

Characterization of *N*-alkanes and Polycyclic Aromatic Hydrocarbons in Water Solution of 180[#] Fuel Oil dealt with and without Dispersants

T. Pan, G.H. Ding^{*}, C. Li, L.L. Lian, N.N. Zhang
Dalian Maritime University, Dalian, China

Y.Y. Wei, J. Zhang^{*}
Dalian University, Dalian, China

ABSTRACT: In order to analyze the concentration changes of *n*-alkanes and PAHs in water solution of oil treated with and without dispersant, 180[#] fuel oil was tested with two kinds of dispersants. It was shown that addition of dispersants caused a marked increase in the concentrations of *n*-alkanes and PAHs in chemically enhanced water-accommodated fractions (CEWAFs) of oil compared to the untreated water-accommodated fractions (WAFs). The times of increase of concentrations were related with the type of dispersant, the dispersed oil, and the ratio of dispersant to oil. As more PAHs were dissolved in CEWAFs, the ecological risk of dispersed oil in water column should be highly concerned.

KEYWORD: *n*-alkane; Polycyclic aromatic hydrocarbons; 180[#] fuel oil; Dispersant

1 INTRODUCTION

Oil spills occur during exploitation, transportation and storage of oil. One primary source of accidental oil input into seas is associated with heavier fuel oil used by large ships. Marine oil spills may result in oil pollution over large areas and present serious environmental hazards, both on marine ecosystems and economic resources such as fisheries, aquaculture, and tourism. Following a spill of oil onto the sea surface, oil slick will form and some of the oil in the resultant slick may disperse naturally into the water column.

In order to respond to oil spill, dispersants will always be used. Dispersants are designed to enhance natural dispersion by reducing the surface tension at the oil/water interface. They may rapidly disperse large amounts of certain oil types from the sea surface by transferring it into the water column. They will cause the oil slick to break up and form water-soluble micelles that are rapidly diluted. The oil is then effectively spread throughout a larger volume of water than the surface from where the oil was dispersed.

However, laboratory experiments showed that dispersants increased toxic hydrocarbon levels in water-accommodated fraction and may cause serious adverse effects on marine organisms (Ramachandran et al., 2004; Anderson et al., 2009; Hook & Osborn, 2012). Anderson et al. (2009) reported that treatment with the dispersant COREXIT 9500 resulted in greater hydrocarbon concentrations in chemically

enhanced water-accommodated fractions (CEWAFs) of oil, relative to the untreated water-accommodated fractions (WAFs). Topsmelt (*Atherinops affinis*) embryo development and survival to hatching were significantly inhibited in CEWAF, while minimal effects on embryo-larval survival were observed in WAF. Increased hydrocarbon concentrations in the CEWAF also caused cardiovascular and other abnormalities in developing topsmelt embryos.

Increase toxicity of dispersed oil should be related with the content changes of hydrocarbon. Therefore, characterizing the content changes of hydrocarbon is very important. However, there are many kinds of dispersants used for oil spill response, and a few studies have characterized the content changes of hydrocarbon after the use of dispersants in detail (Ramachandran et al., 2004; Couillard et al., 2005; Lee et al., 2013). Therefore, in the present study, the content changes of typical hydrocarbons, *n*-alkanes and polycyclic aromatic hydrocarbons (PAHs), in water solution of 180[#] fuel oil dealt with and without two different dispersants were investigated, which may be useful for ecological risk assessment of these dispersants.

2 MATERIALS AND METHODS

2.1 Test chemicals

The 180[#] fuel oil was purchased from China Marine Bunker (Petro China) Co., Ltd. with NO.

GX381374. Two kinds of dispersants, Bailing 919 and GM2, were used in the present study.

Calibration standards used for the determination of *n*-alkanes from C8 to C40 and 23 PAH standards were purchased from Accustandard, Inc., USA. Twenty three PAHs were naphthalene, acenaphthylene, acenaphthene, fluorene, 1-methylfluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(*a*)anthracene, chrysene, benzo(*k*)fluoranthene, benzo(*b*)fluoranthene, benzo(*a*)pyrene, dibenzofuran, dibenzothiophene, 2-methylphenanthrene, 1-methylphenanthrene, 3,6-dimethylphenanthrene, retene, 1-methylpyrene, dibenz(*a,h*)anthracene, dibenzo(*a,h*)pyrene. Internal standards, *n*-tetracosane-d50, naphthalene-d8, acenaphthene-d10, chrysene-d12, 4-terphenyl-d14, phenanthrene-d10, perylene-d10, 1,4-dichlorobenzene-d4 were also purchased from Accustandard, Inc. Distilled chromatographic solvents were used without further purification, which were purchased from J&K Scientific Ltd.

