium homeostasis play an important role in the induction of immunotoxicity in mice by atrazine as depicted by Gao et al. (2016). It is also found to elicit immunotoxic effects on murine lymphocytes, and its presence in the environment might compromise immune function in organisms (Chen et al. 2015a, b). Atrazine is known to reduce the mating rate, number of progeny and competitive fertilization ability; it also alters gene expression and production of proteins in *Drosophila melanogaster* (Vogel et al. 2015). Marcus and Fiumera (2016) observed reduced pupation rate, emergence rate and longevity of adult in *D. Melanogaster* after atrazine exposure. Atrazine was also reported to be endocrine disrupters and significant decrease in steroid levels (testosterone and 17β-estradiol), and total proteins were also noted; the histology of ovotestis showed degenerative changes including azoospermia and oocytes deformation (Omran and Salama 2016). 57% reduction in testicular volume was marked in atrazine exposed tadpoles. Also, primary spermatogonial cells and nurse cells were reduced by 70 and 74%, respectively (Tavera-Mendoza et al. 2002). Toxicity profiles of atrazine against microorganisms, aquatic lower invertebrates, higher vertebrates and humans are presented in Table 2.

The prime target of chlorinated atrazine on humans and mammals is the disruption of the endocrine system (Jin et al. 2014; Kroon et al. 2014; Weber et al. 2013). Secondly, it also induces oxidative stress by formation of reactive oxygen species resulting in the reduced semen quality sperm dysfunction and infertility of amphibians, rats and pigs (Gely-Pernot et al. 2015; Jestadi et al. 2014; Kniewald et al. 2000). In females, pesticides imbalances sexual hormones intervene androgen or estrogens receptors for improper function, irregularities of ovarian cycles, instinctive abortion, defect in developmental births, etc. (Bohn et al. 2011). Atrazine forms ROS, which cause single- and double-strand breaks in DNA and thus is genotoxic (Yang et al. 2010). The working of cardiovascular system also gets affected by atrazine exposure (Lin et al. 2016a, b, c; Cosselman et al. 2015). Atrazine is known to cause hepatic damage, as liver is the primary organ for atrazine metabolism in mammals (Campos-Pereira et al. 2012; Gojmerac and Kniewald 1989). Atrazine is

Table 2 Toxicity and adverse effects of atrazine on humans, aquatic lower invertebrates, higher vertebrates and soil microorganisms

Living groups	Scientific name	Common name/category	Mechanism of toxicity	References
Algae	*Pseudokirchneriella subcapitata*	Micro algae	Inhibition in population growth	Khilji (2011)
	Selenastrum capricornutum	Green algae	Algal population growth inhibition (IC50-cell counts), percent lethality (LC50-flow cytometry derived) and photosynthetic electron transport inhibition	Caux et al. (1996)
	Raphidocelis subcapitata	Microalgae	Decreased in PSII yield	Baxter et al. (2016)
	Diporeia sp.	Microalgae	Cell division was majorly affected	Ralston-Hooper et al. (2009)
	Diporeia sp.	Microalgae	Photosynthetic process, cell division, lipid synthesis were majorly affected	Ma et al. (2006)
Annelid	*Eisenia fetida*	Redworm	Atrazine was more toxic to earthworm than chlorotoluron. Combination showed synergistic effect. SOD activity shows increase	Xu et al. (2006)
	Eisenia fetida	Redworm	Binary mixtures of chlorpyrifos with atrazine and cyanazine demonstrated greater than additive toxicity	Lydy and Linck (2003)
	Nsukkadrilus funmie	Nigeria earthworm	Chloragogenous layer and epithelial tissue damage; prominent vacuolations and pyknotic cells	Oluah et al. (2016)
Mollusca	*Lampsilis siliquoidea* (Glochidia and juvenile stage)	Fatmucket clam	Median effective concentrations for chlorpyrifos were 0.43 mg/L for glochidia at 48 h, 0.25 mg/L for juveniles at 96 h, and 0.06 mg/L for juveniles at 21 days	Bringolf et al. (2007)
	Corbicula fluminea	Freshwater clam	Leading to lipid peroxidation	Dos-Santos and Martinez (2014)
	Crassostrea gigas	Pacific oyster	Detrimental effects on digestive gland by modulating important molecular and biochemical parameters	Lee et al. (2017)
Arthropod	*Chironomus tentans*	Midge	Not acutely toxic at even higher levels but combination with chlorpyriphos, methyl parathion, malathion decreases the EC50	Belden and Lydy (2001)
	Daphnia magna	Water fleas	The interactive effect of all the three pesticides was synergistic and have negative effect on liver, kidneys, etc.	Kungolos et al. (1999)
	Neohelice granulata	Estuarine crab	Significant decrease in glycogen content and significant diminished content of vitellogenin proteins in ovary	Silveyra et al. (2017)
	Drosophila melanogaster	Fruit fly	Reduces the mating rate, number of progeny and competitive fertilization ability; also alters gene expression and production of proteins in	Vogel et al. (2015)
	D. melanogaster	Fruit fly	Atrazine exposure reduces pupation rate, emergence rate and longevity of adult	Marcus and Fiumera (2016)
	Hyalella azteca	Scud	Significant *H. azteca* 96-h mortality occurred within the first 2 h of amendment at the upstream amendment site	Ralston-Hooper et al. (2009)

Table 2 continued

Living groups	Scientific name	Common name/category	Mechanism of toxicity	References
Amphibian	*Rana pipiens*; *Bufo americanus*	Leopard frog; American toads	Older amphibian larvae were more sensitive. The toxicity of 50:50 mixture of atrazine and alachlor was greater than additive	Howe et al. (1998)
	Lithobates catesbeianus	Bull frog	Pessimistic effect on biochemical parameters, lipid peroxidation, and survival in tadpoles	Dornelles and Oliveira (2014)
	Xenopus. Laevis	African clawed frog	Decrease in levels of serum lipids and liver enzymes	Hayes et al. (2002)
Reptilian	*Trachemys scripta*	Red-eared slider	Lowered serum complement and lysozyme activities, reduced leukocyte number as well as their phagocytic activity	Soltanian (2016)
Pisces	*Rhamdia quelen*	Cat fish	Histopathological changes in liver revealed leukocyte infiltration, hepatocyte vacuolization like steatosis and necrosis areas, leading to raised lesion index levels in all tested concentrations; process of osmoregulation was disturbed and gills showed changes in pavement cells and chloride cells	Mela et al. (2013)
	Channa punctatus	Snakehead	Significant rate of micronuclei and nuclear abnormalities	Nwani et al. (2011)
	Tor grypus	Shabout	Hematological parameters like hemoglobin, hematocrit and RBCs were significantly decreased	Zadeh et al. (2016)
	Plotosus lineatus	Eel cattlefish	Enzyme inhibitor, impairing hepatic metabolism and produces genotoxic damage to different cell types	Santos and Martinez (2012)
	Ctenopharyngodon	Grass carp	Decline in levels of total protein and serum albumin	Khan et al. (2016a, b)
	Oreochromis niloticus	Tilapia	Significant rate of micronuclei and nuclear abnormalities	De Campos et al. (2008)
	Cyprinus carpio	Common carp	Effect of atrazine and chlorpyrifos on the mRNA levels of HSP70 and HSC70 in the liver, brain, kidney and gill of common carp	Xing et al. (2013)
	Oncorhynchus mykiss	Rainbow trout	Rainbow trout appeared to be less sensitive than amphibian larvae	Howe et al. (1998)
	Ictalurus punctatus	Channel catfish	Channel catfish appeared to be less sensitive than amphibian larvae	Howe et al. (1998)
	Danio rerio	Zebra fish	Influence on the oxidative stress markers and detoxifying enzyme	Blahová et al. (2013)
	Prochilodus lineatus	Ray-finned fish	Enzyme inhibitor, impairing hepatic metabolism, and produces genotoxic damage to different cell types	Santos and Martinez (2012)
	Danio rerio	Zebra fish	Alters hormone networks via convergence of NR5A activity and cAMP signaling, to potentially disrupt normal endocrine development and function in lower and higher vertebrates	Suzawa and Ingraham (2008)
	Caspian kutum	Caspian white fish	Gill respiration and ion regulation function of fingerlings affected by damaging tissue, pavement cells, and ionocytes	Khoshnood et al. (2015)

