

Evaluation of Tracers for Use in the International Field Experiment on CO₂ Ocean Sequestration

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Introduction

An international field experiment is scheduled to take place off of the west coast of the big island of Hawaii during the second half of 2001 (Adams, et al., 1999; Herzog, et al., 2000). Scientists representing some dozen institutions in five countries on four continents are expected to participate. The experiment will involve several sub-experiments in which CO₂ will be released at a depth of 800 m as a buoyant liquid at rates of 0.1 to 1.0 kg/s. The releases will each be made for a duration of about one hour using nozzles with differing diameters and numbers of ports. Moored and mobile platforms will be used to measure ambient physical, chemical, biological and sedimentary properties, and the changes in these properties, if any, due to the CO₂ release over a spatial scale of about 100 m. The experiment can be viewed as a full-scale test of one nozzle out of perhaps 100 to 1000 nozzles that could serve a 500 MW coal-fired electric power plant whose total CO₂ flow rate would be of order 100 kg/s.

In this paper we review six tracers that have been considered by participating scientists for measuring the rates of CO₂ mixing and dissolution, two processes which are important for determining the concentrations of excess CO₂ and associated changes in pH. The comparison considers dissolved inorganic carbon (or total carbon, C_T), pH, labeled and natural carbon isotopes (¹³C and ¹⁴C) and two introduced tracers (fluorescent dye and SF₆). The tracers are compared with respect to their ability to trace the injected CO₂, the method of measurement, precision and response time, whether or not the measurement can be performed *in situ*, and other factors such as permitting.

The tracers

When CO₂ is added to seawater it reacts to form aqueous CO₂ and bicarbonate, carbonate and hydrogen ions,



The distribution among the dissociation species is governed by equilibrium constants that depend on temperature and salinity, as well as ambient carbon chemistry parameters such as C_T and alkalinity (Morel and Hering, 1993). While the kinetics of CO₂ dissociation in isolation are quite fast, Zeebe et al. (1999) suggests that the carbon chemistry couples with other chemical systems

in the ocean [e.g., H_2O , $\text{B}(\text{OH})_3$] such that the time constant of the CO_2 dissociation reaction may be much larger than the time constant of any single reaction in the system. They estimate the relaxation time for CO_2 equilibrium at the ocean surface (25°C) is about 16s. While still relatively quick, this time-scale approaches that of some plume processes.

Following dissociation, the carbon that is actually discharged can be found in one of four states, CO_2 , H_2CO_3 , HCO_3^- and CO_3^{2-} , the sum of which is termed dissolved inorganic carbon or total carbon, C_T . Because C_T is conserved, it is a fundamental measure of the perturbation to the system, and hence a logical tracer of the injected CO_2 . C_T is best measured in the lab (on board ship) using coulometry to a precision of about 1-2 μM , which is comparable to ambient variability (see further discussion below). pCO_2 sensors are also available for *in situ* measurements, but their response time appears too slow (Walt, 1993).

Along with possibly pCO_2 itself, pH (the negative log of the H^+ concentration) is one of the important variables determining biological response of injected CO_2 (Angel, 1996; Auerbach et al., 1997). Hence it is also a fundamental tracer. But unlike C_T , pH can be easily measured *in situ*, using, for example, a glass electrode probe (e.g., SeaBird SB-18) or the solid state ISFET probe developed recently by CRIEPI. Probe precision is about 0.03 and 0.01 respectively, and each has a reported time constant of order seconds, though lab experiments by IOS suggest the response time of the SeaBird probe may be closer to 30 s (C.S. Wong, personal communication). *In situ* pH measurements may be complemented by more precise shipboard measurement using photometric techniques with precision of about 0.001. Like C_T , the accuracy of measured pH may be limited by ambient variability in carbon chemistry.

Carbon isotopes can also be used as direct measures of injected CO_2 . ^{13}C is a stable isotope whose concentration, relative to ^{12}C , varies with the source of carbon. The isotopic fraction is written as

$$f = \frac{{}^{13}\text{C}}{{}^{12}\text{C}} \quad (2)$$

or, with relationship to a standard isotope fraction,

$$\delta = \left(\frac{f}{f_{std}} - 1 \right) \times 1000 \quad (3)$$

While the injected ^{13}C is initially associated with the CO_2 , it rapidly becomes equilibrated with the other carbon species, and hence becomes a measure of C_T . Hence by measuring the isotopic fraction, using mass spectrometry, one can infer the concentration of excess CO_2 . The precision in the measurement of delta ^{13}C is about 0.1 per mil, similar to ambient variability.

