Int. J. Environ. Sci. Technol. (2015) 12:4025–4036
DOI 10.1007/s13762-015-0866-2

REVIEW

Addressing the environmental impacts of butachlor and the available remediation strategies: a systematic review

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Received: 22 January 2015 / Revised: 16 June 2015 / Accepted: 14 July 2015 / Published online: 28 September 2015

Abstract Butachlor, a chloroacetanilide herbicide, used extensively all over the world as pre-emergence control of unwanted weeds. As a consequence, concerns about its potential adverse effects on the ecosystem and toxicity have risen. Several techniques have been used or are being investigated for effective removal of butachlor from the contaminated sites. This review reports the various toxicological studies conducted so far on the butachlor and the removal technologies available for its decontamination for better understanding. A new insight was also proposed after critical analysis of the merits and demerits of the removal technologies elucidated in the literature. An attempt was made to summarize the currently available analytical techniques reported for determination of butachlor in the environmental samples.

Keywords Butachlor · Contamination · Herbicide · Toxicity

Introduction

Pesticides contribution to the global environmental pollutants has reached great heights due to industrial and intensive agricultural activities (Rajasankar et al. 2013; Buric et al. 2013; Chen et al. 2014). With the increase in pesticide consumption, the herbicide classification tops the group due to their integral part in modern intensive cropping systems (Sarma et al. 2015). Among the commonly used herbicides, the chloroacetanilide group viz., acetochlor, alachlor, butachlor and metachlor, propachlor, are the most consumed chemicals all over the world in agriculture. About 14 million pounds of chloroacetanilide herbicides were consumed in the European Union member states alone (Eurostat 2007). They act by inhibiting the biosynthesis of lipids, alcohols, fatty acids, proteins, isoprenoids and flavonoids (Heydens et al. 2002). The chloroacetanilide herbicides are suspected as endocrine disruptors and have also been classified by US EPA as B-two carcinogen (PAN UK 2001). They contaminate the aquatic environment via agricultural run-off and leaching. These herbicides and their degradation products are often detected in the ground and surface waters and are highly toxic and persistent in the water (Mirbagheri and Monfared 2009; Fenoll et al. 2011; Atar et al. 2011; Santhanam et al. 2014; Abigail et al. 2014; Samuel et al. 2015a, b).

Among this class of herbicides, butachlor (N-(butoxymethyl)-2-chloro-2′,6′-diethyl acetanilide) is a widely recommended herbicide for use in rice cultivation. It is a systemic selective pre-emergent herbicide applied on rice, tea, wheat, beans and other crops viz. corn, soybean (Dwivedi et al. 2012). Butachlor is most commonly used to control a wide range of annual grass and broad leaf weeds (Wang et al. 2013) as well as submerged macrophytes in freshwater fish ponds. The mode of action of butachlor is by inhibiting the elongase responsible for the elongation of very long-chain fatty acids and the geranylgeranyl pyrophosphate cyclization enzymes (Götz and Böger 2004). It also affects the various other metabolic processes and redox homeostasis adversely, in addition to lipid biosynthesis (Agrawal et al. 2014). Butachlor primarily

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enters the environment through various agricultural, horticultural and forestry practices, where inappropriate water management and rainfall contribute to butachlor runoff from the agricultural fields to the watersheds and aquatic ecosystems (Ok et al. 2012). The half-life of butachlor ranges from 1.65 to 2.48 days in field water and 2.67–5.33 days in soil (Huarong et al. 2010). The consumption of butachlor is approximately 4.5×10^7 kg per year in Asia alone (Ateeq et al. 2002). In India, nearly 6750 metric tons of butachlor are applied annually, as it was the first rice herbicide to be introduced (Verma et al. 2014; Tilak et al. 2007). The recommended field dosage of butachlor ranges from 10 to 150 μM (Alla et al. 2008; Chen et al. 2007). The short half-life period ($t_{1/2}$) of butachlor and its biodegradability marked for its extensive use in rice cultivation, especially in south-Asian countries (Mohanty et al. 2004; Ateeq et al. 2002). It is a suspected carcinogen known to stimulate cell proliferation and induce malignant transformation in vitro (Xu et al. 2007b). Its vast application in agricultural soil has been reported to be deleterious to the natural amphibian population in the soil (Xue et al. 2005). Butachlor is a known retardant of growth and reproduction in earthworms viz. *Eisenia fetida* and *Perionyx sansibaricus* (Gobi and Gunasekaran 2010). The ecotoxicological studies suggest that butachlor may be harmful to aquatic invertebrates (Vallotton et al. 2009), microbial communities (Widenfalk et al. 2008) and also a possible carcinogen in animals and humans (Geng et al. 2005a). It is reported as a neurotoxin (Rajyalakshmi et al. 1996), genotoxin (Ateeq et al. 2005; Geng et al. 2005a) and carcinogen (Dwivedi et al. 2012). Many countries have enacted correlative environmental laws for controlling herbicide toxicity. According to the European Union, the pesticide levels in drinking water should not exceed 0.1 μg/L (Dong et al. 2009). Being a persistent agrochemical in soil, it poses serious threat to the agro-ecosystem and to the human health via food chains (Wang et al. 2007). Therefore, the residual harmful effects of butachlor have raised concerns for the cleanup of butachlor contaminated fields. A complete knowledge on butachlor properties will enable the researchers to understand and explore all the feasible ways to control its contamination. This review also gives an insight on the harmful effects caused by butachlor on exposure via. either point or non point sources. In addition, an account on the reported ways for removing butachlor from the contaminated sites are also summarized. In order to enrich the study further, the analytical techniques described till date for butachlor determination in the environmental samples are also listed. Thus, the present review aims to give an overview on the toxicology, remediation strategies and the analytical methods available till date for butachlor determination as well as elimination from the contaminated sites.