Table 2 continued

Living groups	Scientific name	Common name/category	Mechanism of toxicity	References
Rodentia	*Rattus norvegicus*	Male Wistar rats	Affects both germ cells as reduces motility and sperm counts in male rats	Victor-Costa et al. (2010) and Pogrmic et al. (2009)
			Inhibits the release of Gonadotropin-releasing hormone (GnRH), which decreases the secretion of LH that may lead to increased abortions in male	Stoker et al. (2002)
	Mus musculus	Male mice	Atrazine interferes with normal meiosis, which affects spermatozoa production	Gely-Pernot et al. (2015)
	Mus musculus	Mice	Atrazine leads to oxidative stress and disruptions in calcium homeostasis which induces immunotoxicity	Gao et al. (2016)
	Rattus norvegicus	Male Sprague–Dawley rat	Non-dopaminergic cells respond and hypoactivity-inducing effect	Rodriguez et al. (2017)
Primates	*Homo sapiens*	Postmenopausal women	endocrine disrupting effects	Inoue-Choi et al. (2016)
		Human primary hepatocytes	Short and chronic exposures leads to cellular impact on human primary hepatocytes and HepaRG cells	Nawaz et al. (2014)
		Human neuroblastoma	Induces apoptosis of SH-SY5Y human neuroblastoma cells via the regulation of Bax/Bcl-2 ratio and caspase-3-dependent pathway	Abarikwu and Farombi (2015)
			Induces SH-SY5Y human dopaminergic neuroblastoma cells via microglial activation	Ma et al. (2015)
			Induces aromatase expression is SF-1 dependent and endocrine disruptor	Fan et al. (2007)
			Disrupts the hypothalamic control of pituitary–ovarian function	Cooper et al. (2000)

also responsible for cardiotoxicity and hepatotoxicity in mice by disruption of ionic balance (Lin et al. 2016a, b).

The negative effects of atrazine on soil and aquatic biota are enormous. The above studies decipher a clear picture about the vulnerability of atrazine to terrestrial and aquatic life forms. The detection of atrazine with better accuracy and reliability is thus essential for safety of human health, biota and environment.

Analytical methods for monitoring atrazine in ecosystems

Basically, single environmental matrix can contained multiple pesticides (Kaur et al. 2017; Kumar et al. 2016, 2017; Singh et al. 2016). The extraction, cleanup and pre-treatment procedure depend upon the physiochemical nature of pesticides and environmental matrix (Kaur et al. 2017; Kumar et al. 2016, 2017). There are number of methods described for the analysis of different classes of pesticides in different matrices (AOAC 1993; Kumar et al. 2015a, b, c, d; Prasad et al. 2013; Kumar and Singh 2016; Singh et al. 2017). In day-to-day laboratory analysis, AOAC method is most authentic. Most common steps for the extractions of pesticides including atrazine have been described by Kumar et al. (2015a, b, c, d) as per the guidelines of AOAC (AOAC 1993; Kumar et al. 2015a, b, c, d; Prasad et al. 2013; Singh et al. 2016, 2017).

Highly sensitive and rapid analytical methods are essential for monitoring of residual atrazine and its metabolites in soil and water bodies (Table 3). It is monitored by using spectroscopic, immunogenic and chromatographic methods which include infrared (IR) spectroscopy, high-performance liquid chromatography (HPLC)/HPLC–MS/HPLC–MS/MS, HPLC, enzyme-linked immunosorbent assay (ELISA) and gas chromatography GC/GC–MS/GC–MS/MS (Miensah et al. 2015; Williams et al. 2014; Bonansea et al. 2013). Recently nano-based solid-based extractions ultra-performance liquid chromatography (UPLC) and GC/LC–MS methods have been developed with very good recovery and detection limits up to ppb (Table 3). The detection of atrazine in

Table 3 Analytical techniques applied for the detection and quantitative estimation of atrazine and derivatives in various ecosystems