Radiocarbon, ^{14}C , can also be used as a tracer, and is measured onboard using mass spectrometry. The concentration of ^{14}C in fossil sources of CO_2 is zero so, like ^{13}C , measurements of natural ^{14}C can be used to trace plume concentrations of C_T . However, the precision of such measurements is less than using natural ^{13}C or C_T . Much greater sensitivity

can be obtained if ^{14}C is added to the discharge by labeling some of the injected CO_2 . Although the resulting radioactivity is small compared with ambient radioactivity, e.g., from ^{40}K , a drawback of using labeled ^{14}C is the public perception of adding radioactivity to the ocean.

Water-soluble fluorescent dyes such as fluorescein and Rhodamine WT are frequently used as tracers. Illuminated by incident light of a specified excitation frequency, they re-emit light at a lower emission frequency. Fluorometers can be used to rapidly measure fluorescent tracers *in situ* as part of a standard instrument package (i.e., along with temperature, conductivity, pressure, pH) with a precision of order 0.1 ppb. If injected passively as a neutrally buoyant solution near the nozzle, the dye will become entrained in the rising plume, and provide a useful measure of plume entrainment/dilution. However, the CO_2 droplets and the entrained seawater eventually separate, due to effects of ambient stratification (Asaeda and Imberger, 1993; Socolofsky and Adams, 2001a) and/or current (Hugi, 1993; Socolofsky and Adams, 2001b). After separation, the dye will mark the water and not the CO_2 . Indeed, it can be envisioned that, after a certain elevation, most of the entrained seawater will have detrained (peeled) from the plume, taking the dye with it, thus leaving much of the CO_2 droplets to rise without dye. Thus dye is not a good measure of CO_2 fate. However, it can be used as a diagnostic: models that purport to describe plume behavior must be able to represent phase separation and hence measurements of both dye and pH (or C_T) are complementary. Injecting dye in the early part of plume ascent (before peeling) can also serve to determine the rate of CO_2 dissolution, by measuring both pH and fluorescence, as dual tracers. Before peeling, the integrated flux of dye should be conserved, while the integrated flux of excess C_T should increase with elevation, reflecting dissolution of CO_2 . The variation of this ratio can be used to measure variation in CO_2 dissolution with height and, with the help of models, the rate of dissolution with time. Such an experiment is being planned by researchers from CRIEPI.

Finally, SF_6 is another introduced tracer. Using gas chromatograph with electron-capture detection, it can be measured in volumes down to about 10^{-17} mole (Ledwell et al., 1998) or in concentrations about one million times smaller than fluorescent dye. Like dye there is essentially no background concentration. Because of its strong sensitivity, SF_6 has been used to measure oceanic mixing over time scales of a year or more (Ledwell et al., 1998). However, SF_6 must be analyzed on board and hence is not suitable for rapid plume surveying. Like dye, if injected into the entrained seawater, it will mark entrained seawater and not excess C_T *per se*. However, because SF_6 is more soluble in CO_2 than in seawater, it could conceivably be incorporated into CO_2 before injection so as to more directly track injected CO_2 (van Scoy, 1996). In the early phases of our experimental planning (Adams and Herzog, 1997) it was envisioned that an SF_6 experiment would make a nice complementary study of far field mixing and such a study would still be useful as part of a later, more comprehensive, field survey.

The concept of dilution

Because a major objective of a tracer is to measure dilution, we must define dilution. The dilution S of a volume V_o of discharged fluid, mixed with a volume $V_m - V_o$ of ambient fluid, can be written

$$S = \frac{V_m}{V_o} \quad (4)$$

Assuming conservative behavior (no reactions or decay), the concentration of mixed fluid is a weighted average of the discharge concentration and the ambient concentration or

$$C_m = \frac{C_o V_o + C_a (V_m - V_o)}{V_m} \quad (5)$$

Combining with Eq. 4,

$$S = \frac{C_o - C_a}{C_m - C_a} \quad (6a)$$

Eq. 6a can be used directly with C_T , using appropriate values for C_o , C_m and C_a . Since $C_o \gg C_a$, Eq. 6a can be approximated as

$$S \approx \frac{C_o}{C_m - C_a} \quad (6b)$$

Eqs 6a and 6b would also pertain to the introduced tracers (dye and SF_6), to the extent that these trace C_T (see above discussion).