Physical and chemical properties of butachlor

Butachlor was originally developed by Monsanto Co. (USA) in 1968 and commonly used as a post-emergence herbicide in Asia and Africa (Liu et al. 2011). It is produced by the reaction of chloroacetyl chloride with the azomethine of 2,6-diethylaniline and formaldehyde, followed by treatment with n-butanol. Butachlor was first introduced in Japan in 1973 for weed control in transplanted rice paddies. The physical and chemical properties of butachlor are represented in Table 1.

Butachlor released into the air, at a vapor phase of 2.90×10^{-6} mm Hg at 25 °C, will exist in both vapor and particulate phases. The Henry's law constant for butachlor is 5.10×10^{-8} atm-cu m/mol at 25 °C. It is stable to UV light (Beestman and Deming 1974) and gets decomposed at temperatures greater than or equal to 165 °C. Butachlor gets disintegrated while heating and emits toxic fumes of hydrogen chloride and nitrous oxides.

Environmental fate of butachlor

Release of butachlor to the environment is either by various waste streams from its production industry or by its release as pre-emergence herbicide. In the air, butachlor gets degraded by photochemically produced hydroxyl radicals, where there half-life is about 6.8 h. On the other hand, at particulate-phase it gets removed by wet and dry deposition from the environment (Meylan and Howard 1993). Butachlor is

Table 1 Physico-chemical properties of butachlor

Chemical name	N-(butoxymethyl)-2-chloro-N-2,6-dimethyl acetanilide
Molecular formula	$C_{17}H_{26}NO_2Cl$
CAS No.	23184-66-9
Molecular weight	311.9
Physical state	Clear amber liquid at room temperature
Odor	Faint, sweet odor
Density	1.070 g/ml at 25 °C
Boiling point	156 °C
Melting point	0.5–1.5 °C
Decomposing point	165 °C
Saturated vapor pressure (25 °C)	6.0×10^{-4} Pa
Water solubility (20 °C)	20 mg/L
Vapor pressure	1.8×10^{-6} mm Hg at 25 °C
Viscosity	37°Cp at 25 °C
Acute oral LD50	2 g/kg (rat)
Adsorption coefficient (Koc)	700.0
Water partition coefficient (Kow)	4.5

expected, not to undergo direct photolysis as it does not absorb UV light (>290 nm). Based on the soil adsorption coefficient (Koc) of 700.0, butachlor is expected to have no mobility in the soil (Swann et al. 1983). The Henry's law constant of butachlor (Table 1) does not allow volatilization of butachlor in moist soils. If released into water, it gets adsorbed to the sediment and suspended solids, where the half-life is approximately 1.11–1.2 days (Chen and Fan 1988). A high BCF value (1500) indicates the bioconcentration of butachlor in aquatic life (Franke et al. 1994).

Toxicological properties of butachlor

Acute toxicity

Butachlor causes slight erythema and edema in rabbits when exposed to 24 h continuously. On a scale of 8.0, butachlor was found to have a primary irritation index of 3.5 (Wilson and Takei 2000). It was also found to cause primary ocular irritation in 2 of 6 white rabbits tested. But the cornea or iris was not affected. It is also considered to cause dermal sensation in guinea pig, where the dermal hypersensitivity was checked in a modified Buehler assay. The guinea pigs, when challenged with 50 % butachlor, moderate-to-severe erythema with edema were noticed on the third application. The results of butachlor acute toxicity results are given in Table 2.

Chronic toxicity

Butachlor was found to cause chronic toxicity in Sprague–Dawley (S–D) rats, when administered at a concentration of 0, 100, 1000 and 3000 ppm for 26 months. The body weight reduced at a concentration of 1000 and 3000 ppm dietary level in male and at 3000 ppm dietary level in females. Neoplastic changes were observed in the nasal mucosa, thyroid gland and glandular stomach at very high levels (>1000 ppm) of butachlor. In a second chronic study, the effect of butachlor on the liver and kidney was monitored. The highest incidence of hepatocellular swelling was noticed in the male at the lowest dose (100 ppm) and also apparent chronic nephropathy was observed in case of both sexes. Therefore, the level of butachlor chronic toxicity in S–D rats was set at 1.0 mg/kg/day for males and 1.2 mg/kg/day for females. On prolonged exposure (24 months) to butachlor at 50, 500 and 2000 ppm, mean weight was noticed in 100 male and female CD-1 mice which were taken for the study. The levels of serum alkaline phosphatise, glutamic oxaloacetic transaminase and glutamic-pyruvic transaminase were found increased than the control mice. At 2000 ppm, evidence of microcytic anemia in both sexes was found. Increased incidence of retinochoroidal degeneration and cataracts at week 53 and 104 were reported in the mice exposed from 500 to 2000 dietary levels of butachlor (Wilson and Takei 2000).

