

Speciation and stable isotope study for iron in aerosols from various sources to determine their contributions to HNLC region

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In the North Pacific, three sources of iron (Fe) transported via atmosphere can be suggested: (a) mineral dust from East Asia, (b) anthropogenic Fe, and (c) aerosols from volcanic origin. Considering these different sources, Fe can be found and transported in a variety of chemical forms, both water-soluble and -insoluble. It is generally believed that only the soluble fraction of Fe can be considered as bioavailable for phytoplankton. To assess the biogeochemical impact of the atmospheric input, attempt was made to determine Fe species by X-ray absorption fine structure spectroscopy (XAFS) and its water solubility, in particular to compare the three sources. In particular, it was found that Fe stable isotope contribute to determination of Fe emitted from anthropogenic sources.

(i) Iron species and soluble Fe content in aerosol collected at Tsukuba (Japan) through a year were investigated to compare the contributions of mineral dust and anthropogenic components. It was found that the soluble Fe content is correlated with those of sulfate and oxalate originated from anthropogenic sources, suggesting that soluble Fe is mainly derived from anthropogenic sources, which was supported by XAS analysis showing presence of Fe(III) sulfate. Moreover, soluble Fe content was closely correlated with that of Fe(III) sulfate. In spite of supply of high concentrations of Fe in mineral dust from East Asia, anthropogenic Fe fraction is important due to its high water solubility by the presence of Fe(III) sulfate.

(ii) Marine aerosol samples originated from volcanic ash were collected in the western North Pacific during KH-08-2 cruise (August, 2008). XAFS suggested that Fe species of volcanic ashes changed during the long-range transport, while dissolution experiment showed that Fe solubility of the marine aerosol is larger than that of volcanic ashes, possibly due to the transform of insoluble Fe in volcanic ashes into highly soluble Fe such as Fe(II) sulfate. It was found that the soluble Fe content in the aerosol supplied as volcanic ashes should be important due to its very high content of soluble Fe.

(iii) A series of recent studies showed that Fe in anthropogenic aerosols is more soluble than that in natural aerosols (Takahashi et al., 2013) and has lower isotopic ratio (Mead et al., 2013). However, the difference between Fe isotopic ratio ($\delta^{56}\text{Fe}$: $[(^{56}\text{Fe}/^{54}\text{Fe})_{\text{sample}}/(^{56}\text{Fe}/^{54}\text{Fe})_{\text{IRMM-14}}]-1$) of two origins reported in Mead et al. (2013) is not so large compared with the standard deviation. Therefore, the aim of this study is to determine Fe species and $\delta^{56}\text{Fe}$ in anthropogenic aerosols more accurately and to evaluate its contribution to the ocean surface.

Dominant Fe species in the samples were, ferrihydrite, hematite, and biotite. It was also revealed that coarse particles contained more biotite and that fine particles contained a larger amount of hematite, which suggested that anthropogenic aerosols were emitted during combustion processes. In addition, results of Fe isotopic ratio analysis suggested that $\delta^{56}\text{Fe}$ of coarse particles were around +0.25‰, whereas that of fine particles were from -0.5 to -2‰, which was lower than the $\delta^{56}\text{Fe}$ in anthropogenic aerosol by Mead et al. (2013). The size-fractionated sampling made it possible to determine the $\delta^{56}\text{Fe}$ in anthropogenic aerosol. Soluble component in fine particles extracted by simulated rain water also showed much lower $\delta^{56}\text{Fe}$ ($\delta^{56}\text{Fe} = -3.9\text{‰}$), suggesting that anthropogenic Fe has much lower isotopic ratio. The remarkably low $\delta^{56}\text{Fe}$ may be caused by the anthropogenic combustion process. The $\delta^{56}\text{Fe}$ in anthropogenic aerosol measured here is important to model the budget of iron in the surface ocean.

Keywords: Iron, Aerosol, HNCL, XAFS, Fe stable isotope

Impact of the Coastal Oyashio water on spring bloom on the Oyashio area

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The Coastal Oyashio water (COW) flowed out of the Okhotsk Sea to the Northwestern Pacific during winter-spring and is characterized typically by temperature and salinity less than 2 °C and 33, respectively, colder and less saline than the Oyashio water. The COW includes rich nutrients and dissolved iron, which are essential for growth of phytoplankton. Distribution of the COW is generally thought to be limited to the coastal and shelf region off the Hokkaido and Sanriku coasts. Therefore, there have been few studies that quantitatively examined contribution of the COW to spring bloom over the Oyashio area offshore of the shelf region. Synthesizing previous studies, this study proposed a hypothesis that the COW can control formation of the spring bloom on the Oyashio area. To validate this hypothesis, we analyzed in situ monitoring data in May of 1990-2016 on the A-line, encompassing the Oyashio and Mixed Water Region off the southeastern coast of Hokkaido, and revealed relationships between presence of spring bloom and temperature-salinity properties, which were tightly linked with the COW or its modified water. Moreover, using historical temperature-salinity data across the Northwestern Pacific, we will demonstrate spatial extent of the water mass that was potentially linked with the spring bloom to discuss possible contribution of the COW to the whole of the Oyashio area.

