ABSTRACT: Container ships have been widely recognized as an important emission source within maritime transport. Heavy fuel oil (HFO) and diesel oil (DO) are the two most commonly used fuels. This study reports the characteristics and toxicities of particulate matter (PM) emissions from HFO and DO combustion in a typical container ship. The PM number size distribution possesses a bimodal structure with peaks at ~20 nm and ~100 nm. The PM$_{2.5}$ emission factors (EFs) are 3.15 ± 0.39 and 0.92 ± 0.02 g/kg fuel for HFO and DO, respectively. The benzo[a]pyrene equivalent carcinogenic potency (BaP$_{eq}$) of 16 polycyclic aromatic hydrocarbons contained in HFO and DO PM$_{2.5}$ is approximately 0.81 ± 0.10 and 0.12 ± 0.04 mg/kg fuel, respectively. BaP$_{eq}$ concentration shows an increasing tendency with decreased PM size. The reactive oxygen species activity and cytotoxicity of HFO PM$_{2.5}$ samples are ~2.1 and ~2.5 times higher than those of DO PM$_{2.5}$ samples, respectively. These health risks are both significantly attributed to the BaP$_{eq}$ content in PM$_{2.5}$ with correlations of 0.86–0.92. Furthermore, the examined biological effects are much greater than those of atmospheric PM$_{2.5}$ collected in Shanghai. Our results imply that better fuel quality is important for improving air quality and reducing health risks.
be studied in the field to improve the understanding of such variables. Most maritime traffic involves the utilization of heavy fuel oil (HFO); this fuel can generate a high amount of fine and ultrafine PM, which contains organic carbon (OC), elemental carbon (EC), transition metals, and polycyclic aromatic hydrocarbons (PAHs). There are very limited field-based studies on the effect of oil quality on PM emissions. Epidemiology studies have reported that the chemical components of fine PM, including EC, OC, metals and PAHs, can induce biological effects, such as oxidative stress and cytotoxicity. Previous studies have commonly focused on using atmospheric and health risk models to determine PM concentrations and estimate the premature mortality of regional shipping-related health impacts, particularly in European regions or the western United States. However, no report has explained the relationship among fuel quality, chemical characteristics of PM, and toxicity effect. With the limited current knowledge, the mechanism and extent to which such exhausts affect human health have not been revealed. Hence, a detailed quantitative study of PM emissions and their toxicity effect would be highly significant.

Aiming at identifying the influence of fuel qualities on PM emission characteristics and their toxicity effects, this study systematically investigated the chemical compositions and toxicity effects of PM emitted from a typical marine diesel engine with typical operating conditions. One type of HFO and one type of DO, as two typical marine fuels, were comparatively operated in one typical container ship. The physical characteristics (including the PM number size distribution and morphology) and chemical characteristics of size-segmented PM samples were analyzed. Toxicity effects, including oxidative stress and cytotoxicity, were further evaluated in experiments and analyzed based on their correlation with chemical composition.

## MATERIALS AND METHODS

### Tested Container Ship and Campaign Route.

One bulk cargo ship, representative of modern container ships in China, was selected for the field study in the coastal area of Shanghai (see Figure S1). The length and width of the selected ship (a gross tonnage of ~1925, a capacity of ~182 TEUs) are 83.5 and 12.6 m, respectively. The main propulsion engine is a 4-stroke six-cylinder in-line medium-speed marine diesel engine (EA6300ZC, build: Ningbo Power and Machinery Group Co., Ltd.). The engine’s rated power is 735 kW, and its speed is 500 rpm. During the sampling period, the engine load was stable at operation at ~80% of maximum power, approximately 380 rpm.