Table 2 Acute toxicity level of butachlor

Species	Route of administration	Median lethal dosage
Rat	Oral	2620 mg/kg
	Dermal inhalation	>5.3 mg/l
Mouse	Oral	4140 mg/kg
Rabbit	Dermal inhalation	13,000 mg/kg

Microbial toxicity

Butachlor is known to impart toxicity and mutagenicity in *Nostoc muscorum* (Vaishampayana 1985). It also affects the growth, nitrogen fixation and photosynthesis of many cyanobacterial species viz. *Anabaena doliolum* and *Nostoc* (Chen et al. 2007; Pandey and Rai 2002). He et al. (2013) studied butachlor induced toxicity on cyanobacteria, *Nostoc* sp., where significant changes in the growth rate, synthesis of pigments, and photosynthesis system (II) activities were noticed. Dramatic intracellular antioxidant response was also observed in the cells. In another study, the butachlor degradative properties in wheat rhizosphere, non-rhizosphere and inoculated rhizosphere soils were assessed. Results showed enhanced butachlor degradation in wheat rhizosphere soil and in the rhizosphere which was inoculated with butachlor-degrading bacterial community designated as HD. The study reminded the cost-effective use of microorganisms-degrading target herbicides for rapid herbicide degradation from soil (Yu et al. 2003). In 2005, a strategy was investigated to improve the ecological viability of diazotrophic cyanobacterial biofertilizer strains under herbicide stress. For the study, four widely used herbicides including butachlor were taken. The cyanobacterial strains viz. *Nostoc punctiforme*, *N. calcicola*, *Anabaena variabilis*, *Gloeocapsa* sp., *Aphanocapsa* sp. and laboratory strain *N. muscorum* ISU (*Anabaena* ATCC 27893) were taken in both free and immobilized forms. Among all the strains tested, *A. variabilis* exhibited maximum tolerance toward all the herbicides tested. It was also observed that the growth performance of immobilized and free cells had no difference in lethal as well as sub-lethal dosages (Singh and Datta 2005). Wang et al. (2007) conducted a study on the effect of butachlor on soil enzyme activities and microbial community structure in phaeozem soil. The activities of urease and phosphatase were significantly reduced in the presence of higher concentrations of butachlor (50 mg/kg soil). It was also noticed that the microbial community diversity was greatly affected in the presence of butachlor and cadmium.

Phytotoxicity

Butachlor affects the lipid synthesis of isolated leaf cells of *Phaseolus vulgaris* L. and also alleviates the glutathione and its associated enzymes in butachlor tolerant plants (Alla et al. 2007). In another study, it was noticed that butachlor, when applied at recommended field dose resulted in differentially less shoot fresh and dry weight after about 16 days of exposure in the test plants (Alla et al. 2008). Pan et al. (2009) studied the physiological effects of 4 herbicides including butachlor on three submerged macrophytes such as *Ceratophyllum demersum, Vallisneria natans* and *Elodea nuttallii*. The chlorophyll a content and relative growth rate were analyzed in the plants at a lower herbicide concentration (0.0001 mg/L). The results suggested that the growth of aquatic macrophytes is greatly affected by the herbicides present in water bodies. It was concluded that these macrophytes can be used as biomarker for assessing the ecological herbicide contamination risk. In Italian rye grass, the effects of butachlor on its growth, physiology and biochemistry were examined. At a dosage of 5 mg/L, the plant exhibited >50 % reduction in the fresh biomass, which increased with increase in butachlor concentration. Among all the plant parts, root was found to be more sensitive to butachlor followed by the shoot. Significant cell damage noticed in the plants on exposure to butachlor might be closely related to the hydrogen peroxide-induced oxidative stress than the superoxide-induced oxidative stress (Wang et al. 2013). The effect of butachlor on the photosynthesis, protein synthesis, RNA synthesis and lipid synthesis using isolated leaves of red kidney beans (*Phaseolus vulgaris* L.) was tested. At 100 μM concentration, butachlor was found to inhibit all the above mentioned processes. At a concentration of 50 μM, the protein and RNA synthesis of rice (Oryza sativa L.) and barnyardgrass (*Echinochloa crusgalli L.*) root and shoot segments were inhibited (Chang et al. 1985).

