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Enrichment and physiological responses of dechlorane plus on juvenile marine macroalgae (*Ulva pertusa*)

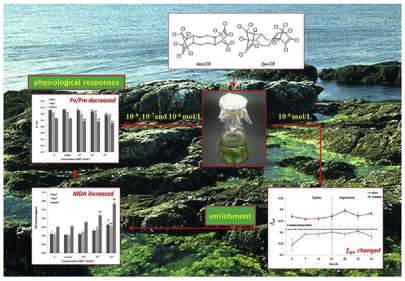
Ning Gong [a, b, *], Kuishuang Shao [c], Xu Han [a, b], Yukun Zhang [a, b], Yeqing Sun [a, b, **]

[a] Institute of Environmental Systems Biology, Dalian Maritime University, Dalian 116026, China
[b] College of Environmental Science and Engineering, Dalian Maritime University, Dalian 116026, China
[c] National Marine Environmental Monitoring Center, Dalian 116023, China

HIGHLIGHTS

- Marine macroalgae accumulated DP during the 21 d uptake and 21 d depuration.
- *Anti*-DP dominated in the juvenile macroalgae.
- DP exposure altered algal photosynthetic efficiency.
- The decrease of F_v/F_m may ascribe to the oxidative damage caused by DP exposure.

GRAPHICAL ABSTRACT



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ABSTRACT

Dechlorane Plus (DP), a chlorinated flame retardant, is increasingly reported in aquatic ecosystems worldwide. But little information is available regarding the toxicity of DP in marine organisms, especially in macroalgae. The objective of this study was to investigate effects of DP exposure on photosynthesis, oxidative stress and its enrichment in juvenile marine macroalgae (*Ulva pertusa*). Following 21- day uptake and 21- day depuration (10^{-8} mol/L), algae accumulated 1.18 times of DP compared to the initial concentration. Anti-DP was prone to accumulate in juvenile macroalgae. The enrichment of DP affected the physiological responses in algae. After 1, 7 and 14 days DP exposure (10^{-8}, 10^{-7} and 10^{-6} mol/L), antioxidant enzymes (SOD and CAT) activities and MDA content changed in a dose and time depended manner. Chlorophyll fluorescence parameters, including F_v/F_m, Φ_{PSII} and ETR decreased with the increasing DP concentration. It indicated that DP leads to a low rate of light energy utilization in algae which may ascribe to the oxidative damage induced by DP enrichment. Present study provides insight into the toxicological effects of DP on marine macroalgae, which is useful for risk assessment of DP in intertidal zone ecosystems.

Dechlorane Plus (DP) is a highly chlorinated compound that has been manufactured since the 1960s as a replacement to Dechlorane (Mirex) (Fang et al., 2014). Commercial DP mixtures contain two stereriosmers (*syn*- and *anti*-DP) in a ratio of approximately 1: 3 (Xian et al., 2011). Nowadays, it is mainly used as additive flame retardant in electrical wire and cable coating, computer connectors and plastic roofing materials and its estimated global annual

* Corresponding author. Institute of Environmental Systems Biology, Dalian Maritime University, Dalian 116026, China.
** Corresponding author. Institute of Environmental Systems Biology, Dalian Maritime University, Dalian 116026, China.
E-mail addresses: cospar06@dlmu.edu.cn (N. Gong), yqsun@dlmu.edu.cn (Y. Sun).

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production volume is 5000 tons (Hoh et al., 2006). Usages of DP are expected increasing because of the bans of some brominated flame retardants in the European Union, such as Octa-, Deca and Penta-bromodiphenyl ether (BDE) technical mixtures (Muñoz-Arnanz et al., 2011). Therefore, it is necessary to understand the potential effects of DP to wild organisms.

Due to its high hydrophobicity (log *KOW* is 9.3) (Xian et al., 2011), DP exhibits long half-life in the environment. After its first detection in the Great Lakes region, USA in 2006 (Hoh et al., 2006), DP has been reported as ubiquitous xenobiotics in different environmental media. In a very recent study, an increasing trend of DP level has been revealed from the mid-1950s to present sediment core samples collected across the Southern Yellow Sea, China (Wang et al., 2017). Although DP concentrations are usually low in surface water (up to 1.4 and 1.8 ng/L (Xiang et al., 2014)) or surface sediments (64.4 pg/g dw (Sun et al., 2016)) from China Sea, high levels of DP have been detected in tissues of aquatic species. For instance, the DP concentrations reached to 9630 ng/g lw in water snake and mud carp from an electronic waste recycling workshop of South China (Wu et al., 2010). Also, the levels of DP in marine organisms including green macroalgae (4.84 ng/g ww) (Gong et al., 2013) and marine bivalves, such as *Crassostrea gigas* (4.1 ng/g ww) (Jia et al., 2011), *Meretrix meretrix* and *Ruditapes pholippnarum* (13–37 ng/g lw) (Sun et al., 2015) were reported, which indicated the potential risks of DP on marine biota.