Keywords: Oyashio area, Spring bloom, Coastal Oyashio water

Evaluation of the origin of the Coastal Oyashio Water using fluorescent dissolved organic matter

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The western subarctic Pacific Ocean is a region where largest seasonal pCO₂ drawdown by biological activity is evident. The Coastal Oyashio Water (COW), characterized by low temperature and low salinity, is distributed at off eastern Hokkaido in spring and possibly affect massive spring phytoplankton bloom in this region. Although riverine waters and/or sea-ice melt water have been considered as freshwater end-members of the COW, the contribution and temporal/spatial distribution of each freshwater end-member has not been well documented. In this study, to evaluate the origin of the COW distributed at off eastern Hokkaido, we used humic-like fluorophores in dissolved organic matter (DOM) as a tracer of freshwater end-member. Since humic-like fluorophore in riverine water is refractory, a negative correlation is generally observed between humic-like fluorescence intensity and salinity in coastal environments. While, levels of humic-like fluorophores in sea-ice melt water are low compared with seawater, because DOM are ejected with brine during sea-ice formation. Thus, it would be able to evaluate the contribution of freshwater end-members of the COW from the relationship between humic-like fluorescence intensity and salinity.

Seawater samples were collected during the *Hakuho-Mar* KH-15-1 cruise conducted at off eastern Hokkaido during March 6 to 26, 2015. As freshwater end-members, riverine waters and sea-ice samples were also collected. The riverine waters were collected from streams/rivers at the eastern Hokkaido during September 18 to 21, 2011. The sea-ice samples were collected during the *Soya* cruise on February 14, 2012, February 25 and 28, 2013, and February 16, 2014. The sea-ice sample was melted in an acid-cleaned PTFE beaker in a dark at room temperature. Dissolved organic carbon (DOC) concentration, excitation-emission matrix (EEM) fluorescence, and absorbance were measured. The EEMs were decomposed into individual fluorescent components using parallel factor analysis (PARAFAC). According to Hanawa and Mitsudera (1987), water masses were classified into three water masses, namely, the COW (T<2.0 °C, S<33.0), the Oyashio Water (T<7.0 °C, S=33.0-33.7, Sigma-theta<26.7), and the Low-layer Water (Sigma-theta>26.7). Four fluorescent components, obtained by EEM-PARAFAC, were categorized as two terrestrial humic-like components (C1 and C2), marine humic-like component (C3) and tryptophan-like component (C4) based on spectral comparisons with previous studies. In the COW, negative correlations were evident between salinity and fluorescence intensity of terrestrial humic-like components. In addition, the intercepts of the regression lines between salinity and terrestrial humic-like fluorescence intensities were within the range of the fluorescence intensities observed in the riverine waters. Since terrestrial humic-like fluorescence intensities in sea-ice samples were lower than those in seawater, the COW observed in this study was considered to be strongly influenced by riverine water. In addition, the intercepts were close to the value observed in the Kushiro River flowing through wetlands, implying that major freshwater end-member of the COW observed in this study originated from riverine water which is strongly influenced by wetlands.

Keywords: Coastal Oyashio Water, freshwater end-member, Fluorescent dissolved organic matter

Influences of organic Fe-binding ligands on natural phytoplankton growth in the western subarctic Pacific

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The influence of organic ligands on natural phytoplankton growth was investigated in high-nitrate low chlorophyll (HNLC) waters and during a phytoplankton bloom induced by a mesoscale iron enrichment experiment (SEEDS II) in the western subarctic Pacific. The growth responses of the phytoplankton in the treatments with iron complexed with model ligand were compared with those with inorganic iron or a control. Desferrioxamine B and protoporphyrin IX were used as models for hydroxamate-type siderophore and tetrapyrrole-type cell breakdown ligand, respectively. In the HNLC water, iron associated with protoporphyrin IX especially stimulated smaller phytoplankton (<10 μ m) growth, 1.5-fold more than did inorganic iron, suggesting that these cell breakdown ligands might be more bioavailable for them. The protoporphyrin IX's stimulatory effect on small phytoplankton was also observed during bloom initiation and development phases, whereas not observed during steady and decline phases. The growth of phytoplankton was inhibited in the treatment with desferrioxamine B-complexed iron, suggesting its low bioavailability for the natural phytoplankton community. Its inhibitory effects were particularly pronounced in pico-eukaryotic phytoplankton. During the iron-induced bloom, the phytoplankton's iron-stress response gradually increased with the desferrioxamine B concentration, suggesting that the competition for iron complexation between natural ligands and desferrioxamine B affected phytoplankton growth. However, the nano-eukaryotes and cryptophytes did seem better able to utilize the desferrioxamine B-complexed iron during the bloom-developing phase. These results indicate that the iron bioavailability for phytoplankton differs between bloom-developing and bloom-decline phases.

