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Druffel, Ellen RM
Williams, Peter M

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warming in UCHI is 0.39 °C, considerably higher than that in RCHI. For this region, UCHI is the only series for which warming is statistically significant. The Chinese results may, at first glance, seem somewhat surprising, as 24 of the stations used in ref. 1 are among the 42 urban sites. In refs 1 and 4, average temperatures for these sites generally come from airport sites, which may be in rural areas. In many parts of the world, city-centre observatories were relocated to airport sites during the 1950s and 1960s. That temperature records from many sites are a combination of information from various locations within a city or town emphasizes the need to assess the homogeneity of individual site records[5,6].

In none of the three regions studied here is there any indication of significant urban influence in either of the two gridded series[1,2,4] relative to the rural series. Earlier work on the contiguous United States[9,10] showed an urban influence of 0.15 °C over the period 1901-84. (The results of this work are summarized in Table 1.) The United States result therefore does seem to be somewhat atypical compared with other industrialized regions of the world. The results from the United States clearly represent an upper limit to the urban influence on hemispheric temperature trends.

In total, the three regions and the contiguous United States encompass 82 grid points (22 over the western USSR, 14 over eastern Australia, 16 over eastern China and 30 over the contiguous United States) on a resolution of 5° latitude by 10° longitude. The three Northern Hemisphere regions in total comprise about 20% of the landmass of the hemisphere, and the eastern Australian region comprises 10% of the landmass in the Southern Hemisphere. Thus there seems to be little urbanization influence in three regions of the world that, when taken together, are twice the size of the contiguous United States.

It is unlikely that the remaining unsampled areas of the developing countries in tropical climates, or other highly populated parts of Europe, could significantly increase the overall urban bias above 0.05 °C during the twentieth century. A bias of this order is an order of magnitude smaller than the hemispheric and global-scale warming trend observed over the last 100 years. The bias will be further halved in hemispheric and global temperature estimates that incorporate marine as well as land temperatures.

We emphasize, however, that our results do not imply that urban warming influences in observations of local temperature will remain inconsequential in global averages in the future. Indeed, careful selection, inspection and monitoring for urbanization influences in the climate record will be required. This concern could be greatly lessened by an international effort to monitor and place observing stations outside urban areas. □

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Identification of a deep marine source of particulate organic carbon using bomb [14]C

Ellen R. M. Druffel* & Peter M. Williams†

* Woods Hole Oceanographic Institution, Woods Hole, Massachusetts 02543, USA
† Scripps Institution of Oceanography, University of California at San Diego, La Jolla, California 92093, USA

THE influx of bomb radiocarbon (^{14}C) into the oceanic food chain has been evaluated by radiocarbon dating of pelagic organisms in the North Pacific[1,2]. These studies found a significant gradient with depth of $\Delta^{14}C$ (the per mil deviation from the 'standard' activity of nineteenth century wood). Such a gradient is not expected according to long-standing assumptions about carbon cycling in the water column[3-5]; instead, one could expect the $\Delta^{14}C$ of organisms throughout the water column to have become equal to that in surface-water dissolved inorganic carbon (DIC) by about 1970 (10–20 years after the production of bomb radiocarbon). Here we present $\Delta^{14}C$ values measured in the profiles of suspended and sinking particulate organic carbon (POC) from an open-ocean site and a coastal basin. The ^{14}C activity of suspended POC decreases significantly with depth, as is observed in organisms, whereas that of sinking POC is only slightly lower than that in surface DIC and surface suspended POC. All POC $\Delta^{14}C$ results, however, are greater than the corresponding pre-bomb, surface-derived DIC values, and therefore contain bomb [14]C. This decrease in ^{14}C activity requires a deep source (or sources) of carbon to sub-surface POC pools. Adsorptive processes involving low-^{14}C-activity dissolved organic carbon (DOC) may provide a mechanism for lowering $\Delta^{14}C$ values in suspended and (to a lesser extent) sinking POC.