Aquatic toxicity

As a consequence of being a common contaminant in the groundwater and surface water, butachlor poses potential threat to the aquatic ecosystem. When the individual and joint toxicity of three chloroacetanilide herbicides viz. alachlor, acetochlor and butachlor, to a fresh water cladoceran *Daphnia carinata* was assessed, the common specific target site of these herbicides which inhibit the synthesis of very long-chain fatty acids was revealed (He et al. 2013). Butachlor has been proven to be genotoxic and cytotoxic in catfish *Clarias batrachus*, and the concentration of butachlor was found proportional to the extent of DNA damage (Zheng et al. 2012). In another study, butachlor was found to cause remarkable protein loss in *C. batrachus* at both lethal and sub-lethal concentration which might be due to increased proteolysis (Muley et al. 2007) or by metabolic utilization of ketoacids to glucogenesis pathway for synthesis of glucose (Rajput et al. 2012). In order to study the reproductive toxicity and endocrine-disrupting effects of butachlor, zebra fish (*Danio rerio*) was chosen as model organism due to its small size, short life cycle, prolific egg production and ease of culture maintenance. The results demonstrated adverse effects of butachlor on the normal reproductive process of zebra fish and also found to disrupt the thyroid and sex steroid endocrine systems when exposed to butachlor for 30 days (Chang et al. 2013). The toxicity of technical grade and commercial formulation of butachlor was conducted on *Channa punctata* (Bloch) with the help of static and continuous flow systems. Prolonged butachlor exposure at sub-lethal concentrations led to increase in the accumulation of residue, which was quantified using high-pressure liquid chromatography (HPLC) and thin layer chromatography (TLC). The accumulated residues in different tissues of the fish, resulted in biomagnification of butachlor via the food chain (Tilak et al. 2007). The possible mutagenicity of butachlor and other chloroacetanilide herbicides were tested in *Salmonella typhimurium* strains TA98 and TA100 indicating induction of base-pair substitution mutations. The effect of chloroacetanilides and their metabolites were tested on isolated and peripheral lymphocytes (mostly T cells) from two human donors. All the tested compounds including butachlor were toxic to lymphocytes, but the sister chromatid exchange induction was not directly linked to the mitotic index and increased duration of the cell cycle (Hill et al. 1997). Farombi et al. (2008) conducted a study to investigate the influence of butachlor on the antioxidant enzyme system and lipid peroxide formation in African cat fish (*Clarias gariepinus*). The fish were exposed to sub-lethal concentrations of butachlor (1, 2, 2.5 ppm) for 24 h and then were killed for observing the changes in the liver, kidney, gills and heart of the fish. An increased malondialdehyde formation, glutathione level, glutathione-S-transferase activity, superoxide dismutase and catalase activity were observed in the fished exposed to butachlor. From the results, it was concluded that butachlor induced oxidative stress in the fish at various tissues due to the depression of the glutathione detoxification system. Although the exact mechanism for butachlor carcinogenicity is not known, the formation of 2,6-diethylbenzoquinone imine, a DNA-reactive metabolite, was the only possible mechanism known (Coleman et al. 2000; Ou et al. 2000). The biological and biochemical toxicity of butachlor on freshwater snails viz. *Pila globosa* and *Biomphalaria alexandrina* were reported by Tantawy (2002). The toxicity of butachlor to marine flatfish was first studied by Huarong et al. (2010), where the inhibition of ATP

supply in pillar cells due to antioxidant enzyme inhibition was noticed.

Animal toxicity

Butachlor was noticed to exert detrimental effects on beneficial organisms like earthworms (Dwivedi et al. 2012). It exhibited mutagenic effects in primary rat tracheal epithelial cells and in Chinese hamster ovarian cells (Hill et al. 1997). It is also known cause stomach tumors in rats (Xu et al. 2007a). On prolonged exposure, it was found to be toxic to spotted snakehead fish (*Channa punctata*) and also accumulates via the food chain (Tilak et al. 2007). Butachlor has been reported to be a neurotoxin to land snails and as a genotoxin to toads, frog tadpoles, flounder and catfish (Rajyalakshmi et al. 1996; Ateeq et al. 2005; Geng et al. 2005b). It is also an indirect mutagen to hamsters and rats (Hsu et al. 2005). The acute toxicity of butachlor was investigated on four species of anurans viz. *Bufo melanostictus*, *F. multistriata, Polypedates megacephalus*, and *Microhyla ornate*, and their sensitivity to butachlor was found to be related to the body size, larval period and habitat use (Geng et al. 2005b). Yin et al. (2008) also reported the genotoxic nature of butachlor to *P. megacephalus* and *Bufo gargarizans*. In another study pond breeding amphibian, alpine cricket frog tadpole (*Fejervarya limnocharis*), was examined for growth, development, time to metamorphosis and survival rate when exposed to realistic concentrations of butachlor. The researchers documented negative effects of butachlor on the time to metamorphosis, development and survival of the amphibian. The DNA damage in the tadpoles was also observed at concentrations less than 4.8 mg/L. But unlike the organophosphorous insecticides, butachlor did not depress the cholinesterase activity of the tadpoles. From the study, it was reported that butachlor has widespread negative impacts on the amphibians present in the paddy field (Liu et al. 2011).