Analytical technique	Detector	Method	Source	Sample detection	Percentage recovery	References
Gas Chromatography (GC/GC–MS)	GC–NPD	Liquid–liquid extraction with diethyl ether	Urine	1 μg/L	100%	Ikonen et al. (1988)
	NPD	Liquid–liquid extraction with ethyl acetate	Water	1.5 ng/L (NPD)	88–96%	Dalluge et al. (1999)
	GC–NPD	Solid-phase microextraction	Water	7.4 ng/L	Not reported	Ferrari et al. (1998)
	GC–NPD GC–ECD GC–MS	Filtered onto SPE matrix	Surface and ground waters	2 ng/L	85–110%	Albanis et al. (1998)
	GC–NPD	Liquid–liquid extraction	Surface water	0.4 ng/L	67–100%	Sabik and Jeannot (1998)
	GC–ECD	Liquid–liquid extraction	Sediment aquatic plants	Not reported	90%	Bennett et al. (2000)
	GC–NPD	Solid-phase extraction	Water	100 ng/L	Not reported	Amistadi et al. (1997)
	GC–NPD	Solid-phase extraction	Soil	1.0 μg/kg	Not reported	Amistadi et al. (1997)
	GC–MS	Solid-phase microextraction	Water	40 ng/L	Not reported	Hernandez et al. (2000)
	GC–MS	Solid-phase microextraction	Soil	> 3 μg/kg	> 80%	Hernandez et al. (2000)
	GC–MS	Liquid–liquid extraction	Blood plasma	100 ng/mL	84–97%	Brzezicki et al. (2003)
	GC–ECD	SPE extraction followed by hexane elution	Soil	Not reported	Not reported	Ahel et al. (1992)
	GC–ECD		House hold dust	0.21 ng/cm^2	Not reported	Lioy et al. (2000)
	GC–ECD	NIOSH method	Air	0.2 μg/sample	Not specific	NIOSH (1998a)
	GC–ECD	Derivatizing in diazomethane	Hand contamination	0.01 μg/mL	87.1–103%	NIOSH (1998b)
	GC–MS	Solid-phase extraction	Water	0.05–0.10 μg/L	85.3–98%	Yokley et al. (2000)
	GC/GC–MS	AOAC method	Water/soil/food/drugs	0.25–5.0 μg/L	65–89.6%	AOAC (1993)
High Performance Liquid Chromatography (HPLC/HPLC–MS/UPLC–MS)	HPLC–DAD	Solid-phase extraction	Water	0.3–40.0 ng/mL	81.3–120.3%	Caoa et al. (2017)
	HPLC	Extraction with dichloromethane	Blood plasma, organ tissues	14.25 ng/mL	58–61%	Pommery et al. (1993)
	HPLC–MS	Nano-based solid-phase extraction	Fruit/vegetables/water	1–200 ng/mL	88–101.9%	Zhao et al. (2012)
	HPLC–MS	Nanotube-based solid-phase extraction	Water	0.0005–0.005 μg/L	85–112%	Tan et al. (2015)
	HPLC–MS	Magnetism-enhanced monolith-based nanotube solid-phase microextraction	Water	0.074–0.23 μg/L	75–119%	Mei et al. (2016)
	HPLC–UV	Extraction with dichloromethane	Liver microsomes	2–5 pmol	96–103%	Lang et al. (1996)

Table 3 continued

Analytical technique	Detector	Method	Source	Sample detection	Percentage recovery	References
	HPLC	Supercritical fluid extraction	Eggs	100 µg/kg	90.4%	Pensabene et al. (2000)
	HPLC/ HPLC–MS	Liquid–liquid extraction	Surface waters	0.6 ng/L	67–100%	Sabik and Jeannot (1998)
	HPLC/ HPLC–MS	AOAC method	Water/soil/food/drugs	0.25–5.0 µg/L	65–89.6%	AOAC (1993)
	UPLC–MS	Solid-phase extraction	Water	0.023–0.657 µg/L	80.3–99.8%	Gonzáleza et al. (2016)
	UPLC–MS	Solid-phase extraction	Water	0.2–30.0 µg/L	70.5–112.1%	Chen et al. (2015a, b)
	HPLC	Molecular-imprinted solid-phase extraction	Blood serum and urine	0.001 µg/mL	94.8%	Peighambarzadeh et al. (2011)
Enzyme-linked immunosorbent assay (ELISA)	ELISA	Direct method	Saliva	0.22 µg/L	Not reported	Denovan et al. (2000)
		EPA-approved method	Food	0.1 µg/L	Not reported	SDI (1999)
		RAPID assay ELISA kit	Water	50 ng/L	Not reported	Amistadi et al. (1997)
		RAPID assay ELISA kit	Soil	200 ng/kg	Not reported	Amistadi et al. (1997)
		Proprietary ELISA method	Water and soil	0.1 µg/L	Not reported	SDI (1998)
		Optical wave Guide Mach–Zehnder immunosensor	–	–	0.1 pg/L	Schipper et al. (1997)
		Ampherometric immunosensor	–	–	Nanomolar range	Lopez et al. (1998)
		SPR	–	–	–	Kim et al. (2003)
		Immobilzation of PPO	–	–	–	Kaoutit et al. (2004)
		Sheep antibodies	–	–	0.03 bp	Wüst and Hock (1992)
		ICG strips	–	–	3 ng/L	Shim et al. (2006)
		Immunomagnetic electrochemical sensor	–	–	10–600 ng/L	Helali et al. (2006)
		Coating with hapten	–	–	0.02–0.7 ng/L	Suri et al. (2008)
		Chemiluminensce	–	–	142 ng/L	Beale et al. (2009)
		Electrochemical Sensor	–	–	10^{-9} mol/L to 1.5×10^{-2} mL	Pardieu et al. (2009)
		Impedance spectroscopy transduction	–	–	10 pg/mL	Ionescu et al. (2010)
		Antibody replicas	–	–	–	Yaqub et al. (2011)
		Molecular-imprinted polymer	–	–	1.8 mM	Zhang et al. (2011)
		Vinyl-substituted zinc proto porphyrin	–	–	1.8 mM	Ionescu et al. (2010)
		Immobilization of gold nanoparticles	–	–	0.016 ng/mL	Liu et al. (2014)

Table 3 continued

Analytical technique	Detector	Method	Source	Sample detection	Percentage recovery	References
		Plastic antibody-based surface plasmon nanosensors	–	–	–	Yilmaz et al. (2017)
		Modified self-ordered Nb_2O_5 nanotube arrays	–	–	–	Yang et al. (2017)
		Detection based on tyrosinase and carbon-based SPE biosensors	–	–	–	Tortolini et al. (2016)
		Detection by phage anti-immuno complex assay	–	–	–	González-Techera et al. (2015)
		Label-free disposable immunosensor	–	–	–	Belkhamssa et al. (2016)

AOAC Association of Official Analytical Chemists, *ECD* electron capture detection, *ICG* immunochromatographic strips, *MS* mass spectrometry, *NIOSH* National Institute for Occupational Safety Chromatography, *NPD* nitrogen–phosphorus detector, *SPE* solid-phase extraction, *ECD* electron capture detection, *ELISA* enzyme-linked immunosorbent assay, *EPA* Environmental Protection Agency, *GC* gas chromatography, *HPLC* high-performance liquid chromatography, *UV* ultraviolet

biological media is quantified using GC coupled with MS including different detectors like flame ionization detector (Haiyan and Center 2015), electron capture detector (ECD) (Miensah et al. 2015), nitrogen-phosphorus detector (NPD) (Bonansea et al. 2013) and GC coupled with mass spectrometer (Williams et al. 2014).

Quantification of atrazine was also done by a diode array (Yang et al. 2014) and a UV detector (Kong et al. 2016). Immunogenic methods are usually based on ELISA using sheep-based antibodies to atrazine (Na et al. 2012). Other immunogenic methods have been developed in which the antibody is bound to a "dipstick," and this is used to evaluate concentrations of atrazine in water or liquid food samples (Kaur et al. 2007), while other sampling approaches have used immuno-affinity systems to concentrate atrazine prior to analysis by GC (Tran et al. 2013).

