

Article

Molecular Distributions and Compound-Specific Stable Carbon Isotopic Compositions of Plant Wax *n*-Alkanes in Marine Aerosols along a North–South Transect in the Arctic–Northwest Pacific Region

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Abstract: A geographical source of *n*-alkanes in marine aerosols was assessed along a North–South transect in the Arctic–Northwest Pacific region. Marine aerosol samples were collected during the ARA08 cruise with the R/V Araon between 28 August and 28 September 2017. We investigated molecular distributions of *n*-alkanes (homologous series of C_{16} to C_{34}) and compound-specific stable carbon isotopes (δ^{13} C) of *n*- C_{27} , *n*- C_{29} , and *n*- C_{31} . Unresolved complex mixtures (UCM) showed a latitudinal trend from the Arctic Ocean to the northwest Pacific Ocean, highlighting an increasing influence of the plume of polluted air exported from East Asian countries. The anthropogenic input was further evidenced by high U/R ratios (>5) and low CPI_{17–23} (0.6–1.4). The occurrence of high molecular weight (HMW) *n*-alkanes with high CPI_{27–31} (>3) indicated the biogenic input of terrestrial higher plant leaf waxes in all studied samples. The δ^{13} C of HMW *n*-alkanes was influenced by both the relative contributions from the C₃/C₄ plant sources and from fossil fuel combustions. The back-trajectory analyses provided evidence that changes in molecular distributions and δ^{13} C of *n*-alkanes were due to the long-range atmospheric transport of anthropogenic and biogenic organic materials from North American and East Asian countries to the Arctic Ocean and the remote northwest Pacific Ocean, respectively.

Keywords: marine aerosol; *n*-alkanes; compound-specific carbon isotopes; Arctic Ocean; northwest Pacific Ocean

1. Introduction

The *n*-alkanes originate from both anthropogenic and biogenic sources, including petroleum residue [1], biomass burning [2], and terrestrial plant wax, fungi, bacteria, algae, and plankton [3]. High molecular weight (HMW) *n*-alkanes (>*n*-C₂₅) are typical land-derived lipid biomarkers which can be carried from adjacent continents to remote oceanic settings by long-range atmospheric transport [4–7]. Investigations of HMW *n*-alkanes in marine aerosols have been widely conducted in the Atlantic Ocean [5,8,9], the Pacific Ocean [10–12], and the Southern Ocean [11]. HMW *n*-alkanes are also often found in marine surface sediments close to continental land in the Atlantic Ocean [13–15], the Pacific Ocean [16,17], and the Southern Ocean [18], reflecting latitudinal vegetation changes on the continent. Hence, the distributions and isotopic signatures of HMW *n*-alkanes extracted from marine sediment cores have successfully been used to reconstruct changes in terrestrial vegetation



as part of paleoclimatological reconstructions [19–23]. Although long-range atmospheric transport is an important pathway for the land-derived HMW *n*-alkanes over the Arctic Ocean, there have been very few marine aerosols observed in the Arctic Ocean [24]. In particular, no studies have examined isotopic signatures of HMW *n*-alkanes in marine aerosols in the Arctic Ocean. Hence, our knowledge of the sources and transport pathways of HMW *n*-alkanes in marine aerosols is still limited in this body of water.

In this study, we collected marine aerosol samples along a North–South transect in the Arctic–Northwest Pacific region in August and September 2017. This study compares variations in molecular distributions and carbon isotope compositions of HMW *n*-alkanes in marine aerosols over the Arctic Ocean and the northwest Pacific Ocean by using air-mass back trajectories. This study provides an insight into the potential sources of marine aerosols and the atmospheric transport pathways of land-derived HMW *n*-alkanes over the Arctic Ocean and the remote northwest Pacific Ocean.

