Radiocarbon evidence that carbon from the Deepwater Horizon spill entered the planktonic food web of the Gulf of Mexico

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Received 23 July 2012
Accepted for publication 19 October 2012
Published 6 November 2012
Online at stacks.iop.org/ERL/7/045303

Abstract
The Deepwater Horizon (Macondo) oil spill released large volumes of oil and gas of distinct carbon isotopic composition to the northern Gulf of Mexico, allowing Graham et al (2010 Environ. Res. Lett. 5 045301) to use stable carbon isotopes ($\delta^{13}C$) to infer the introduction of spilled oil into the planktonic food web. Surface ocean organic production and measured oil are separated by 5–7‰ in stable carbon isotope ($\delta^{13}C$) space, while in radiocarbon ($\Delta^{14}C$) space these two potential sources are separated by more than 1000‰. Thus radiocarbon isotopes provide a more sensitive tracer by which to infer possible introduction of Macondo oil into the food web. We measured $\Delta^{14}C$ and $\delta^{13}C$ in plankton collected from within 100 km of the spill site as well as in coastal and offshore DIC (dissolved inorganic carbon or $\text{CO}_2$) to constrain surface production values. On average, plankton values were depleted in $^{14}C$ relative to surface DIC, and we found a significant linear correlation between $\Delta^{14}C$ and $\delta^{13}C$ in plankton. Cumulatively, these results are consistent with the hypothesis that carbon released from the Deepwater Horizon spill contributed to the offshore planktonic food web. Our results support the findings of Graham et al (2010 Environ. Res. Lett. 5 045301), but we infer that methane input may be important.

Keywords: radiocarbon, carbon isotope, petroleum hydrocarbon, methane, Gulf oil spill

1. Introduction

It is estimated that some 750 000 m$^3$ of oil (Adcroft et al 2010) and up to 500 000 m$^3$ of hydrocarbon gas (Joye et al 2011, Kessler et al 2011) were released over the 85 days of the Deepwater Horizon (DWH) oil spill in the northern Gulf of Mexico. This organic material (petro-carbon) contributed to microbial growth in the Gulf potentially affecting higher trophic levels (Hazen et al 2010, Redmond and Valentine 2011). The oil and gas have unique isotopic compositions, both in terms of $\delta^{13}C$ and $\Delta^{14}C$, effectively making the Deepwater Horizon oil spill a large-scale tracer release. Because both oil and gas carbon are depleted in $^{13}C$ relative to surface production, Graham et al (2010) used measurements of $\delta^{13}C$ in plankton to suggest that oil carbon was being transferred into the planktonic food web.

Surface production in the open ocean has a $\delta^{13}C$ value between −20 and −22‰ (Chanton and Lewis 2002, Chasar...
et al. 2005) while Macondo oil $\delta^{13}C$ was measured to be $-27\%e$ (Graham et al. 2010). Thus, the effective distance between possible endmember $^{13}C$ sources to plankton is about 5–7\%e and the difference between surface production and Macondo-methane $^{13}C$ ($-57.4\%e \pm 0.5$, Joyce and Chanton 2011) is about 30\%e. However, differences in $^{14}C$ for these carbon source endmembers are much greater. Surface carbon $\Delta^{14}C$ is in the range of +40\%e, while fossil carbon has an expected $\Delta^{14}C = -999\%e$. Because the endmembers are so well separated, $^{14}C$ provides a much more sensitive tracer to estimate petro-carbon contributions to the planktonic food web. The large pulse of carbon from the spill that has entered the marine environment provides an opportunity to better understand the functioning of coastal ecosystems and investigate the effects of the spill on coastal food webs and fisheries.

2. Materials and methods

Radiocarbon data are expressed in $\Delta^{14}C\%e$ notation, which is defined as the difference between sample activity and an international standard (1950) corrected for age and $^{13}C$ (following Suiver and Polach 1977). We measured $\Delta^{14}C$ values in plankton collected in eleven tows using a 300 $\mu$m net (in all cases) from an area about 100 km north of the DWH well-head from June 2010 through May 2011. Samples from 2010 were not divided into size fractions, while samples from 2011 were filtered through 600 $\mu$m (large fraction) and 125 $\mu$m (small fraction) mesh. Plankton samples were dried at 60°C and treated with dilute HCl to remove carbonates. A 5–10 mg aliquot of dried sample was placed into break seals with 1 g CuO and 0.5 g silver foil. The tubes were then evacuated, flame sealed and combusted at 580°C followed by cryogenic distillation. The evolved CO2 gas (30–100 $\mu$mol) was transferred to individual break seals, analyzed for $\Delta^{13}C$, and then sent to the Woods Hole National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) facility for radiocarbon analysis. The $\delta^{13}C$ values were measured on a CHN analyzer coupled to a Thermoelectron IRMS at the National High Magnetic Field Laboratory.

