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Microbial Transformation of Chiral Organohalides: Distribution, Microorganisms and Mechanisms

Qihong Lu[a,b], Lan Qiu[a], Ling Yu[a,b], Shangwei Zhang[d], Renata Alves de Toledo[e], Hojae Shim[e], Shanquan Wang[a,b,c*]

[a]School of Environmental Science and Engineering, Sun Yat-Sen University, Guangzhou, China 510275

[b]Environmental Microbiome Research Center, Sun Yat-Sen University, Guangzhou, China 510275

[c]Guangdong Provincial Key Laboratory of Environmental Pollution Control and Remediation Technology, Guangzhou, China 510275

[d]UFZ Department of Ecological Chemistry, Helmholtz Centre for Environmental Research, Permoserstraße 15, Leipzig, Germany 04318

[e]Department of Civil and Environmental Engineering, Faculty of Science and Technology, University of Macau, Macau SAR, China 999078

[*]Corresponding author: Shanquan Wang (wangshanquan@mail.sysu.edu.cn)

Highlights

- Worldwide field assessments of chiral organohalides in soil and sediments have been summarized.
- Microorganisms play a pivotal role in enantioselective transformation of chiral organohalides.
- A few amino acid residues in functional enzymes have a key role in mediating the enantioselectivity.

Abstract

Chiral organohalides including dichlorodiphenyltrichloroethane (DDT), Hexabromocyclododecane (HBCD) and polychlorinated biphenyls (PCBs) raise a significant concern in the environmental occurrence, fate and ecotoxicology due to their enantioselective biological effects. This review provides a state-of-the-art overview on enantioselective microbial transformation of the chiral organohalides. We firstly summarized worldwide field assessments of chiral organohalides in a variety of environmental matrices, which suggested the pivotal role of microorganisms in enantioselective transformation of chiral organohalides. Then, laboratory studies provided experimental evidences to further link enantioselective attenuation of chiral organohalides to specific functional microorganisms and enzymes, revealing mechanistic insights into the enantioselective microbial transformation processes. Particularly, a few amino acid residues in the functional enzymes could play a key role in mediating the enantioselectivity at the molecular level. Finally, major challenges and further developments toward an in-depth understanding of the enantioselective microbial transformation of chiral organohalides are identified and discussed.

Keywords: chiral organohalides; enantioselectivity; microbial transformation; enantioselective dehalogenation; enantiomeric fraction (EF).

Contents

1. Introduction

The term chirality is derived from the Greek (*kheir*) "hand". It describes an object (here a molecule) that has a non-superimposable mirror-image, which is caused by asymmetric center. A chiral compound and its mirror-image are referred to as enantiomers, which differ in their optical activity but display identical physical and chemical properties [1]. Due to the different absolute configuration, the (*R*)/(*S*) system is a way to name an optical isomer based on the atomic number of the stereocenter substituents [2]. On the other hand, enantiomers capable of rotating polarized light clockwise and anticlockwise are labeled as (+) and (-), respectively [2]. Depending on the exact ligands, an (*R*)-enantiomer can be either (+)- or (-)-isomer [3,4]. The enantiomeric composition could be described by using enantiomer fraction (EF) as shown in Eq.1 [5].

$$EF = \frac{\mathrm{A}(+)}{\mathrm{A}(+)+\mathrm{A}(-)} \quad \text{(Eq.1)}$$

Where A(+) and A(-) represent the (+)- and (-)-enantiomers, respectively. If optical rotation is unknown, the two parameters are the first-eluting and second-eluting enantiomers, respectively.

Individual enantiomers may exhibit different biological and toxicological behaviors due to their enantioselective interactions with enzymes and other chiral macromolecules [6]. Take 'Thalidomide (Contergan) Tragedy' for example, only (*R*)-(+)-enantiomers have therapeutic effects, whereas the (*S*)-(-)-thalidomide has teratogenic effects and causes congenital malformations [7]. Therefore, the chirality needs to be taken into consideration in the risk assessment upon exposure to chiral pollutants [8]. Moreover, chirality could be further investigated to gain insights into the enantioselective biotransformation and the corresponding environmental fates, in contrast to the physical and chemical processes which will generally not change enantiomeric compositions [9].

Organohalides are a large group of organic compounds with halogens (e.g. fluorine, chlorine and bromine), which normally present in the environment as

pollutants and are recalcitrant to environmental attenuation due to their inherent stability [10]. Up to date, over 5,000 organohalides have been identified and generated from anthropogenic and natural sources [11,12]. Among them, more than 30% are chiral, and consequently the environmental fate and ecotoxicology become a public concern due to their enantioselective biological effects [13,14]. Chiral organochlorine pesticides, for instance, were massively introduced into environment as racemate (i.e. EF = 0.5) [13]. The enantiomers of chiral organohalides usually have different ecotoxicities [15], and consequently the understanding of the enantiomer-specific bioconversion and the environmental fate of those chiral organohalides are of great importance [16-19].

Stereoisomer analysis has been widely employed as a tool to characterize bioprocesses changing enantiomeric compositions of chiral organohalides in contaminated environment [5,20,21]. Many studies reported the enantiomeric distribution of chiral organohalides in a variety of environmental matrices, including water [22,23], activated sludge [24], soils [25,26], sediments [27,28] and air [29,30]. The results suggested that changes in the enantiomeric compositions of chiral organohalides at contaminated sites were mainly associated to the bioaccumulation and microbial transformation processes. To date, many studies have demonstrated the enantioselective bioaccumulation of chiral organohalides in humans and wildlife (e.g. fish and birds) [31,32]. In addition, enantioselective microbial conversion processes including degradation and enantiomerization of chiral organohalides were also identified in a variety of environmental samples, particularly in soils and sediments [33-44]. Notably, enantiomeric enrichment was observed very recently in organohalide-respiring bacteria, which plays a critical role in the global cycle of organohalides [45,46]. Several excellent reviews and book chapters have been published to provide critical views in the environmental occurrence and fate of chiral pollutants [9,20,47]. Nonetheless, recent progresses in enantioselective microbial transformation, as well as the corresponding mechanisms, remain unreviewed. Therefore, this review provides a state-of-the-art of microbial transformation of chiral

organohalides with three major foci. First, we comprehensively summarize the information on enantiomeric compositions of major chiral organohalides at contaminated sites. Second, we emphasize the enantiomer-specific microbial transformation of chiral organohalides in both mixed and pure cultures, discussing how microorganisms mediate the enantioselective transformation of chiral organohalides. Furthermore, we critically review the functional enzymes, as well as the underlying mechanisms, involved in the enantioselective microbial transformation of chiral organohalides.

2. Chiral organohalides and their environmental contamination

A broad range of solvents, plastics, pesticides and pharmaceutical agents are (or originate from) organohalides, which are consequently a fundamentally important class of hydrocarbons [11,48-50]. Many of organohalides are listed as persistent organic pollutants (POPs), raising public concerns due to their adverse impacts on human health and the environment [8,15,20]. With the consideration of extensive applications and toxicological effects of chiral organohalides, their representatives (Table 1) are given and discussed in this review.