2. Experiments

2.1. Aerosol Sample Collection

Six aerosol samples were collected along a North–South transect in the Arctic–Northwest Pacific region during the ARA08 cruise with the R/V Araon between 28 August and 28 September 2017 (Table 1, Figure 1). The sampling conditions were almost homogeneous without any severe weather heterogeneity [25]. Air sampling was performed on a Pallflex quartz fiber filter ($20 \text{ cm} \times 25 \text{ cm}$) using a high-volume air sampler (HV-1000R, Sibata Scientific Technology Ltd., Soka, Japan). The aerosol sampling inlet was placed on the front deck of the ship (13 m above sea level), ahead of the ship's engines, and a wind controller was used to avoid contamination from ship-engine exhaust during the cruise. In addition, kitchen ventilation systems were connected by a plastic cylindrical pipe (~15 m length) and moved back on the deck (far away from the sampling inlet) to minimize the potential effects of cooking emissions on the atmospheric measurements during the sampling periods. Similar to another study [9], the aerosol collector was connected to a wind vane programmed to have the unit switched on when wind was from a predetermined arc of 100 degrees to each side from the front of the ship's chimney. The sampling flow rate was 1000 lpm and the total sampling time was 2–3 days. After sampling, the sample filters were stored on board at -20 °C until analysis in the laboratory.



Figure 1. (**A**) Cruise tracks of the ARA08 cruise corresponding to each sample with the quartz fiber filter identification numbers used. (**B**) Detailed cruise tracks for the Arctic samples with the quartz fiber filter identification numbers used.

| Sample No. | Starting Point | | | | End Point | | | | 37.1 |
|----------------|----------------|-----------|----------------------|---------------|-----------|-----------|----------------------|---------------|-------------------|
| | Latitude | Longitude | Date (yyyy.mm.dd) | Time (UTC) | Latitude | Longitude | Date (yyyy.mm.dd) | Time (UTC) | (m ³) |
| ARA08 QFF-1 | 70.60 | -139.30 | 2017.09.03 | 16:00 | 69.88 | -139.10 | 2017.09.05 | 15:02 | 2632 |
| ARA08 QFF-2 | 70.50 | -139.00 | 2017.09.07 | 16:18 | 71.00 | -148.50 | 2017.09.13 | 16:12 | 3051 |
| ARA08 QFF-3 | 71.00 | -148.70 | 2017.09.13 | 17:10 | 66.77 | -168.40 | 2017.09.15 | 16:45 | 2755 |
| ARA08 QFF-4 | 55.86 | 170.17 | 2017.09.20 | 20:20 | 49.43 | 158.14 | 2017.09.22 | 20:21 | 2686 |
| ARA08 QFF-5 | 42.88 | 146.19 | 2017.09.24 | 20:59 | 40.16 | 138.14 | 2017.09.26 | 9:30 | 2107 |
| ARA08 QFF-6 | 40.09 | 138.01 | 2017.09.26 | 10:23 | 34.90 | 127.70 | 2017.09.28 | 1:00 | 2267 |

Table 1. Information on marine aerosol sampling.

2.2. Backward Air-Mass Trajectory Analysis

The geographical source areas of tropospheric air that arrived at the ship during sampling periods for each aerosol sample were estimated from air-mass back-trajectory analyses using version 4 of the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model [26]. The 2-day air-mass back trajectories (48 h) were determined at hourly intervals from the ship's position at an arrival height of 50 m to estimate the transport history of the air masses arriving at the observation site [25,27]. The potential origins of the aerosols were divided into four categories based on the residence time of the 2-day back trajectories over the three major domains: Arctic Ocean (including the Beaufort Sea, the Chukchi Sea, and sea-ice region), Pacific Ocean (including the Bering Sea and the Sea of Okhotsk), East Asia (including China and the eastern part of Siberia), and North America (including Alaska and Canada). Geographical information about the ocean, land, and sea-ice was obtained from the sea-ice index, which was provided by the National Snow and Ice Data Center (NSIDC). The sea-ice extent was defined as the area having an ice concentration of $\geq 15\%$ [28].