Dissolved inorganic carbon (DIC) from coastal and offshore waters was analyzed in surface waters collected via Niskin bottles attached to CTD casts. Water samples were acidified with 30% phosphoric acid, brought to gauge pressure with helium, and the water was allowed to equilibrate with the helium. A 10 $\mu$l aliquot of the resulting headspace was direct injected on the GC IRMS for $\delta^{13}C$ analysis. The remaining sample was then vacuum extracted, and the CO2 cryofocused and collected in break seals. The break seals were sent to NOSAMS for $\Delta^{14}C$ analysis. A Student $t$-test was used to compare DIC isotope values for coastal and offshore samples.

3. Results and discussion

Stable carbon isotopes ($\delta^{13}C$) ranged from $-25.3\%e$ to $-20.8\%e$ for all plankton samples (table 1). Radiocarbon values ($\Delta^{14}C$) ranged from $-15.1\%e$ to $+58.2\%e$ and were linearly correlated with $\delta^{13}C$ (figure 1, $r = 0.61$, $p < 0.01$). Lighter $\delta^{13}C$ values in plankton corresponded to more negative $\Delta^{14}C$ values (figure 1). The results indicate the admixture of $^{13}C$ and $^{14}C$ depleted material with modern planktonic water column production. The $\Delta^{14}C$ of DIC from coastal and offshore waters was also similar ($p > 0.1$, $t = 3.182$) and averaged $+41.0\%e \pm 14$ (table 1). Thus, while light

### Table 1. Stable and radiocarbon isotope results for plankton and DIC samples collected from the northern Gulf of Mexico. Size fractions are as described in the text, ‘mixed’ indicates that samples from 2010 were not filtered into separate size fractions and represent composites of total 300 $\mu$m tow contents. DIC were collected in Pensacola and Apalachicola Bays (‘coastal’) and ‘offshore’ in Desoto Canyon.

| Date              | Type     | Latitude | Longitude | $\Delta^{14}C$ | $\delta^{13}C$ |
|-------------------|----------|----------|-----------|----------------|--------------|
| 02 June 2010      | ‘Mixed’  | 30.1609  | 88.1229   | 35.20          | -20.83       |
| 14 June 2010      | ‘Mixed’  | 30.1609  | 88.1229   | 25.58          | -21.28       |
| 14 June 2010      | ‘Mixed’  | 30.0902  | 88.2116   | 44.49          | -21.04       |
| 28 June 2010      | ‘Mixed’  | 30.1609  | 88.1229   | -15.07         | -25.31       |
| 13 July 2010      | ‘Mixed’  | 30.0902  | 88.2116   | 26.20          | -20.82       |
| 20 September 2010 | ‘Mixed’  | 29.7989  | 88.2083   | 58.19          | -22.84       |
| 2 December 2010   | ‘Mixed’  | 30.0902  | 88.2116   | 17.50          | -22.97       |
| 15 May 2011       | 600 $\mu$m | 29.2050  | 87.0006   | 38.02          | -21.10       |
| 15 May 2011       | 125 $\mu$m | 29.2050  | 87.0006   | 25.12          | -22.00       |
| 16 May 2011       | 600 $\mu$m | 30.1670  | 86.6630   | 16.65          | -24.25       |
| 16 May 2011       | 125 $\mu$m | 30.1670  | 86.6630   | -3.39          | -24.43       |
| 17 May 2011       | 600 $\mu$m | 28.8259  | 86.2678   | 44.38          | -20.88       |
| 17 May 2011       | 125 $\mu$m | 28.8259  | 86.2678   | 14.89          | -22.05       |
| 18 May 2011       | 125 $\mu$m | 29.1832  | 87.7487   | -8.16          | -22.15       |
| DIC               | Coastal  | 30.3287  | 87.3142   | 46.86          | 1.60         |
| 29 April 2011     | Coastal  | 30.3287  | 87.3142   | 40.50          | 1.64         |
| 01 May 2011       | Coastal  | 29.6162  | 84.9593   | 36.31          | 0.13         |
| 15 May 2011       | Offshore | 29.2050  | 87.0006   | 39.37          | 1.17         |
| 16 May 2011       | Offshore | 30.1670  | 86.6630   | 39.76          | 1.75         |
| 17 May 2011       | Offshore | 28.8259  | 86.2678   | 37.56          | 2.05         |
| 18 May 2011       | Offshore | 29.1832  | 87.7486   | 43.15          | 1.56         |
| 18 May 2011       | Offshore | 29.2050  | 87.7486   | 45.03          | 1.30         |
The equation of the line fit to the data is $\Delta^{14}C = 9.1x + 226.2$.