2.1 Dichlorodiphenyltrichloroethane (DDT)

DDT was a typical organochlorine pesticide widely applied in agriculture, forestry and horticulture until its ban in the United States and many other industrialized countries in early 1970s [50]. However, DDT is still in the list of persistent organic pollutants (POPs) to be removed from the environment. Depending on conditions, its soil half-life ($t_{1/2}$) can range from 22 days to 30 years [51].Technical DDT is a mixture of various isomers of which *p,p'*-DDT is the most prevalent (65%-80%), followed by *o,p'*-DDT (15-21%) and *o,o'*-DDT (trace amounts) [51]. The *o,p'*-DDT is a chiral molecule, which can be reductively dechlorinated to chiral *o,p'*-DDD (Dichlorodiphenyldichloroethane) and *o,p'*-DDE (Dichlorodiphenyldichloroethylene) [52]. The *o,p'*-DDT isomer has the strongest estrogen-like properties among all the DDT-related compounds, which affects on the reproductive system [51]. Though

produced as a racemic mixture, enantiomers of *o,p'*-DDT have been characterized to have distinct toxicities. In fact, the estrogenic activity of the (+)-enantiomer is significantly lower than the (-)-enantiomer and racemic *o,p'*-DDT both in rats and human breast carcinoma cell line [17,53,54]. There have been many enantioselectivity assessments of the chiral *o,p'*-DDT in surface environments, particularly in sediments and soils (Fig. 1A) [25,33,35,37,55-70].The observed enantioselective signature of chiral *o,p'*-DDT is used as an indicator for tracking the fate and sources of the DDT in the environment [59,71]. In most cases, the EF values of *o,p'*-DDT at contamination sites are close to 0.5, which together with the high DDT/(DDE+DDD) ratios might suggest either the recent contamination or the slow bioconversion of the racemic pesticide [35,72]. On the other hand, significant preferential accumulation of (-)-*o,p'*-DDT (EF ≈ 0.13) was observed in many sediment samples collected from Yueqing and Sanmen Bay [57]. Similar preference was observed in Qiandao Lake sediment [73]. In comparison, comparatively faster attenuation of (-)-*o,p'*-DDT was observed in soil samples collected from Pearl River Delta [35]. In addition, preferential transformation of both enantiomers of *o,p'*-DDT (EF < 0.5 or EF > 0.5) were observed in contaminated soils (Fig. 1A) [25,33,35]. For instance, enantioselective attenuation of *o,p'*-DDT was observed in 11 out of 17 soils from the US corn belt, of which five soil samples were showed to preferentially attenuate the (-)-enantiomer of *o,p'*-DDT [33]. Similar enantioselective degradation of *o,p'*-DDT has been observed in sediments from UK and Canada, and global background soils [25]. Given this, the different enantioselectivities of *o,p'*-DDT biotransformation suggest that a variety of bioprocesses could involve in the enantioselective transformation of the chiral *o,p'*-DDT.

2.2 Hexachlorocyclohexane (HCH)

HCH has been massively manufactured as technical HCH with a production of several million tons globally, and extensively used as an insecticide since 1940s [50]. Although the amount of utilization and environmental contamination of HCH have dramatically decreased, HCH is still a contaminant of concern [74]. *α*-HCH as the

only chiral isomer of HCH is a major component of the technical HCH (55-80% in weight), which has been extensively found in worldwide air, water, soil and sediment samples [16,23,25,75,76]. As shown in Fig. 1B, preferential attenuation of (+)-*α*-HCH (EF < 0.5) was observed in sediment samples of Qiandao Lake, Yueqing Bay and Sanmen Bay [57,73]. Similar preferential depletion of (+)-*α*-HCH (EF = 0.39) was observed in surficial sediments of Northwater Polynya [77]. Interestingly, this lower EF value compared to that of water column samples from the same site (i.e. EF = 0.45) suggested the higher extent of enantiomeric enrichment of (-)-*α*-HCH in sediments [77,78]. By contrast, enrichment of (+)-*α*-HCH was observed in soil samples from Fraser Valley in British Columbia [66], Pearl River Delta [35] and a contamination site near a former HCH factory in Norway [79]. Nonetheless, racemic *α*-HCH (EF ≈ 0.5) was observed in most soil cores from a variety of continental geographical sites [25,33]. Therefore, the enantioselective transformation of *α*-HCH seems to be site-specific, which may depend on the involved biological processes [25].

2.3 Chlordane (CHL)

Chlordane with an environmental half-life of 10-20 years [80] was one of the most heavily used pesticides either as a single congener (*trans*- and *cis*-isomers) or as a mixture (i.e. heptachlor, chlordane and nonachlor) [81]. The production of chlordane was subsequently banned globally in 1997, due to the environmental persistence and the bioaccumulation and biomagnification in food webs [82,83]. Technical chlordane is racemic, containing 1:1 mixtures of both enantiomers of each chiral compound, including *t*-CHL, *c*-CHL and heptachlor [84]. Analyses of the enantiomeric compositions of *t*-CHL and *c*-CHL in sediment and soil samples (Fig. 1C and D) suggested their distinct EF distributions at most contaminated sites: (+)-*t*-CHL was preferentially depleted (EF < 0.5), in contrast to the preferential attenuation of (-)-*c*-CHL (EF > 0.5) [25,29,37,64]. Similar trends of enantioselective transformation of chiral chlordanes have been observed in previous studies [83,85]. Nonetheless, there is no clear explanation for the observed phenomenon, awaiting further investigation. In addition, racemic *t*- and *c*-CHLs were observed in the sediment cores

of Long Island Sound and Toronto lakes, which might be due to fresh residues of chlordane from sources such as house foundations [37,86].

2.4 Dichlorprop (DCPP)

DCPP is a phenoxyalkanoic acid herbicide widely used to control grasses and broad-leaf weeds in planting wheat, corn, sorghum and olive trees [87]. Frequent detections of DCPP in groundwater and soil samples are raising concerns due to its detrimental effects on non-target plants and putative side effects on human beings via food chains [88]. DCPP exists in the environment in two stable enantiomeric forms, i.e. (*R*)-(+)- and (*S*)-(-)- enantiomers, yet only the (*R*)-(+)-enantiomer is active as herbicide [89]. Thus far, data on the enantiomeric compositions of DCPP in sediment and soil samples is limited, because of the short half-life of DCPP under aerobic conditions ($t_{1/2}$ = 3-16 days) [38,90,91]. Investigation on the enantiomeric distribution of DCPP in Brazilian soil indicated the preferential degradation of the (-)-enantiomer of DCPP in most pasture soils (93% of all tested samples), in contrast to the preference of (+)-DCPP and (-)-DCPP in 13% and 38% of the forest soil samples, respectively [90]. Furthermore, an in-depth study on the relationship between functional microorganisms and their enantioselectivities was performed with soil samples collected from Norway, North America and Brazil. The 16S rRNA gene amplicon sequencing data suggested that the enantioselectivity mainly depended on the activation of metabolically quiescent microbial communities or the induction of enantiomer-specific enzymes [90]. For the first time, this study confirmed that the functional microorganisms/enzymes could be activated by a specific environmental variable, and consequently change the enantioselectivity. Additionally, a five-year study (2003-2007) on enantiomeric compositions of DCPP in Ontario streams suggested the enantioselective degradation of DCPP in the watershed and streams (average EF = 0.3 in 2003-2004; average EF = 0.352 in 2006-2007) [91].

