^{234}Th and POC data in the North Pacific in 2002–2008

1. Introduction

Global warming resulting from the increase in greenhouse gases, such as carbon dioxide, is of great concern to the world community. In the last few decades, the carbon cycle in the ocean has been studied to clarify the balance of carbon dioxide between the atmosphere and the ocean. One important issue is the quantification of the role played by the biological pump: how much atmospheric CO_2 is assimilated in the sunlit layer (euphotic zone) and how much carbon is exported to the deep ocean?

The short-lived radionuclide ^{234}Th (half-life, 24.1 days) serves as a valuable tracer for studying the rates of particle-associated scavenging and the subsequent particle export from the euphotic zone (Coale and Bruland, 1985; Buesseler, 1998). This tracer is produced in the water column as a dissolved species by radioactive decay of the conservative ^{238}U in seawater and is redistributed between the dissolved and particulate phases depending on particle reactivity and the availability of particle surfaces.

Particulate organic carbon (POC) fluxes, calculated using the ^{234}Th method, have been reported from oceans worldwide: North Atlantic (Buesseler *et al*., 1992), Equatorial Pacific (Buesseler *et al*., 1995; Bacon *et al*., 1996; Murray *et al*., 1996), Middle Atlantic (Michaels *et al*., 1994; Buesseler, 1998), Arabian Sea (Lee *et al*., 1998; Buesseler *et al*., 1998), Northeast Polynya off Greenland (Cochran *et al*., 1995), Antarctic Ocean (Rutgers van der Loeff *et al*., 1997), the northeastern North Pacific (Charette *et al*., 1999), North Pacific Subtropical Gyre (Benitez-Nelson *et al*., 2001), and Southern Ocean (Buesseler *et al*., 2001a; Coppola *et al*., 2005). Buesseler (1998) proposed that the export ratio (*e*-ratio), which is the ratio of POC flux to primary production, would be less than 5–10% in much of the oceanic area of the world, but would be significantly higher at high latitudes and during episodic export pulses such as spring blooms. Charette *et al*. (1999) and Amiel *et al*. (2002) reported the importance of diatoms in elevating POC export.

The northern North Pacific Ocean, especially its western part, experiences intense winter cooling and receives large supplies of nutrients through upwelling, resulting in high productivity in spring and summer. It is well documented that spring blooms, consisting mainly of diatoms, occur only in the western part of the subarctic Pacific

(Saito *et al*., 2002; Yamaguchi *et al*., 2002). It has been suspected that diatoms in this area play a key role in transporting POC to the deep ocean, because of their relatively large size and resultant high settling velocity (*e.g*., Tsunogai and Noriki, 1991; Kemp *et al*., 2000; Smetacek, 2000; Honda *et al*., 2002). The large decrease of nutrients and surface pCO_2 from spring to autumn also support the high activity of the biological pump in the northwestern North Pacific (Louanchi and Najjar, 2000; Wong *et al*., 2002; Takahashi *et al*, 2002).

Since October 2002, we have made time-series observations in the northwestern North Pacific. High intensities of biological pump have been estimated from sediment traps (Honda *et al*., 2006 and 2009), seasonal variability of nutrients (Honda and Watanabe, 2007; Kawakami *et al*., 2007). Kawakami and Honda (2007) reported that seasonal variability in POC fluxes estimated from ^{234}Th was large (54–179 gC m^{-2} d^{-1}) and annual POC fluxes were estimated to be 31 gC m^{-2} y^{-1} at station K2 (47°N, 160°E). In this dataset, we present vertical profiles of ^{234}Th, POC, and PON in the northern North Pacific. These data will help further understanding of particle dynamics at the euphotic layer.

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3. Water sampling and sample analysis

Samples were collected during 12 cruises of R/V *Mirai*, *Natsushima*, and *Kairei* since October 2002 in the northern North Pacific. The cruises were MR02-K05 Leg2 (Oct.–Nov. 2002; doi: 10.17596/0001778), MR03-K01 (Feb–Mar. 2003; doi: 10.17596/0001783), NT03-07 (Jul. 2003; doi: 10.17596/0000370), KR03-11 (Sep.–Oct. 2003; doi: 10.17596/0001006), NT03-12 (Nov. 2003; doi: 10.17596/0000379), MR04-02 (Mar.–Apr. 2004; doi: 10.17596/0001785), NT04-05 (May–Jun. 2004; doi: 10.17596/0000388), MR04-04 (Aug. 2004; doi: 10.17596/0001786), MR05-04 (Sep.–Oct. 2005; doi: 10.17596/0001793), MR06-03 Leg1 (May–Jun. 2006; doi: 10.17596/0001796), MR06-03 Leg2 (Jun.–Jul. 2006; doi: 10.17596/0001797), MR07-05 (Sep.–Oct. 2007; doi: 10.17596/0001803), and MR08-05 (Oct.–Nov. 2008; doi: 10.17596/0001809).