The vessel carried goods along the Yangtze River channel from Daishan (30.14° N, 122.09° E) to Taicang (31.46° N, 121.13° E). The campaign route is illustrated in Figure S2. The vessel started on June 18th, 2017, in the Qugang Harbor in Daishan, crossed Hangzhou Bay, and finally arrived at Taicang, Jiangsu province, along the Yangtze River waterway. During the campaign, the same engine was tested with HFO and DO combustion in Hangzhou Bay and the Yangtze River, respectively. The fuel change took approximately 30 min when the ship entered the Yangtze River waterway. The viscosity was 19.30 mm²/s for HFO and 2.93 mm²/s for DO at 40°C. The carbon residue and content of ash and vanadium(V) were lower for DO than those for HFO, as described in Table 1.

### Field Sampling Method.

The sampling system is schematically shown in Figure S3. A flue gas analyzer (Testo 350, Germany) was employed to monitor gaseous pollutants, including CO, NO, NO₂, and SO₂. The flue gas analyzer was zeroed using standard air before sampling. The average EFs for these gaseous pollutants (i.e., CO, NO, NO₂, and SO₂) during HFO combustion were 11.90 ± 1.26, 5.159 ± 6.53, 1.93 ± 0.24, and 28.63 ± 4.23 g/kg fuel, respectively, while for DO combustion, the average EFs were 11.94 ± 1.08, 58.15 ± 2.70, 2.83 ± 0.19, and 14.19 ± 0.59 g/kg fuel, respectively. Volatile organic compounds (VOCs) were sampled via a polynvinyl fluoride film sampling bag (Tedlar, DuPont, USA) with a standard volume of 3.0 L. Samples were concentrated by a preconcentrator (Entech 7100, Entech Inc., USA), and then after examined by gas chromatography/mass spectrometry (6890GC-5973MS, Agilent, USA).

A flue gas sampler (Dekati model 4000, Finland) was employed as the online dilution system with a dilution ratio of 1:40. A scanning mobility particle sizer (SMPS, TSI 3082, USA) with a condensation particle counter (TSI 3775, USA) was employed to examine the PM size distributions in the range of 10–500 nm. SMPS were performed with consecutive runs in each operating condition more than 1 h. The total suspended PMs were sampled by a homemade particulate sampler, while the PM₁,₅ samples were collected on quartz fiber filters (QFFs, Whatman 1851-865, UK) using a PM₁,₅ cyclone (2000-30EH, URI Inc.). Additionally, samples on Teflon filters (Whatman 7592-104, UK) were collected for each fuel type for subsequent gravimetric, water-soluble ion and elemental analysis. Size-segregated PM samples ranging from 0.056 to 18 µm in aerodynamic diameter were collected by a micro-orifice uniform deposit impactor (MOUDI, Model 110, MSP Corp., USA) with a fixed flow rate of 30 L/min. The QFFs were preheated at 450°C for 6 h and put in clean plastic Petri dishes before sampling, while they were reserved at ~20°C refrigerator until analysis after sampling. Three successful samples in parallel were performed for each test.

### Estimation of Emission Factors.

The fuel-based EFs were determined by carbon balance, using the same formula as that used in previous studies. All carbon in fuels was converted to carbon-containing gaseous species (including CO₂, CO, and hydrocarbons) and carbonaceous PM during fuel combustion. CO₂ EF (EFCO₂/ g/kg fuel) was calculated via the following equation: $\Delta(\text{CO}_2) = \gamma \times (\Delta(\text{CO}_2)/\Delta(\text{CO}) + \Delta(\text{NO}) + \Delta(\text{PM}) + \Delta(\text{NO}_2))$, where $\gamma$ is the mass ratio of carbon in fuel (gC/kg fuel), while $\Delta(\text{CO}_2), \Delta(\text{CO}), \Delta(\text{NO})$, and $\Delta(\text{PM})$ are the changes in mass of CO₂, CO, NO, and PM, respectively.
concentrations. After incubation for 24 h, cell viability was assessed by a trazolium bromide assay. The optical emission intensity of 570 nm wavelength was detected via a microplate reader (H1Multimode, BioTek, Winooski, VT). The intracellular reactive oxygen species (ROS) generation was detected by dichlorofluorescein staining. The fluorescence intensity (488 and 525 nm) of the dichlorofluorescein was determined using the microplate reader. A more detailed description can be found in previous studies.44-46 The end point of cell viability was calculated by the IC50 value (the concentration causing 50% inhibition of cell viability).46 The results of oxidative stress were shown via the EC15 value (1.5-fold increase in ROS generation relative to control).46 Three successful analyses in parallel were performed for each test.

