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REVIEW

Recent insights into the microbial catabolism of aryloxyphenoxy-propionate herbicides: microbial resources, metabolic pathways and catabolic enzymes

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Abstract

Aryloxyphenoxy-propionate herbicides (AOPPs) are widely used to control annual and perennial grasses in broadleaf crop fields and are frequently detected as contaminants in the environment. Due to the serious environmental toxicity of AOPPs, there is considerable concern regarding their biodegradation and environmental behaviors. Microbial catabolism is considered as the most effective method for the degradation of AOPPs in the environment. This review presents an overview of the recent findings on the microbial catabolism of various AOPPs, including fluazifop-*P*-butyl, cyhalofop-butyl, diclofop-methyl, fenoxaprop-*P*-ethyl, metamifop, haloxyfop-*P*-methyl and quizalofop-*P*-ethyl. It highlights the microbial resources that are able to catabolize these AOPPs and the metabolic pathways and catabolic enzymes involved in their degradation and mineralization. Furthermore, the application of AOPPs-degrading strains to eliminate AOPPs-contaminated environments and future research hotspots in biodegradation of AOPPs by microorganisms are also discussed.

Keywords Aryloxyphenoxy-propionates · Biodegradation · Microbial resource · Degradation pathway · Catabolic enzyme

Introduction

More than 400 types of chemical herbicides are being widely used for increasing crop yields throughout the world. In 2007, the global pesticides market was approximately $39.4 billion with herbicides occupying the largest portion of 40%, followed by insecticides, fungicides and other types of pesticides (Grube et al. 2011). Aryloxyphenoxy-propionate herbicides (AOPPs) based on 4-oxyphenoxypropanoic acid as their skeletal structure are one of the most widely used herbicide classes around the world after glyphosate. In 2014, worldwide sales volume of AOPPs reached $12.17 billion with 4.6% of the global herbicide market. As selective post-emergent herbicides registered for applications in controlling annual and perennial grassy weeds in many crops, AOPPs interfere with fatty acid biosynthesis by inhibiting acetyl-coenzyme A carboxylase (Donald and Shimabukuro 1980; Lucini and Molinari 2011). After the application of AOPPs on farmland, they can be rapidly transformed to acidic forms via hydrolysis of their ester bonds by plants or soil microorganisms, which could increase their polarity and solubility, but does not influence bioactivity (Ahmad Hamdani and Powles 2013; Luks et al. 2016). At present, the AOPPs with the largest market share are fluazifop-*P*-butyl, cyhalofop-butyl, diclofop-methyl, fenoxaprop-*P*-ethyl, haloxyfop-*P*-methyl and quizalofop-*P*-ethyl (Wang et al. 2017).

While AOPPs are relatively safe for crops, their residues in the ecological environment can harm following crops or non-target organisms. For example, AOPPs can reduce germination rates, mitotic frequency and α-amylase activity

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of lentil seeds (Aksoy et al. 2007). Moreover, it was also found to significantly increase the percentage of DNA damage, as indicated by the tail length and tail moment in the comet assay on silkworm hemocytes in a low doses of clodinafop-propargyl (30 mg/L) (Yin et al. 2011). More seriously, AOPPs are detrimental to aquatic organisms and human health, and can induce liver injury (Cai et al. 2008; Ioannis et al. 2007). For instance, the 96 h LC_{50} value of 6-chloro-2,3-dihydrobenzoxazol-2-one (CDHB) for tadpoles was 30.4 mg/mL (Jing et al. 2017). In addition, the degradation products of AOPPs in the ecological environment may possess even stronger toxicity. Fenoxaprop acid (FA), the main degradation product of fenoxaprop-*P*-ethyl (FE), can be further transformed to 2-benzoxazolinone (BOA), which in turn can be absorbed and translocated into other crop plants, causing physiological disturbances and a decline of crop yields (Wink and Luley 1988; Chiapusio et al. 2004). Toxicity studies on *Daphnia magna* showed that 4-[(6-chloro-2-benzoxazolyl)oxy] phenol (CBOP) (48 h EC_{50} of 1.49–1.64 mg/L) and hydroquinone (48 h EC_{50} of 0.25–0.28 mg/L) were more toxic to *Daphnia magna* than the parent FE (48 h EC_{50} of 4.2–6.9 mg/L) (Lin et al. 2008). Therefore, it is crucial to eliminate the harm that AOPPs and their degradation intermediates cause to the ecological environment.