In water samples, atrazine was detected with GC equipped with nitrogen phosphate detector (NPD) and the percentage recovery is very high 96–98% (Nsibande et al. 2015). In sub-surface waters, the atrazine was quantified by both the techniques, i.e., HPLC and GC equipped with NPD, ECD and MS detectors (Barchanska et al. 2014). In aquatic plants and sediments, the concentration of atrazine was quantified by GC coupled with ECD detectors and the recovery percentage is near about 90% (Bennett et al. 2000). In water and soil samples, the solid-phase extraction method is used to concentrate the samples prior for analysis, all the three methods, i.e., GC coupled with all three detectors mentioned above, ELISA and HPLC equipped with UV detector (Hernandez et al. 2000; Lioy et al. 2000). The detection limit of atrazine in biological media moves to a greater extent as it was 0.1 µg/L in the year 2000 (Yokley et al. 2000) and it moves to 50 ng/L in the year 2008 (Gervais et al. 2008). It is all due to the new innovations in day-to-day life. In 2000, the detection was only SPE and GC based. Using styrene di-vinyl benzene sorbents, the detection limits increase to 10 ng/L (Bruzzoniti et al. 2006). Tandem mass spectroscopy combined with ultra-performance liquid chromatography detects up to 50 ng/L of the atrazine in biological media (Kuklenyik et al. 2012).

Qie et al. (2013) developed a technique direct competitive ELISA method (dcTELISA) based on thermistor enzyme for faster detection of atrazine in large-scale samples. In this method, ATZ competes for β-lactamase-labeled ATZ (ATZ–E) for the binding sites on anti-ATZ monoclonal immune response (mAb) which is covalently linked to form immunocomplexes from immune reactor with β-lactamase-labeled ATZ and atrazine. The detection limit was very good with high recovery rate (88–107%) in silage and fresh corn stalk samples. Another novel method for detection of atrazine was based on the SPR (Sepia

pterin reductase) determination of P450 mRNA levels in *Saccharomyces cerevisiae*. The selected oligonucleotide probe that exhibits specificity for P450 mRNA was successfully immobilized on the sensor chip. The mRNA was quantified. It is a highly sensitive and rapid method that permits the detection of atrazine within 15 min (Kim et al. 2003). Kaoutit et al. (2004) also gave a simple conducting polymer-based biosensor approach. A glassy carbon electrode was prepared which is operated at open circuit and served for the immobilization of the enzyme polyphenol oxidase (PPO) during the anodic electropolymerization of polypyrrole (PPy). The concentration of atrazine in aqueous solution is attributed to its inhibitory power toward the catalytic activity of PPO. This biosensor helps in easy detection of photosynthetic inhibiting herbicide monitoring because of its analytical performance and simplicity. A protein-based conjugate method was developed for binding of atrazine with anti-atrazine monoclonal antibodies. Here immobilization was done on gold particles based on test strip method assessed with a photometric device to detect atrazine in very low limits (130 ng/mL) (Byzova et al. 2010). An immunochromatography (ICG) strip test for detection of atrazine in water samples was also developed. Monoclonal antibody (MAb) specific to atrazine was produced from the cloned hybridoma cell (AT-1-M3) and used to develop a direct competitive enzyme-linked immunosorbent assay (DCELISA) and ICG strip. The limit of detection was 3 ng/mL, and it requires only 10 min getting the results and that too in a single step. It came out to be a sensitive and accurate technique (Shim et al. 2006). A disposable immunomagnetic electrochemical sensor involving magnetic particles was developed for the detection of atrazine. The sensor was based on a magnetic monolayer of magnetic particles coated with streptavidin, formed on a gold electrode after application of a magnetic field. The atrazine interacts with biotinyl–Fab fragment K47, and the immune reactions were characterized by impedance spectroscopy. A decrease in electron transfer resistance was observed which could be attributed to rearrangements in the magnetic monolayer. The limit of detection is in the range 10–600 ng/ml; it is a sensitive approach for detection of atrazine acting as an antigen (Helali et al. 2006). Another novel immunoassay was formulated that involved direct coating of haptens on microtiter plates for detection of atrazine. The assay allows hapten-coated plates and uses affinity-purified atrazine which showed very high sensitivity. The limit of detection for atrazine is in the range 0.02–0.7 ng/mL (Suri et al. 2008). Detection of atrazine and triazines in water has also been carried out flow injection chemiluminescence analysis. The aliphatic amines in traizines react with tris(2,2′-bipyridyl)ruthenium(III) to produce chemiluminescence. The presence of natural organic matter (NOM) significantly increased the chemiluminescence, masking the signal generated by atrazine. Isolating the target analyte via solid-phase extraction (SPE) prior to analysis removed this interference and concentrated the samples. The detection limit is 14 ± 2 ng/L (Beale et al. 2009). Pardieu et al. (2009) devised an electrochemical sensor based on molecularly imprinted conducting polymer (MICP). The recognition of atrazine can be quantified by the variation of the cyclic voltammogram of MICP. It shows selectivity toward triazine family and shows a large range of detection from 10^{-9} to 1.5×10^{-2} mol/L. Impedance spectroscopy transduction combined with the immunosensor technology has been used for the determination of atrazine. The immunoreaction of atrazine on the attached anti-atrazine antibody leads to an increase in the charge transfer resistance which is proportional to the concentration of atrazine. Its limit of detection was 10 pg/mL (Ionescu et al. 2010). Another approach based on antibody replicas for atrazine detection was formulated by Schirhagl et al. (2011). Antibodies were used to pattern the nanoparticles for surface imprinting the polymer layer to produce replicas. Liu et al. (2011) constructed a MIP (molecularly imprinted polymers) chemosensor from a core–shell nanostructure. Vinyl-substituted zinc(II) protoporphyrin (ZnPP) was used as both fluorescent reporter and functional monomer to synthesize atrazine-imprinted polymer shell. The limit for detection is 1.8 mM. Bioluminescent reported bacteria are also utilized for detection of atrazine. Increase in bioluminescent signals is recorded for *E. coli*. For better interaction between insoluble atrazine and bacterial cells, centrifugation of bacterial cells and analyte dilutions can be performed (Jia et al. 2012). An electrochemical immunosensor for atrazine detection was developed by immobilization of gold nanoparticles on the gold electrode surface. The increase in surface area of work electrode leads to more anti-atrazine monoclonal antibodies capture. Ferricyanide was used as an electrochemical redoxindicator; immunosensor was characterized by cyclic voltammetry and electrochemical impedance spectroscopy. The limit for detection is as low as 0.016 ng/mL (Liu et al. 2014). A field effect transistor was developed based on network of single-walled carbon nanotubes which constitute carbon nanotubes field effect transistors and act as conductor channel for the determination of atrazine in various biological samples with detection limit up to 0.001 ng/mL (Belkhamssa et al. 2016).