2.3. Analysis of n-Alkanes

All six quartz fiber filters were freeze-dried, cut into small $(1 \text{ cm} \times 1 \text{ cm})$ pieces, and ultrasonically extracted (5×) with a mixture of dichloromethane (DCM):methanol (MeOH) (2:1, v:v) for 20 min. The total lipid extracts were concentrated under a gentle N₂ stream and passed over a small Na₂SO₄ Pasteur pipette column. The extracts were separated into apolar and polar fractions on an activated Al₂O₃ column using hexane:DCM (9:1, v:v) and DCM:MeOH (1:1, v:v), respectively. The apolar fraction containing *n*-alkanes was dried and further purified over an Ag+ impregnated silica pipette column to separate aliphatic and aromatic hydrocarbons using hexane as eluent.

The apolar fractions were analyzed with an Agilent 7890A gas chromatograph (GC, Agilent Technologies, Santa Clara, CA, USA) equipped with a flame ionization detector (FID) using a DB–5 column fused silica capillary column (30 m length, 0.25 mm internal diameter, and 0.25 μ m film thickness, Agilent). The samples were injected under constant flow at an initial oven temperature of 70 °C in a splitless mode with helium as a carrier gas. The GC oven temperature was subsequently raised to 130 °C at a rate of 20 °C/min, and then to 320 °C at 4 °C/min, with a final hold time of 45 min. Quantification of chromatographically resolved aliphatic hydrocarbons was made by using external standards (solution of *n*-alkanes from C₈ to C₄₀, pristane, and phytane; Supelco 502065, AccuStandard, New Haven, CT, USA). The concentration of unresolved complex mixtures (UCM) was calculated with the mean response factors of *n*-alkanes. The apolar fractions were also analyzed with an Agilent 7820A GC coupled to an Agilent 5977E MSD mass spectrometer (MS, Agilent Technologies, Santa Clara, CA, USA) operated at 70 eV with a mass range of *m*/*z* 50–800. The samples were subjected to the same temperature conditions and capillary column described for GC analysis. Compound identifications

were based on a comparison of relative GC retention times and mass spectra of the *n*-alkane mixture (C_8-C_{40}) analytical standards (Supelco 502065).

The average chain length (ACL) [29], the carbon preference index (CPI) [30], the percentage of wax *n*-alkanes (%Wax) [31], and the percentage of petrogenic *n*-alkanes (%PNA) [32] were calculated as follows:

ACL =
$$\frac{[27 \times C27 + 29 \times C29 + 31 \times C31]}{[C27 + C29 + C31]}$$
(1)

$$CPI = \frac{1}{2} \times \left[\left(\frac{C27 + C29 + C31}{C26 + C28 + C30} \right) + \left(\frac{C27 + C29 + C31}{C28 + C30 + C32} \right) \right]$$
(2)

Wax - Cn = [Cn] -
$$\left[\frac{Cn + 1 + Cn - 1}{2}\right]$$
 (3)

$$\% Wax = \frac{\Sigma Wax - Cn}{\Sigma NA} \times 100$$
(4)

$$PNA = 100 - Wax$$
 (5)

where Cn is the concentration of the n-alkane containing n carbon atoms, Σ Wax-Cn is the concentration sum of wax *n*-alkane contribution arising from all odd *n*-alkanes, and Σ NA is the concentration sum of total *n*-alkanes in the range of C₂₆ to C₃₂.

2.4. Compound-Specific Stable Carbon Isotope Analysis

The δ^{13} C values of *n*-alkanes were determined using an isotope ratio mass spectrometer (IsoPrime GV Instruments, Manchester, UK) connected with a GC (Hewlett Packard 6890 N series, Agilent Technologies, Santa Clara, CA, USA) via a combustion interface (glass tube packed with copper oxide–CuO, operated at 850 °C) [17]. The samples were subjected to the same temperature conditions and capillary column described for the GC and GC-MS analyses. Isotopic values are expressed as δ^{13} C values in per mil relative to the Vienna-Pee Dee Belemnite (VPDB). Isotope values of the dominant C₂₇, C₂₉, and C₃₁ homologues reported were determined by averaging duplicate analyses whenever concentrations were sufficient. Standard deviations of carbon isotope measurements were generally better than ±0.4‰, as determined by repeated injections of the standard.