Utilizing microorganisms for the elimination of AOPPs-contaminated soil has some significant advantages, including cost-effectiveness and environmental-friendliness (Hussain et al. 2015). Therefore, a series of microorganisms with excellent degradation capacity for different AOPPs have been isolated in recent years. Furthermore, the partial degradation pathway and mechanism of AOPPs degradation by microorganisms were elucidated, which will provide biological resources with clear degradation characteristics for bioremediation of AOPPs-contaminated environments. This review presents an overview of the recent insights into the microbial catabolism of AOPPs and proposes new prospects for further research on the biodegradation of AOPPs.

Microbial resources involved in degradation of AOPPs

Microbial resources are the basis for further study of the mechanisms of AOPPs biodegradation and bioremediation of AOPPs-contaminated soil. In recent years, many consortia and strains with excellent AOPP degradation ability have been isolated and characterized (Table 1). Most of these are bacteria, indicating that bacteria play a very important role in AOPPs degradation in the environments.

A consortium consisting of *Chryseomonas luteola* and *Sphingomonas paucimobilis* was isolated for diclofop-*P*-methyl degradation, which was able to utilize it as the sole source of carbon and energy for growth (Grenier and Adkins 1995). The two strains were able to completely transform 1.5 mg/L diclofop-*P*-methyl to diclofop acid within 71 and 54 h, respectively (Grenier and Adkins 1995). Hoagland and Zablotowicz (1998) isolated four strains (*Pseudomonas fluorescens* BD4-12, RA-2, UA5-40 and *P. putida* M-17) for fenoxaprop-*P*-ethyl degradation. When the herbicide was ^{14}C-labeled in either the dioxyphenyl or the chlorophenyl ring, it could be seen that resting cells rapidly hydrolyzed FE to fenoxaprop acid (FA), but cleavage of the ester bond proceeded slowly. Song et al. (2005a) reported that *Alcaligenes* sp. strain H was able to degrade 25 mg/L fenoxaprop-*P*-ethyl with a degradation percentage of 69.5% and utilize it as the sole carbon source for growth. However, poor efficient degradation of low concentration of AOPPs were observed from these early reports. In recent years, some microorganisms with excellent AOPPs degradation ability were isolated from long-term AOPPs-contaminated environments. An efficient FE-degrading strain, *Rhodococcus* sp. T1, was isolated from the enrichment culture and identified. It was able to degrade 94% of 100 mg/L FE within 24 h and the resulting metabolites FA were identified by HPLC/MS analysis (Hou et al. 2011). *Rhodococcus ruber* JPL-2 was also able to utilize 100 mg/L FE as the sole carbon source for growth with a degradation percentage of 94.6% (Liu et al. 2015). Nie et al. (2011) isolated five AOPP degrading strains from rice field soil using cyhalofop-butyl as the substrate, and identified them as *Agromyces* sp., *Stenotrophomonas* sp., *Aquamicrobium* sp., *Microbacterium* sp. and *Pseudomonas azotoformans*. All of these strains were able to degrade most AOPPs, including fenoxaprop-*P*-ethyl, haloxyfop-*P*-methyl, quizalofop-*P*-ethyl, cyhalofop-butyl and clodinafop-propargyl. For example, a total of 100 mg/L of AOPPs was degraded by stain JPL-2 with degradation percentages of 83.7, 71.7, 92.4, 51.8, 57.5 and 67.7% for clodinafop-propargyl, cyhalofop-butyl, quizalofop-*P*-ethyl, diclofop-methyl, haloxyfop-*P*-methyl and fluazifop-*P*-butyl, respectively (Liu et al. 2015). However, these AOPPs were only converted to the corresponding acids, were not completely degraded, which may actually increase the potential ecotoxicity instead of reducing it. Jing et al. (2017) concluded that metabolites were more toxic than the parent compound fenoxaprop-ethyl to tadpoles because FA were hardly detectable in tadpoles after aqueous solution exposure, while CDHB was accumulated and eliminated as first-order kinetics with half-life of 37.1 h.