Seawater samples (30 L) were collected from eight depths between 10 and 200 m by Niskin bottle samplers attached to CTD sensors (SBE 911plus Sea-Bird Electronics Inc., SBE 19plus Sea-Bird Electronics Inc., or 8001-ICTD Falmouth Scientific Inc.) that recorded salinity, temperature, and depth. The seawater samples were filtered through polypropylene cartridge filters with a pore size of 0.8 μm (for dissolved ^{234}Th) and Whatman GF/F glass fiber filters (0.7 μm nominal pore size) of 25-mm diameter (for chlorophyll *a*). Filtering was done on board the research vessel immediately after collection. After filtration, water samples were acidified to pH 1 by the addition of concentrated HCl solution, and the ^{230}Th yield tracer (2.5 dpm) and 100 mg of Fe (as $FeCl_3$) were added. After the samples were shaken and allowed to stand for about half a day, ammonia was added to the water samples to precipitate the iron. The coprecipitated ^{234}Th and iron in the water samples were collected using polypropylene cartridge filters with pore size of 3 μm. Particulate samples for the analysis of ^{234}Th, POC, and particulate organic nitrogen (PON) content were taken from the same depths as the seawater samples using *in situ* pumping systems (Large Volume Pump WTS-6-1-142V, McLane Inc.). At each depth, approximately 200 L of seawater was filtered through a pre-combusted (450 °C for 4 h) glass-fiber filter with a nominal pore size of 0.7 μm. In addition, approximately 1000 L of seawater was filtered through a pre-washed (0.1N HCl) nylon mesh screen filter with a nominal pore size of 53 μm (first filter) and a pre-combusted glass-fiber filter with a nominal pore size of 3 μm (second filter). Soon

after sampling, particles larger than 53 μm were rinsed from the nylon mesh screen onto a pre-combusted Whatman 47 mm GF/F filter with a nominal pore size of 0.7 μm. Sinking particles were sampled by PITS-type drifting sediment traps (Knauer *et al*. 1979), which were deployed at depth of 55, 100, 150, and 200 m for 24 h during each observation. No preservative was added for the deployments. Sinking particles caught in the drifting sediment traps (DST) were filtered through Whatman 47 mm GF/F filters for ^{234}Th and pre-combusted 25 mm GF/F filters for POC. Although zooplankton that sometimes appeared in DST samples were removed with forceps, it is possible that some contamination with zooplankton carbon occurred.

^{234}Th beta background for glass-fiber filters was reported to be likely higher than that for quartz fiber filters (Benitez-Nelson *et al*., 2001; Buesseler *et al*., 2001b); however, because in this study we conducted beta-counting for particulate ^{234}Th without the filter after the purification, this background was negligible.

For POC and PON measurement, a stainless-steel cork borer was used to cut out subsamples of diameter 21 mm from the filter samples delivered by *in situ* pumping. To measure particulate ^{234}Th, the rest of the sample was digested with a mixture of concentrated HCl and HNO_3 (3:1, v/v) in the presence of the ^{230}Th yield tracer (2.5 dpm). Radiochemical separation and purification of these nuclides were achieved by procedures similar to those of Anderson and Fleer (1982) using the anion exchange technique. A column separation was carried out on board to remove ^{238}U from the dissolved samples within two days after the iron precipitation. The rest of the sample purification for determination of dissolved and particulate ^{234}Th was performed in the land-based laboratory.

In the laboratory, ^{234}Th of each phase was electroplated onto stainless-steel planchets (Narita *et al*., 2003). The planchets were covered with polyethylene sheets (50 μm thick) and first beta-counted using a low-background (0.1–0.3 cpm) anticoincidence gas-flow beta detector (LBC-470, Aloka Co. Ltd.) to determine their ^{234}Th activity, and then alpha-counted with silicon surface barrier detectors (Octéte, Seiko EG&G Co. Ltd.) to determine the yield from the ^{230}Th activity. The recovery of ^{230}Th usually ranged from 25% to 55%. The concentration of ^{234}Th was calibrated against deep-water samples equilibrated with ^{238}U. The analytical precisions (1σ) for dissolved and particulate ^{234}Th determinations were about 3.5% and 4.5%, respectively.

Samples for POC and PON analysis were stored in a freezer before analysis. POC

and PON were measured with an elemental analyzer (Model 2400II, PerkinElmer Inc.). Before measurement, the samples were treated with concentrated HCl vapor for 24 h to remove calcium carbonate and dried at 50 °C for 3 h. The repeatability (1σ) of POC and PON measurements was usually less than 3%.

The concentration of chlorophyll *a* in seawater samples was measured by fluorometric determination (Suzuki and Ishimaru, 1990). The precision (1σ) based on replicated measurements was usually better than 3%.