Using pH as a tracer, the change in measured pH relative to ambient, $\Delta pH = pH_a - pH_m$, can be related to the change in C_T (excess C_T), $\Delta C_T = (C_m - C_a)$, as

$$\Delta pH = \alpha \Delta C_T \quad (7)$$

so that Eq. 6b can be written

$$S = \frac{\alpha C_o}{\Delta pH_m} \quad (8)$$

where C_o refers to the discharged concentration of C_T .

If C represents the concentration of $^{12}C \cong C_T$ and fC represents the concentration of ^{13}C or ^{14}C then the fraction of ^{13}C (or ^{14}C) in a mixture can be expressed

$$f_m = \frac{V_o f_o C_o + (V_m - V_o) f_a C_a}{V_o C_o + (V_m - V_o) C_a} \quad (9)$$

Assuming $S \gg 1$, S can be evaluated as

$$S = \frac{V_m}{V_o} = \frac{C_o(\delta_o - \delta_m)}{C_a(\delta_m - \delta_a)} \quad (10)$$

Maximum dilution

The accuracy and sensitivity of the various tracers depends on the accuracy with which the concentrations/pH/isotopic fraction can be measured, and with the associated ambient variability of the concentration/pH/isotope fraction. For example, denoting uncertainty in measured concentration by σ_m and variability in ambient concentration by σ_a , the maximum dilution which can be determined to within a precision of p from measuring C_T , dye or SF_6 concentration, can be determined from Eq. 6b as

$$S_{\max} = \frac{pC_o}{\sqrt{\sigma_m^2 + \sigma_a^2}} \quad (11)$$

When pH is used to measure changes in C_T , the maximum dilution depends on the ambient variability of C_T (denoted by σ_a), the accuracy of the pH measurement (denoted by $\sigma_{\Delta pH}$) and the uncertainty in the relationship between ΔpH and ΔC_T (denoted by σ_α), or

$$S_{\max} = \frac{pC_o}{\sqrt{\sigma_a^2 + (\alpha\sigma_{\Delta pH})^2 + (\sigma_\alpha\Delta pH)^2}} \quad (12)$$

Using carbon isotopes, the limiting dilution comes from Eq. 10. Assuming $(\delta_o - \delta_m) \gg (\delta_m - \delta_a)$, the maximum dilution is

$$S_{\max} = \frac{p(C_o / C_a)\delta_o}{\sqrt{\sigma_{\delta_m}^2 + \sigma_{\delta_a}^2}} \quad (13)$$

Ambient variability

As indicated above, precision in the measurement of dilution by a given tracer reflects spatial and temporal variability in the ambient concentration of the particular tracer. In principle, temporal variability can be eliminated by measuring ambient concentrations during the experiment. Spatially, we focus on vertical variability because it is expected to be much more significant than horizontal variability over the respective scales of the plume. We assume that the plume may mix over a height of order 100 m and that the ambient tracer concentration varies linearly over this height. Because of uncertainty regarding the exact vertical distribution of entrainment into the plume, the associated uncertainty in the average concentration of entrained seawater is taken as 10-20 percent of the plume height (10-20 m) times the gradient in ambient

concentration. Measurements collected by IOS during the ambient survey of August 1999 suggest gradients of ambient C_T concentration of about 0.1 $\mu\text{M}/\text{m}$ (Miller et al., 2000), while corresponding gradients of ambient ^{13}C fraction analyzed by NRL were about 0.1 per mil (Coffin, et al., 1999). The estimated gradient in ambient ^{14}C fraction is 2 per mil (K. Grabowski, personal communication).