Human toxicity

Butachlor exposed cultured mammalian cells exhibited DNA strand breaks and chromosomal aberrations (Panneerselvam et al. 1999). Dwivedi et al. (2012) assessed the butachlor associated risks to humans in human peripheral blood mononuclear cells (PBMN). The results revealed the role of butachlor in triggering necrosis in human PBMN cells due to their oxidative role in intracellular reactive oxygen species (ROS) production, and the consequent mitochondrial dysfunction, oxidative DNA damage and chromosomal breakage.

Available butachlor remediation strategies

Adsorption

The adsorption of butachlor by clays and organoclays was investigated by Pal and Vanjara (2001). The surfactant pretreated organoclays adsorbed more butachlor than malathion, which might be due to the higher hydrophobicity of butachlor. The results suggested that the clays viz. kaolin, bentonite and montmorillonite and their respective organoclays can be applied efficiently for the removal of poor water soluble pesticide from aquifers. Xu et al. (2005) studied the adsorption behavior of butachlor using humic acids (HAs) from three different soils in China. HAs from different soils exhibited different butachlor adsorption capacities based on their carbonyl group. The results confirmed the adsorption mechanism as hydrogen bond formation between the C=O, phenolic and alcoholic groups of HAs and butachlor molecules. The net contributions of minerals to butachlor adsorption in natural soils were investigated with various degrees of organomineral aggregation. The clay microaggregates of smallest size sorbed about 58–71 % of butachlor, while the fine sand fraction sorbed less. A higher ratio of clay to soil organic carbon and soil sorption coefficients (K_d and K_{oc}) suggested that minerals can protect favorable sorption sites within soil organic matter physically. The researcher also proposed a new adsorption model for quantifying the net contribution of minerals to butachlor sorption (He et al. 2014).

Biodegradation

The most important route for herbicide degradation and dissipation in ecosystems is through microbial transformation (Martín 1994; Rajasankar et al. 2013). Zheng et al. (2012) proved that microbial degradation to be the promising way for chloroacetamide herbicide cleanup from the contaminated environment. But, in general, there is sparse or no systematic study to the best of our knowledge on butachlor biodegradation. In earlier reports, few microorganisms have been reported for their capability for degrading butachlor (Table 3). Dwivedi et al. (2010) reported a bacterial strain *Stenotrophomonas acidaminiphila* JS-1 which was capable of utilizing butachlor as a sole source of carbon and energy. The JS-1 strain removed butachlor from soil at a rate constant of 0.17 d^{-1} and half-life of 4.0 days. In addition, the JS-1 strain had the ability for butachlor remediation with a distinctive auxiliary attribute of plant growth stimulation. In bioaugmented soil, JS-1 strain completely degraded butachlor within 20 days at ambient temperature, whereas

Table 3 Reported work on butachlor degradation by microorganisms

Microorganisms	Source of isolation	References
Bacteria		
Stenotrophomonas acidaminiphila JS-1	Contaminated soil of wheat rhizosphere	Dwivedi et al. (2010)
Paracoccus sp. Y3B-1	Activated sludge of wastewater plant	Ni et al. (2011)
Catellibacterium caeni sp DCA-1^T	Activated sludge of wastewater plant	Zheng et al. (2012)
Paracoccus sp. FLY-8	Rice field soil	Zhang et al. (2011)
Fungi		
Trichoderma viride and *Pseudomonas alcaligenes*	Contaminated agricultural soil	Abd-Alrahman and Salem-Bekhit (2013)
Fusarium solani and *Fusarium oxysporum*	Soil	Chakraborty and Anjan (1991)

in case of unsterilized soil degradation up to 31 % was noticed under alike conditions. The researcher also supported the findings of Madhaiyan et al. (2006), which states the inhibitory effect of butachlor at higher concentrations, on indole-3-acetic acid synthesis. Ni et al. (2011) reported another bacterial strain, *Paracoccus* sp. Y3B-1, was isolated from activated sludge of a waste water plant. This strain, Y3B-1, could degrade three chloroacetamide herbicides viz. acetochlor, butachlor and pretilachlor with degradation rate of 86.7, 65.5 and 69.1 % after 3 days at optimum pH (7.0) and temperature (30 °C).

Two soil fungi, *Fusarium solani* and *Fusarium oxysporum*, were found to effectively degrade butachlor to at least 30–32 kinds of metabolites via dechlorination, hydroxylation, dehydrogenation, debutoxymethylation, C-dealkylation, N-dealkylation, O-dealkylation and cyclization detected by GC–MS via direct comparison with authentic samples for 23 metabolites. The structures of the remaining nine metabolites have not yet been determined. Hence, a plausible degradation pathway was proposed via. gas chromatography-mass spectroscopy (GC–MS) by Chakraborty and Anjan (1991). On the basis of the metabolite detection and enzyme assays, a degradation pathway for butachlor was elucidated in *Paracoccus* sp. FLY-8, isolated from rice field soil. The FLY-8 could utilize six chloroacetamide herbicides as carbon source. It was noticed that the molecular structure of the herbicides had influence on the microbial degradation rate where the substitutions in the alkoxymethyl side chain with alkoxyethyl side chain exhibited low degradation efficiency followed by the length of amide nitrogen's alkoxymethyl chain. But the phenyl alkyl substituents were not found to have significant influence on the degradation efficiency. In this strain, butachlor was converted to alachlor via partial C-dealkylation and then to 2-chloro-N-(2,6-dimethylphenyl) acetamide by N-dealkylation, which was subsequently converted to 2,6-diethylaniline and finally degraded to aniline and catechol followed by ortho-cleavage pathway (Zhang et al. 2011).