However, a few recent studies showed that certain microbial consortia can indeed completely mineralize AOPPs. A FE-degrading consortium designated W1 was enriched from FE-polluted soil, and was able to completely degrade 0.18 mg/L FE at 30 °C and pH 7.0 after 7 days of incubation (Dong et al. 2015a). In addition, Dong et al. (2017) also obtained a microbial consortium, ME-1, which achieved a degradation percentage of > 95% with 100 mg/L metamifop

Table 1 Microbial resources for the biodegradation of AOPPs degradation

AOPP	Microorganism	Source	Concentration	Incubation time	Degradation percentage (%)	References
Fluazifop-*P*-butyl	*Aquamicrobium* sp. FPB-1	Legume field	100 mg/L	40 h	96	Wang et al. (2017)
Haloxyfop-*P*-methyl	*Aquamicrobium* sp. FPB-1	Legume field	100 mg/L	40 h	97	Wang et al. (2017)
Diclofop-*P*-methyl	*Aquamicrobium* sp. FPB-1	Legume field	100 mg/L	40 h	99	Wang et al. (2017)
	Chryseomonas luteola	Manitoban soils	1.5 µg/mL	71 h	99	Grenier and Adkins (1995)
	Sphingomonas paucimobilis	Manitoban soils	1.5 µg/mL	54 h	99	Grenier and Adkins (1995)
Quizalofop-*P*-ethyl	*Aquamicrobium* sp. FPB-1	Legume field	100 mg/L	40 h	98.5	Wang et al. (2017)
	Pseudomonas sp. J-2	Sewage outfall				Zhang et al. (2017)
	Rhodococcus sp. JT-3 and *Brevundimonas* sp. JT-9	Wastewater treatment facility	100 mg/L	60 h	99	Zhang et al. (2016a)
	Ochrobactrum sp. QE-9	Wastewater treatment facility	50 mg/L	5 days	99	Zhang et al. (2016b)
Fenoxaprop-*P*-ethyl	*Aquamicrobium* sp. FPB-1	Legume field	100 mg/L	40 h	97	Wang et al. (2017)
	Rhodococcus ruber JPL-2	Wheat field	100 mg/L	54 h	94.6	Liu et al. (2015)
	Acinetobacter sp. DL-2	Wheat field	50 mg/L	5 days	95.2	Dong et al. (2015b)
	Rhodococcus sp. T1	Wheat field	100 mg/L	24 h	94	Hou et al.(2011), Hou (2011)
	Fluorescent pseudomonas BD4-13, RA-2, UA5-40 and *Pseudomonas putida* M-17	Soil				Robert and Robert (1998)
	Alcaligenes sp. H	Industrial waste water	25 mg/L	5 days	69.5	Song et al.(2005a, b)
Cyhalofop-butyl	*Aquamicrobium* sp. FPB-1	Legume field	100 mg/L	40 h	96	Wang et al. (2017)
	P. azotoformans QDZ-1	Rice field	100 mg/L	5 days	84.5	Nie et al. (2011)