3. Dataset

Data obtained from cruises were electrically compiled as an excel file "234Th_data_2002-2008.xls", and were depth, potential temperature (Theta), salinity, potential density (Sigma-theta), POC, PON, particulate ^{234}Th (P-234Th), dissolved ^{234}Th (D-234Th), and chlorophyll *a*. The data of depth, potential temperature, salinity, and potential density were measured by CTD sensors. The error of P-234Th and D-234Th was estimated from counting error. In the size fraction data sheet, POC and ^{234}Th of particles >3 μm were calculated from the sum of >53 μm particles (on nylon mesh screen) and 3–53 μm particles (on 3 μm glass-fiber filter). In the drifting sediment trap data sheet, the ratio of POC and particulate ^{234}Th in the sinking particles (POC/234Th-p) was shown.

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References

Amiel, D., Cochran, J.K., Hirschberg, D.J., 2002. $^{234}Th/^{238}U$ disequilibrium as an indicator of the seasonal export of particulate organic carbon in the North Water. Deep-Sea Research II 49, 5191–5209.

Anderson, R.F., Fleer, A.P., 1982. Determination of natural actinides and plutonium in marine particulate material. Analytical Chemistry 54, 1142–1147.

Bacon, M.P., Cochran, J.K., Hirschberg, D., Hammar, T.R., Fleer, A.P., 1996. Export flux of carbon at the equator during the EqPac time-series cruises estimated from ^{234}Th measurements. Deep-Sea Research II 43, 1133–1154.

Benitez-Nelson, C., Buesseler, K.O., Karl, D.M., Andrews, J., 2001. A time-series study of particulate matter export in the North Pacific Subtropical Gyre based on ^{234}Th: ^{238}U disequilibrium. Deep-Sea Research I 48, 2595–2611.

Buesseler, K.O., 1998. The decoupling of production and particulate export in the surface ocean. Global Biogeochemical Cycles 12, 297–310.

Buesseler, K.O., Bacon, M.P., Cochran, J.K., Livingston, H.D., 1992. Carbon and nitrogen export during the JGOFS North Atlantic Bloom Experiment estimated from ^{234}Th: ^{238}U disequilibria. Deep-Sea Research I 39, 1115–1137.

Buesseler, K.O., Andreews, J.A., Hartman, M.C., Belastock, R., Chai, F., 1995. Regional estimates of the export flux of particulate organic carbon derived from thorium-234 during the JGOFS EqPac program. Deep Sea-Research II 42, 777–804.

Buesseler, K.O., Ball, L., Andreews, J., Benitez-Nelson, C., Belastock, R., Chai, F., Chao, Y., 1998. Upper ocean export of particulate organic carbon in the Arabian Sea derived from thorium-234. Deep-Sea Research II 45, 2461–2487.

Buesseler, K.O., Ball, L., Andreews, J., Cochran, J.K., Hirschberg, D.J., Bacon, M.P., Fleer, A., Brzezinski, M., 2001a. Upper ocean export of particulate organic carbon and biogenic silica in the Southern Ocean along 170°W. Deep-Sea Research II 48, 4275–4297.

Buesseler, K.O., Benitez-Nelson, C., Rutgers van der Loeff, M., Andrews, J., Ball, L., Crossin, G., Charette, M.A., 2001b. An intercomparison of small- and large-volume techniques for thorium-234 in seawater. Marine Chemistry 74, 15–28.

Charette, M.A., Moran, S.B., Bishop, J.K.B., 1999. ^{234}Th as a tracer of particulate organic carbon export in the subarctic northeast Pacific Ocean. Deep-Sea Research II 46, 2833–2861.

Coale, K.H., Bruland, K.W., 1985. ^{234}Th: ^{238}U disequilibria: within the California Current. Limnology and Oceanography 30, 22–33.

Cochran, J. K., Barnes, C., Achman, D., Hirschberg, D. J., 1995. Thorium-234/Uranium-238 disequilibrium as an indicator of scavenging rates and particulate organic carbon fluxes in the northeast water polynya, Greenland. Journal of Geophysical Research, 100, 4399–4410.

Coppola, L., Roy-Barman, M., Mulsow, S., Povinec, P., Jeandel, C., 2005. Low particulate organic carbon export in the frontal zone of the Southern Ocean (Indian sector) revealed by ^{234}Th. Deep-Sea Research I 52, 51–68.

Honda M.C., Watanabe, S., 2007. Time-series water sampling by Remotely Access Sampler (RAS) and its application for the study of biogeochemical cycle. Journal of Oceanography 63, 349–362.

Honda, M.C., Imai, K., Nojili, Y., Hoshi, F., Sugawara, T., Kusakabe, M., 2002. The biological pump in the northwestern North Pacific based on fluxes and major components of particulate matter obtained by sediment-trap experiment (1997-2000). Deep-Sea Research II 49, 5595–5625.