$\Delta^{14}C$ of POC and DOC was measured in samples collected from two areas in the North Pacific Ocean. An oligotrophic site (31°00′ N, 159°00′ W) in the North Central Pacific (NCP) was occupied during June–July 1987 (bottom depth 5,760 m) and a series of profiles was taken from May 1986 to October 1987 in the centre of the Santa Monica Basin (SMB), a moderately eutrophic basin off the coast of California (33°50′ N, 118°50′ W, bottom depth 900 m). Suspended POC was collected using in situ pumps[6] deployed for 2-8 hours at eleven depths in the North Central Pacific during 1987 and for 2-6 hours at four depths in the Santa Monica Basin during October 1986. During each deployment, 600–4,500 l of sea water were filtered through 0.8-μm pore-diameter, pre-combusted quartz-fibre filters (Whatman ultra-pure QM-A), which were then frozen at −20 °C. Sinking POC was collected at 600 m and 1,600 m from the bottom (5,165 and 4,165 m depth) in the North Central Pacific and at 100 or 200, 500, 700 and 850 m depths in the Santa Monica Basin using paired Soutar traps[7] deployed for periods of two weeks (North Central Pacific) and three months (Santa Monica Basin). Mercuric chloride was used in all deployments as a trap poison. Sinking POC in the North Central Pacific samples was concentrated by filtration onto pre-combusted quartz filters. The filters were acidified with 5% H_3PO_4 for 24 h to remove the carbonates, dried under vacuum and combusted in double quartz tubes with CuO and silver according to standard techniques[8]. Aliquots of the sinking POC from SMB samples were acidified with 5% H_3PO_4 and dried at 60 °C before combustion as above. The Santa Monica Basin seawater samples were filtered on board ship from a 12-l Go-Flo Niskin bottle, and DOC was oxidized in the laboratory to CO_2 by photo-oxidation using previously reported techniques[9]. DIC was extracted from 150-ml aliquots (SMB) of the above unfiltered Niskin samples after acidification with 5% H_3PO_4, or absorbed into $SrCl_2$–NH_4OH solution on board ship from 200 l of the NCP Gerard

barrel samples after acidification with concentrated H_2SO_4 (ref. 10). These latter CO_2 samples were measured by conventional gas proportional-counting techniques[11]. The CO_2 from DIC (SMB), DOC and POC were converted to graphite[12], and ^{14}C was measured using accelerator mass spectrometry (AMS) at the University of Arizona[13].

The suspended POC $\Delta^{14}C$ values in the North Central Pacific ranged from $+139 \pm 9‰$ at 20 m to $+43 \pm 28‰$ at 5,700 m, and decreased gradually from the surface to the deep sea (Fig. 1a). The value at 20 m is equivalent to the average of sixteen $\Delta^{14}C$ measurements of DIC ($+132 \pm 6‰$ (1σ)) from 3-m samples taken every other day throughout the 1987 cruise. Similarity of $\Delta^{14}C$ values in the euphotic zone indicates that suspended POC had been formed recently during photosynthetic fixation of DIC in the surface waters.

$\Delta^{14}C$ of sinking POC collected in 1987 from the North Central Pacific was $+99 \pm 12$ and $136 \pm 14‰$ at 4,165 and 5,165 m depth, respectively. The 4,165-m sample had an activity 81‰ higher than that of suspended POC from the same depth, and the 5,165 m value was higher by 86‰, indicating that rapidly sinking, surface-derived particles contribute to the ^{14}C activity of abyssal POC. These elevated ^{14}C activities in the North Central Pacific sinking POC relative to the corresponding suspended POC suggest that there is more reworking within the suspended POC pool than within the sinking pool, so that fewer labile constituents (recently derived from surface waters) remain in the suspended POC pool than in the sinking POC.