Comparison

Table 1 uses Eqs. (11-13) to estimate S_{max} for each of the six tracers, assuming $p = 0.1$. A number of other tracer attributes are also summarized, from which we can draw the following conclusions:

- While the source strength of fluorescent dye and (particularly) SF_6 can be adjusted at will to provide any reasonable level of sensitivity, these tracers monitor the entrained seawater, and not excess C_T ; hence they are not suitable as the primary tracer of the plume. However, by measuring dye along with pH, one has a useful field measurement of CO_2 dissolution, as well as a complementary diagnostic of overall plume behavior.
- With 10% precision, measurement of excess C_T can resolve dilution up to about 10^6 . This corresponds to an estimated average dilution (Eq. 4) in a volume 100m long by 40m wide by 50m high, containing CO_2 discharged at a “low” volume flow rate of $10^{-4}\text{m}^3/\text{s}$ (0.1kg/s) for a period of 2000 s in a current of 5 cm/s. This volume is consistent with 3D numerical predictions of CO_2 plume behavior in a current made (Alendal and Drange, 2001; Sato, 2000). Assuming the same mixing volumes, the estimated average dilution for a “high” volume flow rate of $10^{-3}\text{m}^3/\text{s}$ (1 kg/s) is 10^5 . Thus 100m downstream from the discharge, C_T could resolve the spatial features of a high flow rate plume, but possibly not a low flow rate plume.
- Based on the measured ambient variability and measurement precision of ^{13}C , slightly lower dilutions ($\sim 3 \times 10^5$) can be resolved using natural ^{13}C . The ambient variability of ^{13}C needs to be checked during the actual survey.
- Because the discharge concentration can be adjusted at will (and it traces excess C_T directly) ^{14}C offers considerably more sensitivity. Using a discharge enrichment factor of 100 yields an order of magnitude greater sensitivity than that obtained with C_T or with natural ^{13}C . However, there are several “issues” associated with the use of ^{14}C : how to introduce it to the tank, permitting, and public perception concerning use of radioactive materials.
- ^{13}C , ^{14}C and C_T can not be measured *in situ*, or with real time output, so they must be supplemented with other measurements.
- A pH probe can provide *in-situ*, real time measurements. With in-place calibration, such probes can provide accuracy of 0.01 units, yielding similar dilution sensitivity as obtained with C_T (i.e., accuracy will be limited by spatial variability in C_T). The finite response time of the pH probes could limit spatial resolution somewhat, but any error can be corrected during data analysis. Shipboard measurements of pH should provide useful calibration, but it appears that ambient variability in C_T will control the sensitivity of pH.
- Consistent with the above discussion, our experiment will include four of the six tracers discussed herein: C_T , pH, natural ^{13}C and dye.

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Table 1. Tracer Comparison

Tracer	Method	<i>In-situ?</i>	Real time?	Disch Conc	Amb Conc	Precision	Ambient Var	Max. Dil. S_m	Response Time	Cost/effort
DIC	coulometry	no	no	$C_o \cong 20M$	$C_a \cong 2mM$	$\sigma_m \cong 1 - 2\mu M$	$\sigma_a \cong 1 - 2\mu M$	1E6	NA	moderate
pH	SeaBird	yes	yes	NA	NA	0.03	related to variability in C_T	3E5	15-45s	low
	CRIEPI	yes	yes	NA	NA	0.01		1E6	< 10 s	low
	photometric	no	no	NA	NA	0.001		1E6	NA	moderate
Nat ^{13}C in C_T	MS	no	no	$\delta_o \cong -24$ to -32	$\delta_a \cong 0$	$\sigma_{\delta m} \cong 0.1$	$\sigma_{\delta \alpha} \cong 0.1$	3E5	NA	moderate
Dead ^{14}C	MS	no	no	$\delta_o \cong -1000$	$\delta_a \cong -200$	$\sigma_{\delta m} \cong 10$	$\sigma_{\delta \alpha} \cong 2$	E5	NA	moderate
Lab ^{14}C (100x)	MS	no	no	$\delta_o \cong 10^5$	$\delta_a \cong -200$	$\sigma_{\delta m} \cong 10$	$\sigma_{\delta \alpha} \cong 2$	E7	NA	high
Dye	fluorometer	yes	yes	adjustable	small	.01 to .1ppb	small	adjustable	fast	moderate
SF ₆	GC	no	no	adjustable	v. small	v. high	v. small	v. high	NA	high