Keywords: Organic ligand, Iron, Phytoplankton, Western subarctic Pacific, Desferrioxamine B, Protoporphyrin IX

Higher temperature accelerate the growth of iron-limited phytoplankton communities in the subarctic Pacific

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Iron is one of the key element determining the carrying capacity of primary production in the marine ecosystem. Because of iron scarcity in certain oceanic regions, phytoplankton communities were dominated by small-sized non-diatom species and thus less efficient trophic transfer and biological carbon pump. However, the effect of climate change such as warming on iron-limited phytoplankton is poorly investigated. This study investigated that the effect of higher temperature (+ 4–5°C relative to controls) and iron addition on the growth dynamics of phytoplankton communities in the subarctic Pacific. Two experiments were conducted during summer in 2014 aboard R/V *Mirai* (MR14W: 47°N, 160°E; MR14E: 47°N, 148°W) and another one experiment was conducted during late winter in 2015 aboard R/V *Hakuho-Maru* (KH15: 42°N, 146°E). The addition of iron enhanced the specific growth rate of larger phytoplankton groups in all three experiments whereas smaller phytoplankton groups were rarely affected. In MR14W and KH15 experiments, higher temperature enhanced the growth of phytoplankton in both unamended controls and iron-added treatments. The magnitude of growth enhancement by the temperature increases was larger in smaller phytoplankton groups relative to the larger groups in the KH15 experiment. According to the relative growth rate analysis (between higher temperature (+ 4–5°C) treatment to control temperature under each iron conditions, and between iron-added to non-iron-added treatment under each temperature conditions), we found that the summer phytoplankton communities were iron-limited rather than temperature-limited whereas late winter phytoplankton community was temperature-limited rather than iron-limited. Our results suggest that the temperature conditions could modify the dynamics of iron-limited phytoplankton communities, especially for the low-temperature conditions. In addition, future global warming may enhance the growth of phytoplankton even in the iron-limited open ocean. Given the higher temperature could enhance the growth of smaller phytoplankton groups relative to the larger ones as observed in the KH15 experiment, not only climate change but also seasonal warming from winter to summer may play a key role in the dynamics of community composition in the ocean.

Keywords: Global warming, phytoplankton, subarctic Pacific Ocean

Effect of optical properties variability on retrieval of chlorophyll *a* from ocean color data in Oyashio and coastal Oyashio waters in early spring

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Massive phytoplankton bloom occurs in Oyashio and coastal Oyashio waters off Kushiro during spring. Ocean color images also illustrates the spring bloom as high chlorophyll *a* (chl.*a*) concentration. While a validation result showed the estimated chl.*a* concentrations in these waters are within a range of +/-35% of in situ values, effects of Tokachi river plume on chl.*a* estimation were anticipated. However, little is known about optical properties in this region. We measured remote sensing reflectance (R_{rs}), absorption coefficient, backscattering coefficient (b_{bp}) and chl.*a* of the waters during the cruise of R/V Hakuho-maru in March 2015 and investigated the effects of the optical properties on chl.*a* estimation from satellite data.

In the coastal stations of study area where was highly turbid for a few days due to passing of a low pressure during 10–13 March, absorption coefficient of non-algal particles (a_d) accounted for >60% of that of particulate matters (a_p) and b_{bp} was also higher than those in offshore stations. These optical properties induced high R_{rs} and resulted in overestimation of chl.*a* concentration by 2-3 folds when the standard ocean color chl.*a* algorithm was applied to the R_{rs} . On March 20, however, ratio of a_d and b_{bp} decreased and estimated chl.*a* concentration using the algorithm coincided with *in situ* data.

Phytoplankton absorption coefficient at 443 nm ($a_{ph}(443)$) and $b_{bp}(555)$ were linearly correlated with chl.*a* concentration and $a_d(443)$, respectively. Estimated values of chl.*a* concentration and $a_{CDOM}(443)$ applying these relationship to satellite ocean color data indicated that relatively higher ocean color chl.*a* in offshore region had interferences by non-algal particles and CDOM advected from coastal region. In this study region, satellite chl.*a* images should be carefully used and retrieval of chl.*a* from a_{ph} is better than using standard band-ratio algorithm because spatio-temporal variability in optical properties are dynamic and complicated not only in coastal region but also in offshore.