Furthermore, the isomer-selective accumulation has been observed in wild life and aquatic food web (Xian et al., 2011; Sverko et al., 2011; Zhao et al., 2014). f_{anti} values (fraction of anti-DP to total DP) were reported to decrease in species occupying higher trophic levels. But there are some contradictory results on the bioaccumulation pattern even in the same species (Xian et al., 2011). Laboratory tests showed that stereoselective enrichment occurred under high DP exposed concentrations but not for lower DP in rats and quails (Li et al., 2013a, 2013b). In our previous studies, however, it is showed that anti-DP tended to accumulate in both field and laboratory samples in adult marinealga (Zhao et al., 2014; Gong et al., 2017). Whether there is the same tendency of DP isomer accumulation in juvenile marinealga is unknown.

The basic toxicities of DP are provided by OxyChem Company and High Production Volume Information System (HPVIS) of the US EPA (OxyChem, U.S. EPA). The toxicity data of DP from peer review papers on rodent and chicken showed little acute toxicity on tested organisms (Brock et al., 2010; Crump et al., 2011). But it was found that an oral exposure to DP could induce oxidative damage and perturbations of signal transduction in mouse livers (Wu et al., 2012) and earthworms *Eisenia fetida* (Zhang et al., 2014). Recent studies also indicated that DP is genotoxic to luminous bacteria (Dou et al., 2015), earthworms (Yang et al., 2016) and Mediterranean mussels (Barón et al., 2016). These studies indicate that although DP had no obvious acute toxicity, its subchronic toxicities deserved attention. Since the available data on toxicity of DP in marine organisms is still limited, it is urgent to fulfill these knowledge gaps.

Marine macroalgae could be important ecotoxicological models, as they constitute the main source biomass production and thus support the structure and function of the coastal marine ecosystem. In this way, adverse effects of many kinds of environmental factors on macroalgae may have a potential impact on not only themselves but also other levels of organisms. *Ulva pertusa* is a ubiquitous green alga distributed from northern Yellow Sea to the Southern China Sea. It has been used as a source of food, feed and medicine in Asian for several centuries. Besides, it is well-known to respond to a wide array of contaminants, e.g., the industrial effluents from a textile and leather products manufacturing complex (Yoo et al., 2013). The adverse effects of copper on the growth, chlorophyll concentrations, photosynthesis activity, antioxidant capacity and nitrate reductase activity in *U. pertusa* were also observed (Han et al., 2008). In our previous study, it was found that DP impaired growth and reproductivity in adult *U. pertusa* (Zhao et al., 2014; Gong et al., 2017). But whether subchronic levels of DP induce the physiological responses in juvenile macroalgae is unclear.

Therefore, the objective of the present study was to evaluate DP accumulation pattern in juvenile *U. pertusa* as well as its physiological responses to DP exposure. 10^{-8} mol/L DP was used for 21 d uptake and 10^{-8}–10^{-6} mol/L DP were used for the 14 d subchronic exposure. Concentrations chosen here were close to the DP environmental occurrence and did not induce the obvious morphological damage or death in macroalgae according to our previous study. To assess the effect of DP on photosynthesis in macroalga, we monitored the changes of several chlorophyll fluorescence parameters. The activities of antioxidative enzymes, including catalase (CAT) and superoxide dismutase (SOD), as well as the maleic dialdehyde (MDA) content were also measured to understand the toxicological mechanisms of DP in macroalgae.

1. Materials and methods

1.1. Chemicals and reagents

DP was obtained from Anpon Electrochemical Co., Ltd. (purity > 99%; Jiangsu, China). Standards for individual *syn*- and *anti*-DP were purchased from Wellington Laboratories (Guelph, Ontario, Canada). Polychlorinated biphenyls 155 (CB-155) and octachloronaphthalene (OCN) purchased from Accustandard Inc. (New Haven, CT) were used as the surrogate and internal standards for DP measurement. Silica gel (100–200 mesh) was purchased from Merck (Merck, Germany). All reagents (dichloromethane, hexane, isooctane and methanol) used in these experiments were of analytical grade. Due to the low solubility of DP in water, acetone (purity > 99.8%) was chosen as solvent carrier. The DP stock in acetone was 10^{-3} mol/L (653.72 mg/L).

1.2. The collection of adult U. pertusa

The adult *U. pertusa* samples were collected from rocky intertidal zone of Heishijiao, Dalian, China (121.56N, 38.87E). The individual specimens were immediately transported to the laboratory. Algae were washed with filtered seawater and the detritus were removed carefully with a soft brush. And then algae were rinsed in the filtered seawater containing 1% KI–I_2 for 5 min twice. The cleaned algae acclimatized in a tank with 10 L of filtered seawater, where they were maintained at 15 ± 1 °C, 20 μmol/m^2 s with a photoperiod of 12 h of light/12 h of darkness (12:12 h L:D) for 3 days.

1.3. The formation of reproductive cells in U. pertusa

The healthy adult *U. pertusa* were selected and cut into fragments of 1–5 mm length by razor blade. The fragments were incubated in Petri dishes with filtered seawater containing PES culture medium at 25 ± 1 °C, 40 μmol/m^2 s and 14:10 h L: D. After 3-5 d, the vegetative cells from margin to center of the fragments gradually transform into the gametocytes, where the motile zoospores released and adhered to the bottom of the dishes soon. The fragments were removed once most of the cells in fragments formed into reproductive cells.

1.4. The growth of juvenile U. pertusa

After adhering, the spores of *U. pertusa* germinated and divided into uniseriate filaments. Subsequently these filaments were detached from dishes and transferred into flasks of 1 L with aerated