



Advance in the toxic effects of petroleum water accommodated fraction on marine plankton

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ABSTRACT

Recently, the impact of petroleum pollution on marine plankton has been complemented by a great concern. This review summarizes the reports about toxic effects of oil water accommodated fraction (WAF) on marine phytoplankton, zooplankton and early life stage of animal. For the oil WAF, toxicants are mainly composed of the aromatic hydrocarbons, such as the benzene hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) with 2–5 rings. The oil WAF, especially the PAHs, can be accumulated in plankton due to their great lipophilic abilities, and thus elicits various deleterious effects. Toxicological tests show that marine plankton is very sensitive to the petroleum WAF, as the order of median effective/lethal concentration is merely $\mu\text{g/L}$ or mg/L . There are species and developmental stages differences of plankton tolerance to petroleum WAF, and the toxicity of different oil WAF is various. Generally, its toxicity enhances with increasing carbonic chain length and benzene ring number. Many studies on the acute and sub-acute toxic effects of oil WAF have been done, however few researches on its chronic toxic effects has been carried out till now. Besides, most reports focused on the levels from molecule to individual, though very little work of petroleum toxic effects has ever been performed on the marine plankton population or community levels. Therefore, it is necessary to continue these studies in future.

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1. Introduction

With the rapid economic development and energy demand, petroleum import amount is growing dramatically in China. Marine petroleum transportation and harbor throughput increase year after year, causing the frequency oil spill accident. Besides, oil pollution discharge from ship and crude oil exploration gradually increase. So the risks of marine oil pollution become more and more serious [1]. The import amount of crude oil was about 200 million in China in 2008 according to the statistics, above 90% of which was transported by sea. The realization of China's Petroleum Strategy Reservation Plan and the increase of crude oil demand in future will accelerate the oil transportation amount by sea. Therefore, the risks of marine oil pollution will continuously climbing in China, and the problem of marine ecological safety can not be optimistic. China marine environmental quality communiqué in 2008 [2] showed that oil still was the one of three main pollutant (the other two were nitrogen and phosphorus) in coastal areas, especially in some important half blocked bay with less water exchange. This ecological risk due to the long term accumulation of oil pollution is severe and can not be ignored [3].

Marine phytoplankton, as the most important primary productivity, can offer food to zooplankton and larvae and juvenile fish [4]. Zooplankton can influence or control the primary productivity by top-down effects [5] in return, and its population dynamic change can influence the biomass of other marine animals like fish by bottom-up effects [6]. Once the community of plankton changed by the effects of oil pollution, the structure, stability and function of marine ecological system can be changed as well [7]. It is necessary and crucial to study the impact of oil pollution to marine plankton in view of the serious oil pollution of coastal areas in China and the ecological system function and status of marine plankton. Current researches focus on the impact of crude oil water accommodated fraction (WAF) to marine phytoplankton [8–11], zooplankton [12,13], and animals in early life stages [14,15]. This paper summarized the research results about the influence of oil WAF on marine plankton both at home and abroad, and prospected the study points in future, to further promote the quantified evaluation of the damage by oil pollution to marine ecology.

2. The composition and main toxic substances of marine petroleum WAF

Petroleum (crude oil) is a complex mixture that consisted of hydrocarbon (including alkanes, cycloalkanes and aromatic hydrocarbons) and non-hydrocarbon (including resin and asphalt). A

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series process of physics, chemistry and biology diversifications happen after crude oil entering the ocean, including spread, evaporation, dissolution, emulsification, disperse, absorption, sedimentation, biological decomposition and photo-oxidation [16]. These oil substances will be partially physically transferred and biologically decomposed, and the rest will dissolve in the seawater. Different kinds of crude and refined oil have different compositions, water solubilities (generally $\leq 200 \times 10^{-6}$ mg/L [17]), and WAF components. However, WAF is mainly constitute of BTEX (the general term of benzene, toluene, ethylbenzene and xylene), alkylation of benzene homologues, polycyclic aromatic hydrocarbons (PAHs), petroleum hydrocarbon and some unresolved complex mixtures (UCMs) through chromatogram [18]. The mainly toxic substances are some aromatic hydrocarbons, such as BTEX and PAHs. The PAHs in WAF are mostly 2–5 rings [18] and the PAHs with ± 6 rings are little, because the rest PAHs with more rings can not dissolve in water for their highly lipophilic ability (high log K_{ow} value). Heterocyclic compounds of N, P, S in petroleum also has contribution on the toxicity, such as thiophene and its alkylated homologues, quinoline, acridine and other components with high water solubility and toxicity [19]. And these heterocyclic compounds can be gradually accumulated in the process of oil weathering [20]. But, generally speaking, the heterocyclic compounds are much less than BTEX and PAHs in oil [21], so they are relatively lowly toxic in the total toxicity. The resin and asphalt are hard for the living organism absorption, due to their high molecular weight (700–1000 of resin and 1000–10,000 of asphalt [22]). So they are also less toxic to marine plankton. The PHAs with >2 rings mainly have chronic toxic effects to the environmental damage and organism hurt [23,24], for they are difficultly decomposed [25]. The BTEX and the naphthalene with 2 rings and its homologues have acute toxic effects, due to their high concentration and water solubility and easily volatile that cannot stay long in the water [25].