Keywords: optical property, ocean color remote sensing, Oyashio

Interannual variation of seasonality of primary production in the subarctic region of western North Pacific

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The subarctic region of western North Pacific is one of High Nutrient Low Chlorophyll (HNLC) seas because iron is consumed by phytoplankton during spring and primary productivity is restricted even if macro nutrients and light are sufficient. In the strait of the Kuril Islands, vertical mixing generated by internal waves broken at complicated ocean topography is bringing intermediate water to the surface. However, little is known about relationship between primary production and nutrients exported by intermediate water and vertical mixing. In this study, we classified study area with similarity analysis of seasonal change in primary production climatology and then determined its seasonality (peaks, period) to investigate interannual change in the seasonality and relation to nutrients.

We used the remote sensing reflectance and photosynthetic available radiation of the MODerate resolution Imaging Spectroradiometer (MODIS)/Aqua for 13 years from 2003 to 2015. Absorption coefficient of phytoplankton was retrieved from remote sensing reflectance using the Quasi-Analytical Algorithm (QAA). Absorption Based Production Model was applied to the absorption coefficient to derive daily net primary production. Climatological value of primary production for each week was calculated as a logarithmic mean for the 13 years dataset. Sea ice concentration of AMSR-E/Aqua from 2003 to 2010, sea surface temperature of AVHRR/NOAA from 2003 to 2012, net heat flux of the NCEP from 2003 to 2015 and the Pacific Decadal Oscillation (PDO) index from 2002 to 2015 were also analyzed. Based on the similarity of the seasonal variability in the primary production climatology, study area was classified using the cluster analysis (K-means method). Then, we defined 3 terms (1st term: width of 1st peak, 2nd term: period from the end of 1st peak and the start of 2nd peak, 3rd term: width of 2nd peak).

The study area was classified into 12 regions. In the region covered by sea ice seasonally, primary production increased immediately after sea ice retreat. Around the northern Kamchatka Peninsula, peaks in spring and autumn with similar level of production were recognized. The second peak was higher than the first peak around the southernmost part of the Kamchatka peninsula and the Aleutian Islands. In the central and eastern part of the Okhotsk Sea, the western and central part of the Bering Sea, and Oyashio region, the first peak was higher than the second peak.

In all regions, increase of primary production for the first term started, when the net heat flux and SST in winter show minimum values, probably due to stop of cooling and mixing. Principal component analysis for the interannual variability of the primary production showed a contribution rate of the 1st mode was more than 70% for each term. While the PDO had antiphase against SST and the net heat flux during the 1st and 2nd terms, significant relationship between PDO and primary production was found. Therefore, it was suggested that the interannual variability of primary production from spring to summer in the 1st and 2nd terms are greatly affected by climate change.

Keywords: Primary Production, Remote sensing, HNLC sea

Abundance and distribution of dimethylsulfoniopropionate-degrading bacteria in the Oyashio water off the coast of Hokkaido, northern Japan

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Bacterial community in the ocean involves in biological production of dimethylsulfide (DMS) from dimethylsulfoniopropionate (DMSP), a major osmolyte accumulated in phytoplankton cells. DMS emission from the ocean to the atmosphere plays a significant role in the production of secondary aerosols and subsequent cloud formation. Also, DMS is reportedly a signaling molecule used by some seabirds, crustaceans and marine mammals, suggesting the importance of its dynamics to understand biological interactions in the ocean ecosystems. Three metabolic pathways have been currently known as major processes of bacterial DMSP degradation. Two pathways can contribute to DMS production. The first one is the DMSP cleavage into DMS and acrylic acid and the second one is the cleavage into 3-hydroxypropionate and DMS after condensation of DMSP and acyl-CoA. The third pathway can contribute to a sink of DMS, because DMSP is degraded into methyl methylsulfoniopropionate and then methionine by serial demethylation. The goal of this study is to reveal the relationship between DMS emission and DMSP-degrading bacteria and to determine environmental factors controlling this relationship. Here we report abundance and distribution of DMSP degradation genes and the corresponding bacterial community structure during the spring bloom of coastal Oyashio water. Seawater samples were collected from the surface and subsurface chlorophyll maximum layers at 17 stations off the east coast of Hokkaido during the KH-15-1 R/V Hakuho-maru cruise in March 2015. The water was serially passed through 3.0 μm and 0.22 μm pore-size filters to collect particle-associated and free-living bacteria. After extracting DNA, DMSP lyase genes (*dddP* and *dddD*), DMSP demethylase gene (*dmdA*) and 16S rRNA gene were quantified by qPCR. As for the *dmdA*, 7 primer sets were used to differentiate diverse phylotypes. Also, amplicon sequencing of 16S rRNA gene was performed to determine bacterial community structure. As a result, two phylogenetic groups of *dmdA*, C/2 and D/1 clades were mainly detected in addition to *dddP* and *dddD*. The copy number of *dmdA* was higher than those of *dddP* and *dddD* in the Oyashio water, whereas *dmdA* copy number was lower than *dddP* and *dddD* copy numbers in the coastal Oyashio water. The *dmdA* copy number detected in this study was ca. 10^3 - 10^4 copies/ml. This value was one order lower than previously reported values (ca. 10^4 - 10^5 copies/ml) including our data in the tropical and subtropical Pacific Ocean and Tohoku coastal waters. Sequences of *dmdA* C/2 and D/1 clades were possessed by 1b and 1a subclades of *Pelagibacter* (SAR11) group bacteria, respectively. Although they often dominate bacterial assemblages in the ocean, they must be less abundant than usual in the Oyashio water of this study. Also, previous studies reported that *dddP* was the major DMSP lyase gene in the ocean and *dddD* was rather minor. However, we found the area where *dddD* was the major DMSP lyase gene. Since the *dddD* dominance in DMSP lyase genes was observed in the other Oyashio water off Tohoku area, this might be a specific feature of the Oyashio water. Furthermore, sequencing and phylogenetic analysis of *dddD* revealed that the gene originated from bacteria closely related to the genus *Porticoccus* (SAR92) belonging to the class *Gammaproteobacteria*. In this study, we found distinctive community structure of DMSP-degrading bacteria in the Oyashio water from previously reported structures. Further studies should be aimed to compare the change of bacterial communities with the change of DMSP and DMS concentrations and determine how bacterial gene type and abundance control