2.2 Preparing the WAFs and CEWAFs

WAF and CEWAFs were prepared by following standardized methods of Singer et al. (2000) and Barron & Ka'ahue (2003). WAFs were created by layering a known mass of 180[#] fuel oil onto a standard volume (1750mL) of 0.45 μ m filtered natural seawater (30psu; fully aerated) in a 2-L glass bottle (resulting in a standardized 22-23% headspace, by volume) with an oil loading 25 g/L, and mixing this with magnetic stirrers at a rate sufficient to create a vortex 20-25% of water depth to provide sufficient mixing energy for dispersion. The bottle was covered with a cap, sealed and wrapped with aluminum foil during the mixing. The mixture was stirred for 18 h and allowed to settle for 6 h for the separation of the water and oil phases.

For preparation of CEWAFs, the dispersants, Bailing 919 or GM2 were added to the surface of the seawater and the oil-water mixture at a ratio of 1:5 dispersant: oil, respectively. CEWAF were prepared in much the same way as WAFs. The aqueous layer was drained off and transferred into a clean amber glass bottle and then stored at 4 °C for analyses.

2.3 Extraction

WAF or CEWAF samples (100mL) were shaken and extracted twice with 10mL of hexane. The organic extracts were combined and made up to final volume of 25mL. The organic extracts were rotary-evaporated to ~1mL. Then the concentrated extracts was loaded on preconditioned 3-g silica gel

fractionation columns. Saturated and aromatic hydrocarbons were eluted with hexane (12mL) and 50% dichloromethane (DCM) in hexane (v/v, 15mL). The fractions were concentrated to appropriate volumes, spiked with internal standards and then adjusted to an accurate pre-injection volume of 1.00mL for further instrumental analysis. The hexane fraction was analyzed for *n*-alkanes compounds. The DCM fraction was analyzed for unsubstituted PAHs and alkyl homologous PAHs.

2.4 Analyses of *n*-alkanes

Analyses for *n*-alkanes were performed on an Agilent 6890 gas chromatograph equipped with a flame-ionization detector (GC-FID). The DB-5 MS Ultra capillary column (30m \times 0.25mm i.d., 0.25 μ m film thickness) were used for GC-FID and GC-MS analyses. The oven temperature was programmed to start initially at 50 °C (2min), increased to 300 °C at 6 °C/min, and held for 16 min. Injector temperature was set at 290 °C and detector temperature at 300 °C. GC-FID analysis provided a baseline resolution of *n*-alkanes from *n*-C8 to *n*-C40. Quantization of the analytes was based on the internal standard compound (*n*-tetracosane-d50).

2.5 Analyses of PAHs

An Agilent 6890/5975 GC/MS instrument was used for analyses of unsubstituted PAHs and alkyl homologous PAHs. The GC column was held at 50 °C for 2 min, ramped to 150 °C at 8 °C/min, hold 3 min at 150 °C, increased to 300 °C at 3 °C/min, and held for 15 min. The MS was scanned over *m/z* 35–550, with a 150-threshold count and 3 min solvent delay. The quadrupole was held at 150 °C with the ion source at 230 °C. Quantification and identification of target PAHs was performed on a GC/MS in both the scan mode and the selected ion monitoring (SIM) mode with specific ions and retention windows applied for each compound. Quantization of the analytes was based on the internal standard compound (4-terphenyl-d14).

2.6 Quality assurance/quality control

Matrix spikes, laboratory sample duplicates, and laboratory blanks were processed with each batch of samples as part of the laboratory internal quality control. All the quality control procedures satisfied their acceptable ranges. The recoveries of *n*-alkanes (C8-C40) were from 80.59% to 114.24%, and the recoveries of PAHs were in the range of 53.34%-98.43%.