3. The toxic effects of oil WAF to marine phytoplankton

Different kinds of oil WAF have different toxicity to phytoplankton, and generally, the longer the carbon chain is, the more benzene ring has, and the more toxic the oil is. The order of toxicity (Table 1) to phytoplankton usually is ortho xylenes > toluene [10], benzo(a)pyrene (5 rings) > pyrene and fluoranthene (4 rings) > anthracene and the phenanthrene (3 rings) > naphthalene (2 rings) > BTEX (1 ring) [10,26–29], heavy oil > light oil [30,31], aromatic hydrocarbons > alkanes [31]. Besides, different phytoplankton species has different tolerance to oil WAF toxicity, representing different median effective concentration (EC_{50}) of growth (Table 1). Phytoplankton community happen abnormal succession under the stress of oil pollution that the dominant degree of less tolerant species gradually decreases, even vanishes, while more tolerant species gradually become the dominant ones [8,9,31–33]. The field investigation after oil spill accident of “TASMAN SEA” tanker showed that diversity of phytoplankton community decreased around the pollution area, and species number and cell density reduced to 1/2 of pre-accident, especially diatom, the dominant species in population, its species number climbed down from 40 to 18. Contrarily, the species number of dinoflagellates did not change [1].

Both laboratory researches and field investigations showed that low concentration of WAF in seawater had less influence on phytoplankton, even could promote its growth [9,34,35]. The stimulative effects were related to the bacteria in water and algae itself [34,35]. The bacteria would decompose the oil WAF to the algae utilized carbon. And some species of phytoplankton, such as *Chlamydomonas*, *Chlorella*, *Navicula*, *Nitzschia* and *Cyclotella*, could decompose WAF by themselves and realize the biological transformation [29,36,37], consequently achieve the biological restoration of oil pollution area. But if the oil concentration was too high, it could restrain the algae growth [11,38,39]. Therefore, it is

Table 1

EC_{50} of growth inhibition for different phytoplankton species under different toxicants exposure.

Species	Toxicant	72 h- EC_{50} ^a	Reference
<i>Pheodactylum tricornutum</i>	Phenanthrene	154 ± 3.1 µg/L	[26]
	Anthracene	123 ± 5.5 µg/L	
	Fluoranthene	103 ± 9.1 µg/L	
	Pyrene	119 ± 1.2 µg/L	
<i>Skeletonema costatum</i>	Phenanthrene	47 ± 5.5 µg/L	[27]
	Anthracene	39 ± 2.4 µg/L	
	Fluoranthene	18 ± 2.9 µg/L	
	Pyrene	24 ± 2.0 µg/L	
<i>Thalassiosira pseudonana</i>	Fluoranthene	1031 µg/L	[28]
	Pyrene	260.3 µg/L	
	Benzo(a)pyrene	55.24 µg/L	
<i>Cyclotella caspia</i>	Fluoranthene	0.20 mg/L ^a	[29]
<i>Chlorella uvlgaris</i>	0 [#] Fuel oil WAF	12.11 mg/L	[30]
	0 [#] Marine fuel oil WAF	12.22 mg/L	
	Heavy fuel oil WAF	18.73 mg/L	
<i>Tetraselmis chuii</i>	BTEX	62.91% WAF ^a	[31]
	Mixture of aromatics with C ₉ –C ₁₁	28.59% WAF ^a	
	Raw naphtha	27.84% WAF ^a	
	Light naphtha	28.59% WAF ^a	
	Heavy naphtha	4.91% WAF ^a	
	Mixture of aromatic hydrocarbons of C ₉	4.79% WAF ^a	
	Mixture of C ₆ –C ₈ hydrocarbons, paraffin and isoparaffin	19.92% WAF ^a	
<i>Zooxanthella croadriz tica</i> , <i>P. tricornutum</i> , <i>Nitzschia closterium minutissima</i> , <i>S. costatum</i> , <i>C. uvlgaris</i> , <i>Platymonas subcordiformis</i>	Toluene	34.10–114.00 mg/L	[10]
	Naphthalene	3.90–7.30 mg/L	
	Ortho xylenes	1.69–3.03 mg/L	
	Phenanthrene	0.60–1.92 mg/L	

^a Exposure duration for 24 h.

[#] Unmarked letter indicated 72 h- EC_{50} .

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