Photochemical degradation of atrazine

Several chemical methods have been developed for the degradation during time to time. Konstantinou et al. (2001) have studied the photocatalytic degradation of atrazine and

other s-triazine herbicides by using particulate TiO_2 as photocatalyst under simulated solar light. The degradation process is highly efficient with traces of atrazine (at ppb level) being decomposed in very short times to less than 0.1 ppb. The process has been shown to lead to the formation of 2,4,6-trihydroxy-1,3,5-triazine (cyanuric acid) as the final product of the degradation process for all the investigated herbicides with several intermediates, rather than to the complete mineralization often observed for other classes of substrates. Monitoring of degradation products has been done using liquid, gas and ion chromatography, and the overall degradation process has been monitored through dissolved and particulate organic carbon measurements.

Atrazine degradation by Fenton's reagent has been determined as a function of reagent's concentration and ratios and pH in batch treatments (Barbusiński and Filipek 2001). The actual number and nature of oxidation products have been shown to vary with the concentration. The optimum Fenton's reagent treatment has been achieved with 1:l molar ratios of $FeSO_4$ and H_2O_2 (2.69 mM), producing two main terminal products viz, 2-chloro-4,6-diamino-s-triazine (23%) and 2-acetamido-4-amino-6-chloro-s-triazine (28%). Chloride release of $55 \pm 9\%$ indicated that dehalogenated s-triazines accounted for the balance of ^{14}C. Atrazine degradation has been found to be pH dependent and decreases from 99% at pH 3 to 37% at pH 9.

In a modified approach, the effects of an inorganic ligand tetrapolyphosphate on the molecular oxygen activation and the subsequent aerobic atrazine degradation by $Fe@Fe_2O_3$ core–shell nanowires were investigated at a pH range of 6.0–9.0 (Wang et al. 2014a, b). It was observed that the addition of tetrapolyphosphate enhanced the rate of aerobic atrazine degradation dramatically (955 times) which was even 10 times that of the traditional organic ligand ethylenediamine tetraacetate. The rate enhancement has been attributed to enhanced reduction in Fe(III) to Fe(II) and the subsequent activation of molecular oxygen, owing to the suppressed hydrogen evolution, in the presence of tetrapolyphosphate, from the reduction in proton by $Fe@Fe_2O_3$ core–shell nanowires, making more electrons available for the reduction in Fe(III). Moreover, the complexation of tetrapolyphosphate with ferrous ions ensures enough soluble Fe(II) for Fenton reaction and also provides another route to produce more hydroxyl ($^{\cdot}OH$) radicals in the solution via the single-electron molecular oxygen reduction pathway, thus increasing the rate dramatically.

Ozone being a powerful oxidant has been used in the presence of hydrogen peroxide for degradation of atrazine. Tandem solid-phase extraction procedure was used which includes a C_{18} reverse-phase support and a strong cation exchanger (Nélieu et al. 2000). It was found that ammeline (2, 4-diamino-6-hydroxy-s-triazine) is the major end product (20% at pH 8) and 2-chloro-4,6-diamino-s-triazine as competitor whose ratio was dependent on the hydroxyl radical content. A number of new intermediates identified were aminoaldehydes and a carbinolamine (Nélieu et al. 2000). Triazine has also been degraded by electrochemical advanced oxidation processes such as anodic oxidation, electro-fenton and photoelectro-fenton using a small open and cylindrical cell with a boron-doped diamond anode. Anodic oxidation has been carried out either with a stainless steel cathode or an O_2 diffusion cathode able to generate H_2O_2 formed at the boron-doped diamond surface in all electrochemical advanced oxidation processes. In the bulk form, Fenton's reaction between added Fe^{2+} and electrogenerated H_2O_2 in electro-Fenton and photoelectron-Fenton, Hydroxyl radical ($^{\cdot}OH$) is the main oxidant (Borras et al. 2010). It has been observed that almost overall mineralization (94%) is achieved. Atrazine decay always follows a pseudo-first-order reaction, being more rapidly destroyed from $^{\cdot}OH$ in bulk than at the boron-doped diamond surface. The formation of dealkylated aromatic intermediates such as desethylatrazine and desethyldesisopropylatrazine and cyanuric acid has been revealed by reverse-phase HPLC, and short linear carboxylic acids such as formic, oxalic and oxamic have been identified and quantified by ion-exclusion HPLC. It has been observed that all initial nitrogen is transformed into NO_3^- and NH_4^+ ions (followed by ionic chromatography) in electro-fenton and photoelectro-fenton but not in anodic oxidation, where 36% of nitrogen is released from the solution probably as volatile NO_x species.

The recent results showed approximately 80% of atrazine was degraded by ozonation in the presence of hydroxylamine, while only 20% was degraded by ozonation alone. The atrazine degradation involved dealkylation, dechlorination–hydroxylation and olefination (Yang et al. 2016a, b). It has been found that at lower pH the degradation efficiency of atrazine was enhanced by UV/chlorine compared to UV or chlorine alone. The oxidation products of atrazine resulting from dealkylation, dechlorination–hydroxylation, alkylic-hydroxylation, alkylic-oxidation, alkylic-hydroxylation dehydration, deamination–hydroxylation and dechlorination–hydrogenation in UV/chlorine process were detected, which were slightly different from those formed in UV/H_2O_2 (Kong et al. 2016). Similar products were noticed when nitrite was added to enhance atrazine degradation during ozonation (Yang et al. 2016a, b). The experimental results of electrophotocatalytic reduction (hydroxyl radical reduction) of atrazine with an initial concentration of atrazine (100 mg/L) show that more than 99% of atrazine oxidation was obtained after 30 min of treatment and reaction kinetic constant was about 0.146/min. The analysis with liquid chromatography

Table 4 Microorganisms involved in biodegradation of atrazine under in situ and experimental conditions