the dynamics of these ecologically important organic sulfur compounds.

Keywords: Oyashio, DMSP, Bacteria

Marine and atmospheric observations of volatile organic compounds during early spring in the Oyashio region

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A variety of volatile organic compounds (VOCs), including dimethylsulfide (DMS), isoprene and acetone, are emitted from the ocean to the atmosphere, and have strong influence on photochemical oxidation and aerosol formation. Since these marine VOCs are originated from microbial metabolisms of phytoplankton and bacteria, the VOC concentrations in seawater show seasonal and latitudinal variations associated with microbial activity and taxonomy as well as ocean physics. However, it has been largely unknown whether the variations of VOCs in seawater due to microbial activity affect the variations and distributions of VOCs in the air.

In order to examine the linkage between biological activities and VOCs dynamics both in the ocean and atmosphere, we made observations of spatial and temporal variations of VOCs during KH-15-1 cruise by R/V *Hakuho Maru* on March 2015 in the Oyashio region, western subarctic Pacific. The VOCs concentrations in the surface seawater and the overlying atmosphere were continuously measured by Proton Transfer Reaction-Mass Spectrometry during the cruise.

Phytoplankton (measured as Chl. *a* concentrations) gradually increased from the beginning to end of March. This seems a sign of springtime phytoplankton bloom in the Oyashio region. With the increase in Chl. *a*, the concentrations of several microbiologically produced VOCs (i.e., DMS, methanethiol, acetone, isoprene, acetaldehyde and propene) in the surface seawater increased. The VOCs concentrations in the air did not show clear increase except for DMS. The DMS concentration in the air showed positive correlation with that in the seawater, suggesting that marine organisms (i.e., phytoplankton) contributed to the increase of DMS concentrations in the air.

Keywords: volatile organic compounds, Oyashio region, Sea-Air flux

Linkages between atmospheric organic aerosols and surface seawater during phytoplankton blooms in spring

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Ocean-derived atmospheric aerosols can affect radiative forcing via formation of cloud droplets as well as biogeochemical cycle of bioelements. Marine atmospheric aerosols are known to largely consist of organics associated with phytoplankton and dissolved organic matter in seawater. The current climate models parameterize marine emissions of organic aerosol based on surface chlorophyll *a* concentrations and wind speeds. However, recent field studies have suggested that other chemical/physical/biological processes affecting marine aerosol production may also be missing in current emission parameterizations, such as chemical/biochemical forms of organics associated with microbial activity in surface seawater. Studies are very limited with respect to direct linkage between biochemical characteristics of organics in seawater and ambient atmospheric organic aerosols.

Observational study during the R/V *Hakuho-maru* cruise from March 6 to 26, 2015, investigated the contribution of microbial activity in surface seawater to the formation of atmospheric organic aerosols by direct comparison of chemical/biogeochemical characteristics of organics aerosol with those of particulate/dissolved organics in surface seawater. On average, organics accounted for the majority (~40%) of the submicron particle mass, which was attributable to dissolved organic carbon (DOC) and particulate organic carbon (POC) in the sea surface based on the measurement of stable carbon isotopic ratios of water-soluble organic carbon (WSOC) aerosols ($\delta^{13}\text{C}_{\text{WSOC}}$). We present a general overview of atmospheric observations during the cruise and discuss (1) chemical characterization of ocean-derived submicron WSOC compared with biogeochemical characterization of DOC measured by excitation emission matrix (EEM) fluorescence, and (2) comparison between organic aerosol mass and the fraction of POC linked to the development/aging of diatom bloom.