after incubation for 6 days. Furthermore, a mixed microbial flora consisting of three species of bacteria, *Acinetobacter* sp. DL-2, *Pigmentiphaga* sp. DL-8 and *Taonella mepensis* H1, was able to completely degrade FE (Dong et al. 2015a; Xi et al. 2013). Strain DL-2 could convert FE to FA, which was followed further transformation to 6-chloro-2,3-dihydrobenzoxazol-2-one (CDHB) and 2-(4-hydroxyphenoxy)-propionic acid (HPP), which were degraded completely by strains DL-8 and H1, respectively. A quizalofop-*P*-ethyl (QE)-degrading consortium consisting of *Rhodococcus* sp. JT-3 and *Brevundimonas* sp. JT-9 was obtained from QE-polluted soil, and was able to degrade 100 mg/L of QE in 60 h (Zhang et al. 2016b). Strain JT-3 initiated the catabolism of QE to quizalofop acid (QA), which in turn was used by strain JT-9 as a carbon source for growth and to simultaneously feed strain JT-3 (Zhang et al. 2016a). However, other than the above-mentioned consortium, we are not aware of any other reports on the complete mineralization of AOPPs by microorganisms.

Many degrading microbial strains have been inoculated on the bioremediation of herbicide-contaminated sites in laboratory, pot and field experiments. For instance, the inoculation of *Rhizobium* species has the potential to clean up fluazifop-*P*-butyl in contaminated soil and increased the root, shoot and total dry weights of faba bean plants after 60 and 90 days from sowing (Metwally and Shalby 2007). However, the fate and ecological behaviours of microorganisms introduced into soil remain still needs further research.

Microbial AOPPs degradation pathways

Exploring the microbial degradation pathways of the organic pollutants is considered as an important aspect of bioremediation, especially in the view of the fact that the eco-toxicity of intermediate metabolites may be stronger than that of the original structure, such as CBOP (48 h EC_{50} of 1.49–1.64 mg/L) and hydroquinone (48 h EC_{50} of 0.25–0.28 mg/L) were more toxic to *Daphnia magna* than the parent FE (48 h EC_{50} of 4.2–6.9 mg/L) (Lin et al. 2008). At present, there are few reports on the microbial degradation pathways of AOPPs. While the upstream degradation pathway of AOPPs has largely been determined, the following pathways involved in downstream degradation are not yet clear. The reported metabolic pathways of AOPPs are summarized in Fig. 1, among which the microbial degradation pathway of FE is the best understood.

Rhodococcus sp. T1 (Hou et al. 2011) and *Acinetobacter* sp. DL-2 (Dong et al. 2015b) were found to be able to transform fenoxaprop-*P*-ethyl (FE) to FA and ethanol by hydrolyzing the ester bond. Consortium W1 (Dong et al. 2015a) broke the C–O–C bond of FA to form 6-chloro-2,3-dihydro benzoxazol-2-one (CDHB) and 2-(4-hydroxyphenoxy) propionate (HPP). In the next step, *Pigmentiphaga* sp. DL-8 was able to completely mineralize CDHB and HPP and utilize them as carbon sources for growth. CDHB was first converted to 2-amino-5-chlorophenol (2A5CP) (Dong et al. 2016), which is further completely mineralized via the 2A5CP biodegradation pathway as described by Wu et al. (2006). Interestingly, strain DL-8 may promote the formation of 9-chloro-2-amino-3H-phenoxazin-3-one (CAPO), which is not known to be degraded further, with high concentrations (> 0.072 mg/L) of 2A5CP. During the degradation process of HPP by strain DL-8, hydroquinone (HQ) was identified as the main intermediate metabolite, generated through the cleavage of the C–O bond of HPP. In addition, GSH conjugation (predominantly glycylcysteine conjugates arising from FE or FA) was shown to be the mechanism by which the benzoxazolyl-oxy-phenyl ether bond was cleaved (Hoagland and Zablotowicz 1998). Finally, a relatively complete microbial degradation pathway of FE was proposed by Dong et al. (2015b, 2016). Recently, Dong's group has revealed the first known biodegradation pathway of another AOPP, metamifop, by consortium ME-1 (Dong et al. 2017).