Microbial species	Enzymes and genes involved	Degradation products	Accession numbers	References
Agrobacterium radiobacter J14a	AC (*atzA*), HAEA (*atzB*), IAIA (*atzC*), CAH (*atzD*) BH (*atzE*), AH (*atzF*)	Hydroxyatrazine, deethylatrazine and deethyl-hydroxyatrazine	–	Struthers et al. (1998) and De Souza et al. (1998)
Alcaligenes sp. SG1	AC (*atzA*), HAEA (*atzB*), IAIA (*atzC*), CAH (*trzD*) BH, AH	–	–	K.L.Boundy-Mills (unpublished) and Zhang et al. (2011)
Arthrobacter sp.	–	–	–	Wang et al. (2013)
Arthrobacter sp. C3	*trzN*	Dechlorination		Wang et al. (2016)
Arthrobacter sp. strain DAT1	*trzN*, *atzB*, *atzC*	–	JN833464.1	Wang and Xie (2012)
Arthrobacter sp.	–	Cyanuric acid	HQ665017	El Sebai et al. (2011)
Arthrobacter strain DNS 10	–	Cyanuric acid	HQ914648	Zhang et al. (2011)
Arthrobacter sp. T3AB1	–	–	GU459313.2	Liu et al. (2010)
Arthrobacter sp. GZK-1	–	–	FJ766438	Getenga et al. (2009)
Arthrobacter sp. AD26	–	–	–	Qingyan et al. (2008)
Arthrobacter strain HB5	–	Hydroxyatrazine, cyanuric acid	–	Wang et al. (2006)
Arthrobacter sp. MCM	–	–	AY589014	Vaishampayan et al. (2007)
Arthrobacter strain MCM B-436	–	–	–	Vaishampayan et al. (2007)
Arthrobacter nicotinovorans HIM	–	1,3,5-Trimethyl-1,3,5-triazone-2,4,6(1H,3H,5H)-trione	–	Aislabie et al. (2005)
Arthrobacter sp. strain DNS10	*strzN*, *atzB* and *atzC*	–		Zhang et al. (2011)
Arthrobacter sp. AD1		–	–	Cai et al. (2003)
Arthrobacter aurescens TC1	AC (*trzN*), HAEA (*atzB*) IAIA (*atzC*)	Isopropylamine	–	Strong et al. (2002)
A. radiobacter J14a	–	Hydroxyatrazine, deethylatrazine and deethyl-hydroxyatrazine.	–	Struthers et al. (1998)
Aminobacter aminovorans	–	Cyanuric acid	–	Rousseaux et al. (2001)
Arthrobacter crystallopoietes	–	Cyanuric acid	–	Rousseaux et al. (2001)
Bacillus subtilis strain HB-6	–	Hydroxyatrazine, cyanuric acid	HM116874	Wang et al. (2014a, b)
Bacillus licheniformis	–	Deetylatrazine, deisopropylatrazine and hydroxyatrazine	–	Marecik et al. (2008)
Bacillus megaterium	–	Deetylatrazine, deisopropylatrazine and hydroxyatrazine	–	Marecik et al. (2008)
Botrytis cinerea	–	Deetylatrazine, deisopropylatrazine and hydroxyatrazine	–	Marecik et al. (2008)
Comamonas sp. A2	–	Hydroxyatrazine, *N*-isopropylammelide, and cyanuric acid	EU016085	Yang et al. (2010)
Chelatobacter heintzii	–	Cyanuric acid	–	Rousseaux et al. (2001)

Table 4 continued

Microbial species	Enzymes and genes involved	Degradation products	Accession numbers	References
Clavibacter michiganese ATZ1	AC (*atzA*), HAEA (*atzB*)	–	–	De Souza et al. (1998)
E. cloacae strain JS08	trZD	Hydroxyatrazine (HA) *N*-isopropylammelide deethylatrazine (DEA), deisopropylatrazine (DIA), and cyanuric acid	FJ810807	Solomon et al. (2013a, b)
Enterobacter cloacae 99	CAH (*trzD*), BH, AH (*trzF*)	Hydroxyatrazine, deethylatrazine and deethyl-hydroxyatrazine.	–	Cheng et al. (2005), Eaton and Karns (1991), Cook and Hutter (1984) and Beilstein et al. (1981)
Ensifer sp.	*atzA*, *atzB*, *atzC*, *atzD*, *atzE* and *atzF*	Cyanuric acid	–	Ma et al. (2017)
Hendersonula toruloide	–	Cyanuric acid and CO_2	–	Wolf and Martin (1975)
Klebsiella sp. KB02	–	–	HM989008	Sopid (2012)
Klebsiella sp. A1	–	Hydroxyatrazine, *N*-isopropylammelide, and cyanuric acid	EU016084	Yang et al. (2010)
Klebseilla pneumonia 99	*trzC*, *rzD*, *trzE*	Ammelide or cyanuric acid	–	Karns and Eaton (1997)
Nocardioides sp. SP12	–	–	–	Piutti et al. (2003)
Nocardia sp.	–	Cyanuric acid	–	Giardina et al. (1980)
Nocardia sp.	–	2-Hydroxy-4,6-bis(alkylamino)-s-triazines	–	Giardina et al. (1979)
Nocardia sp. AM	–	–	–	Giardina et al. (1985) and Giardina et al. (1982)
Nocardioides EAA-3 and EAA-4	*trzN*, *atzB*, and *atzC*	Hydroxyatrazine, desethylatrazine, and desisopropylatrazine	–	Omotayo et al. (2016)
Nocardioides sp.	AC (*trzN*)	Hydroxyatrazine,	–	Topp et al. (2000b)
Proteobacteria	*rzN-atzBC-trzD*	–	–	Udiković-Kolić et al. (2010)
Actinobacteria	*trzN-atzABC-trzD*			
Bacteroidetes	*trzN-atzABCDEF-trzD*			
Pseudaminobacter C147	AC (*atzA*), HAEA (*atzB*), IAIA (*atzC*), CAH, BH, AH	Hydroxyatrazine	–	Topp et al. (2000a)
Pseudomonas ADP	AtzA, AtzB, AtzC, CAH (*atzD*), BH (*atzE*), AH(*atzF*)	Hydroxyatrazine and CO_2	–	Mandelbaum et al. (1995)
Pseudomonas ZXY-1	–	–	–	Zhao et al. (2017)
Pseudomonas YAYA6	–	Cyanuric acid	–	Yanze-Kontchou and Gschwind (1994)
Pseudomonas putida	–	Deisopropylatrazine and deethylatrazine	–	Behki and Khan (1986)
Pseudomonas fluorescens	–	Deisopropylatrazine and deethylatrazine	–	Behki and Khan (1986)
Pseudomonas stutzeri	–	Deisopropylatrazine and deethylatrazine	–	Behki and Khan (1986)
Pseudomonas huttiensis NRRLB-12228	EAA, IAIA (*trzC*), CAH (*trzD*), BH,a AHa	–	–	Eaton and Karns (1991) and Cook and Hutter (1984)