Keywords: Atmospheric organic aerosols, Phytoplankton bloom, Biogeochemical linkage between atmosphere and ocean

Number-size distribution and cloud condensation nuclei (CCN) activity of marine aerosol over the northern North Pacific in spring

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Aerosol particles in the atmosphere affect the climate directly by absorbing/scattering solar radiation and indirectly by acting as cloud condensation nuclei (CCN) and affecting cloud formation. Because the estimate of the radiative effect by aerosol via cloud formation are highly uncertain, to clarify the CCN activity of atmospheric aerosol and the characteristics of CCN is important for the assessment of global climate. The sources of aerosols in the marine atmosphere are primary emission as sea spray and secondary formation from volatile compounds. In spring, emission/formation of primary/secondary particles containing biogenic organic components in association with the enhancement of the biogenic activity in the ocean would affect the characteristics of the number concentrations of aerosol particles and CCN. In this study, the number concentration and number-size distribution of aerosol particles and the number concentration and activity of CCN were investigated, based on a shipboard measurement of atmospheric aerosols over the northern North Pacific.

The atmospheric observation on R/V *Hakuho-maru* was performed from 6 to 26 March, 2015. Aerosol particles passed through a cyclone (50% cut-off diameter: 2.5 micrometer) were introduced to the instruments in the laboratory, and the number-size distribution of the aerosol was measured every 5 min using a scanning mobility particle sizer. Further, the CCN efficiency spectra (the ratios of CCN to aerosol particles at respective diameters) at 0.1%, 0.2%, and 0.6% supersaturations were also measured every 1 h using a scanning mobility CCN analysis system, by switching the supersaturation conditions every 20 min.

The number-size distribution was bimodal on the average. Based on the characteristics, the observed aerosols are categorized to 3 types: (a) the number concentration was low and the peak of the size distribution was in the accumulation mode (diameter: >100 nm); (b) the number concentration was high and the peak of the size distribution was in the Aitken mode (diameter: <100 nm); (c) peaks were both in the Aitken and accumulation modes. Based on the backward trajectory analysis of the studied air masses, it is inferred that the transport of terrestrial aerosols in addition to clean maritime aerosols affected the number-size distributions. The hygroscopicity parameter calculated from the CCN efficiency spectra were lower than literature values for clean marine aerosols enriched in inorganic salts. This result suggests that the presence of organic components of terrestrial origin or those from the sea surface resulted in the decrease of the CCN activity of aerosol particles. The CCN number concentrations tended to be high, as compared to literature values for the clean marine atmosphere. The obtained data would be useful to assess the contributions of marine biota to the CCN number concentrations and those of physical factors (the number concentration and number-size distribution) and chemical factors (the chemical composition and hygroscopicity) to the CCN concentrations.

Size distributions and CCN activities of marine aerosols obtained in the longitudinal observation over the Pacific Ocean

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Atmospheric aerosols play an important role in controlling radiative properties and lifetime of clouds by acting as cloud condensation nuclei (CCN). Given that the ocean covers about 70% of the Earth's surface, oceanic aerosols contribute significantly to the CCN budget in the marine environment. Marine particulate organics and precursor gases generated by marine biota may affect concentrations, size and chemical composition of the oceanic aerosols. Thus, it is important to understand the relationship between marine primary productivity and aerosol properties related to CCN activities over the open ocean. In this study, size distributions and CCN activities of aerosols over the Pacific Ocean are characterized, and factors controlling the spatial variation of the aerosol characteristics are discussed.

Atmospheric measurements were conducted during R/V Hakuho-maru KH-13-7 and leg 2 of KH-14-3 cruises. Ambient air was sampled continuously through the inlets via silicon tubing and then dried with a diffusion dryer. The dried air samples were introduced to a scanning mobility particle sizer to measure number size distributions of the ambient aerosols. CCN concentrations were measured with a continuous flow thermal gradient CCN counter during the leg 2 of KH-14-3. Concentrations of atmospheric trace gases (O₃ and CO) and radon daughters, those can be tracers for land-origin and/or anthropogenic air masses, were also measured continuously along the cruise tracks.

The aerosol number concentrations varied from <100 to 3000 cm⁻³ and the spatial variations could not be explained only by the transport of land-origin air masses. This result suggests that it is necessary to consider the supply of marine origin material to the atmosphere. The aerosol number size distributions showed bimodal with a gap around 100 nm in diameter, which is characteristic of clean maritime air, in most of the oceanic region. The Aitken mode (diameter less than 100 nm) contributed greatly to the number of aerosols in the regions where the influence of land-origin air masses were small, indicating that the regions were suitable for the condensation and growth of fresh particles. Actually, a few typical events of new particle formation were observed in the South Pacific. In the arctic region, a spontaneous enhancement of aerosols with diameter around 100 nm was observed. Because there were not major anthropogenic sources of pollutants around the arctic region, the enhanced particles might be come from biogenic sources. Analysis based on CCN activation ratio suggests that these increased fine particles were rich in organics.