2.5 Polychlorinated biphenyls (PCBs)

PCBs are a family of 209 congeners, which were massively produced as commercial mixtures (e.g. Aroclor 1260) for industrial usages [49]. PCBs as POPs

persist in the environment and pose health threat to human beings via bioaccumulation in food webs [92]. It was reported that PCBs could persist in a human body with a half-life of 10-15 years [93]. Out of the 209 PCB congeners, 78 PCBs display axial chirality and exist as rotational isomers [94]. While only 19 out of the 78 chiral PCBs are known to form stable atropisomers under the ambient condition, and constitute a large part of the commercial mixtures [30]. For instance, the technical PCB mixture - Aroclor 1260 contains up to 33% chiral PCBs by molar concentration (mol%), of which each chiral PCB is commonly constituted by 1:1 mixture of both enantiomers [18,95]. Fig. 2 summarizes the concentrations and EFs of six major chiral PCBs (i.e. PCB91, PCB95, PCB132, PCB136, PCB149 and PCB174) in worldwide soil and sediment samples [24,27,30,37,70,72,96-105]. The survey results suggested that the enantioselective transformation of chiral PCBs might take place at very low concentrations. For example, chiral PCBs in topsoil samples collected from sits near Birminghan, UK showed non-racemic PCB95, PCB136 and PCB149 (EF = 0.39-0.45) at pg/g concentrations [103]. Additionally, the non-racemic PCB174 (EF > 0.5) suggested the preferential attenuation of (-)-PCB174 in soil samples [99, 100], in line with the enantioselective dechlorination of PCB174 in the organohalide-respiring *Dehalococcoides* [45]. In contrast to PCB174 as a bioconversion substrate, PCB95 could be a substrate, or an intermediate from dechlorination of highly chlorinated PCBs [45,95]. Therefore, accumulation of (-)-PCB95 (EF < 0.5) might be a result of dechlorination of highly chlorinated PCBs, or due to a combination of both enantioselective production and attenuation of PCB95 [27,37,99]. By contrast, the racemic PCBs detected in suburban soil samples from Birmingham, UK and Toronto, Canada indicated the fresh input and slow bioconversion of PCBs [27,37,102].

3. Microbial transformation of chiral organohalides in the environment and in laboratory studies

Microbial processes may alter the enantiomeric compositions of chiral

organohalides as a result of the enantioselective biotransformation, in contrast to the non-enantioselective abiotic processes [20]. Consequently, enantioselectivity can serve as an indicator of microbial transformation of chiral organohalides [5]. To better understand the enantioselectivity of bioattenuation of chiral organohalides at contaminated sites, laboratory experiments could be performed under well-controlled conditions to mimic the enantioselective transformation processes in natural environments, which predominantly include oxidative degradation and anaerobic microbial conversion.

3.1 Oxidative degradation

Microbial transformation of chiral organohalides in surface environment (e.g. freshwater, river estuary and topsoil) usually proceeds aerobically, and might result in enantiomer-specific oxidative degradation. There have been many studies confirming the enantioselective aerobic biodegradation of chiral organohalides (Table 2) [34,36,43,78,84,89,90,95,106-113]. For example, investigation on the stereochemical fate of α-HCH in aerobic marine sediment and surface water from the North Sea firstly suggested the higher degradation activity of (+)-α-HCH compared to that of the (-)-α-HCH [110]. Later on, similar enantiomeric enrichment of the (-)-α-HCH was observed in other aerobic microcosms established with surface seawater or soil samples [108], in line with results obtained in field studies [34,78]. All these evidences working together suggested the important role of aerobic microorganisms in the enantioselective HCH degradation in surface environments (Fig.1B) [57,59,73]. Nonetheless, information on the microbial community composition of these microcosms, as well as taxonomy of the key functional microorganisms, remain scarce [84,110]. Recently, Xu and colleagues reported the correlation of a HCH degrading *Sphingomonas* with the stereoselective accumulation of HCHs in nationwide agricultural soils in China [114]. In this study, the microbial community composition was determined by using 16S rRNA gene amplicon sequencing, and the community-impacting factors including soil moisture and temperature were comprehensively evaluated. Interestingly, results suggested that increasing soil

moisture would benefit the growth of HCH-degrading populations, and consequently affect the enantioselective biodegradation. Though with a wide range of EF values (0.10-0.84), the EFs > 0.5 observed in most soil samples indicated the preferential degradation of (-)-α-HCH in agricultural soils [114]. On the other hand, the racemic α-HCH at contaminated sites might be due to either the fresh inputs of α-HCH with negligible biodegradation activities, or the neutralized enantioselectiveities of distinct enzymatic processes [34,106]. Therefore, it is challenging to predict the enantioselective bioconversion of chiral organohalides in complex microbial communities, since the observed enantiomeric compositions epitomize all enantioselective bioconversion processes in the investigated communities.

The enantioselectivity of aerobic attenuation of several other organohalides including *o,p'*-DDT, CHL and DCPP, have been also evaluated in laboratory studies. For example, Ali and colleagues investigated the oxidative degradation of *o,p'*-DDT in a water-sediment system using sediment cultures amended with plant extract [43]. Both uptake and degradation efficiencies of (-)-*o,p'*-DDT were observed to be slightly higher than these of (+)-*o,p'*-DDT (EF > 0.5). Similar preferential degradation of the (-)-*o,p'*-DDT was observed in a microcosm established with soil collected from Luddington, UK [106]. Nonetheless, in the assessment of global distribution of the chiral *o,p'*-DDT (Fig.1A), the distinct enantiomeric enrichments of (+)/(-)-*o,p'*-DDT were driven by the microbial community compositions at different geographical locations [36,64,106]. Pertaining to CHL, several aerobic cultures established with soil samples were enriched to enantioselectively degrade the CHLs [36,106]. Interestingly, in line with observations in environmental surveys (Fig. 1C and D), both (-)-*c*-CHL and (+)-*t*-CHL were identified to be preferentially degraded in enrichment cultures (Table 2) [36,115]. The enantioselective biodegradation of the easily-degrading DCPP has been extensively studied [90,107,109,111,116]. As early as 1992, the aerobic degradation of racemic DCPP was investigated for the first time in a marine microbial community [107], in which microorganisms exclusively degraded the (+)-DCPP. In contrast, the (-)-DCPP was preferentially and completely

degraded within 7 days by microorganisms in activated sludge samples under aerobic conditions [109]. Later, Lewis and colleagues confirmed that the enantioselective degradation of DCPP was influenced by the microbial communities, while significant environmental changes such as tropical deforestation and global warming may substantially alter the enantiomeric enrichment of chiral DCPP by changing the microbial community composition [90].

3.2 Anaerobic microbial transformation

Microbial transformation of chiral organohalides also occurred in anaerobic environmental matrices, including soils, sediments and sewage sludge. Under anaerobic conditions, microorganism-mediated conversion processes like dehydrohalogenation and reductive dehalogenation play major roles in the attenuation of organohalides [117,118]. Compared with the oxidative degradation, reductive bioprocesses usually take a much longer time and require strict ecological niches. Therefore, available information on the anaerobic enantioselective transformation of chiral organohalides is comparatively limited (Table 2). Buser and Müller reported that the HCH dechlorination rates in anaerobic enrichment cultures established with sewage sludge were in the order of γ-HCH > (+)-α-HCH > (-)-α-HCH > δ-HCH > β-HCH [113]. Similar preferential degradation of (+)-α-HCH was observed in anaerobic soil samples collected from Kintyre Peninsula, Scotland [36]. Interestingly, the preferential conversion of (+)-α-HCH in the microbial reductive dechlorination process is in line with the enantioselective aerobic degradation of the (+)-α-HCH [84,107], suggesting the impacts of molecular structure properties (e.g. molecular structure and energy barrier of a specific enantiomer) in the enantioselective transformation of α-HCH.