Abd-Alrahman and Salem-Bekhit (2013) isolated six bacterial and few fungi strains from a butachlor contaminated agricultural soil, which could utilize butachlor as a sole source of carbon and energy. Among the isolated strains, *Trichoderma viride* and *Pseudomonas alcaligenes* were found to quickly degrade butachlor up to 98–75 % after 15 and 21 days, respectively. The butachlor residue analysis proved the *Trichoderma* genus as excellent butachlor degrader which could be due to the presence of enzymes viz. cellulases and chitinases, available in its mycelium. In another study, a novel *Catellibacterium caeni* sp. nov DCA-1^T was investigated for butachlor degradation. The DCA-1^T strain could degrade 81.2 % of 50 mg/L butachlor in 84 h over a wide range of pH and temperatures (Zheng et al. 2012). Based on GC–MS analysis, five metabolites viz. N-hydroxymethyl-2-chloro-N-(2,6-diethyl-phenyl-)-acetamide, 2-chloro-N-(2,6-diethyl-phenyl-)-acetamide, (2,6-diethyl-phenyl-)-ethoxymethyl-carbamic acid, N-(2,6-diethyl-phenyl-)-N-hydroxymethyl-acetamide and N-(2,6-diethyl-phenyl-)-N-hydroxymethyl-formamide were found to be produced by the DCA-1^T during butachlor degradation. Although the degradation pathway of butachlor differs among different microorganisms, a probable degradative pathway for bacterial strain DCA-1^T is depicted clearly in Fig. 1. The strain DCA-1^T was also bioaugmented in three different soils, where 57.2–90.4 % of 50 mg/kg butachlor was removed in 5 days, demonstrating the potential use of the strain in the cleanup of butachlor contaminated sites. A study was conducted using micropaddy lysimeters (MPL) under ambient temperature in two rice crop seasons, where it was concluded that MCL as a valuable tool for herbicide measurement loss during different seasons. It was also noticed that the dissipation of butachlor from rice paddy fields was faster during summer than in spring (Ok et al. 2012).

Phytoremediation

Researchers have demonstrated that plant growth enhances in-soil degradation of butachlor in the rhizosphere (Yu