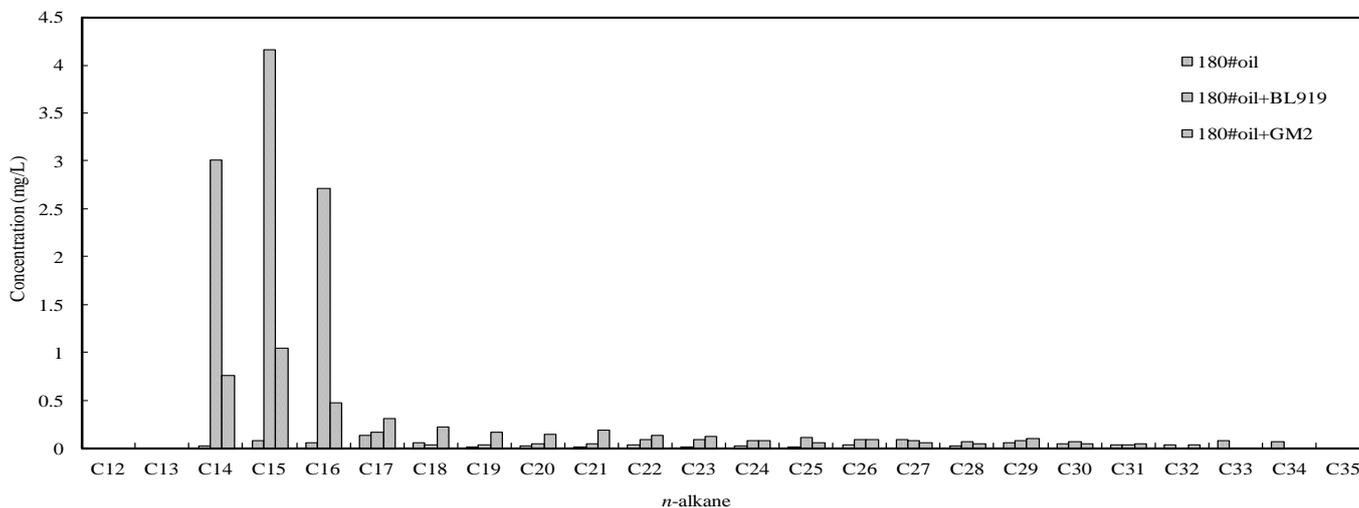


Figure 1. The content changes of target *n*-alkanes in WAF and CEWAFs

3 RESULTS AND DISCUSSION

3.1 The content changes of *n*-alkanes with dispersants

The content changes of *n*-alkanes in WAF and CEWAFs were shown in Figure 1. The total concentration of *n*-alkanes in WAF was measured to be 0.827 mg/L. The total concentration of *n*-alkanes in CEWAFs treated by dispersants BL919 or GM2 were 10.914 and 4.021 mg/L, respectively. It indicated that dispersants can effectively enhance the dissolution of *n*-alkanes in water phase, and BL919 caused more *n*-alkanes dissolved in water phase than GM2 dispersant.

For individual *n*-alkane in WAF, the concentrations of them were in the range of not detected (n.d.) to 0.123 mg/L, with the maximum value of C17. The primary *n*-alkanes in WAF were C15-C18, which might be related with higher volatility of shorter *n*-alkanes and lower solubilities of longer *n*-alkanes.

After BL919 dispersant was used, the concentrations of C14-C16 *n*-alkanes markedly increased, which changed to be the primary fractions of *n*-alkanes in CEWAF. The concentration of *n*-tetradecane increased from 0.0158 to 3.008 mg/L,

with an increment about 200-fold. As for GM2, the concentrations of C14-C27 *n*-alkanes raised at different degree, with C14-C16 also to be the primary fractions of *n*-alkanes in CEWAF. It was detected that *n*-pentadecane raised from 0.077 to 1.042 mg/L, to be the maximal concentration of *n*-alkane in CEWAF of GM2. Comparing the CEWAFs of two dispersants, BL919 made more *n*-alkanes dissolved in CEWAF than GM2.

3.2 The content changes of PAHs with dispersants

The content changes of PAHs in WAF and CEWAFs were shown in Figure 2. The total concentration of PAHs in WAF was measured to be 71.735 μ g/L. The lower molecular weight of PAHs, such as naphthalene and acenaphthene, were the primary fractions of PAHs in WAF. For the individual PAH in WAF, the highest concentration was measured to be 15.11 μ g/L for naphthalene, which was in agreement with the results of Gardiner et al. (2013).