Due to the inherent stability, PCBs are difficult to be eliminated from environmental matrices, and the microbial reductive dechlorination mediated by organohalide-respiring bacteria is the major process responsible for the PCB attenuation in natural anoxic environments [117,119]. Nonetheless, the slight

enantiomeric enrichment of chiral PCBs or non-racemic PCBs at worldwide contamination sites (Fig. 2) might suggest the low PCB dechlorination activity or the non-enantioselective PCB dechlorination [27,97,100-102,120]. By contrast, experimental evidences to support enantioselective dechlorination of chiral PCBs remain scarce. The enantiomeric enrichment of chiral PCBs (e.g. PCB132 and PCB149 in Aroclor 1254) was observed for the first time in a microcosm study with sediment from Lake Hartwell, SC. In the microcosm, PCB132 was dechlorinated to PCB91 and PCB51 via removing *meta*-chlorines, while PCB149 was dechlorinated to PCB95 and PCB51 via attacking *para*- and *meta*-chlorines, respectively. Interestingly, no enantioselectivity was observed in reductive dechlorination of PCB132 and PCB149, in contrast to the enantioselective dechlorination of the dechlorination intermediates, i.e. PCB91 (EF < 0.5) and PCB95 (EF > 0.5) [95]. In Aroclor 1254-spiked microcosms, reductive dechlorination of PCB149 was also non-enantioselective. It has been speculated that the dechlorinating microorganisms/enzymes responsible for the PCB132/PCB149-dechlorination bind to the two enantiomers equally [18,95]. The non-enantioselective dechlorination of parent PCB congeners followed by enantioselective dechlorination of daughter dechlorination products possibly emphasized two different metabolic pathways involved in the PCB dechlorination. Notably, the authors also implied that the enantioselective dechlorination of chiral PCBs might depend on the chlorine substitution pattern of the chiral PCBs, as well as the microbial community composition [95,120].

4. Enantioselective biotransformation of organohalides: functional microorganisms, enzymes and mechanistic scenarios

Studies on the enantiomeric compositions of chiral organohalides in both environmental surveys and laboratory assays suggested a variety of bioprocesses mediated by distinct microorganisms or enzymes for the enantioselective transformation. Nonetheless, specific mechanisms for these enantioselective

bioprocesses remain largely unknown, due to challenges in identifying enantioselectivity of the complicated microbial communities. By contrast, investigations on the isolated organohalide-converting microorganisms or purified functional enzymes (Table 3) may provide mechanistic insights into the enantioselective bioprocesses [9,45,121-128].

4.1 Functional microorganisms

Several aerobic microorganisms in pure cultures have been identified to enantioselectively degrade DCPP (Table 3). For example, an *alpha*-Proteobacteria bacterium, *Sphingomonas herbicidovorans* MH, isolated from soil-column enrichment [129] is a versatile phenoxy-alkanoic acid degrader. Strain MH could completely degrade both enantiomers of DCPP, with a preference of the (*S*)-(-)-enantiomer over the (*R*)-(+)-enantiomer [130]. The enantioselectivity of strain MH was explained to be due to the two different inducible substrate-transport systems involving the enantioselective DCPP-degradation [130,131]. Later on, the discovery of two α-ketoglutarate-dependent dioxygenases (i.e. SdpA and RdpA) for catalyzing the enantioselective DCPP-degradation in strain MH provided molecular evidences for above-mentioned cultivation observations [121]. Similar functional enzymes for DCPP-degradation were identified from *Delftia acidovorans* MC1, an isolate from herbicide-contaminated building site [122]. Nonetheless, in contrast to the preference of the (-)-enantiomer in strain MH, MC1 selectively eliminated the (+)-enantiomer [122]. Other isolated aerobic DCPP-degrading bacteria exclusively convert a single enantiomer, e.g. the ether-bond cleavage of (-)-DCPP in *Ralstonia eutropha* JMP134 and *Burkholderia cepacia* RASC, and the (+)-DCPP conversion in *Alcaligenes denitrificans* EST4002 [123].

For the enantioselective degradation of HCH, several strains of *Sphingomonas paucimobilis* were isolated and characterized (Table 3) [124,132,133], particularly the extensively studied *S. paucimobilis* UT26 [134] and B90A [135]. Both UT26 and B90A could degrade a variety of HCHs (i.e. α-HCH, δ-HCH and γ-HCH) and their metabolites (e.g. α-PCCH, β-PCCH and γ-PCCH) into products including

1,2,4-trichlorobenzene (TCB) [136]. Interestingly, no enantiomeric enrichment was observed for the *α*-HCH transformation by strain B90A, which was identified to harbor two functional enzymes (i.e. LinA1 and LinA2) involving the enantioselective degradation of *α*-HCH [127,137]. One reason for the non-enantioselective degradation in strain B90A might be the equal expression of LinA1 and LinA2, and consequently the homogenization of the degradation of both (+)- and (-)-enantiomers. Notably, strain B90A converted the (+)-*α*-HCH and (-)-*α*-HCH to *β*-(*3S,4S,5R,6S*)-1,3,4,5,6-PCCH and *β*-(*3R,4R,5S,6R*)-1,3,4,5,6-PCCH, respectively [124]. Thus far, the enantioselectivity of anaerobic transformation of HCH in pure cultures had only been tested in *Clostridium pasteurianum* DSM525, which was shown to be non-enantioselective (Table 3) [126]. As early as 2002, the enantioselectivity of PCB conversion was reported for the first time in an aerobic pure culture *Jonibacter sp.* MS3-02 [127], showing the non-enantioselective degradation of seven chiral PCBs (Table 3). Almost at the same time, non-enantioselective degradation of chiral PCBs was also reported in aerobic pure cultures, *Arthrobacter sp.* B1B and *Rhodococcus sp.* ACS (Table 3) [128]. By contrast, enantioselective PCB-degradation was observed in other three aerobic bacterial lineages, i.e. *Ralstonia euthrophus* H850, *B. cepacia* LB 400 and *Rhodococcus globerulus* P6, with distinct enantiomeric preferences (Table 3) [128]. The enantioselectivity of these PCB-converting bacteria might be both cell structure-specific and PCB congener-specific [128]. For example, similar enantioselectivities were observed within Gram-negative bacteria (e.g. strains H850 and LB400) or Gram-positive bacteria (e.g. strains B1B and ACS) (Table 3). One exception was that the Gram-positive *R. globerulus* P6 shared similar enantiomeric preference with the Gram-negative bacteria in conversion of chiral PCBs, which might be due to their employment of similar biphenyl dioxygenases (BphA) [128,138]. Interestingly, the enantioselectivity of these aerobic PCB-converting bacteria could be altered by co-substrate addition. For instance, a significant shift in the enantioselectivity of PCB45 degradation was observed in biphenyl-fed pure cultures of *R. globerulus* P6, *R. euthrophus* H850 and *B. cepacia* LB400, compared to them grown on tryptic soy

broth (TSB) medium, carvone or cymene [128]. In addition, the enantioselectivities of carvone-fed strains B1B and ACS could be altered when changing to the TSB medium [128]. A mechanistic reason might be that the added co-substrate potentially modified the conformation of the PCB-converting enzyme, and consequently shifted the enantiomeric specificity [139,140]. Therefore, these experimental evidences suggested that the enantioselective degradation of chiral PCBs in aerobic microorganisms could be a synergistic result of the varied differences in functional microorganisms and enzymes, as well as the presence of isozymes and their active sites. In contrast to the extensive investigations on the aerobic degradation of chiral PCBs, information on the enantioselectivity of anaerobic PCB dechlorination remain scarce, particularly the environmentally relevant PCBs. Until very recently, Yu and colleagues reported the enantioselective dechlorination of chiral PCBs in *Dehalococcides mccartyi* CG1 [45], in which strain CG1 was shown to preferentially remove chlorines from the (-)-enantiomers of all GC-resolved chiral PCBs. Nonetheless, whether the enantioselectivity observed in this study presents a common enantioselective pattern for PCB dechlorination warrants future analyses. In conclusion, the enantioselective transformation of chiral organohalides in the characterized microorganisms may proceed in three different avenues: (1) Microorganisms express two functional enzymes, and each of them converts only a single enantiomer, e.g. the equally expressed LinA1 and LinA2 in *S. paucimobilis* B90A result in non-enantioselective degradation of α-HCH, whereas the differently expressed SdpA and RdpA lead to enantioselective transformation of DCPP in *S. herbicidovorans* MH and *D. acidovorans* MC1 [14,121,130]. (2) Microorganisms express a single functional enzyme for exclusively transforming a single enantiomer, e.g., TfdA expressed in *R. eutropha* JMP134, *B. cepacia* RASC and *A. denitrificans* EST4002 [123]. (3) Microorganisms express a single functional enzyme to convert both enantiomers, but, at different rates, e.g., PcbA1 expressed in *D. mccartyi* CG1 [45].