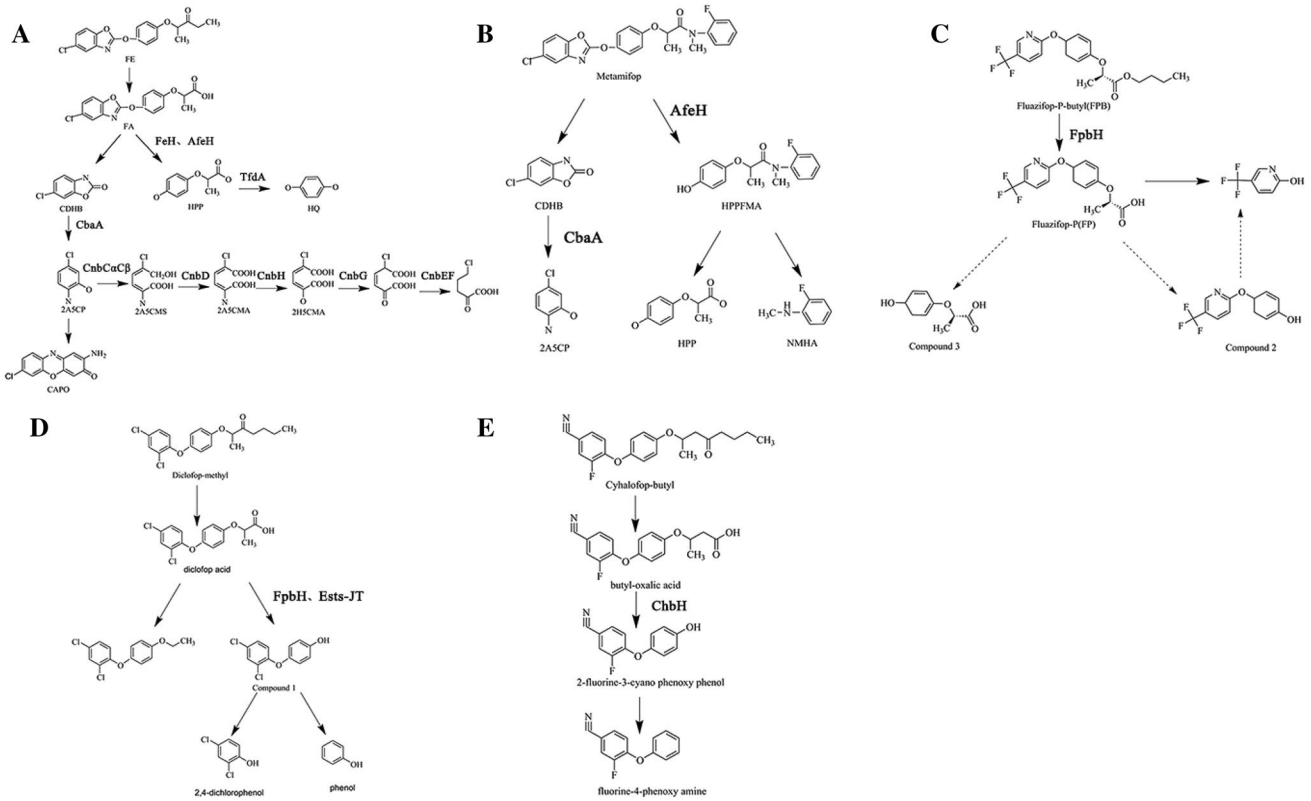

Fig. 1 The reported metabolic pathways of AOPPs by microorganisms. **A** Degradation pathways of fenoxaprop-*P*-ethyl (FE); **B** degradation pathways of metamifop; **C** degradation pathways of fluazifop-*P*-butyl (FBP); **D** degradation pathways of diclofop-methyl; **E** Degradation pathways of cyhalofop-butyl by microorganisms. Solid lines represent observed microbial degradation steps. Punctuated lines represent theoretical degradation steps not confirmed in this study. Compound 2 means 4-{[5-(trifluoromethyl)-2-pyridinyl]oxy} phenol; Compound 3 means 2-(4-hydroxyphenoxy)propanoic acid

Consortium ME-1 firstly transformed metamifop into CDHB and HPPFMA, which were further degraded to HPP and NMFA, respectively. The degradation pathways of CDHB and HPP were consistent with that of FE, but the further degradation process of NMFA has not been reported.