FIGURE 1. Number size distribution of PMs emitted from ship exhaust resulting from HFO and DO combustion.

RESULTS AND DISCUSSION

Bimodal Distribution of Submicron PMs. Ship-exhaust PM number and size distributions of HFO and DO combustion in the size range 10-500 nm are characterized in Figure 1. Surface and volume distribution of PM from ship

Figure 1. Number size distribution of PMs emitted from ship exhaust resulting from HFO and DO combustion.

Particle Emissions and Chemical Composition. The EFs of total suspended primary PM were 5.93 ± 0.48, 1.45 g/kg and 2.02 ± 0.01 g/kg fuel for HFO and DO combustion, respectively. The EFs of primary PMs obtained in this study were 3.15 ± 0.65 g/kg for HFO, whereas they were 0.92 ± 0.02 g/kg fuel for DO. The EFs of primary PMs obtained in this study are in agreement with that in the literature. The average EFs for n-alkanes resulting from HFO and DOC smog were 0.48 ± 0.08 and 0.16 ± 0.01 g/kg fuel,

ΔCtOC represents the concentrations of CO2, CO, PM, and VOCs, respectively, with the background concentrations subtracted (g/m³). Other gaseous species EFs were calculated via the equation EFX = EFCO2 × Δ(X)/Δ(CO2), where EFX is the fuel-based EF for species X, and Δ(X) represents the concentration of species X.

Transmission Electron Microscopy Analysis. Copper 230-mesh transmission electron microscopy (TEM) grids were fixed in the center of an impactor sampler to collect PMs in flue plume. The morphology of individual carcinogenic PMs was investigated by TEM. The microstructure and components of single carcinogenic PMs were analyzed by EDS and selected-area electron diffraction, as well as a field emission high-resolution TEM (FE-HRTEM, JEOL-2100F) equipped with an Oxford EDS, as detailed in a previous work.37

Analysis of Chemical Compositions. Each quartz filter sample was divided into quarters and analyzed for the following chemical compounds. Sixteen US EPA priority PAHs (see Table S1) were determined via using the Agilent 6890GC-5973MS. The details for extracting and analyzing the 16 PAHs were described in our previous study.38 BaP (benzo[a]pyrene) has been regarded as one of the most carcinogenic PAH species, and the toxic equivalent factors (TEFs) for individual PAH species relative to BaP were adopted from a previous study.39 The cancer risk of the 16 PAHs were described in our previous study.38 BaP (benzo[a]pyrene) has been regarded as one of the most carcinogenic PAH species, and the toxic equivalent factors (TEFs) for individual PAH species relative to BaP were adopted from a previous study.39 The cancer risk of the 16 PAHs was evaluated via BaP-equivalent carcinogenic potency (BaPeq) EFs. The BaPeq value is possibly a little bit higher than the actual value due to some of the gas phase PAHs possibly being adsorbed in the filters during sampling.27 An energy-dispersive X-ray fluorescence (XRF) spectrometry (NAS100, Nayur, China) was employed to analyze a variety of selected elemental compositions in the Teflon-filter PM2.5 samples. The elemental densities in the samples were directly analyzed after the filter was placed on the sample stage without any sample pretreatment; the details are described elsewhere.40 A total of 7 elements, including Si, S, Cl, K, Ca, V, and Fe, were effectively examined in this study and compared with the results obtained for blank filters.