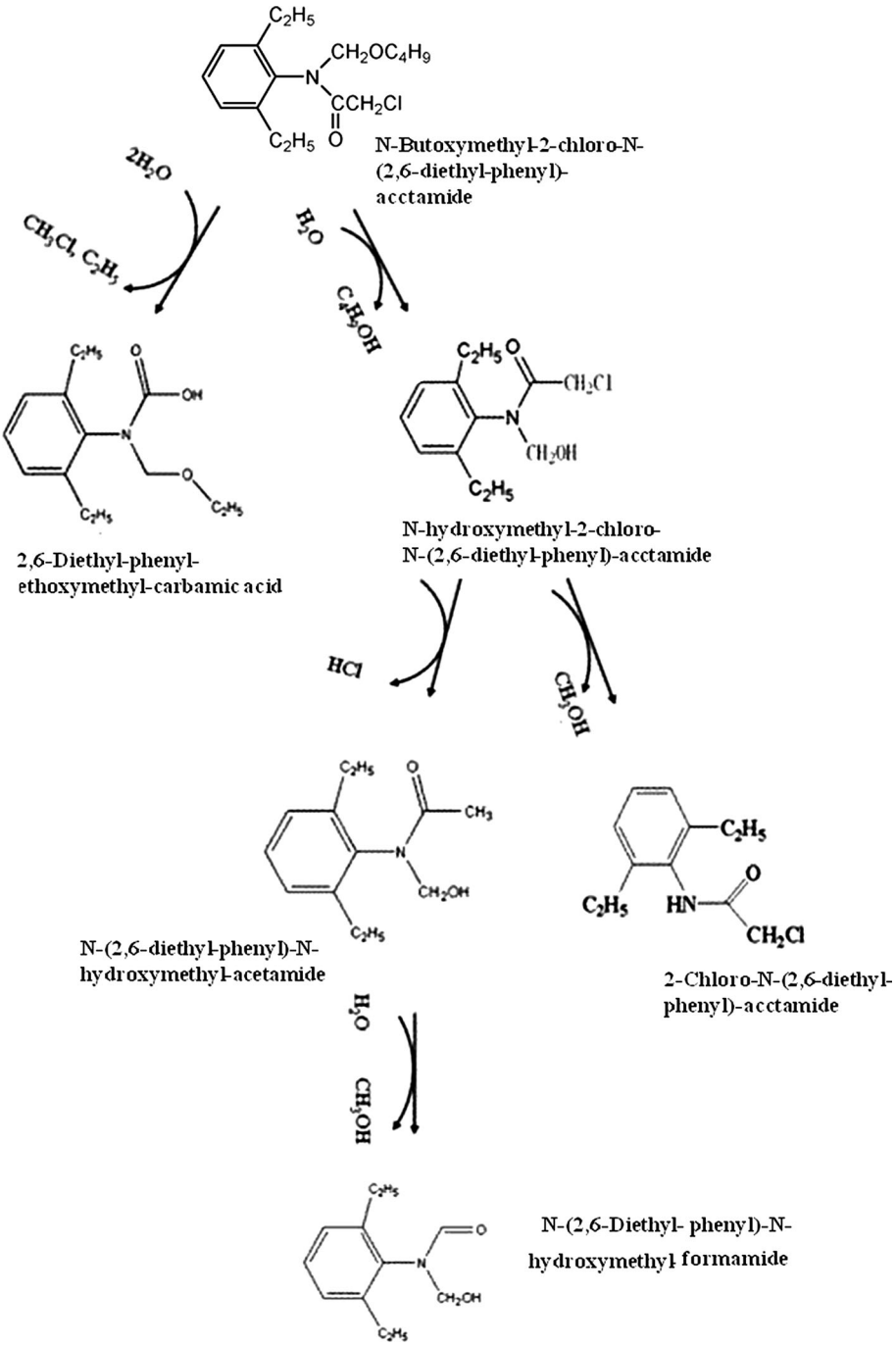

Fig. 1 Butachlor degradation pathway for DCA-1^T strain (Zheng et al. 2012)

et al. 2003; Wang et al. 2013). Wang et al. (2013) stated that understanding the tolerance of specific plant for butachlor is necessary for evaluating its aptness for being used as a bio-remediating plant species. He also reported phytoremediation as a cost-effective method for removing butachlor from the contaminated sites. An investigation was carried out by Yang et al. (2011) for observing the butachlor biodegradation dynamics and its related microbial ecophysiological responses in riparian soil. Different plants such as *Phragmites australis, Zizania aquatica*, and *Acorus calamus* were used for assessing their butachlor degradation efficiency. Based on the results, *A. calamus* was found to exhibit greater degradation efficiency than the other two plants tested and hence could be used for butachlor remediation of agricultural nonpoint pollution.

Nanoremediation

Several studies have reported the fascinating properties of nanomaterials in remediation of environmental pollutants

Table 4 Comparison of the reported butachlor available strategies

Remediation strategy	Advantages	Reported work on butachlor
Adsorption	Effective at even low concentration, selective, regenerative and cost effective	Clays, organoclays, humic acids (Pal and Vanjara 2001; Xu et al. 2005)
Biodegradation	Breakdown from higher to low molecular weight compounds, forms mineralized products such as CO_2, H_2O and biomass	Bacteria and Fungi (Table 3)
Phytoremediation	Environmentally friendly, cost-effective, non-intrusive technique	*Phragmites australis, Zizania aquatica*, and *Acorus calamus* (Yang et al. 2011; Wang et al. 2013)
Nanoremediation	Reduces cleanup time, certain contaminant concentration reduced to zero level, need for treatment and disposal of contaminated soil reduced	Titanium dioxide nanoparticle (Mahmoodi et al. 2007)

(Yola et al. 2014a, b; Yola and Atar 2014). A study was conducted to degrade and mineralize butachlor from aqueous solution using immobilized titanium dioxide nanoparticle by Mahmoodi et al. (2007). The photocatalytic degradation kinetics was found to follow a first-order model. Results revealed that thin-film coating of photocatalyst may resolve the problem of the suspension system of butachlor degradation where maximum butachlor degradation was observed when the hydrogen peroxide concentration was increased from 0 to 3.5 mM. It was also reported that the nanophotocatalysis using immobilized titanium dioxide nanoparticle could remove butachlor effectively from polluted waters. The nanophotocatalysis technique may be a viable one for the treatment of large volumes of butachlor polluted water and could also be used for the degradation of other chloroacetanilide herbicides. A detail comparative description of the available remediation strategy is also tabulated in Table 4.

Analytical methods for butachlor determination

The commonly employed methods for herbicide analysis in environmental samples include gas chromatography (GC), liquid chromatography (LC) and immunoassay (Zhao et al. 2006). A description of the methods used for butachlor determination is elaborated in this section.

Residual analysis from soil

Butachlor extraction from humic acids (HAs) has been demonstrated by Xu et al. (2005) using high-performance liquid chromatography (HPLC). Different kinds of china soil viz. phaeozem, fluvo-aquic, krasnozem and humic acids (HA) were taken for analyzing the adsorption capacity of butachlor onto them. The HAs adsorbed butachlor was separated by centrifugation for 15 min and a Hypersi BDS 200 mm: 4.0 mm C_{18} reverse-phase packing column was used for the determination. Acetonitrile (80 %) and water (20 %) was used as mobile phase. An UV–Vis detector was used to detect butachlor at 215 nm. In another study, butachlor was extracted from the soil sample by compactly packing in a glass column and eluting with hexane–acetone (1:1 v/v) mixture. The soil was mixed with 0.5 g of activated charcoal, 0.5 g Florisil and 10 g of anhydrous sodium sulfate, prior to elution. The extracted sample was analyzed for butachlor concentration by HPLC using a UV diode array detector at 210 nm. Acetonitrile: water (80: 20) was the used isocratic mobile phase (Bhupander et al. 2011).