Honda, M.C., Kawakami, H., Sasaoka, K., Watanabe, S., Dickey, T., 2006. Quick transport of primary produced organic carbon to the ocean interior. Geophysical Research Letter 33, 10.1029/2006GL026466.

Honda, M.C., Sasaoka, K., Kawakami, H., Matsumoto, K., Watanabe, S., Dickey T.D., 2009. Application of underwater optical data to estimation of primary productivity. Deep-Sea Research I 56, 2281–2292.

Kawakami, H., Honda, M. C., 2007. Time-series observation of POC fluxes estimated from ^{234}Th in the northwestern North Pacific. Deep-Sea Research I 54, 1070–1090.

Kawakami, H., Honda, M.C., Wakita, M., Watanabe, S., 2007. Time-series observation of dissolved inorganic carbon and nutrients in the northwestern North Pacific. Journal of Oceanography 63, 967–982.

Kemp, A.E.S., Pike, J., Pearce, R.B., Lange, C.B., 2000. The "Fall dump" – a new perspective on the role of a "shade flora" in the annual cycle of diatom production and export flux. Deep-Sea Research II 47, 2129–2154.

Knauer, G.A., Martin, J.H., Bruland, K.W., 1979. Fluxes of particulate carbon, nitrogen, and phosphorus in the upper water column of the northeast Pacific. Deep-Sea Research A 26, 97–108.

Lee, C., Murray, D.W., Barber, R.T., Buesseler, K.O., Dymond, J., Hedges, J.I., Honjo, S., Manganini, S.J., Marra, J., Moser, C., Peterson, M.L., Prell, W.L., Wakeham, S. G., 1998. Particulate organic carbon fluxes: compilation of results from the 1995 US JGOFS Arabian Sea Process Study – By the Arabian Sea Carbon Flux Group. Deep-Sea Research II 45, 2489–2501.

Louanchi, F., Najjar, R.G., 2000. A global monthly climatology of phosphate, nitrate, and silicate in the upper ocean: Spring-summer export production and shallow remineralization. Global Biogeochemical Cycles 14, 957–977.

Michaels, A.F., Bates, N.R., Buesseler, K.O., Carlson, C.A., Knap, A.H., 1994. Carbon-cycle imbalances in the Sargasso Sea. Nature, 372, 537–540.

Murray, J.W., Young, J., Newton, J., Dunne, J., Chapin, T., Paul, B., 1996. Export flux of particulate organic carbon from the central equatorial Pacific determined using a combined drifting trap-^{234}Th. Deep-Sea Research II 43, 1095–1132.

Narita, H., Abe, R., Tate, K., Kim, Y-I., Harada, K., Tsunogai, S., 2003. Anomalous large scavenging of ^{230}Th and ^{231}Pa controlled by particle composition in the northwestern North Pacific. Journal of Oceanography 59, 739–750.

Rutgers van der Loeff, M.M., Friedrich, J., Bathmann, U.V., 1997. Carbon export

during the spring bloom at the southern polar front, determined with the natural tracer ^{234}Th. Deep-Sea Research II 44, 457–478.

Saito, H., Tsuda, A., Kasai, H., 2002. Nutrient and plankton dynamics in the Oyashio region of the western subarctic Pacific Ocean. Deep-Sea Research II 49, 5463–5486.

Smetacek, V.S., 2000. The giant diatom dump. Nature, 406, 574–575.

Takahashi, T., Sutherland, S.C., Sweeny, C., Poisson, A., Metzl, N., Tilbrook, B., Bates, N., Wanninkhof, R., Feely, R.A., Sabine, C., Olafsson, J., Nojiri, Y., 2002. Global sea-air CO_2 flux based on climatological surface ocean pCO_2, and seasonal biological and temperature effects. Deep-Sea Research II 49, 1601–1622.

Tsunogai, S., Noriki, S., 1991. Particulate fluxes of carbonate and organic carbon in the ocean. Is the marine biological activity working as a sink of the atmospheric carbon?. Tellus 43B, 256–266.

Wong, C.S., Waser, N.A.D., Nojiri, Y., Whitney, F.A., Page, J.S., Zeng, J., 2002. Seasonal cycles of nutrients and dissolved inorganic carbon at high and mid latitudes in the North Pacific Ocean during the *Skaugran* cruises: determination of new production and nutrient uptake ratios. Deep-Sea Research II 49, 5317–5338.

Yamaguchi, A., Watanabe, Y., Ishida, H., Harimoto, T., Furusawa, K., Suzuki, S., Ishizaka, J., Ikeda, T., Takahashi, M.M., 2002. Structure and size distribution of plankton communities down to the greater depths in the western North Pacific Ocean. Deep-Sea Research II 49, 5513–5530.