Table 4 continued

Microbial species	Enzymes and genes involved	Degradation products	Accession numbers	References
Pseudomonas sp. CN1	IAIA (*atzC*), CAH, a BH a AHa	–	–	De Souza et al. (1998)
Rahnella aquatilis		Deetylatrazine, deisopropylatrazine and hydroxyatrazine	–	Marecik et al. (2008)
Ralstonia brasilensis M91	3 AC (*atzA*), HAEA (*atzB*) IAIA (*atzC*), CAH (*trzD*), BH, a AHa	–	–	Cheng et al. (2005), De Souza et al. (1998) and Radosevich et al. (1995)
Ralstonia picketii D	CAH (*atzD*), BH (*atzE*) AH (*atzF*)	–		Cheng et al. (2005)
Rhizobium sp. PATR	AC (*atzA*)	–	–	Bouquard et al. (1997)
Rhodococcus N186	BCD, AM (*thcB*)	–	–	Shao and Behki (1996)
Rhodococcus MB-P1	Plasmid coded	Deethylatrazine' and deisopropylatrazine	–	Batra et al. (2009)
Rhodococcus corallinus	*trzA*, NRRLB-15444R TC (*trzA*), DIHA	–	–	Shao and Behki (1995)
Rhodococcus B30	–	2-Chloro-4-amino-6-(isopropylamino)-s-triazine 2-chloro-4- [(l-hydroxyprop-2-yl)aminol-6-(isopropylamino)-s-triazine	–	Behki and Khan (1994)
Rhodococcus sp. TE1	AM (*atrA*)	–	–	Shao and Behki (1995) and Behki et al. (1993)
Stenotrophomonas maltophilia	–	Cyanuric acid	–	Rousseaux et al. (2001)
Stachybotrys chartarum	–	Cyanuric acid and 2-chloro-4,6-diamino-s-triazine	–	Wolf and Martin (1975)
Stenotrophomonas maltophilia	–	Deetylatrazine, Deisopropylatrazine and hydroxyatrazine	–	Marecik et al. (2008)
Umbelopsis isabellina	–	Deetylatrazine, Deisopropylatrazine and hydroxyatrazine	–	Marecik et al. (2008)
Volutella ciliata	–	Deetylatrazine, Ddeisopropylatrazine and hydroxyatrazine	–	Marecik et al. (2008)
Xanthomonas sp. ARB2	–	Deethylatrazine (DEA) and deisopropylatrazine (DIA)	–	Sawangjit (2016)

AC atrazine chlorohydrolase, *HAEA* hydroxyatrazine ethylaminohydrolase, *IAIA N*-isopropylammelide isopropylamidohydrolase, *TC s*-triazine chlorohydrolase, *AM* atrazine monooxygenase, *DEAM* eethylatrazine monooxygenase, *DIHA* deisopropyhidroxylatrazine amidohydrolase, *EAA N*-ethylammelide amidohydrolase, *TH s*-triazine hydrolase, *CAH* cyanuric acid hydrolase, *BH* biuret hydrolase, *AH* allophanate hydrolase

technique permits to identify, quantify and see the evolution of atrazine by-products which are generated by dechlorination, dealkylation and alkylic-oxidation mechanisms (Komtchou et al. 2016). The photodegradation study of atrazine was demonstrated using either Pt–TiO_2 or TiO_2 as a photocatalyst under 352 nm light irradiation. The Pt–TiO_2-catalyzed atrazine degradation reached 76% in 3 h without adding H_2O_2 solution or aeration, which was more than 10% higher than the TiO_2-catalyzed reaction. The decomposition product of Pt–TiO_2-catalyzed atrazine degradation was mainly cyanuric acid (Chen et al. 2017). Shamsedini et al. (2017) noticed the maximum atrazine removal rate was at pH = 11 in the presence of Fe^{3+}–TiO_2 catalyst = 25 mg/L and the initial concentration of atrazine equal to 10 mg/L.

Microbial degradation of atrazine

Microorganisms are endowed with enormous and remarkable metabolic capabilities to utilize xenobiotics which are their carbon and energy source. A number of microbial

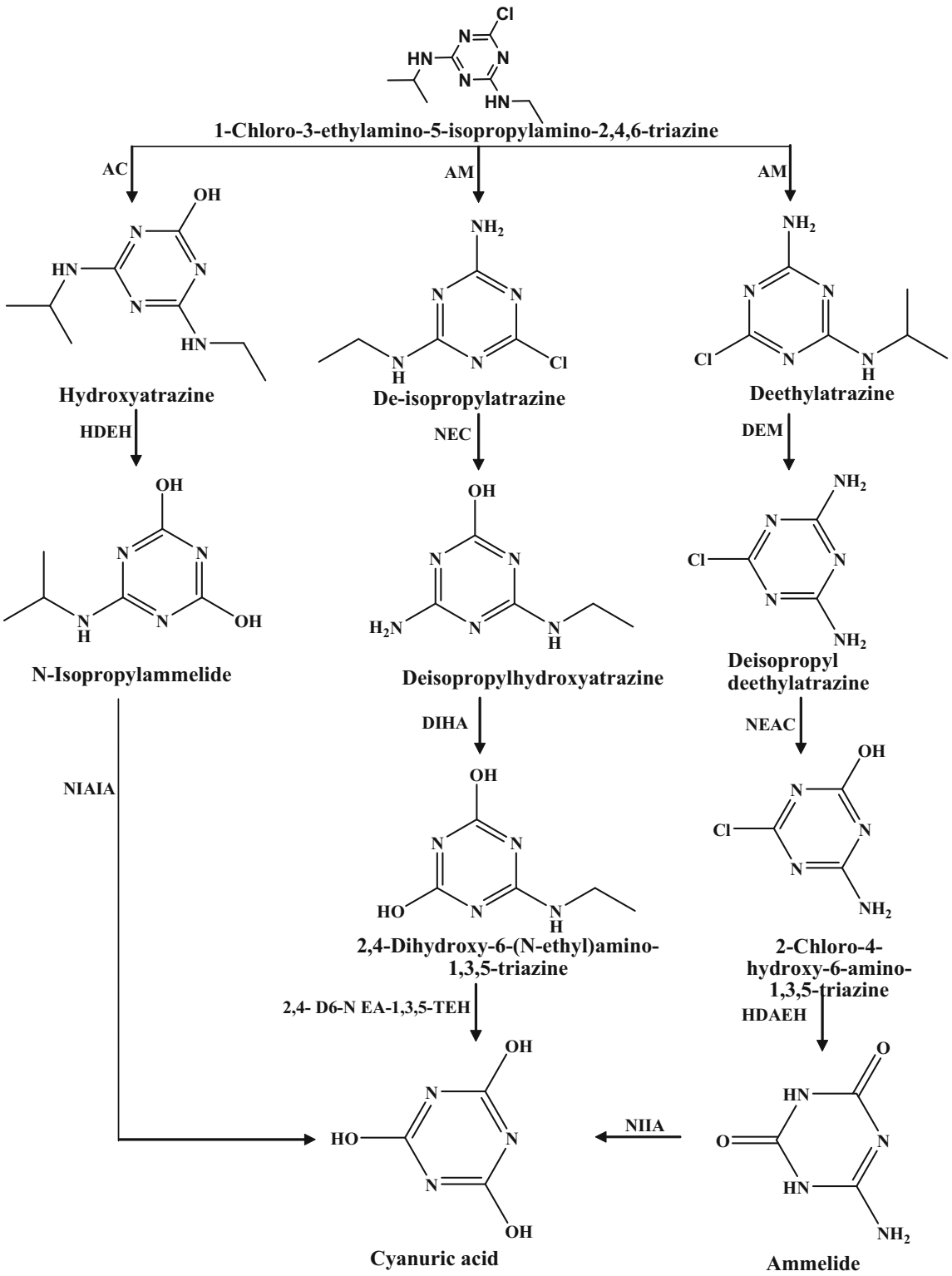

Fig. 2 Physical and biochemical pathways involved in the microbial biodegradation of atrazine. *AC* atrazine chlorohydrolase, *AM* atrazine monooxygenase, *HDEH* hydroxyl dechloroatrazine ethylaminohydrolase, *NEC* N-ethylammeline chlorohydrolase, *DEM* deethylatrazine monooxygenase, *NIAIA* *N*-isopropyl ammelide Isopropyl aminohydrolase, *DIHA* deisopropylhydroxyatrazine aminohydrolase, *NEAC* N-ethylammeline chlorohydrolase, 2, 4 D6 NEA 1, 3, 5 TEH = 2, 4-dihydroxy-6-(N′-ethyl) amino-1, 3, 5-triazine ethylaminohydrolase, *HDAEH* hydroxydechloro atrazine ethylaminohydrolase, *NIIA* *N*-isopropylammelide isopropylaminohydrolase