4.2 Enantioselective enzymes

Functional enzymes play a key role in mediating the enantioselective transformation of chiral organohalides, on which information has hitherto been limited (Table 3). Pertaining to the enantioselective degradation of DCPP, two distinct *α*-ketoglutarate-dependent dioxygenases (i.e. RdpA and SdpA) were purified and characterized from both *S. herbicidovorans* MH and *D. acidovorans* MC1 for exclusively converting the (*R*)-(+)- and (*S*)-(-)-DCPP, respectively (Table 3; Fig. 3) [121,122,141-144]. Further experiments of substrate docking and site-directed mutagenesis of SdpA and RdpA from strain MH suggested that the specific residues might be involved in substrate binding and enantiospecificity [144]. For instance, RdpA residues Gln93, Ile106 and Phe171 could sterically hinder the binding of the (-)-enantiomer, whereas SdpA residues Glu69, Asn98, Arg207 and His208 may prevent binding of the (+)-enantiomer. Moreover, RdpA is compatible with the (*R*)-(+)-mecoprop interacting with the guanidino group of Arg285, hydroxyl group of Tyr221 and the amide nitrogen of Ser114. Likewise, the (*S*)-(-)-mecoprop interacts with the amide nitrogen of Ser105, hydroxyl group of Tyr109, guanidine nitrogen of Arg274 and additional active site of SdpA residues His272/208 [144]. These results suggested that protein residues play distinctive roles in binging correct/incorrect enantiomers, and consequently result in the enantioselectivity. In addition, several *α*-ketoglutarate-dependent 2,4-D dioxygenases (TfdA) have been identified from phylogenetically diverse lineages (e.g. *R. eutropha* JMP134, *B. cepacia* RASC and *A. denitrificans* EST4002) (Table 3), forming a separate cluster for enantioselective degradation of DCPP (Fig. 3B) [123]. Interestingly, although TfdAs of *B. cepacia* RASC and *A. denitrificans* EST4002 share the higher sequence similarity (i.e. 95% similarity over 282 amino acids), TfdAs of *B. cepacia* RASC and *R. eutropha* JMP134 show identical enantiomer-specificity for exclusive degradation of (-)-DCPP, in contrast to (+)-DCPP degradation catalyzed by the TfdA of *A. denitrificans* EST4002. Moreover, the substrate binding residues of TfdA were identified as Arg278, His214 and Lys71 [145], while Arg278 and His214 residues have direct counterparts in the RdpA (i.e. Arg285 and Tyr221) and SdpA (i.e. His208 and Arg274). These experimental evidences suggested that the amino acid residues have a

crucial effect on the enantioselective transformation of DCPP, irrespective of the amino acid sequence similarity [123,144,145]. Notably, above-mentioned enantioselective dioxygenases have different enzyme structures, which might exert impact on their enzymatic enantioselectivity. For instance, the RdpAs of *S. herbicidovorans* MH and *D. acidovorans* MC1 are homotrimers [122], whereas other *α*-ketoglutarate-dependent dioxygenases enzymes are either monomers (e.g. SdpA) [122] or homodimers (e.g. TfdA) [146].

The characterized enzymes for enantioselective degradation of *α*-HCH are dehydrochlorinases (LinAs), which have been identified firstly in *S. paucimobilis* UT26 and B90A [124, 132]. In contrast to a single *linA* gene of strain UT26, strain B90A harbors two different *linA* genes i.e. *linA1* and *linA2* [137,147], of which *linA2* share 99% sequence similarity (over 154 amino acids) with the *linA* of strain UT26 [125]. In terms of amino acid sequence similarity, LinA1 and LinA2 were 90% identical to each other (Fig.3), with 11 amino acid differences in the beginning 1-148 amino acid sequence, but significantly different in the remaining sequence region [148,149] . Further investigation on the enantioselective transformation of *α*-HCH by heterogeneously expressed LinA1 and LinA2 demonstrated that LinA1 preferentially converted the (+)-*α*-HCH, in contrast to LinA2 for (-)-*α*-HCH degradation [124]. Moreover, the non-enantioselective degradation of *α*-HCH in strain B90A suggested that LinA1 and LinA2 were equally active in strain B90A [124]. Interestingly, a *linA* gene encoding dehydrochlorinase for exclusive degradation of (+)-*α*-HCH was identified from metagenomic data of a HCH-contaminated site [150], which has only a single amino acid difference in the 1-148 amino acid sequence region with $LinA1_{B90A}$ and the remaining region is identical to the corresponding region of $LinA2_{B90A}$ [148]. Consequently, residues in the 1-148 amino acid sequence region may be responsible for the enantioselectivities of LinA1 and LinA2. The site-directed mutagenesis analyses allowed a closer look at the binding site of LinAs, suggesting the involvement of His73 and Asp25 in the stereoselectivity of LinAs [151]. Nonetheless, the results of sequence homology analysis revealed that His73 and

Asp25 were conserved [148]. To further investigate the key amino acid residues responsible for the enantioselective transformation of *α*-HCH, *in silico* docking analyses were performed recently [42], which identified four amino acids (i.e. Lys20, Leu96, Ala131 and Thr133) in LinA2 as the key residues for selective binding of the enantiomers of *α*-HCH. Mutagenesis experiments revealed that a combined change of three amino acids (i.e. Lys20Gln, Leu96Cys, and Ala131Gly) caused a reversal in enantioselectivity from the (-)-enantiomer to the (+)-enantiomer [42]. This preference was enhanced by the additional amino acid changes (e.g. Thr133Met). Moreover, amino acid residues further away from the active site might be involved in enhancement of enantioselectivity [42].

Thus far, information on enzymes for enantioselective degradation of chiral PCBs was mostly obtained from cultivation experiments, rather than with purified enzymes [45, 128, 138]. BphAs from aerobic *R. globerulus* P6 and *B. cepacia* LB400 share only 66% amino acid sequence similarity with each other, and have distinctive patterns of enantioselective degradation of chiral PCBs (Table 3) [128,138]. For the anaerobic dechlorination of chiral PCBs, recent experimental evidences showed that a predominant PCB reductive dehalogenase (i.e. PcbA1) in *D. mccartyi* CG1 catalyzed the enantioselective dechlorination of chiral PCBs (Table 3) [45]. The observation of a single reductive dehalogenase for dechlorination of both enantiomers but with different rates might suggest a different enzymatic model for enantioselective transformation of chiral organohalides, compared to above-discussed single enantiomer-specific enzymes. For instance, the enantiomer-specific binding of mecoprop to a single enantioselective enzyme (e.g. RdpA or SdpA) should be expected to interact with the carboxylic acid, the oxygen atom in the ether group, and the methyl group by multiple residues [144]. By contrast, the organohalide-respiring bacteria employ periplasmic, outward-oriented, membrane-bound reductive dehalogenases to catalyze halogen removal from organohalides without destroying the corresponding backbone carbon structure (e.g. the biphenyl in PCBs) [152]. The comparatively fewer substrate-enzyme residue interactions might result in the less

enantioselectivity in the microbial reductive dehalogenation. Therefore, it is possible that the extent of enantioselectivity may be positively correlated with the number of substrate-interacting residues. Nonetheless, due to the challenge of heterogeneous expression and subsequent characterization of PCB RDases, information on enzyme-substrate binding remains scarce. Further studies based on purified enzymes, as well as mutagenesis analyses, may help to clarify the mechanism underlying the enantioselective transformation of chiral PCBs.