$\Delta^{14}C$ profiles of POC in the Santa Monica Basin are shown in Fig. 1b. Sinking POC $\Delta^{14}C$ values from three cruises (May 1986, October 1986 and October 1987) display a decrease from an average of $+86 \pm 11‰$ ($N = 2$) at 100 m to an average of $+41 \pm 10‰$ ($N = 3$) at 850 m. The differences between these profiles are significant and are apparently not solely a function of the seasonal cycle. The $\Delta^{14}C$ values at 100 m and 200 m for the sinking (78 ± 8, 94 ± 8 and $101 \pm 8‰$) and suspended ($110 \pm 13‰$) POC at the 900-m station in the Santa Monica Basin are similar to that of the DIC at 5 m ($96 \pm 6‰$), indicating that both POC phases are recent products of photosynthetically produced carbon from surface-water DIC. The sinking POC $\Delta^{14}C$ values are biased, however, because of appreciable numbers of small
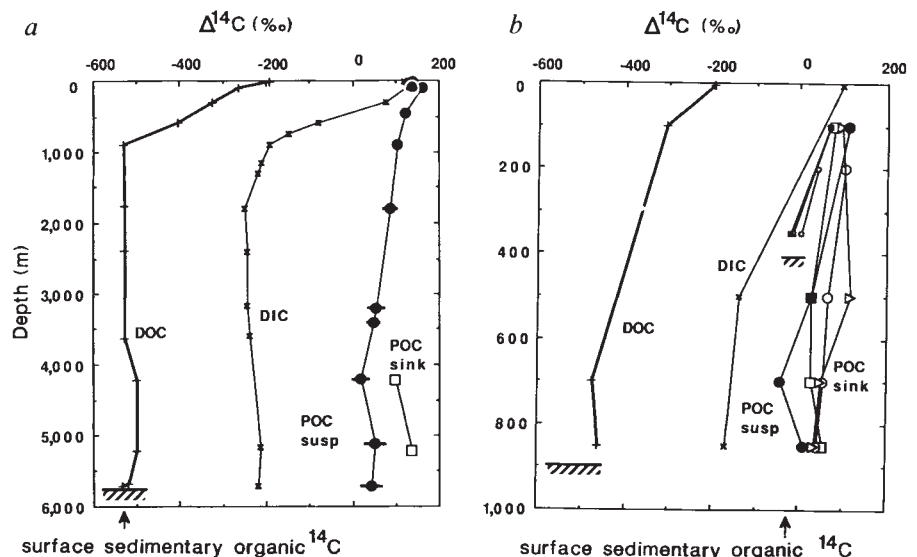
(<1 cm) swimmers in these shallow (100 m, 200 m) trap samples. These swimmers, primarily copepod nauplii, are estimated to account for 10–20% of the total carbon measured.

The $\Delta^{14}C$ values for suspended POC in the Santa Monica Basin were significantly lower than those for all three sinking POC $\Delta^{14}C$ profiles, where the largest difference found between sinking and suspended samples was from the same cruise (October 1986; suspended $\Delta^{14}C$ was 42–120‰ lower). These lower $\Delta^{14}C$ values are due at least in part to episodic resuspension of surficial sediment from the shelf[15,16], which carries low ^{14}C-activity sediment into the Basin. This is consistent with the lower $\Delta^{14}C$ values measured for suspended and sinking POC collected at 100 or 200 and 350 m from the eastern shelf of the basin in 400-m-deep water (Fig. 1b). Both the $\Delta^{14}C$ results from the shelf and other chemical data, including $\delta^{13}C$ and $\delta^{15}N$ signatures[15], suggest that terrestrial input from the Los Angeles area into the basin waters was minimal, at least during the 1986–87 period. Given the differences in many physical, chemical and biological properties between the NCP and SMB sites, there is a remarkable correspondence in their DOC and suspended and sinking POC ^{14}C activities (Fig. 1), both in profile and in ^{14}C content. Total ultraviolet-oxidizable DOC and suspended POC concentrations below the photic zone are similar at comparable depths at both sites. It is clear that open-ocean ultraviolet-oxidizable DOC is being recycled into the coastal basin and that local perturbations, including higher productivity, do not necessarily dominate deep-basin organic chemistry.