Biogeochemical linkages between the ocean and the atmosphere during phytoplankton blooms in the Oyashio region

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The Oyashio is a western boundary current of the western North Pacific, where a large phytoplankton blooms regularly occur in spring. The spring phytoplankton blooms leads to extensive transport of organic carbon to the deep ocean, causing the drawdown of nutrients and $p\text{CO}_2$. Therefore, the Oyashio plays an important role not only in the global carbon cycle, but also in supporting various marine resources. The Coastal Oyashio Water (COW) has the characteristics of low temperature and low salinity. The COW spreads extensively over the Oyashio region and has a great influence on the phytoplankton bloom in the Oyashio region. Regarding the origin of the COW, influence of sea ice melt water from the Sea of Okhotsk and/or the East Sakhalin Current has been proposed, but that has not been fully understood yet. In addition, the COW might be influenced by river water and coastal sediments around the Hokkaido island. Multi-scale vertical and horizontal ocean mixing processes can strongly influence the distribution of dissolved and suspended substances including macro- and micro-nutrient availability, and may impact on the phytoplankton bloom formation. The changes in nutrient dynamics generally affect the abundance, composition and metabolic activity of marine organisms such as phytoplankton and bacteria during the blooms.

Marine phytoplankton can produce volatile organic compounds and marine atmospheric aerosols, which strongly influence on atmospheric chemistry. Primary and secondary organic and inorganic components produced via marine phytoplankton activity can contribute to the formation of cloud droplets and subsequently affect the climate change. Therefore, the biogeochemical cycles related to the phytoplankton blooms have a tight linkage between the ocean and the atmosphere.

In order to investigate "Biogeochemical linkages between the ocean and the atmosphere during phytoplankton blooms", a field campaign in the Oyashio region was carried out using the research vessel Hakuho-maru from March 6 to 26, 2015. In this presentation, we report the outline of the research cruise, especially focusing on the nutrient dynamics in the pre-bloom condition.

Keywords: phytoplankton bloom, linkages between the ocean and the atmosphere, Oyashio - Coastal Oyashio water, micro- and macro-nutrients dynamics

Fine- and micro-scale observations in the Oyashio in winter

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During the R/V Hakuho-maru cruise in Mar. 2015, fine- and microstructure measurements in the Oyashio water were conducted using a CTD/LADCP and vertical microstructure profiler in order to know the spatial variability of wintertime turbulence field, which has not been reported so far at this area. At a station off the shelf break, whose bottom depth is about 530 m, one-day repeated observations were also conducted to know the temporal variability of turbulence intensity.

The energy dissipation rate, ε , was patchily elevated to $O(10^{-8})$ [W/kg] and was typically $O(10^{-10} - 10^{-9})$ [W/kg] in the upper 400 m depth (less dense than $27.0 \sigma_{\theta}$) across the Oyashio. Off the shelf break, where the one-day observation was conducted, strong turbulence with $\varepsilon = O(10^{-7})$ [W/kg] and $K\rho = O(10^{-3} - 10^{-2})$ [m²/s] was observed at around 60 - 70 m depth ($26.4 \sigma_{\theta}$), and $\varepsilon = O(10^{-8})$ [W/kg] and $K\rho = O(10^{-3})$ [m²/s] at around 350 m depth ($26.7 \sigma_{\theta}$) corresponding to the period of isopycnal heaving of about 50m. This strong mixing around $26.4 \sigma_{\theta}$ ($26.7 \sigma_{\theta}$) was enhanced when the along-isobath (down-sill) flow and its associated shear was strengthened. Harmonic analysis shows that the diurnal tidal flow was large in the upper 50 m, while the mean and semi-diurnal flow were also important at around $26.7 \sigma_{\theta}$ suggesting that the tidal flow may impact on the turbulence field at this place.

Keywords: turbulent mixing, Oyashio

Differences in the composition and photosynthetic physiology of spring phytoplankton assemblages between coastal Oyashio and Oyashio waters