Water-soluble ions were analyzed by examining the Teflon-filter samples via an ion chromatograph (940 Professional IC, Metrohm, Switzerland) equipped with a Metrosep A supp 16-250 separation column and a Metrosep C6 analytical column. The corresponding detection limits for major inorganic ions were within 0.47-3.33 ng/mL. Br-, PO43-, Li+, and K+ were below the detection limits. Blank levels are below MDL.

OC and EC fractions of PMs were analyzed by a thermal/optical carbon analyzer (Model 2015, Atmoslytic Inc., CA) according to the IMPROVE protocol. Four OC fractions and three EC fractions (EC1, EC2, and EC3 evolved at 580, 740, and 840 °C in a 98% He/2% O2 atmosphere, respectively) were produced. The MDL for OC determined by using the thermal/optical carbon analyzer was 0.18 ± 0.06 μg/cm², while it was 0.04 ± 0.01 μg/cm² for EC. Blank levels are below MDL.

Evaluation of Toxicity. The cell line of an adenocarcinoma human alveolar basal epithelial (A549) was employed to measure the toxic effects of the PM samples, as described previously in detail.41 Here we briefly outlined the analysis procedures of cell viability and oxidative stress. The PMs were extracted by methanol, and the solvent was then removed by nitrogen. The cells were exposed to PM extracts at different concentrations. After incubation for 24 h, cell viability was analyzed via using 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide assay. The optical emission intensity of 570 nm wavelength was detected via a microplate reader (H1Multimode, BioTek, Winooski, VT). The intracellular reactive oxygen species (ROS) generation was detected by dichlorofluorescein staining. The fluorescence intensity (488 and 525 nm) of the dichlorofluorescein was determined using the microplate reader. A more detailed description can be found in previous studies.44-46 The end point of cell viability was calculated by the IC50 value (the concentration causing 50% inhibition of cell viability).46 The results of oxidative stress were shown via the EC15 value (1.5-fold increase in ROS generation relative to control).46 Three successful analyses in parallel were performed for each test.

FIGURE 1. Number size distribution of PMs emitted from ship exhaust resulting from HFO and DO combustion.

Particle Emissions and Chemical Composition. The EFs of total suspended primary PM were 5.93 ± 0.48, 1.45 g/kg and 2.02 ± 0.65 g/kg fuel for HFO and DO combustion, respectively. The EFs of total primary PM2.5 were 3.15 ± 0.65 g/kg fuel for HFO, whereas they were 0.92 ± 0.02 g/kg fuel for DO. The EFs of primary PMs obtained in this study are in agreement with that in the literature. The average EFs for n-alkanes resulting from HFO and DO combustion were 0.48 ± 0.08 and 0.16 ± 0.01 g/kg fuel,
respectively. The incomplete combustion process of fossil fuels can generate \textit{n}-alkanes and release smaller than C\textsubscript{26} homologues.\textsuperscript{50} EFs for \textit{n}-alkanes of HFO were 3-fold higher than that of DO, which indicated a large amount of incomplete combustion fuel might be emitted along with the exhaust during operation with the HFO. The noncarbonaceous components of PM\textsubscript{2.5} samples were mainly contributed to SO\textsubscript{4}\textsuperscript{2−}, followed by NH\textsubscript{4}\textsuperscript{+}, NO\textsubscript{3}−, Ca\textsuperscript{2+}, Fe, and V; the remaining fraction, including F\textsuperscript{−}, Cl\textsuperscript{−}, Na\textsuperscript{+}, Mg\textsuperscript{2+}, and SiO\textsubscript{2}, was less than 3%. HFO PM\textsubscript{2.5} contained 9.2 ± 0.8% of sulfate, whereas DO PM\textsubscript{2.5} contained 3.4 ± 0.5%. The NH\textsubscript{4}\textsuperscript{+} fraction for HFO PM\textsubscript{2.5} was 1.2 ± 0.6%, while for DO PM\textsubscript{2.5}, it was 3.6 ± 1.3%. NH\textsubscript{4}\textsuperscript{+} is generated when ammonia (NH\textsubscript{3}) reacts with proton donors, it can be inferred where NH\textsubscript{3} was present in the exhaust gas of ship emission. Since NH\textsubscript{3} has a significant impact on air quality, it is necessary to detect it in future work. The concentrations of V and Fe in HFO PM\textsubscript{2.5} are much higher than those for DO PM\textsubscript{2.5}; this possibly is due to element vibrations in two types of fuels, as shown in Table 1. In mass balance calculations, metals commonly found in crustal material are assumed to present as oxides; these oxides are Fe\textsubscript{2}O\textsubscript{3} and V\textsubscript{2}O\textsubscript{5}.