All of the sinking and suspended POC $\Delta^{14}C$ values in the North Central Pacific and Santa Monica Basin are greater than the corresponding pre-bomb surface DIC values of $-50‰$ (ref. 17) and $-70‰$ (ref. 18), respectively. This reflects the presence of post-bomb, and thus surface-derived, carbon acquired within the past 30 years throughout the entire water column in both particulate organic phases. If the residence time of suspended POC is the same as that determined for suspended particles[5] using thorium isotope measurements (5–10 yr), we must assume that suspended POC has turned over at least 2–3 times during the 30-yr lifetime of bomb radiocarbon in the oceans. Furthermore, if all of the POC was surface-derived, we would not expect to see a gradient in $\Delta^{14}C$ from surface to deep. We believe that,

FIG. 1 a, $\Delta^{14}C$ of suspended POC, sinking POC, DIC and DOC as a function of depth at 31°00′N, 159°00′W (North Central Pacific). The value plotted at 1,800 m for the suspended POC is an average of two $\Delta^{14}C$ analyses ($110 \pm 15‰$ and $62 \pm 15‰$). Symbols on the DOC and DIC profiles are from cruise Eve-1, June–July 1987, with the exception of the four symbols between 1,800 m and 3,600 m on the DIC profile, which are from cruise Alcyone-5, October 1985[9]. The shallowest suspended POC value is at 20 m depth. b, $\Delta^{14}C$ of suspended POC (●, Oct 86), sinking POC (○, Oct 87, ▷, Oct 86, □, May 86), DIC (×) and DOC (+) as a function of depth at 33°50′N, 118°50′W (Santa Monica Basin). Small open symbols represent $\Delta^{14}C$ of sinking and suspended POC (as described above) at a 400-m-deep eastern shelf station.

METHODS. $\Delta^{14}C$ of POC were determined using AMS techniques and are corrected to a $\delta^{13}C$ of $-25‰$ (ref. 14). $\delta^{13}C$ of POC was measured on CO_2 obtained from the closed-tube combustion step. Errors for the AMS $\Delta^{14}C$ measurements are ± 5–8‰ and those for the conventional $\Delta^{14}C$ measurements are $\pm 2‰$. $\Delta^{14}C$ values are corrected for blank CO_2 from the quartz combustion tubes and quartz filters. Blanks composed 1–15% of the sample CO_2 volumes, and had $\Delta^{14}C$ values of blank CO_2 samples averaging $-480‰$. The error in $\Delta^{14}C$ for POC is less than or equal to its symbol size except as noted by horizontal bars.

a $\Delta^{14}C$ (‰)

b $\Delta^{14}C$ (‰)

surface sedimentary organic [14]C

surface sedimentary organic [14]C

whereas the 5–10 yr residence time does indeed apply to POC, not all components of the suspended (and to a lesser extent the sinking) POC are directly surface-derived in the two areas studied. This would be consistent with the decrease of ^{14}C activities observed in meso-, bathy- and abyssopelagic fishes and crustaceans[1,2] relative to surface ^{14}C activities.

There are at least three mechanisms that could be responsible for the incorporation of non-surface-derived, low-^{14}C-activity carbon into the suspended and sinking POC pools. First, low-^{14}C-activity DOC may be incorporated into the POC pool by heterotropic uptake of DOC by free-living bacteria in the water column[19]. Also, adsorption of DOC onto sub-micrometre webs used by filter feeders such as pteropods and larvaceans, and onto mucus produced in large amounts by various zooplankton (salps, for example) could have a role in sequestering low-^{14}C-activity DOC (A. Alldredge, personal communication). A mass-balance calculation for the North Central Pacific site requires that only 14% of the deep-sea suspended POC (with an average Δ^{14}C of +46‰ between 1,800 m and 5,700 m) need have originated from deep-sea DOC (average Δ^{14}C of −520‰ for ultraviolet-oxidizable fraction[9]) to have been responsible for the 93% average reduction of surface POC Δ^{14}C values. Fourteen per cent of the deep-sea POC (the mean concentration of which below 1,000 m is ~0.1 μmol l^{-1}) represents only 0.25% of the deep-sea, ultraviolet-oxidizable DOC (~40 μmol l^{-1})[9].