The total concentrations of PAHs were 517.49 μ g/L, a 7.2-fold increase in CEWAF of BL919 compared to WAF. The addition of BL919 dispersant caused a great increase in the concentrations of four target PAHs,

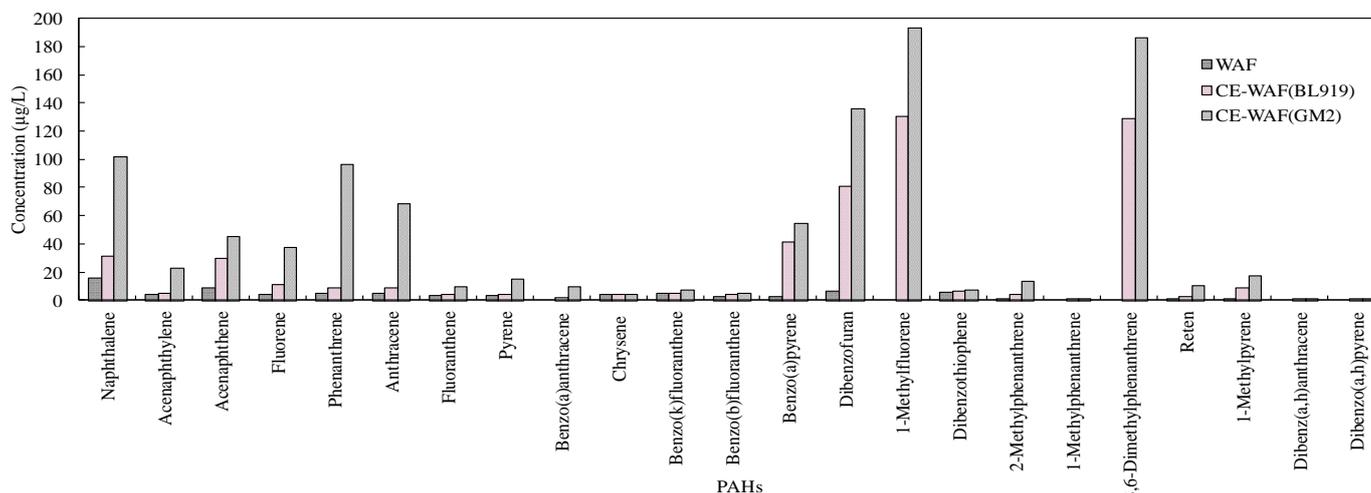


Figure 2 The content changes of target PAHs in WAF and CEWAFs

1-methylfluorene, 3,6-dimethylphenanthrene, dibenzofuran and benzo(a)pyrene. These four PAHs (380.63 $\mu\text{g/L}$) became to be the primary PAHs of CEWAF of BL919, taking up 73.55% total PAHs detected. As for GM2, the concentrations of naphthalene, phenanthrene, anthracene, and fluorene also increased greatly beside the above four PAHs. Therefore, the total concentration of PAHs detected in CEWAFs of GM2 was 1043.88 $\mu\text{g/L}$, greater than that of BL919 (517.49 $\mu\text{g/L}$). The addition of GM2 dispersant caused a 14.6-fold increase in $\sum\text{PAH}$ concentrations in CEWAF compared to WAF. 1-methylfluorene, 3,6-dimethylphenanthrene and dibenzofuran were also the primary PAHs in CEWAF of GM2, taking up 54.58% total PAHs tested. Thus, the profile of PAHs in water phase changed markedly after dispersants were added.

Cohen et al. (2001) found a five-fold increase in total PAH concentrations in CEWAF compared to WAF using Corexit 9527 to disperse Bass Strait crude oil at a 1:30 ratio of dispersant to oil with a much higher oil loading (100 g/L). Couillard et al. (2005) reported that the addition of dispersant Corexit 9500 to weathered Mesa light crude oil with the rate of 1:30 (v/v) at an oil loading of 0.2 g/L caused a 1.6- and five-fold increase in the concentrations of total PAH and high-molecular-weight PAH with three or more benzene rings. In the present study, a higher ratio of dispersant to oil was used, and the higher increase of $\sum\text{PAH}$ concentrations in CEWAF compared to WAF was observed. Therefore, dispersant efficacy may vary as a function of the type of dispersant, of the composition of the dispersed oil, of the ratio of dispersant to oil, and of the energy used to mix the solution.