4.3 Mechanistic scenarios

Experimental evidences suggested that enantiomer-specific functional enzymes have a pivotal role in mediating the enantioselectivity, particularly a few substrate-interacting amino acid residues in the enzymes [42,153]. To provide mechanistic insights into the enantioselectivity, both three-point model [154,155] and four-location model [156] were proposed in previous studies (Fig. 4). In the three-point model (Fig. 4A), the substrate enantiomer binds to three active sites (i.e. A', B' and C') of the functional enzyme, while the opposite enantiomer mismatches with the functional enzyme at the same binding sites, resulting in the enantioselectivity [47]. By contrast, in the four-location model (Fig. 4B), three parts of both enantiomers bind to the same three active sites (i.e. A, B and C) of the functional enzyme, but the enantiomer-specific activity depends on the fourth binding site (i.e. D) [156]. These models improved our mechanistic understanding of enantioselective transformation of chiral compounds. Moreover, current technical developments in enzyme crystallization and gene editing allow in-depth exploration of the enantioselectivity at the molecular level. For example, enzymatic structure analyses showed that the current identified enantiomer-specific functional enzymes are either trimers (e.g. RdpA and LinA) or monomers (e.g. SdpA), while non-enantiomer-specific functional enzymes capable of converting both enantiomers are dimers [45]. On the other hand, a modeling and docking study on rat cytochrome P-450 (CYP) 2B1 isozyme suggested a lower CDOCKER interaction energy (i.e. non-bonded interactions, including van der Waals and electrostatics forces) of

(*S*)-(-)-PCB132, compared to (*R*)-(+)-PCB132, and consequently a higher binding enzyme-substrate affinity of (*S*)-(-)-PCB132 [157]. Similar phenomena were observed for the enantioselective transformation of PCB45 and PCB95 [157]. Recent experimental evidences of preferential dechlorination of (*S*)-(-)-PCB132 in *Dehalococcoides* further built-on that the enantiomer configuration and molecular properties of chiral organohalides could also play a role in affecting the enantioselectivity [45,157,158].

5. Concluding remarks and future perspectives

Both field surveys and laboratory studies all working together suggest that microorganisms are of decisive importance in enantioselective attenuation of chiral organohalides in natural environment and at bioremediation sites. For these enantioselective processes, several models have been proposed to provide mechanistic insights, and amino acid residues in different functional enzymes have been identified to be responsible for mediating the enantioselectivity. Nonetheless, several outstanding questions remain unanswered, and warrant future studies:

(1) Mechanistic insights into the enantioselectivity of microbial transformation of organohalides

The microbial transformation of chiral organohalides is a complex process, involving adsorption, and enzymatic transport and transformation, in which all steps might be enantioselective. Take the adsorption for instance, environmental matrices including soil and sediments generally have the minerals and organic matters with chiral structures [159,160], and might consequently contribute to their enantioselective adsorption of chiral organohalide pollutants [160]. Nonetheless, our current studies have mainly focused on the enantioselective transformation, rather than the whole processes which altogether affect the environmental fate of chiral organohalides. Also, mechanistic understanding of how organohalide enantiomers differentially interact with each other on the molecular level will greatly improve our current knowledge on toxicokinetics and degradation potential of chiral organohalides.

Thus far, it has been confirmed that several amino acid residues in functional enzymes play key roles in mediating the enantioselectivity, and the potential contribution of other amino acid residues still await in-depth analysis [42,144]. Moreover, mechanistic studies on the enantioselective transformation of chiral organohalides in obligate anaerobic microorganisms are still in their infancy stages. For example, investigation on the enantioselective dehalogenation mediated by organohalide-respiring bacteria have been largely hindered by the challenges in growing fastidious dehalogenating bacteria and in harvesting enough amount of the active functional reductive dehalogenases for enzyme structure analysis [45].

(2) Can the enzymatic enantioselectivity be completely converted?

Recent studies implied that the mutated LinA2 could preferentially, but not solely, degrade the opposite enantiomer of α-HCH by changing three amino acid residues [42]. The results indicated that changing amino acid residues can cause the shift of enantioselectivity, while complete reversal of enantioselectivity was not achieved. Is it possible to control both the enantioselective preference and extent by adjustment of amino acid residues in key functional enzymes? It is still a grand challenging question, awaiting answers from close collaborations of biochemists and environmental microbiologists.

(3) Enantiomerization of chiral organohalides

Many chiral hydrocarbons (e.g., pesticides and pharmaceuticals) may undergo enzymatic or non-enzymatic enantiomerization, indicating the reversible conversion of one enantiomer into the other [161-163]. Enzyme-mediated enantiomerization is generally catalyzed by epimerases and racemases through reversibly cleavage of the C-H bond and act at a stereogenic center adjacent to a carbonyl functionality [164]. On the other hand, given proper conditions (e.g., temperature and pH), some enantiomers are configurationally unstable and undergo non-enzymatic interconversion [161,165]. Several laboratory studies have been published to discuss the enantiomerization process in the enantioselective degradation of herbicides

[44,166], fungicides [167] and pesticides [168]. Nonetheless, due to the technical difficulty of source track and the complex field environment, enantiomerization process could be hard to be determined in the filed assessment. Therefore, more attention should be paid to enantiomerization process in field assessment of chiral organohalides, which will broaden our understanding of enantioselectivity.

(4) Enantioselective formation of organohalides

Although microorganisms have been recently shown to produce organohalides including tetrachloroethene (PCE), chloroform, PCBs and PBDEs in natural environment [12,169,170], information on the global cycle, particularly the microbial generation, of chiral organohalides remains elusive. Knowledges on natural sources of chiral organohalides, together with their formation mechanisms and environmental fates, are critical to assess their toxicokinetics and environmental risks. Therefore, studies on the generation of chiral organohalides are required.

(5) Implications in bioremediation of organohalide pollutants

Advances in separation and detection of chiral compounds empower the in-depth analyses of transformation and fate of chiral organohalides at contaminated sites. In site assessments, (non-)racemic compositions of chiral organohalides were utilized to indicate their bioconversion in the environment, which were generally coupled with enantiomer-specific stable carbon isotope analysis (ESIA) to differentiate the distinct biochemical transformation processes [126,171,172]. Combination of these techniques may provide valuable insights into fates of chiral organohalides for environmental bioremediation applications [173].

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Figure Legends

Fig. 1. EFs and concentrations of typical chiral organohalides in worldwide environmental soils and sediments: (A) *o,p'*-DDT, (B) α-HCH, (C) *trans*-CHL, (D) *cis*-CHL.

Fig. 2. EFs and concentrations of six environmentally-relevant chiral PCBs in worldwide environmental soils and sediments.

Fig. 3. Phylogenetic tree of organohalide-converting bacteria (A) and their enantioselective functional enzymes (B).

Fig. 4. Proposed mechanistic models for enantioselective bioconversion of chiral compounds: (A) three-point model, and (B) four-point model. A, B, C, D are the four ligands of the chiral substrate. A', B', C', are the binding sites in the active site of the enzyme. In some case, an additional bind site at the fourth location (D' and D'') is necessary for the selective recognition of an enantiomer.

