

Supporting Information:

Oxygen isotopes ($\delta^{18}\text{O}$) trace photochemical hydrocarbon oxidation at the sea surface

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1. Supplementary Methods and Discussion

1.1 Sample extraction, experimental reproducibility, and QaQc of $\delta^{18}\text{O}_{\text{oil}}$

Surface and deposited oil residues were extracted in a mixture of high-purity dichloromethane and methanol (90:10, v/v). To test potential influence of methanol on the $\delta^{18}\text{O}$ of the oil residue (e.g., potential exchange with OC or carry-over), one deposited oil residue was extracted in three separate trials each using a solvent mixture of dichloromethane and methanol (90:10, v/v) and dichloromethane and acetonitrile (90:10, v/v). Because there was no difference in the $\delta^{18}\text{O}$ composition of the deposited oil residue between solvent mixtures (dichloromethane:methanol = 11.0 ± 0.3 ‰, dichloromethane:acetonitrile = 10.9 ± 0.3 ; $p = 0.8$), the dichloromethane and methanol (90:10, v/v) mixture was used for all surface and deposited oil residues. This test also revealed the experimental reproducibility of $\delta^{18}\text{O}$ for triplicate extractions of the same deposited oil residue to be 0.3‰. Efforts were made to resolve isotopic changes to surface oil in the early stages of oxidation. A batch of sixteen samples with residence times ranging from hours to three days were extracted. These same samples showed first-order exponential growth in oxygen content with increasing residence time on the sea surface (Ward et al., 2018a). However, there was not enough sample mass to resolve a robust $\delta^{18}\text{O}$ value. Based on previous radiocarbon analysis (Aeppli et al., 2012), all carbon in the oil residues can be assumed to be petroleum derived.

Unlike the oil residues, the source oil was not extracted with solvent prior to $\delta^{18}\text{O}$ analysis. This is because the water content in the source oil is negligible, as determined by the Coulometric Karl Fisher technique (Relevant ASTM Methods: D1064, D1533, D6304, D7923). The tests were performed using an Aquapal II by in-house scientists at CSC Scientific Company, the manufacturer of the instrument. The source oil contained $0.02 \pm <0.01\%$ water by mass ($\pm 1\text{SE}$,

N=3), considerably lower than the 0.4% O by mass measured for the source oil. Thus, on average, oxygen from the residual water in the source oil accounts for <5% of total oxygen in the oil.

The oxygen isotope composition of reservoir water in the Macondo well is not known. However, the oxygen isotope composition of water in Miocene-aged reservoirs in the Gulf of Mexico at a similar depth as the Macondo well (~4000 m) is ~3-4‰ (Land and Macpherson, 1992). Conservatively assuming the water content of the source oil was 5% by mass and the isotopic composition was 4‰, the change in the isotopic composition of the source oil when accounting for water (0.2‰), is less than the measurement error of the initial value reported when not accounting for water (0.3‰). Collectively, accounting for water in the source oil had a negligible impact on the oxygen content and isotope composition of the source oil, or the conclusions of the study.

The low water content of the source oil is consistent with expectations based on how the oil was collected and on the water content of other crude oils. The source oil had minimal, if at all, contact with water during collection. It was recovered from an insertion tube that was receiving oil directly from the Macondo well during response operations. Any unbound, free water in the oil was removed via separatory funnels prior to transfer to ampules (see [NIST 2779 certificate](#)). Therefore, the only residual water in the source oil is physically-entrained, emulsified water, which proved to be 0.02% by mass. Similarly, water content in crude oil is known to be very low; the water content of NIST 2722 (heavy sweet crude) and NIST 2721 (light sour crude) is 0.01%.

We took many precautions to minimize absorption of water from the atmosphere onto the capsules during sample preparation and analysis for bulk and isotopic oxygen analysis. All samples and capsules were stored in a desiccator before and after sample prep and then loaded into a pre-warmed sample carousel. These steps minimized absorption as evidenced by the secondary standard results. International reference materials (IAEA 600-602, USGS 35, 42, 43) spanning a $\delta^{18}\text{O}$ range of 75‰ (-3.5 to 71.4 ‰) were analyzed with every sample run and were always within the instrumental error of the known values. These results indicate that water absorption was a negligible contribution to the values reported in this study.

1.2 FTIR analysis

Following exposure to simulated sunlight, the oil in the dark-control and light-exposed treatments was dried with pre-combusted sodium sulfate, solvent exchanged with spectrophotometric grade 1,1,2-trichloroethene, transferred to a 390 μm , potassium bromide, liquid infrared-cell (Harrick Scientific), and analyzed on a Bruker Vertex 70 Fourier transform infrared spectrophotometer. Carbonyl stretching at 1712 cm^{-1} and hydroxyl stretching at 3412 cm^{-1} were normalized to methylene stretching at 2926 cm^{-1} , the tallest peak in the spectrum.

1.3 Isotopic fractionation of $\delta^{18}\text{O}_{\text{O}_2}$ during photochemical oxidation

To determine $\delta^{18}\text{O}$ of O atoms solely by reaction of oil with dissolved O_2 , we characterized closed-system changes in the $\delta^{18}\text{O}_{\text{O}_2}$ with increasing photochemical dissolved O_2 consumption. A 100 μL oil film was placed along the inside of 160 mL borosilicate serum vials, filled completely with air-equilibrated synthetic seawater (no headspace), and exposed in the Atlas XLS+ for up to twelve hours. A similar approach was repeated for Martha's Vineyard Sound dissolved organic carbon

(DOC). Surface water was collected from the Environmental Systems Laboratory at Woods Hole Oceanographic Institution, filtered to isolate the operationally defined 0.22 μm dissolved size fraction (Millipore), and irradiated in the solar simulator for up to 48 hours alongside dark controls.