The majority of the PM\textsubscript{2.5} mass in HFO or DO was carbonaceous, as shown in Figure 2a. Organic matter (OM) was the major component of PM\textsubscript{2.5} in HFO and DO samples. OM values for HFO and DO were calculated from OC via the relationships OM = 1.26 × OC and OM = 1.50 × OC, respectively, where the coefficients used for the relationship between OM and OC were determined by full component analysis of PM\textsubscript{2.5}, including carbonaceous and noncarbonaceous species analysis. The coefficients of OM/OC determined in the study are consistent with the frequently used values in the literature, which ranged from 1.2−1.8.\textsuperscript{51−53} The carbonaceous mass fractions (OM+EC) for HFO were approximately 85.8%, while for DO they were 86.9%. The ratio of OC/EC in this work was 0.93 and 1.19 for HFO and DO, respectively. The lower ratio also suggests lower combustion efficiency for HFO when compared to DO. EC originates from the pyrolysis of fuel droplets. It can be easily formed at a low air-fuel ratio and high combustion temperature condition.\textsuperscript{54} EC can be classified into char-EC and soot-EC. Char-EC is formed at a relatively low combustion temperature via the fuel pyrolysis, while soot-EC is formed at a high combustion temperature via a gas-to-particle conversion.\textsuperscript{55} Char-EC accounted for approximately 46% of EC mass for HFO, whereas it accounted for 33% for DO.

Figure S5 and Figure S6 show the morphology and speciation of HFO and DO PM samples characterized by STEM-EDS analysis. Soot was the predominant type of EC. The HRTEM images of these particles exhibited the disordered graphitic layers with a graphic microstructure. Soot spheres showed onion-like structures. EDS results of soot PMs showed that the particles predominantly contained carbon. Nanometer-sized particles rich in S were observed at the surface of PMs or within PM agglomerates (Figures S5b and S6b). Figure S5c and Figure S5d show high content of Fe and V in HFO PM samples, respectively. The V element can be used as a tracer of HFO combustion and was not present in the DO exhaust. Ca is the main component of the mineral PMs (Figure S6d). The difference in morphology is attributed to their different formation mechanisms.

\textbf{BaP\textsubscript{eq} Fraction in PM\textsubscript{2.5} and Size Segregated PM.} Figure 2b shows the Total-BaP\textsubscript{eq} values of the 16 PAHs in the PM\textsubscript{2.5} samples. The PAH emission characteristics and EFs showed high differences during HFO and DO combustion. PAH EFs of HFO were 4.6-fold higher than that of DO (Figure S8). This result is consistent with a previous study, in which HFO contains a large fraction of aromatic compounds, typically polycyclic aromatics, while DO generally contains higher proportions of aliphatic compounds.\textsuperscript{56} Chry dominated the PAH pattern, followed by Pyr and BaP in HFO PM\textsubscript{2.5}; while for DO PM\textsubscript{2.5}, Pyr dominated the PAH pattern, followed by Chry and BkF. HFO PM samples contained higher ring PAHs than DO samples, such as InP, DahA, and BghiP.