Residual analysis from water

New method for determination of butachlor using single-drop microextraction (SDME) and GC was explained by Zhao et al. (2006) apart from the routine methods viz. extraction, cleanup and extract concentration. These new methods are time consuming, tedious with large amount requirement of organic solvents. A fast, simple, inexpensive and solvent-free sample preparation for butachlor extraction from water could be performed using SDME. The extraction was done using a microdrop of water-immiscible solvent at the tip of a microsyringe needle in the sample for extraction. After extraction, the microdrop could be retracted back into the microsyringe before injecting the sample into GC. For optimal extraction, a appropriate extraction solvent is crucial followed by the extraction time where the extraction efficiency increased with time. The microdrop volume was found directly proportional to the extraction efficiency. The conditions for effective SDME for butachlor were optimized, such as toluene microdrop (1.6 µl), stirring rate (400 rpm), extraction time (15 min). The limit of butachlor detection by this limit was 0.0002–0.114 µg/L. Butachlor recovery in the range of 70–188 % in a concentration of 10–100 ng/ml was observed when enzyme-linked immunosorbent assays were used for analysis of mineral, ground and surface water (Yakovleva et al. 2003). For the assay, environmental water was spiked with butachlor at various concentrations and

was analyzed with ELISA which resulted in better butachlor recovery in all the tested samples. It was also found that the recovery range of butachlor falls between the range of 70–120 % and the direct and indirect ELISAs analyte concentration requirement from 30 ng/ml in accordance with the US Environment Protection Agency (EPA).

Residual analysis from plants

For determining the level of butachlor and two other chloroacetanilide herbicides in *Radis pseudosterllariae*, a medicinal herb, a gas chromatography-mass spectroscopy (GC–MS) analysis was developed. The extracts of the plants were made by accelerating solvent extraction method (ASE), where the optimized conditions of extraction solvent, temperature, cleanup reagent, flush volume, static time and static cycle were used. After extraction, the extract was concentrated and quantified by internal standard method. The GC–MS separation was performed on a HP-5 MS capillary column (30 m × 0.25 mm, 0.25 μm), and temperatures of 250 °C for injection port and 280 °C for transfer line were maintained. Helium was used as the carrier gas, and the ion source was an electron impact ionization source. The detection limit and relative standard deviation for butachlor was 0.18 ng/g and 3.9 %, respectively, with an average recovery of 80.2–104.1 %. This method was reported to be a well-suited method for herbicide analysis in herbs accompanied with ease in operation and good precision (Xu et al. 2007a, b).

Residual analysis from animals

A competitive enzyme-linked immunosorbent assay with photometric detection based on either immobilized antigen or antibody was developed for butachlor (Yakovleva et al. 2003). A detection limit of 0.02 ng/ml was optimized in the study. For the assay, specific polyclonal antibodies for butachlor were obtained from butachlor-3-mercaptopropionic acid immunized rabbits, and best assay sensitivity was noticed against immunogen and immobilized antigen format. The residual levels of butachlor in male and female zebra fish (*Danio rerio*) were analyzed via enzyme-linked immunosorbent assay by Chang et al. (2013). The effects of butachlor on the reproduction and endocrine disruption were analyzed quantitatively. For studying the interaction of butachlor with human DNA and its role on oxidative genotoxicity on human peripheral blood mononuclear (PBMN) cells, techniques such as fluorescence spectroscopy, single-cell gel electrophoresis assay, flow cytometry and cytokinesis-blocked micronucleus assay were used for the first time (Dwivedi et al. 2012). A specific dye probe DCF (2′,7′-dichlorodihydrofluorescein diacetate) was used for visualizing the PBMN cells in the fluorescence microscope at 485 and 530 nm, respectively. For flow cytometry analysis, the DCF florescence in the FL1 log channel via 525-nm band-pass filter in the Coulter EPICS XL/X1-MCL was recorded at 488 nm. The mitochondrial damage caused in butachlor exposed cells was visualized at 520 and 590 nm under fluorescence microscope after staining with rhodamine (Rh123).

Conclusion

The remediation techniques known till date have specific advantages and disadvantages. The bioremediation strategies, although promises effective butachlor removal, are also associated with drawbacks such as long degradation times, low predictability and extensive monitoring techniques. Also, the bioremediation techniques are still studied only at laboratory level and hence, there is a need for extensive field studies using accurate efficiency analysis.

Considering the role of herbicides in food production, their use as agrochemicals cannot be restricted in spite of their association with irrecoverable environmental impacts. Hence, another alternative for effective pesticide usage could be the utilization of nanotechnology for weed control without harming the nature.

Acknowledgments The authors express their sincere thanks for laboratory facility and financial assistance from VIT University.

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