2.5. Statistical Analysis

The fractional abundances of each *n*-alkane component were obtained by normalizing each *n*-alkane concentration to the summed concentration of *n*-alkane compounds ($C_{26}-C_{32}$) considered. To provide a general view of the variability of the distribution of *n*-alkanes, principal component analysis (PCA) was performed on the fractional abundances of *n*-alkanes using the R program [33]. We also performed hierarchical clustering of principal components (HCPC) on the PCA results to cluster samples with similar *n*-alkane distributions.

3. Results

The ship track during sample acquisitions is indicated in Figure 1, and the beginning and ending coordinates are given in Table 1. The air masses mainly came from the north and then passed over the Arctic Ocean to the ship when the marine aerosol samples of QFF-1 and QFF-2 were collected (Figure 2). The back trajectories were different when QFF-3 was collected, showing increased contributions from the Pacific Ocean and the eastern part of Siberia. The air masses mainly originated from the Pacific Ocean, with a minor portion of East Asia, when QFF-4 was collected. The air masses from East Asia increased during the QFF-5 and GFF-6 sample collection.

The resolved *n*-alkanes were detected in a series of C_{16} to C_{34} with a predominance of *n*- C_{27} , *n*- C_{29} , and *n*- C_{31} homologues (Figure 2). All aerosol samples studied showed a broad and unimodal UCM of hydrocarbons eluting between *n*- C_{15} and *n*- C_{25} . The UCM concentrations varied between 4 and 105 ng/m³ (Figure 3A). The ratios of unresolved to resolved hydrocarbon components (U/R)

were in the range of 5.0 to 9.9 (Figure 3B). The concentration of odd-carbon-numbered long-chain *n*-alkanes in C_{27} – C_{31} (ΣC_{27} – $_{31}$) ranged from 0.04 to 2.5 ng/m³, with higher values close to the East Asian continent (Figure 3C). The ACL_{27–31} (Equation (1)) was relatively stable along the North–South transect, with an average of 28.9 ± 0.2 (Figure 3D). The odd to even predominance of the *n*-alkanes, expressed as CPI_{27–31} (Equation (2)), was between 3 and 7 (Figure 3E). The %Wax_{27–31} (Equations (3) and (4)) was in the range of 41–71% (Figure 3F). All *n*-alkane compounds except for *n*- C_{27} , *n*- C_{29} , and *n*- C_{31} were not present in sufficient concentrations to be measurable by GC-IRMS. The δ^{13} C values of the dominant HMW *n*-alkanes (*n*- C_{27} , *n*- C_{29} , and *n*- C_{31}) fell in the range of –32.2‰ to –30.1‰, –33.1‰ to –31.4‰, and –34.8‰ to –31.8‰, respectively (Figure 4).

The PCA results based on the fractional abundances of HMW *n*-alkanes ($C_{26}-C_{32}$) showed that the PC1 (55.5%) was closely related to odd-carbon-numbered long-chain *n*-alkanes (C_{27} to C_{31}) with a negative loading and a positive loading of all even-carbon-numbered *n*-alkanes (C_{26} to C_{32}) (Figure 5). The PC2 (35.4%) predominantly reflected the presence of C_{28} to C_{32} with a positive loading and C_{26} to C_{27} with a negative loading. The subsequent HCPC results showed that all Arctic marine aerosol samples were grouped as one cluster, associated with even-carbon-numbered long-chain *n*-alkanes. The Pacific marine aerosol samples were separately clustered into odd-carbon-numbered long-chain *n*-alkanes.



Figure 2. Backward air-mass trajectories at 50 m above ground level for each sample and fractional abundances of high molecular weight (HMW) *n*-alkanes for the range of C_{26} – C_{32} . The yellow lines indicate the ship track lines.