Figure 2b shows the Total-BaP\textsubscript{eq} values of the 16 PAHs in HFO and DO PM\textsubscript{2.5} samples. The sum of the BaP\textsubscript{eq} values for DahA, InP, BaP, BkF, BbF, and BaA (with TEF more than or equal to 0.1) contributes to ~95% of the BaP\textsubscript{eq} for a total 16 PAH species. The total-BaP\textsubscript{eq} values in HFO and DO PM\textsubscript{2.5} samples per kg fuel mass are shown in Figure S9. The reduction in the BaP\textsubscript{eq} of the DO PM\textsubscript{2.5} sample was 85% compared with the BaP\textsubscript{eq} value of the HFO PM\textsubscript{2.5} sample.

Comparison of BaP\textsubscript{eq} in PM exhausted from various anthropogenic emission sources is shown in Table S2. In order to give the effective comparison to BaP\textsubscript{eq} from different sources, all the values were unified into mg/g PM in the study.
The results showed that the values from residential coal combustion\(^{57}\) were in a much higher level than those of HFO and DO in this study. BaPeq from household fuel combustion\(^{40}\) varied largely with different solid fuels, which might be caused by the different fuel composition. BaPeq from a container ship was slightly lower than that reported in a previous study\(^{58}\); this may be due to operating with different fuel types and marine engines. BaPeq in HFO PM emitted from a container ship was much greater than those from on-road vehicle emissions, including gasoline\(^{59}\) and diesel vehicles\(^{60,61}\), while the value in DO PM was higher than diesel vehicles but at the same level with gasoline vehicles. However, motorcycles showed extremely higher BaPeq values than ships and other vehicles;\(^{62}\) this may be due to their small combustor chamber which limits the combustion efficiency of fuels.\(^{63}\) Besides, the BaPeq values in the lab test were lower than those in the field test, which could underestimate the carcinogenic risk from the real-world emission. Hence, more systematic real-world measurements are urgently needed to improve the circumstances. Since BaPeq from a container ship were higher than many mobile sources, the health effect caused by ships cannot be neglected especially in coastal areas.\(^{64}\) Furthermore, a large amount of toxic heavy metals is also emitted from ship exhausts, which could aggravate the negative health impacts.\(^{65}\)

The total-BaPeq in HFO and DO size-segregated PM is presented in Figure 3a, where all the values were unified into mg/g PM. The total-BaPeq in both HFO and DO size-segregated PM samples possesses peaks at particle aerodynamic diameters of 0.1–0.18 μm. The total-BaPeq was reduced in almost all size ranges except in PM\(_{10–18}\) when operated with DO, and the three highest reductions in emissions were in PM\(_{0.056–0.1}\), PM\(_{0.1–0.18}\), and PM\(_{0.18–0.32}\), which showed percentage reductions of 60.6%, 63.4%, and 62.1%, respectively. It has been shown that the more carcinogenic particulate PAHs are found in smaller PM from HFO and DO, indicating that at a similarly increased concentration of finer PM, the resulting particulate PAHs would have much higher carcinogenicity. This may be resulting from the larger surface area of smaller PM, which creates a higher capacity to absorb and deliver toxic chemicals. Hence, in addition to PM\(_{2.5}\) emitted from ships when using HFO or DO, special attention should be paid to ultrafine PM as well. The total-BaPeq values in HFO and DO PM samples per kg fuel mass are shown in Figure S10.
Toxicity of Primary PM. The biological effects of HFO size-segregated PMs were significantly greater than those of DO PMs. This may be due to varying chemical speciation in relation to different fuel types. Particle constituents, notably PAHs, may elicit distinct biological responses. Oxidative stress exhibited significant differences across size fractions (Figure 3b). The ROS-generating capacity in HFO and DO size-segregated PM samples possesses peaks at 0.1–0.18 μm and 0.056–0.1 μm, respectively, which is consistent with the number and size distribution of HFO and DO PM (Figure 1). The result suggests that, in addition to chemical composition, the particle number and size distribution affect redox activity. The cell viability exhibited a unique pattern of response (Figure 3c). Statistical analysis reveals that the investigation of the ultra fraction, whose oxidative-stress and cytotoxic effects are more evident, is highly significant. The biotoxicity of ultrafine PM was higher than that of large-sized PM, which was consistent with a previous report.66 This may be attributed to the higher ratio of toxic chemical components, as well as the greater surface area of ultrafine particles at the same weight.43