Following irradiation, the $\delta^{18}\text{O}$ of the remaining dissolved O_2 was measured by headspace equilibration (Sutherland et al., 2018). Headspace was created by injection of five mL of ultra-high purity helium into the serum vials, which were equilibrated on a shaker table (120 rpm) at room temperature (22°C) for at least one hour prior to sampling. An aliquot of the headspace gas was sampled using a gas-tight, He-flushed syringe and injected into a modified TraceGas preparation system (Elementar) with manual gas injection-port. Sample O_2 was chromatographically separated from N_2 using a 5\AA molecular sieve column, with continuous monitoring of masses 32, 33, and 34 on a 10-collector IsoPrime 100 isotope ratio mass spectrometer (IRMS) used for calculation of $\delta^{18}\text{O}$ values. Sample isotopic ratios were referenced against laboratory air, which was assumed to be +23.88 per mil (Barkan and Luz, 2005). Simultaneous IRMS monitoring of mass 28, 29, 30 and 40 also allowed determination of N_2 and Ar, respectively.

The fraction of dissolved O_2 remaining was quantified as the ratio of O_2/Ar (Kana et al., 1994), and Rayleigh fractionation of $\delta^{18}\text{O}_{\text{O}_2}$ was quantified using equation S1:

$$\frac{{}^{18}R}{{}^{18}R_0} = f^{18\alpha-1} \quad (\text{S1})$$

where f is the fraction of oxygen remaining (relative to dark-controls), ${}^{18}R$ is the ${}^{18}\text{O}:{}^{16}\text{O}$ isotope ratio at f , and ${}^{18}R_0$ is the isotope ratio of the dark-controls. By plotting $-\ln(f)$ versus

$1000 \cdot \ln(^{18}R/^{16}R_o)$ (Fig. 2c), the isotope effect, $^{18}\epsilon_{\text{oxidation}} (^{18}\alpha-1)$, is determined from the slope. No differences were observed in the oxygen content and isotopic composition between the dark-controls and initial conditions measured immediately after preparing the vials (data not shown). Therefore, we calculated the isotope effect of photochemical oxidation relative to the dark-controls rather than the initial conditions.

1.4 Clarification of the relationship between $\delta^{18}\text{O}_{\text{Oil}}$ and residence time

There are many competing hypotheses to explain the plateaued elemental oxygen content (Ward et al., 2018a) and $\delta^{18}\text{O}_{\text{Oil}}$ after floating for ~five days on the sea surface (Figure 2A in the main text). First, as the surface oil weathered, the film thickness increased from $< 1 \mu\text{m}$ to mm. UV light penetrates only tens of microns, whereas visible light penetrates ~100 microns into an oil film. Therefore, it is probable that photochemical oxidation of the thick surface oil films was limited by self-shading, where the majority of the oil mass does not absorb photons and thus is not oxidized. This hypothesis has previously been proposed (Ward et al., 2018a).

Second, as previously proposed based on laboratory experiments (Lichtenthaler et al., 1989), the rates of photochemical O_2 consumption may exceed the rates of O_2 replenishment, which may, in turn, may limit photochemical oxidation. This is particularly true for thicker, viscous oil films where O_2 diffusion rates are slower. However, in the field we would expect the surface oil to be replenished with O_2 in the evening, resulting in a steady rise in elemental oxygen content and $\delta^{18}\text{O}_{\text{Oil}}$ over time. We did not observe a steady rise in either variable, which suggests that O_2 limitation may not be the primary control on photochemical oxidation.

Third, it is possible that the oil loses its capacity to be photo-oxidized with increasing light exposure. This “dose-dependence” of photochemical oxidation has been observed for other complex organic mixtures, such as dissolved organic carbon (Miller and Zepp, 1995; Cory et al., 2014), but not for crude oil. This potential control is unlikely because the apparent quantum yield for photochemical O₂ uptake was similar for Macondo crude oil and oil that weathered for seven days on the sea surface (Ward et al., 2018a).

Fourth, it is widely known that photochemical oxidation results in the formation of water-soluble compounds (i.e., photo-dissolution). This pathway was first reported in 1974 (Burwood and Speers, 1974). However, as previously discussed (Ward et al., 2018a), no study has quantified apparent quantum yields for the photo-dissolution of surface oil in sunlit waters. Therefore, it is unclear to what extent oxidation of surface oil to water-soluble products impacts the mass balance of the floating oil.

Table S1. Summary of oxygen isotopic composition of organic carbon ($\delta^{18}\text{O}_{\text{oc}}$) reported in this study and in the literature. Colors coded according to Figure 1 in main text. References cited: Gray and Thompson, 1976; Gray and Thompson, 1977; Ramesh et al., 1985; Buhay and Edwards, 1995; Werner et al., 1996; Farquhar et al., 1997; Anderson et al., 1998; Saurer et al., 1998; Barbour et al., 2001; Saurer et al., 2002; McCarroll and Loader, 2004; Matthews, 2010; Tartèse et al., 2016.

Organic Carbon Source	$\delta^{18}\text{O}_{\text{oc}}$ Range (‰)	N
Wood	15 to 28.8	85
Lignin	10.2 to 27.3	58
Cellulose	22 to 33.5	290
Leaf Litter	21	1
Dissolved Organic Matter	4.7 to 10.9	16
Kerogen	13.4 to 14.3	2
Coal	12.7 to 13.5	2
Deepwater Horizon Crude Oil	-0.9 to -0.2	2
Deepwater Horizon Photo-Oxidized Oil	5.5 to 10.2	58
ALL	-0.9 to 33.5	514

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