Figure 3. (A) Concentration of unresolved complex mix (UCM) hydrocarbons, (B) ratio of unresolved to resolved hydrocarbon components (U/R), (C) odd-carbon-numbered long-chain *n*-alkanes in the range of C_{27} – C_{31} (ΣC_{27-31}), (D) average chain length (ACL₂₇₋₃₁), (E) carbon preference index (CPI₂₇₋₃₁), and (F) the percentage of wax *n*-alkanes (%Wax₂₇₋₃₁).



Figure 4. Average δ^{13} C values of each sample for (A) *n*-C₂₇, (B) *n*-C₂₉, and (C) *n*-C₃₁.



Figure 5. (**A**) Results of the Principal Component Analysis (PCA), and (**B**) the Hierarchical Clustering on Principal Components (HCPC) of the fractional abundances of HMW *n*-alkanes for the marine aerosol samples investigated.

4. Discussion

4.1. Anthropogenic Hydrocarbons in Marine Aerosols

Unresolved complex mixtures of hydrocarbons are composed of positional isomers of linear, branched, and/or cyclic alkanes with different carbon numbers and emitted to the atmosphere by incomplete fossil-fuel combustion [34-36]. The UCM hydrocarbons were detected in all marine aerosol samples investigated and showed a latitudinal trend of increasing values towards the south with a maximum value in GFF-6 in the northwest Pacific Ocean (Figure 3A). Our results are in good agreement with previous studies which showed the presence of UCM hydrocarbons in marine aerosol samples collected over the northwest Pacific Ocean, the East China Sea, and the East Sea of Korea [10–12]. The presence of UCM hydrocarbons was also reported in aerosol samples collected from ground stations on Jeju Island in South Korea, on Hokkaido Island, and Chichi-Jima Island in Japan [10,37,38], and in a southeastern coastal city of China (Xiamen) [39]. In general, the UCM concentrations of marine aerosol samples collected over the Northwest Pacific were one order of magnitude higher than those of aerosol samples collected at the Chichi-Jima station located in the remote northwest Pacific Ocean [10,37]. The concentrations of UCM hydrocarbons were three orders of magnitude higher in aerosol samples collected at Alert (82.5° N, 62.3° W) in the Canadian high Arctic [40] than those of the marine aerosol samples collected over the Beaufort Sea. Thus, our results indicate a generally increasing input of anthropogenic pollution from the Arctic Ocean to the northwest Pacific Ocean.

The ratio of unresolved to resolved hydrocarbon components (U/R) >4 can be another sign of a substantial input of fossil-fuel combustion to marine aerosols [41–43]. In our samples, the U/R was on average 5 ± 0.3 in the Arctic Ocean and 9 ± 0.6 in the northwest Pacific Ocean (Figure 3B), providing additional evidence that the marine aerosols investigated were affected by long-range transport of fossil-fuel combustion aerosols. The CPI of *n*-alkanes can be another measure of petroleum inputs. Petroleum-derived *n*-alkanes have a regular distribution with a CPI of 1 [1,44], whereas epicuticular waxes derived from higher land plants generally have CPI values of >4 [41]. The CPI values for the whole range of C₁₇–C₃₃ were 1.2–1.6 in the Arctic Ocean and 3.1–5.0 in the northwest Pacific Ocean. The CPI for the low molecular weight *n*-alkanes (i.e., C₁₇–C₂₃), where the UCM hump occurred, were lower, with values of 0.6–0.7 in the Arctic Ocean and 0.7–1.4 in the northwest Pacific Ocean, confirming anthropogenic inputs from fossil-fuel combustion in the marine aerosols studied.