species and strains have been shown to exhibit atrazine metabolism as listed in Table 4. Prokaryotic (Gram-positive and Gram-negative bacteria) and eukaryotic microbial species are involved in atrazine biodegradation both in situ and under in vitro conditions. Bacterial and fungal species usually dechlorinate the atrazine molecule leading to the formation of hyroxyatrazine, deisopropylatrazine and deethylatrazine. *Xanthomonas* sp. ARB2 (Sawangjit 2016); *Enterobacter cloacae* JS08 (Solomon et al. 2013a, b); *Klebsiella* sp. KB02 (Sopid 2012); *Comamonas* sp. A2 (Yang et al. 2010); *Stenotrophomonas maltophilia, Rahnella aquatilis* (Marecik et al. 2008); *Chelatobacter heintzii, Aminobacter aminovorans, Stenotrophomonas maltophilia* (Rousseaux et al. 2001); *Pseudaminobacter* C147 (Topp et al. 2000a); *Bacillus subtilis* HB-6 (Wang et al. 2014a, b); *Arthrobacter* sp. (Getenga et al. 2009; Liu et al. 2010; El Sebai et al. 2011; Zhang et al. 2011; Wang and Xie 2012; Wang et al. 2013); *Bacillus licheniformis, B. megaterium* (Marecik et al. 2008); *Arthrobacter nicotinovorans* HIM (Aislabie et al. 2005); *Nocardioides* sp. SP12 (Piutti et al. 2003); *Arthrobacter aurescens* TC1 (Strong et al. 2002); *Arthrobacter crystallopoietes* (Rousseaux et al. 2001); and *Nocardioides* sp. (Topp et al. 2000b). Some fungal species, viz. *Umbelopsis isabellina, Volutella ciliate and Botrytis cinerea*, were also found to be involved in degradation of atrazine (Marecik et al. 2008). Microbial species perform atrazine biodegradation by three major pathways out of which one is purely hydrolytic, while remaining two others are mixed (hydrolytic–oxidative) (Fig. 2). The first intermediate product hydroxyatrazine was first extensively converted by *Pseudomonas* spp. ADP consisting of three gene products *atzA*, *atzB* and *atzC* (Martinez et al. 2001). The dechlorination method (hydrolytic) which is catalyzed by enzyme atrazine chlorohydrolase (*atzA* or *trzN* gene product) shows dechlorination followed by elimination of *N* alkyl substituents to yield cyanuric acid (Solomon et al. 2013a, b). These three genes are widespread and almost found in all the atrazine-degrading strains worldwide (Rousseaux et al. 2001; Topp et al. 2000a). Usually in Gram-positive strains, *atzA* is replaced by *trzN* which belongs to hydrolase enzyme which removes several functional groups from the parent compound (Wang et al. 2005; Topp et al. 2000b). The second pathway engrosses the N-dealkylation of the atrazine into deethylatrazine or deisopropylatrazine which is further dealkylated into deisopropyldeethylatrazine or further undergoes hydrolytic to yield cyanuric acid. *Rhodococcus* strains N186 and 21 and SpTE1 show oxidative reactions by producing enzymes AtzA and TriA which actively deaminates the atrazine metabolites (Seffernick et al. 2001). Dechlorination of dealkylated atraizine is commonly shown by *Rhodococcus corallinus* NRRLB-containing hydrolase AtzB (Seffernick et al. 2002). Further, in the upper degradation pathway it gets converted into two different aminohydrolases which is encoded by *atzB* and *atzC*. Then, the final hydrolytic reaction which is encoded by *trzF/atzF, trzD/atzD* and *trzE/atzE* converts cyanuric acid into carbon dioxide (Udiković-Kolić et al. 2010; Wackett et al. 2002).

Nitrogen released from atrazine metabolism serves as a nitrogen source for atrazine-degrading bacteria (Vaishampayan et al. 2007; Dutta and Singh 2013; Yang et al. 2010). Some bacteria initiate degradation of atrazine involving the enzyme atrazine chlorohydrolase through the mechanism of hydrolytic dechlorination. Aminohydrolases catalyze two hydrolytic deamination reactions that hydroxyatrazine undergoes; *N*-isopropylammelide (Getenga et al. 2009; Qingyan et al. 2008) or *N*-ethylammelide (Topp et al. 2000a) is formed as the intermediate metabolites. These ammelides are finally converted to cyanuric acid (Yang et al. 2010). Another route followed for atrazine degradation is N-dealkylation of the lateral ethyl and isopropyl chains to deethylatrazine, deisopropylatrazine and deethyldeisopropylatrazine (Zhang et al. 2011). These dealkylated atrazine metabolites undergo hydroxylation, and cyanuric acid is formed as the ultimate metabolite (Vaishampayan et al. 2007). Cyanuric acid, formed by either of the metabolic routes, is acted upon by cyanuric acid amidohydrolase, biuret amidohydrolase and allophanate hydrolase enzymes leading to the cleavage of the cyanuric acid to carbon dioxide and ammonia (El Sebai et al. 2011).

Conclusion

The demand for pesticides is on rise globally, especially in emerging economies of the world. India is the second most populated country of the world and is at the center of green revolution. It is, however, under ever-increasing demand of fulfilling the food requirements of huge population and thus relying heavily on synthetic herbicides as a weed control measure. As a consequence, environmental pollution, contamination of reservoirs, effect on food chains and life-threatening toxicities are certain to happen. Atrazine and its adverse effects are considered a highlighted threat to the environmental sustainability. Hence, an urgent need is felt to diverted resources and coordinated efforts to minimize its use, and at the same time, it is essential to monitor its impact on vertebrates, invertebrates and, most importantly, on microbial flora. Microbial biodegradation using in situ approach and use of transgenic strains having enhanced enzymatic activities and superior adaptability is considered a valid option for future studies. In future, use of biopesticides is expected to relieve our dependency on atrazine in order to minimize environmental pollution.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Human and animal rights This study does not involve work

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