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Every spring massive diatom blooms occur both in coastal Oyashio (COY) and Oyashio (OY) regions off East Hokkaido. In general, surface COY waters possess lower temperatures and salinities and higher nutrient levels as compared with those in the OY, so that marked differences in the abundance, community composition, and photosynthetic physiology of phytoplankton between the two water masses can be expected. These, in turn, could influence the biogeochemical processes and ecosystems in the two regions. However, such information has still been scarce thus far. Therefore, we carried out field campaigns using the R/V *Hakuho Maru* during 6–26 March 2015 and the TR/V *Misago Maru* during 16–17 April 2015. The abundance and community composition of phytoplankton were assessed from UHPLC pigment analyses. Diatom community composition was also estimated with a DNA metabarcoding technique. Furthermore, we evaluated the photosynthetic physiology of phytoplankton in terms of photosynthesis-irradiance curves, chlorophyll variable fluorescence, and diatom-specific *rbcL* gene expression. During the R/V *Hakuho Maru* expedition, phytoplankton little bloomed at most stations in the COY and OY where diatoms were predominant in the phytoplankton assemblages. On the other hand, diatoms proliferated in COY waters during the TR/V *Misago Maru* observations. The genus *Thalassiosira* was predominated in the diatom assemblages of the COY, whereas a mixture of *Thalassiosira*, *Minidiscus*, and *Fragilariopsis* dominated in the OY. In the 24-h bottle incubation experiments where temperatures increased by +7°C from those of ambient seawater, increases in diatom-specific *rbcL* gene expression and chlorophyll *a*-normalized maximum photosynthetic rate were observed in COY waters, whereas no such temperature effect was confirmed in the OY. Our results suggested that *Thalassiosira* in the COY could respond sensitively to the increase in temperature and then form blooms rapidly.

Keywords: Phytoplankton, Spring bloom, Community composition, Photosynthetic physiology

Nitrogen and Carbon stable isotope ratios of zooplankton in the Oyashio region of the western North Pacific

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Carbon and nitrogen isotope ratios ($\delta^{15}\text{N}$ and $\delta^{13}\text{C}$) of organisms are controlled by not only biological factors, such as catabolism and assimilation, but also physical environmental conditions that influence the isotope ratios of primary producers (phytoplankton). To examine how different water properties (i.e., nutrients and temperature) affect $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ in marine food webs, we measured $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ of zooplankton in three distinct water masses: coastal Oyashio (COY), Oyashio (OY) and warm-core ring (WCR) water along the A-line monitoring transect (38N-42.5N, 144.5-147.5E) in March 6- 26, 2015, cruise of the KH-15-1 of the *R/V Hakuho-maru* of the Japan Agency for Marine-Earth Science and Technology (JAMSTEC), and in February 28 –March 16, 2015, cruise of the WK-15-03 of the *R/V Wakataka-maru* of the Tohoku National Fisheries Research Institute, Japan Fisheries Research and Education Agency (FRA). Zooplankton samples were collected from 150 m depth to the surface using vertical tow of a NORPAC twin net (45cm mouth diameter, 0.355 mm mesh size). After collection, all samples were classified using a stereomicroscope into species or genus level, and only adults were used for isotopic analysis. Water samples were collected from the surface to 250m depth profiles for the measurements of $\delta^{15}\text{N}$ ($\text{NO}_3^+ + \text{NO}_2^-$). We compared the trophic fractionations of carbon and nitrogen isotopes ($\Delta \delta^{13}\text{C}$, $\Delta \delta^{15}\text{N}$) of zooplankton among the three water masses. We found that $\delta^{15}\text{N}$ of chaetognatha at COY tended to be higher than OY and WCR, but a simple relationship between $\Delta \delta^{15}\text{N}$ and $\Delta \delta^{13}\text{C}$, regardless of species or water masses. Combined with this $\Delta \delta^{15}\text{N}$ - $\Delta \delta^{13}\text{C}$ relation, the isotopic ratios of zooplankton would allow us to predict C and N isotope ratios of higher trophic consumers, such as carnivorous fish and seabirds.

Keywords: N and C isotope ratios, food chain, Oyashio region, isotopic fractionation

Contribution for the marine ecosystem at the North East Pacific Ocean by deposition of atmospheric nitrogen compounds

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It has become apparent that deposition of atmospheric species emitted from Asian region is one of pathways for the supply of nutrients and inhibitors in the ocean surface layer. However, there have been a few studies to estimate the contribution of marine ecosystem by the deposition of atmospheric species. In this study, we investigated contribution of deposition of atmospheric nitrogen compounds to the marine ecosystem at the North East Pacific Ocean using 3-D marine ecosystem model (NEMURO) combined with atmospheric regional chemical transportation model (WRF-CMAQ). The 3-D marine ecosystem model indicated that surface chlorophyll concentrations at sub-tropical region in North Pacific Ocean in summer was underestimate to those of the satellite observation by MODIS, suggesting lack of nutrient supply processes in summer. The atmospheric regional chemical transport model indicated that there are sufficient depositions for nitrate and ammonia at sub-tropical region in North Pacific Ocean calculated from 2009 to 2013, suggesting that atmospheric contribution as nutrients is potentially high. In the presentation, we are going to report the results for combination analysis by marine ecosystem model, atmospheric regional chemical transportation model, marine monitoring data by buoys, and satellite observation at sub-tropical region in North Pacific Ocean.

Keywords: atmospheric aerosol, deposition, marine ecosystem