Fig 1

Fig.1

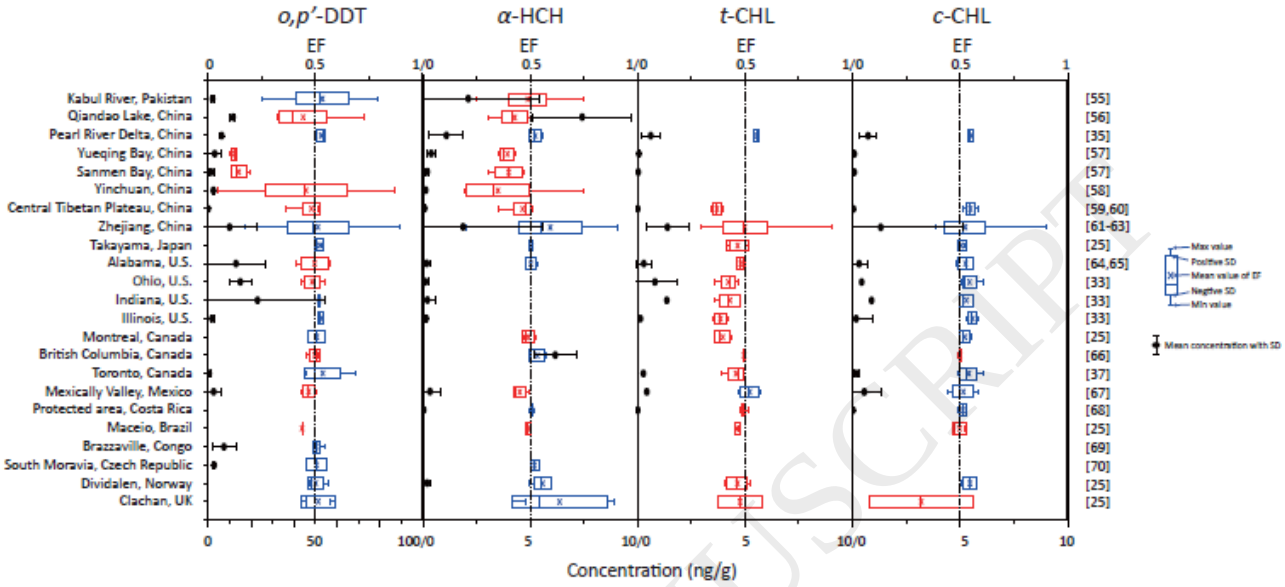


Fig 2

Fig.2

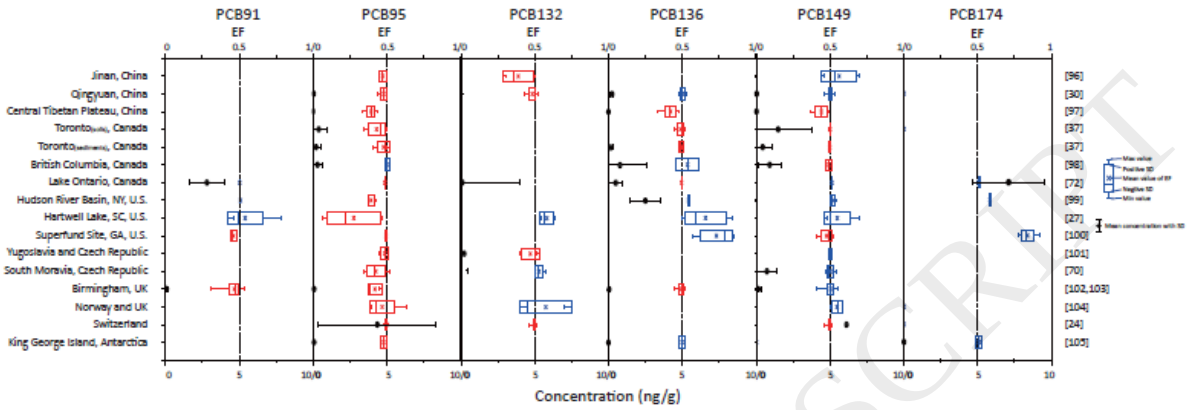


Fig 3

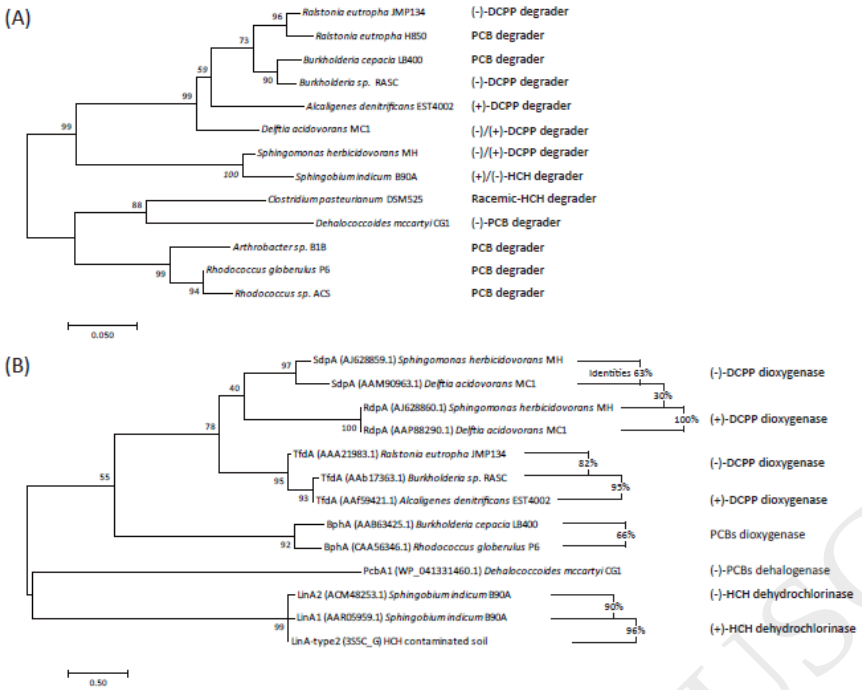


Fig.3

Fig 4

Fig.4

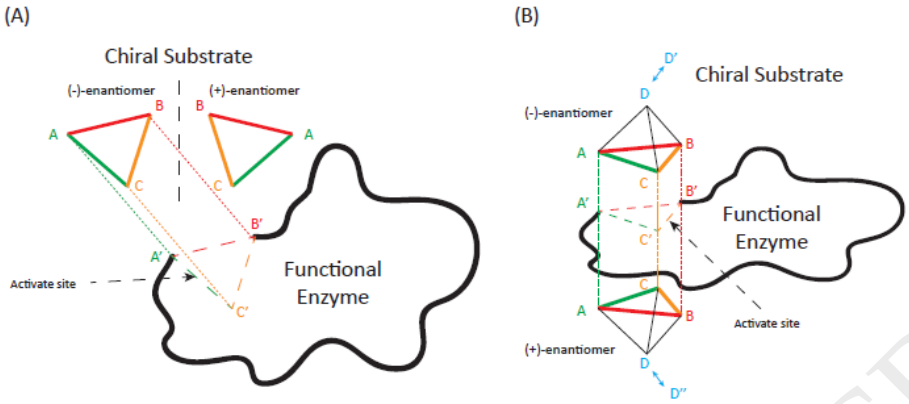
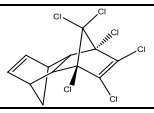
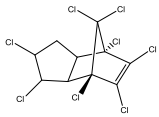
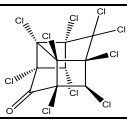
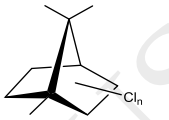
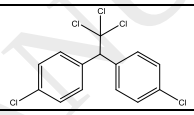
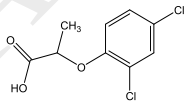
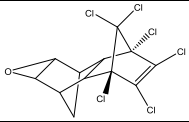
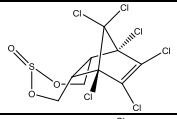
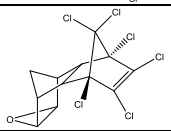
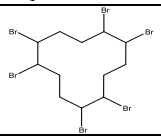
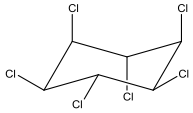
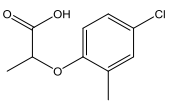
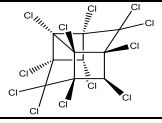
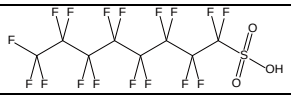
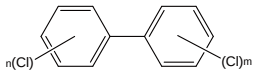


Table 1. Characteristics of environmentally-relevant chiral organohalides.