Compared with BL919, although GM2 render relatively less *n*-alkanes dissolved in CEWAFs, it increased more parent PAHs and alkyl PAHs. There are no data available for the toxicity of 1-methylfluorene, 3,6-dimethylphenanthrene and dibenzofuran. However, it was showed that benzo(a)pyrene, phenanthrene and anthracene were high toxic to aquatic organisms (Mu et al., 2012; Palanikumar et al., 2012). Therefore, the ecological risk of dispersed oil in water column was highly concerned as more PAHs were dissolved.

4 CONCLUSION

In the present study, 180[#] fuel oil was dispersed with two kinds of dispersants. It was shown that addition of dispersants caused a marked increase in the concentrations of *n*-alkanes and PAHs. The times of increase of concentrations were related with the type of dispersant, the dispersed oil, and the ratio of dispersant to oil. As more PAHs were dissolved in CEWAFs, the ecological risk of dispersed oil in water column should be highly concerned.

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REFERENCES

- [1] Anderson BS, Arenella-Parkerson D, Phillips BM, Tjeerdema RS, Crane D. 2009. Preliminary investigation of the effects of dispersed Prudhoe Bay Crude Oil on developing topsmelt embryos, *Atherinops affinis*. *Environ. Pollut.* 157(3): 1058-1061.
- [2] Barron, M.G., Ka'ahue, L., 2003. Critical evaluation of CROSERF test methods for oil dispersant toxicity testing under subarctic conditions. *Mar. Pollut. Bull.* 46, 1191-1199.
- [3] Cohen AM, Nugegoda D, Gagnon MM. 2001. Metabolic responses of fish following exposure to two different oil spill remediation techniques. *Ecotoxicol Environ Saf* 48:306-310.
- [4] Couillard CM1, Lee K, Légaré B, King TL. 2005. Effect of dispersant on the composition of the water-accommodated fraction of crude oil and its toxicity to larval marine fish. *Environ Toxicol Chem.* 24(6):1496-504.
- [5] Gardiner WW, Word JQ, Word JD, Perkins RA, McFarlin KM, Hester BW, Word LS, Ray CM. 2013. The acute toxicity of chemically and physically dispersed crude oil to key Arctic species under Arctic conditions during the open water season. *Environ Toxicol Chem.* 32(10): 2284-2300.
- [6] Hook SE., Osborn HL. 2012. Comparison of toxicity and transcriptomic profiles in a diatom exposed to oil, dispersants, dispersed oil. *Aquat. Toxicol.* 124-125: 139-151.
- [7] Lee KW, Shim WJ, Yim UH, Kang JH. 2013. Acute and chronic toxicity study of the water accommodated fraction (WAF), chemically enhanced WAF (CEWAF) of crude oil and dispersant in the rock pool copepod *Tigriopus japonicus*. *Chemosphere* (92): 1161-1168.
- [8] Mu JL, Wang XH, Jin F, Wang JY, Hong HS. 2012. The role of cytochrome P4501A activity inhibition in three- to five-ringed polycyclic aromatic hydrocarbons embryotoxicity of marine medaka (*Oryzias melastigma*). *Mar Pollut Bull.* 64(7):1445-1451.
- [9] Palanikumar L, Kumaraguru AK, Ramakritinan CM, Anand M. 2012. Biochemical response of anthracene and benzo[a]pyrene in milkfish *Chanos chanos*. *Ecotoxicol Environ Saf.* 75(1):187-197.
- [10] Ramachandran SD, Hodson PV, Khan CW, Lee K. 2004. Oil dispersant increases PAH uptake by fish exposed to crude oil. *Ecotoxicol. Environ. Saf.* 59: 300-308.
- [11] Singer, M.M., Aurand, D., Bragin, G.E., Clark, J.R., Coelho, G.M., Sowby, M.L., Tjeerdema, R.S., 2000. Standardization of the preparation and quantitation of water-accommodated fractions of petroleum for toxicity testing. *Mar. Pollut. Bull.* 40, 1007-1016.