Dose-dependent effects of HFO and DO PM samples were observed in the values of EC1.5 and IC50. The EC1.5 values for HFO PM2.5 and DO PM2.5 were 3.06 ± 1.28 and 6.35 ± 2.34 μg/mL, respectively, whereas the IC50 values were 39.6 ± 18.3 and 97.9 ± 27.8 μg/mL, respectively. It suggests that the HFO PM2.5 would have higher negative biological effects than DO PM2.5. PM exhausted from marine diesel engines when operated with HFO or DO induced greater toxic effects than on-road vehicle emissions, whose EC1.5 values for diesel and petrol emitted PMs were reported to be 25 μg/mL67 and 35 μg/mL,68 respectively; while the IC50 values for petrol exhaust particles and residential solid fuel burning were 250 μg/mL67 and 100 μg/mL44, respectively. The results indicate that it is of great importance to make relative regulations to avoid negative toxic effects caused by ship emissions. The toxicity and health effects might be more negative when changing to lower loads due to higher EFs of pollutants.69 How these differences influence the toxicity and health effects need to be investigated in the future.

Correlation between BaPeq and Biological Effects. Figure 4 shows the linear regression analysis of the biological effects and BaPeq content in HFO and DO PM samples. The biological effects of both HFO and DO PM samples were significantly correlated (p-value <0.01) with the BaPeq values, with correlation coefficients (r) of 86%, 90%, 89%, and 92% for HFO oxidative stress, DO oxidative stress, HFO cytotoxicity, and DO cytotoxicity, respectively. Furthermore, the correlations are more significant in DO samples than those in HFO samples. This is possibly owing to the higher content of other hazardous compounds in HFO PM, such as transition metals (Fe, V), which have been identified to possess significant negative potential impacts on biological effects.55

Environmental Implication. PM2.5 emitted from lower-quality oil (HFO) has greater biological effects than that emitted from higher-quality oil (DO). Furthermore, both of these sources have greater negative health impacts than atmospheric PM2.5 samples collected in January 2016 in the city of Shanghai, as shown in Figure 5. The sampling process is detailed in the SI. EC1.5 values for the atmospheric PM2.5 on heavy- and light-pollution days were 7.60 ± 1.51 and 16.30 ± 2.90 μg/mL, respectively, and IC50 values were 105 ± 20 and 319 ± 45 μg/mL, respectively. The values of HFO PM2.5 were 2.9- and 2.5-fold higher than those of atmospheric PM2.5 on heavily polluted days but 8.7- and 5.3-fold higher than those on lightly polluted days. It has been implied that differences in the
amounts of specific substances associated with particles emitted from container ships could lead to greater oxidative stress and cytotoxicity.

The implications drawn from this field study are that the negative impacts from HFO-operated container ships need to be mitigated and that HFO should be replaced by high-quality refined fuels (high heating value and lower sulfur content fuel) to reduce negative environmental impacts and low effect of public health, particularly in coastal areas and harbor cities. A reduction in the PAH emissions could lead to a reduction of ~85% in BaPeq, which would alleviate potential biological effects. Hence, further regulation of fuel quality (sulfur, aromatic hydrocarbons) is implied to be an effective approach to achieve air quality and health targets by jointly reducing PM and health impacts from shipping emissions. Although DO is a low-sulfur fuel and is widely consumed in sulfur-emission control areas, PM emitted from ships when using DO should not be neglected due to its greater toxic effect relative to atmospheric PM. Furthermore, it is necessary to consider standards based on particle number owing to the differing toxicity of ultrafine PM.

■ ASSOCIATED CONTENT

 Supporting Information

 Ten figures, two tables, and description of atmospheric PM$_{2.5}$ samples collected in Shanghai in 2016 (PDF)

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