Group of Organohalides	Acronym	Chiral Compounds	Molecular Formula	Structure	Usage	Banned Time[a]
Aldrin	HHDN	Aldrin	$C_{12}H_8Cl_6$		Insecticide	1974
Chlordane	CHL	*trans*-CHL, *cis*-CHL, *octa*-CHLs (U81, U82, MC4, MC5, MC7), nonaCHL (MC6), Chlordene, Heptachlor	$C_{10}H_6Cl_8$		Termite-treatment, Insecticides	1988
Chlordecone		Chlordecone	$C_{10}Cl_{10}O$		Insecticide	2009
Chlorinated bornane (Toxaphene like)		B7-515, 1059, 1146, 1453, 531, B8-786, 789, 806, 809, 1413, B8-1414, 1945, 2229, 415, B9-418, 1025, 1679, 2206	$C_{10}H_{10}Cl_8$ (B8-1413)		Insecticide	2004
Dichlorodiphenyl trichloroethane	DDT	*o,p'*	$C_{14}H_9Cl_5$		Insecticide，Control malaria	1972
Dichlorprop	DCPP	Dichlorprop	$C_9H_8Cl_2O_3$		Herbicide，Pesticides	N.A.[b]
Dieldrin	HEOD	Dieldrin	$C_{12}H_8Cl_6O$		Insecticide	2004
Endosulfan		Endosulfan	$C_9H_6Cl_6O_3S$		Insecticide, Acaricide	2011
Endrin		Endrin	$C_{12}H_8Cl_6O$		Insecticide, Rodenticide, Piscicide	1984
Hexabromocyclododecane	HBCD	*α,β,γ*	$C_{12}H_{18}Br_6$		Brominated flame retardant	2013
Hexachlorocyclohexane	HCH	*α*	$C_6H_6Cl_6$		Insecticide	2009
Mecoprop	MCPP	Mecoprop	$C_{10}H_{11}ClO_3$		Herbicide	N.A.
Mirex		Mirex	$C_{10}Cl_{12}$		Insecticide	1976

Perfluorooctane sulfonic acid	PFOS	Perfluorooctane sulfonic acid	$C_8HF_{17}O_3S$		Fluorosurfactant	2009
Polychlorinated biphenyl	PCB	45, 84, 88, 91, 95, 131, 132, 135, 136, 139, 144, 149, 171, 174, 175, 176, 183, 196, 197	$C_{12}H_nCl_{(10-n)}$		Dielectric, Coolant fluids	1978

[a] Banned time in U.S.

[b] N.A., not applicable.

Table 2. Enantioselective transformation of chiral organohalides in microcosms.

Organohalides	Matrices	Intermediates /Products	Enantioselectivity[a]	Redox condition	References
o,p'-DDT	Sediment	N.I.[b]	(-)[c]	Aerobic	[43]
	Soil with sludge	N.I.	(-)	Aerobic	[106]
α-HCH	Sediment	*β*-PCCH	(+)	Aerobic	[107]
	Surface water	N.I.	(+)	Aerobic	[78]
	Surface water	N.I.	(+)	Aerobic	[34]
	Sea water	*β*-PCCH	(+)	Aerobic	[84]
	Soil	N.I.	(+)	Aerobic	[108]
	Soil with sludge	N.I.	(+)/(-) R[d]	Aerobic	[106]
t-CHL	Soil with sludge	N.I.	(+)	Aerobic	[106]
	Soil	N.I.	(+)	Aerobic	[36]
c-CHL	Soil	N.I.	(-)	Aerobic	[36]
	Soil with sludge	N.I.	(-)	Aerobic	[106]
DCPP	Groundwater	N.I.	(+)/(-) R	Aerobic	[89]
	Soil	N.I.	(-)/pasture sample (+)/(-)/forest sample	Aerobic	[90]
	Sewage Sludge	N.I.	(-)	Aerobic	[109]
	Sediment	N.I.	(+)	Aerobic	[110]
	Sediment	N.I.	(-)	Aerobic	[111]
o,p'-DDT	Sediment	*o,p'*-DDD	(+)/(-) R	Anaerobic	[112]
α-HCH	Sewage Sludge	*β*-PCCH	(+)	Anaerobic	[113]
	Soil	N.I.	(+)	Anaerobic	[36]
PCB91	Sediment	PCB51	(+)	Anaerobic	[95]
PCB95	Sediment	PCB53	(-)	Anaerobic	
PCB132	Sediment	PCB91	(+)/(-) R	Anaerobic	
PCB149	Sediment	PCB95	(+)/(-) R	Anaerobic	

[a] Enantioselectivity represents the enantioselective attenuation.

[b] N.I., not yet identified.

[c] Only (-)-enantiomer was attenuated.

[d] R, enantioselective attenuation without enantioselectivity.

Table 3. Isolated bacteria and their functional enzymes for enantioselective transformation.

Organohalides	Microorganisms	Functional enzyme	Enantioselectivity[a]	Redox condition	References
DCPP	*Sphingomonas herbicidovorans* MH	SdpA	(-)[b]	Aerobic	[121]
		RdpA	(+)	Aerobic	
	Delftia acidovorans MC1	SdpA	(-)	Aerobic	[122]
		RdpA	(+)	Aerobic	
	Ralstonia eutropha JMP134	TfdA	(-)	Aerobic	[123]
	Burkholderia cepacia RASC	TfdA	(-)	Aerobic	
	Alcaligenes denitrificans EST 4002	TfdA	(+)	Aerobic	
α-HCH	*Sphingobium indicum* B90A	LinA1	(+)	Aerobic	[124]
		LinA2	(-)	Aerobic	
	Sphingobium indicum UT26	LinA2	(-)	Aerobic	[125]
	Clostridium pasteurianum DSM 525	N.I.[c]	(+)/(-) R[d]	Anaerobic	[126]
PCB45, PCB88, PCB91, PCB95, PCB136, PCB144, PCB149	*Jonibacter* sp. MS3-02	N.I.	(+)/(-) R	Aerobic	[127]
PCB45 PCB84 PCB91 PCB95	*Ralstonia eutrophus* H850	N.I.	E2-PCB45[e] (-)-PCB84 (-)-PCB91 (+)-PCB95	Aerobic	[128]
	Burkholderia cepacia LB400	BphA	E2-PCB45 (-)-PCB84 (-)-PCB91 (+)-PCB95	Aerobic	
	Rhodococcus globerulus P6	BphA	E2-PCB45 (+)/(-)-PCB84 R (+)/(-)-PCB91 R (+)-PCB95	Aerobic	
	Rhodococcus sp. ACS	N.I.	(+)/(-) R	Aerobic	
	Arthrobacter sp. B1B	N.I.	(+)/(-) R	Aerobic	
PCB132, PCB149, PCB174, PCB176, PCB183	*Dehalococcoides mccartyi* CG1	PcbA1	(+)/**(-)**-PCBs[f]	Anaerobic	[45]

[a] Enantioselectivity represents the enantioselective attenuation.

[b] Only (-)-enantiomer was attenuated.

[c] N.I., not yet identified.

[d] R, enantioselective attenuation without enantioselectivity.

[e] Elution orders of (+)- and (-)-enantiomers haven't been identified, E1 stand for first elution enantiomer, E2 stand for second elution enantiomer.

[f] Both enantiomers can be dechlorinated, whereas (-)-enantiomer was preferential dechlorinated.