According to the conclusions reported by many studies, the initial steps in the degradation of most AOPPs are the hydrolysis of ester bonds to form the corresponding acids, such as the conversion of FE to FA (Liu et al. 2015; Dong et al. 2015b), diclofop-methyl to diclofop acid (Grenier and Adkins 1995), cyhalofop-butyl to butyl-oxalic acid (Nie et al. 2011), quizalofop-*P*-ethyl to quizalofop acid (Zhang et al. 2017), fluazifop-*P*-butyl (FPB) to FP (Nora et al. 2015; Wang et al. 2017), and so on. In recent years, there have been some major advances research on the in the degradation of these acids. *Chryseomonas luteola* and *Sphingomonas paucimobilis* isolated from Manitoban soils were capable of degrading diclofop acid to 4-(2,4-dichlorophenoxy)phenol, which could be further converted to 2,4-dichlorophenol and phenol via the cleavage of the phenylene ether bond (Grenier and Adkins 1995). *Pseudomonas azotoformans* QDZ-1was found be able to transform butyl-oxalic acid into 2-fluorine-3-cyano phenoxy phenol by cleavage of the ester bond, which was further degraded to fluorine-4-phenoxy amine by hydrolysis of the nitrile (Nie et al. 2011). This paper revealed that the main product of FPB degradation is FP, which can be further biodegraded to yield 2-hydroxy-5-trifluoromethyl-pyridine (TFMP) at a slower rate. The European Food Safety Authority suggested a theoretical degradation pathway of FP via 4-{[5-(trifluoromethyl)-2-pyridinyl]oxy}phenol to TFMP (European Food Safety Authority 2012). A fourth degradation product, designated 2-(4-hydroxyphenoxy)propanoic acid, is also mentioned by the European Food Safety Authority, but this degradation product was only observed at low concentrations in plant material after spraying with FPB.

In summary, we have obtained some understanding of the upstream degradation pathways of AOPPs, but the knowledge surrounding the microbial degradation pathways of most AOPPs needs to be improved and the eco-toxicity of these catabolic intermediates should be further evaluated. This is the only way to assess the actual environmental toxicity of AOPPs and their degradation intermediates, so that the safety of microbial agents involved in AOPPs-degradation can also be guaranteed.

Microbial enzymes involved in the biodegradation of AOPPs

There are few reports on the key enzymes involved in degradation of AOPPs, and the microbial mechanism of AOPPs degradation will be the focus of future research. At present, the mechanisms involved in the initial steps of AOPP degradation are relatively well-understood, and mainly involve ester bond cleavage by esterases to form the corresponding acids (Table 2).