Second, chemosynthetic production of organic matter from DIC has been suggested[20] to occur at depths of 0–2,000 m in the North Pacific. Deep-sea DIC Δ^{14}C values (−240‰ in the North Central Pacific) are also lower than those of POC (Fig. 1a); but a greater portion of the POC (30% or more) would have had to originate by this mechanism to account for the low suspended and sinking POC Δ^{14}C values in the deep sea. The amount of POC resulting from *in situ* chemosynthesis can, however, be estimated[20] to be only about 5% of the particle flux.

Third, the Δ^{14}C value of sedimentary organic carbon (SOC) at the North Central Pacific site (−541‰ in the upper 1 cm of sediment) is comparable to the ^{14}C activities of the ultraviolet-oxidizable DOC in bottom waters. It is difficult to envisage resuspension of SOC as far up into the water column as 1,000 m below the surface at the NCP site, unless it originated from continental-shelf sediments or hydrothermal vent or ridge regions and was advected laterally into the mid-Pacific. In the Santa Monica Basin, however, intermittent resuspension[15,16] of surficial shelf- and/or slope-derived SOC may contribute to the reduced activity of POC in the water column, especially with respect to the suspended particles. The Δ^{14}C activity of this advected material is likely to be similar to that found for surficial SOC at mid-Basin (−10‰, 0–1.25 cm). There is also the possibility of natural oil seeps[22] on the basin slopes and anthropogenic petroleum products[23] contributing dead carbon (Δ^{14}C = −1,000‰) by adsorption onto particles.

The incorporation of DOC into the POC pool, especially the suspended POC, seems the most reasonable mechanism for lowering POC Δ^{14}C, as only a small fraction of the ubiquitous low-^{14}C-activity DOC would suffice to lower the deep-water POC Δ^{14}C values, whatever the mechanism. Quantification of the various processes proposed above are complicated by the presence of an extra fraction of DOC[24] that was previously undetected by conventional oxidative techniques[25]. As yet, there are no Δ^{14}C measurements for this extra DOC, but it is suspected that the values are different from those found for the ultraviolet-oxidizable fraction because of the correlation between DOC concentration and apparent oxygen utilization at some sites[24], and other isotopic evidence[26]. □

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High-pressure geochemistry of Cr, V and Mn and implications for the origin of the Moon

A. E. Ringwood, T. Kato*, W. Hibberson & N. Ware

Research School of Earth Sciences, Australian National University, Canberra, ACT 2601, Australia

CHROMIUM, vanadium and manganese are present in similar abundances in the Earth's mantle and the Moon, and are substantially depleted relative to their Mg-normalized primordial abundances[1-6]. Experimental studies[7,8] of the partitioning of chromium, vanadium and manganese between molten iron and silicates show that these elements are lithophile at the pressures, temperatures and oxygen fugacities prevailing in the Earth's upper mantle and in the Moon. Here, we show that at much higher pressures, corresponding to those in the Earth's lower mantle, the partitioning behaviour of Cr, V and Mn changes owing to increasing solubility of oxygen in molten iron. Cr and V (and perhaps Mn) are preferentially partitioned into molten iron under these conditions. We therefore attribute the depletions of these elements in the Earth's mantle to their siderophile behaviour during formation of the Earth's core, at pressures that were sufficiently high to cause substantial amounts of oxygen to dissolve in molten metallic iron. Similar depletion patterns of Cr, V and Mn in the Earth's mantle and the Moon strongly suggest that a large proportion of the Moon was derived from the Earth's mantle after the Earth's core had segregated.

Chromium, vanadium and manganese are present in near-chondritic abundances (Mg-normalized) in the eucrite parent body[1-3]. Moreover, Cr and Mn are also present in near-chondritic abundances in the shergottite parent body, believed to be Mars[1,4,5]. (The V abundance in the shergottite parent body is poorly constrained.) But these elements are substantially depleted in the Earth's mantle and the Moon[1-6] and the depletion factors in the Earth's mantle and the Moon are remarkably similar. Seifert and Ringwood[6] estimated the Cr/Mg ratios of the Earth's mantle and the Moon to be 0.49 and 0.36–0.40 of

* Present address: Institute of Mineralogy, Petrology and Economic Geology, University of Tohoku, Sendai 980, Japan.