The back trajectories calculated for the periods of the samples collected in the Arctic Ocean showed that the air masses mainly originated from the Arctic Ocean and North America (Table 2). On the contrary, the air-mass trajectory analyses generally showed that most of the air masses came from the East Asian countries over the northwest Pacific Ocean through the atmosphere under the influence of strong westerly and northerly winds. Accordingly, our results show that the Arctic Ocean and the northwest Pacific Ocean were influenced by the plume of polluted aerosols exported from North American and East Asian countries during the sampling periods, respectively.

| Samula No | Geographical Source Sectors for Air-Mass Trajectories | | | | | | |
|-------------|---|--------------|-----------|---------------|--|--|--|
| Sample No. | Pacific Ocean | Arctic Ocean | East Asia | North America | | | |
| ARA08 QFF-1 | 16.5 | 53.9 | 0 | 29.6 | | | |
| ARA08 QFF-2 | 1.5 | 75.2 | 0 | 23.3 | | | |
| ARA08 QFF-3 | 49.3 | 12.0 | 10.6 | 28.1 | | | |
| ARA08 QFF-4 | 99.7 | 0 | 0.3 | 0 | | | |
| ARA08 QFF-5 | 79.7 | 0.1 | 20.2 | 0 | | | |
| ARA08 QFF-6 | 71.5 | 0 | 28.5 | 0 | | | |

Table 2. Percentages of dominant back trajectories found within each sampling period.

4.2. HMW n-Alkanes in Marine Aerosols

The HMW n-alkanes (C_{27} - C_{31}) were detected in all marine aerosol samples investigated, suggesting an input of terrestrial higher plant leaf waxes [4]. The ΣC_{27-31} was higher in the northwest Pacific Ocean $(1.4 \pm 1.0 \text{ ng/m}^3)$ than in the Arctic Ocean $(0.05 \pm 0.01 \text{ ng/m}^3)$, especially close to the East Asian countries (Figure 3C). The carbon number maxima (Cmax) in the C_{27} - C_{31} range can also give an indication of a significant incorporation of higher land plant waxes [31]. The Cmax at *n*-C₂₇ and $n-C_{29}$ (Figure 2) with the ACL₂₇₋₃₁ of ~29 (Figure 3D) are thus evidence for an origin of epicuticular leaf waxes of higher land plants. Our results are in line with previous studies that reported a Cmax at n-C₂₇ in the Arctic marine aerosols [24] and a Cmax at $n-C_{29}$ or $n-C_{31}$ in the Pacific marine aerosols [10,11]. The HMW *n*-alkanes showed CPI₂₇₋₃₁ of 3.2 ± 0.4 in the Arctic Ocean and of 6.1 ± 1.1 in the northwest Pacific Ocean (Figure 3E). Hence, CPI₂₇₋₃₁ values (>3) demonstrate that the marine aerosols investigated were affected by higher plant waxes. Furthermore, %Wax₂₇₋₃₁, with values of 48 ± 5% in the Arctic Ocean and of $68 \pm 5\%$ in the Northwest Pacific (Figure 3F), provides evidence of an influence of higher plant leaf waxes in the marine aerosols. Our results demonstrate that the marine aerosols studied were influenced by petroleum residues, as shown by the %PNA, with a value of $52 \pm 5\%$ in the Arctic Ocean and $32 \pm 5\%$ in the northwest Pacific Ocean. Thus, the relative contribution of fossil-fuel combustion to the resolved HWM *n*-alkanes was higher in the Arctic aerosols than in the Pacific aerosols, contrary to that of UCM (see Figure 3A).

The carbon isotopic signatures of *n*-alkanes are a useful means to distinguish between sources [45,46]. The *n*-alkane δ^{13} C values of higher land plants that use the Calvin–Benson cycle of carbon fixation (i.e., C₃ plants) were centred at $-34.6 \pm 2.9\%$ for *n*-C₂₇, $-35.1 \pm 2.3\%$ for *n*-C₂₉,