The esterase gene *feh* cloned from *Rhodococcus* sp. T1 encodes the FE-hydrolyzing carboxylesterase (FeH) was responsible for the initial step of the degradation pathway. The substrate preference of FeH followed the order of fenoxaprop-*P*-ethyl>quizalofop-*P*-ethyl>clodinafop-propargyl>cyhalofop-butyl>fluazifop-*P*-butyl>haloxyfop-*P*-methyl>diclofop-methyl, which indicated that the chain length of the alcohol moiety of AOPPs strongly affected the hydrolytic activity of FeH (Hou et al. 2011). The FE-hydrolase AfeH was obtained from *Acinetobacter* sp. DL-2, and was able to hydrolyze various AOPPs with catalytic efficiency in the order of clodinafop-propargyl>fenoxaprop-*P*-ethyl>haloxyfop-*P*-methyl>quizalofop-*P*-ethyl>cyhalofop-butyl (Dong et al. 2015b). In addition, more AOPPs-hydrolases from different microorganisms were identified, such as FpbH, QpeH, EstS-JT and ChbH, which were obtained from *Aquamicrobium* sp. FPB-1, *Pseudomonas* sp. strain J-2, *Rhodococcus* sp. strain JT-3 and *P. azotoformans* QDZ-1, respectively (Wang et al. 2017; Zhang et al. 2016a, 2017; Nie et al. 2011). The common characteristic of these identified strains or esterases are that they all have catalytic activity toward ester bonds of AOPPs. However, their catalytic activities on various AOPPs differed significantly, indicating that strongly affects the biodegradability of AOPPs, while substitutions in the aromatic ring had only a slight influence. For instance, the specific activities of AfeH were 216.39 U/mg (FE), 123.86 U/mg (quizalofop-*p*-ethyl) and 5648.89 U/mg (4-nitrophenyl acetate), respectively (Dong et al. 2015a).

Recently, Dong et al. (2016) elucidated the microbial degradation mechanism of CDHB, a key intermediate during biodegradation of FE, for the first time. The amidohydrolase CbaA, which shares 18 to 21% identity with metal-dependent hydrolases of the PF01499 protein family, was purified and identified from *Pigmentiphaga* sp. DL-8. It was able to catalyze CDHB to 2A5CP with a specific activity of 5900 U/mg protein. Furthermore, the 2A5CP-metabolic gene cluster (*cnbR, cnbC*$_\alpha$*C*$_\beta$, *cnbD, cnbE, cnbF, cnbG, cnbH* and *cnbI*) surrounded by two IS1071 transposable elements was discovered in the DL-8 genome using Local-BLAST. The gene cluster located in the genome of strain DL-8 shares 99% identity with those from *Comamonas* sp. strain CNB-1 (Wu et al. 2005) and *Pseudomonas putida* ZWL73 (Zhen et al. 2006), which are able to degrade 4-chloronitrobenzene (4CNB).

With large amounts of genes involved in the metabolism of chemical compounds being isolated from various microorganism, some herbicide-catabolic genes, such as *feh, atzA, gox* and *gat*, have been introduced into agricultural crops for enhancing herbicide tolerance during the past two decades (Qiu et al.

Table 2 Microbial enzymes involved in biodegradation of AOPPs

Enzyme	Substrate preference	Source strain	Size amino acids	Family	Optimum reaction temperature (°C)	Optimum reaction pH	References
FeH	FE>quizalofop-*P*-ethyl>clodinafop-propargyl>cyhalofop-butyl>fluazifop-*P*-butyl>haloxyfop-*P*-methyl>diclofop-methyl	*Rhodococcus ruber* JPL-2	380	–	30	7.0	Liu et al. (2015)
AfeH	Clodinafop-propargyl>fenoxaprop-*P*-ethyl>haloxyfop-*P*-methyl>quizalofop-*P*-ethyl>cyhalofop-butyl	*Acinetobacter* sp. DL-2	309	Family VII of lipolytic enzymes	50	9.0	Hou et al. (2011)
FpbH	Haloxyfop-*P*-methyl>diclofop-methyl>fenoxaprop-*P*-ethyl>quizalofop-*P*-ethyl>fluazifop-*P*-butyl>cyhalofop-butyl	*Aquamicrobium* sp. FPB-1	265	–	37	7.0	Wang et al. (2017)
QpeH	Fenoxaprop-*P*-ethyl>quizalofop-*P*-tefuryl>QPE>haloxyfop-*P*-methyl>cyhalofop-butyl>clodinafop-propargyl	*Pseudomonas* sp. J-2	309	Family V	30	8.0	Zhang et al. (2017)
Ests-JT	Quizalofop-*P*-ethyl	*Rhodococcus* sp. JT-3	393	Esterase family VIII	35	7.5	Zhang et al. (2016a)
EstQE	Quizalofop-*P*-ethyl>fenoxaprop-*P*-ethyl>clodinafop-propargyl>cyhalofop-butyl>quizalofop-*P*-tefuryl>haloxyfop-*P*-methyl	*Ochrobactrum* sp. QE-9	382	Esterase family VIII	45	8.0	Zhang et al. (2016b)
ChbH	Quizalofop-*P*-ethyl ≈ fenoxaprop-*P*-ethyl>CyB ≈ fluazifop-*P*-butyl>diclofop-methyl ≈ haloxyfop-*P*-methyl	QDZ-1	332	–	50	7.0	Nie et al. (2011)
CbaA	CDHB	*Pigmentiphaga* sp. DL-8	339	PF01499 family	55	9.0	Dong et al. (2016)