$\delta^{13}C$ values in plankton can result from riverine influences (Chanton and Lewis 1999, Fry 2002). $^{14}C$ was not influenced by coastal inputs, supporting the use of $^{13}C$ as a tracer for petro-carbon contributions to foodwebs. The radiocarbon results are consistent with Graham et al (2010) conclusion that the lighter $\delta^{13}C$ they observed in plankton samples is due to the introduction of petroleum carbon into the planktonic food web. The smaller size fraction of plankton had more depleted $\delta^{13}C$ and radiocarbon values, while the larger size fraction had more positive $\Delta^{14}C$. However, $\Delta^{14}C$ for two of the large size fraction samples were still below measured DIC values ($+41\%$) consistent with the hypothesis that petroleum-based carbon of either oil or natural gas origin is influencing both size fractions and making its way into the planktonic food web.

We used a 2 endmember isotope mass balance calculations to evaluate the contributions of fossil carbon for each isotope, $\Delta^{14}C_{%}$ and $\delta^{13}C_{%}$, as shown below:

$$[\text{Plankton observed isotopic value}] = [X \text{ fraction of tissue from fossil carbon input}] \times [\text{fossil carbon isotope value}] + [(1 - X) \text{ fraction of tissue from surface modern carbon input}] \times [\text{surface carbon isotope value}].$$

For radiocarbon endmembers we used $\Delta$ values of 41$\%$ (our DIC average value) for modern surface production and $-999\%$ for fossil petro-carbon. The $^{14}C$ mass balance calculation results indicate that plankton ranged from having no petro-carbon influence to up a high of 5%. For $\delta^{13}C$ we used $-20.4\%$ as a value of modern surface production. This value is the result of the equation fit to the data of figure 1 and it corresponds to a $\Delta^{14}C$ value of 41$\%$. For a petro-carbon endmember we explored two $\delta^{13}C$ values, the petroleum $\delta^{13}C$ value of $-27.2\%$ determined by Graham et al (2010) for weathered oil, and the $\delta^{13}C$ value of $-57.4\%$ determined for Deepwater Horizon-released CH$_4$ (Joye and Chanton 2011). The $\delta^{13}C$ mass balance for the two endmembers of $-20.4\%$ and $-27.2\%$ yielded estimates of petroleum input ranging up to 72%, while the methane-based endmembers of $-20.4\%$ and $-57.4\%$ yielded estimate ranging up to 13.3% petro-carbon in the plankton. Since presumably both the Macondo-methane and petroleum would exhibit similar $\Delta^{14}C$ values of $-999\%$, it would appear from this analysis and the relatively better agreement between the radiocarbon mass balance and the $^{13}C$ mass balance for methane, that perhaps methane was more effective at finding its way into the food web than was petroleum hydrocarbon. Presumably the incorporation of petro-carbon occurred via bacteria that consumed oil and gas and then were themselves incorporated into the planktonic food web.

Acknowledgments

This research was supported by grants from the BP/The Gulf of Mexico Research Initiative through the Florida Institute of Oceanography, the Northern Gulf Institute, the Deep C Consortium administered by Florida State University and by the ‘Ecosystem Impacts of Oil and Gas Inputs to the Gulf (ECOGIG)’ Consortium administered by the University of Mississippi. We thank Yingfeng Xu at the National High Magnetic Field Laboratory for assistance with $^{13}C$ work, and the staff at NOSAMS at Woods Hole for excellent AMS work.

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