and $-35.4 \pm 2.6\%$ for n-C₃₁ [38,47–50]. On the other hand, C₄ plants that use the Hatch–Slack cycle of carbon fixation exhibit the *n*-alkane δ^{13} C values of $-20.8 \pm 2.9\%$ for n-C₂₇, $-20.0 \pm 2.3\%$ for n-C₂₉, and $-20.1 \pm 2.5\%$ for n-C₃₁ [38,47–50]. The δ^{13} C signatures in the Pacific marine aerosols were within a narrow range of $-32.0 \pm 0.1\%$ for n-C₂₇, $-32.0 \pm 0.4\%$ for n-C₂₉, and $-32.0 \pm 0.2\%$ for n-C₃₁ (Figure 4). In contrast, the Arctic marine aerosols showed relatively larger variations in δ^{13} C for n-C₂₉ ($-32.4 \pm 0.7\%$) and n-C₃₁ ($-34.2 \pm 0.6\%$), except for n-C₂₇ ($-30.4 \pm 0.2\%$) (Figure 4). The difference in the same *n*-alkanes between the samples may reflect atmospheric transport pathways and hence differential source areas. However, QFF-1 and QFF-2 collected in the Arctic Ocean showed similar back trajectories with the main sources from the Arctic Ocean and North American countries (Table 2,

see also Figure 2) but revealed differences in δ^{13} C of *n*-C₂₉ and *n*-C₃₁ (see Figure 4). Hence, the relatively high deviation of δ^{13} C values among the Arctic aerosol samples seems to be related to the diversity of the wind directions and thus the source regions.

The relative contributions to the HMW *n*-alkanes from terrestrial C₃ and C₄ plants were estimated by using a simple two-endmember mixing model [51], based on the δ^{13} C values of *n*-C₂₇: C₃ plant *n*-alkanes = -34.6‰ and C₄ plant *n*-alkanes = -20.8‰. Use of the mixing model resulted in estimates of C₄ plant contribution varying from 29% to 32% for the Arctic marine aerosols and 17% to 20% for the Pacific marine aerosols. Accordingly, the mixing model results suggest a higher input of C₄ plants to the Arctic marine aerosols than to the Pacific marine aerosols during the time of sampling. However, it should be noted that there was a negative correlation between δ^{13} C ratios of *n*-C₂₇ against CPI₂₇₋₃₁ (R² > 0.78, *p* < 0.0001) but a positive correlation between δ^{13} C ratios of *n*-C₂₇ against %PNA₂₇₋₃₁ (R² > 0.85, *p* < 0.0001). Notably, the Arctic marine aerosol samples were separately clustered from the Pacific marine aerosol samples in association with even-carbon-numbered long-chain *n*-alkanes (Figure 5). Hence, this line of evidence in addition to lower CPI₂₇₋₃₁ and higher %PNA₂₇₋₃₁ suggests that the contribution of fossil-fuel combustion influenced more strongly the δ^{13} C ratios of *n*-C₂₇ in the Arctic marine aerosols than in the Pacific marine aerosols. Accordingly, it appears that the δ^{13} C signatures of HMW *n*-alkanes contained in the marine aerosols analyzed were affected by the contribution of both C₃/C₄ plants and fossil-fuel combustions.

5. Conclusions

We investigated molecular distributions and δ^{13} C of *n*-alkanes in marine aerosols collected along a transect from the Arctic Ocean to the northwest Pacific Ocean. In all studied samples, the anthropogenic input was evidenced by the presence of UCM, high U/R ratios, and low CPI values for low molecular weight *n*-alkanes. The biogenic input of terrestrial higher plant leaf waxes was predominant for HMW *n*-alkanes in all studied samples, with high CPI values. The δ^{13} C of HMW *n*-alkanes was as a function of the relative contributions from the C₃/C₄ plant sources in addition to the anthropogenic inputs from fossil-fuel combustions. Accordingly, *n*-alkanes in the studied marine aerosol samples originated from mixed sources. The back-trajectory results provided evidence that the atmospheric transport of anthropogenic and biogenic organic materials from North American and East Asian countries contributed to marine aerosols in the Arctic Ocean and the northwest Pacific Ocean, respectively. Accordingly, our results show that changes in molecular distributions and δ^{13} C of *n*-alkanes of marine aerosols were a function of changes in the prevailing wind and hence source regions. Furthermore, our study provides a basis for future paleoclimatological work for understanding the link between land-derived HMW *n*-alkanes in the atmosphere and those in the marine sediments in the Arctic Ocean.

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