2012; Kawahigashi 2009). Transgenic plants expressing this enzymes showed tolerance and phytoremediation activity toward target herbicides. However, only one catabolic gene is transformed and the intermediate metabolite may still toxic. Thus, the more catabolic genes should be constructed in genetically modified crops and to provide a complete detoxification system in the phytoremediation process.

Conclusions and perspectives

AOPPs have become an important tool for boosting food production and so it will continue to be widely used. However, the irrational overuse of AOPPs will inevitably lead to environmental pollution and ultimately constitutes a threat to animals and even human health because AOPPs and their catabolic intermediates are either recalcitrant or have low rates of natural degradation. For example CBOP, which was one of the main intermediates of herbicide FE, was resistant to photodegradation under the irradiation of $\lambda > 290$ nm, and its photolysis rate was seven times slower than the parent under the irradiation of $\lambda > 200$ nm (Lin et al. 2008). Singh et al. (2013) also found that residues of fenoxaprop ethyl and acid dissipated in soil with a half-life of 0.5 and 7.3 days in field experiment, respectively. Due to the serious environmental toxicity of AOPPs, there is considerable concern regarding their biodegradation and environmental behaviors. Although AOPPs can be

degraded via hydrolysis and photolysis, microorganisms are the most key factor in their degradation in the natural environment. The overview of the data on the microbial catabolism of AOPPs presented in this review article highlights that diverse microbial species or consortia have evolved the capacity to degrade AOPPs after long-term exposure.

As can be seen from this review, all the isolated AOPPs-degrading strains are bacterial species, and few articles reported that fungi are involved in the degradation of AOPPs. Considering the importance of fungal populations, further studies should investigate the role of fungi in the catabolism of AOPPs. In addition, although these strains with excellent AOPPs-degradation ability have been widely reported, their utilization mostly remains at the laboratory stage. Moreover, the stability of degradation efficiency was often unsatisfactory when the AOPPs-degrading strains were released into the ecological environment for bioremediation of AOPPs contamination. Metwally and Shalby (2007) concluded that the inoculation of *Rhizobium* species has the potential to degrade fluazifop-*p*-butyl but it needs 60 and 90 days after sowing and a rapid decline in the rate of degradation was observed subsequently. Furthermore, the ecological effects of AOPPs-degrading bacterial agents, including survival dynamics, interactions with indigenous microorganisms, effects of environmental factors on in-situ bioremediation, and so on, also need to be evaluated further.

At present, the mechanism of microbial degradation of AOPPs are still practically a "Black Box". Many genes involved in the initial stages of AOPPs degradation have been identified, and many metabolic pathways of AOPPs utilization by microorganisms have been found in recent years. However, some of the metabolic pathways were proposed based on metabolite identification and lack of enzymological evidence. Moreover, not all of the catabolic genes involved in the pathways have been described. Therefore, further research should be performed to identify the complete set of genes involved in the degradation and mineralization of AOPPs using modern molecular biology technologies, such as genomics, transcriptomics, proteomics, and so on. And these catabolic genes should be used to construct recombinant strains and genetically modified crops for the bioremediation of AOPPs-contaminated areas and yield increase, respectively.

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