Use of SF_6 as a Gas Exchange Rate Tracer in Streams

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Materials Needed

- 5-10 lb tank of SF_6. Price on this varies over short time intervals ($200-$500). A 10 lb tank can last about 5 years (ca.30 reaeration estimates).
- SF_6 regulator.
- Tubing to connect SF_6 regulator to flow meter and air stone.
- Cole-Parmer variable area flow meter with needle valve. Tube is N082-03 with glass float and NPT threaded barbed fittings for tubing.
- Needle valve to precisely control flow. It is not possible to regulate flow without a needle valve. Cole Parmer will give you the calibration curve for air for this flowmeter, but this won't work with heavy SF6--you will need to calibrate it yourself.
- Aquatic Ecosystems Sweetwater AS3 diffuser (has almost no back pressure). Any fine bubble diffuser/airstone will work.
- Wrench to connect SF_6 tank and regulator.
- 60 mL syringes (Fisher# 13-689-8) with 2-way valves -- 1 per SF_6 sample.
- Needles.
- Wheaton 10 mL serum vials (Fisher# 06-406D) with butyl stoppers (Supelco 27232) with aluminum crimps (Supelco 27200). *Note: we also use 7.0 mL BD Vacutainers (BD# 366431 or Fisher# 02-685-B).*
- Equipment needed for chloride or bromide tracer addition and sample collection.
- GC with Electron capture detector set up as follows. Poropak Q column, 6 feet, 80-100 mesh. High-purity N_2 carrier gas at 39 mL/min.
- Gas-tight syringe for injecting 0.1 mL samples into GC.

Methods

Before going to the field:

- Set-up SF_6 tank, regulator, tubing, and flow meter to check for any missing parts.
- Pre-evacuate serum vials or vacutainers.
- Pre-label syringes and serum vials or vacutainers.

In the field:

- Bubble SF_6 through the airstone in-stream at a spot good for mixing.
  - We use about 100 mL/min for a 50-200 L/s stream.
  - In a big stream (say 1000 L/s) we increase to 200-300 ml/min.
  - Mixing may be a problem in big, shallow streams.
- At the same time add chloride or bromide tracer to 1-20 mg Cl/L or 50 µg Br/L.
- Wait for equilibrium downstream (easy to find if you use a hand-held meter to watch for increasing conductivity). Do not turn off SF_6 or tracer until sampling is finished.
- After equilibrium downstream, collect triplicate SF_6 samples from 6 sites downstream of where SF_6 will be fully mixed into the water column.
  - Add 45 mL of water into a 60-mL plastic syringe equipped with a 2-way valve ensuring that there are few gas bubbles in the syringe.
- Collect water samples for salt tracer and analyze on an ion chromatograph.
  - If mixing is a problem or if reaeration is going to be very low, then use the leftover 45 mL of water in the syringes for the salt analysis by filtering the water into a clean nalgene bottle.
- Later (and far away from the stream), suck in 15 mL of air, shake for 10 minutes, and then inject the headspace into the pre-evacuated serum vial (10 mL) or vacutainer (7 mL). Gas samples are good to store at this point for at least 2 months.

In the lab:

- See page 4 for specific GC settings and methods

Calculating reaeration coefficient from SF_6 data:

Plot the decline in peak area (as LN of peak area) of SF_6 downstream from the release site (as in Figure 1). The slope of the line is the SF_6 loss rate (m^{-1}). Multiplying the loss rate by reach velocity (m min^{-1}) gives the reaeration coefficient for SF_6: K_{SF6} (min^{-1}).

The reaeration coefficient for SF_6 is calculated based on Wanninkohf et al. (1990), which is analogous to propane. Given K_{SF6} it is possible to calculate the K for any other gas based on the ratio of their Schmidt numbers (*Sc*), where:

$$\frac{K_{SF_6}}{K_{O_2}} = \frac{Sc_{SF_6}}{Sc_{O_2}}$$

The reaeration rate for O_2 is about 1.4 times higher than SF_6 at the same temperature. Schmidt numbers can be calculated using the following equation:

$$Sc = A - Bt + Ct^2 - Dt^3$$

where t is temperature in degrees Celsius and A-D represent gas-specific constants for freshwater ecosystems (Table 1).

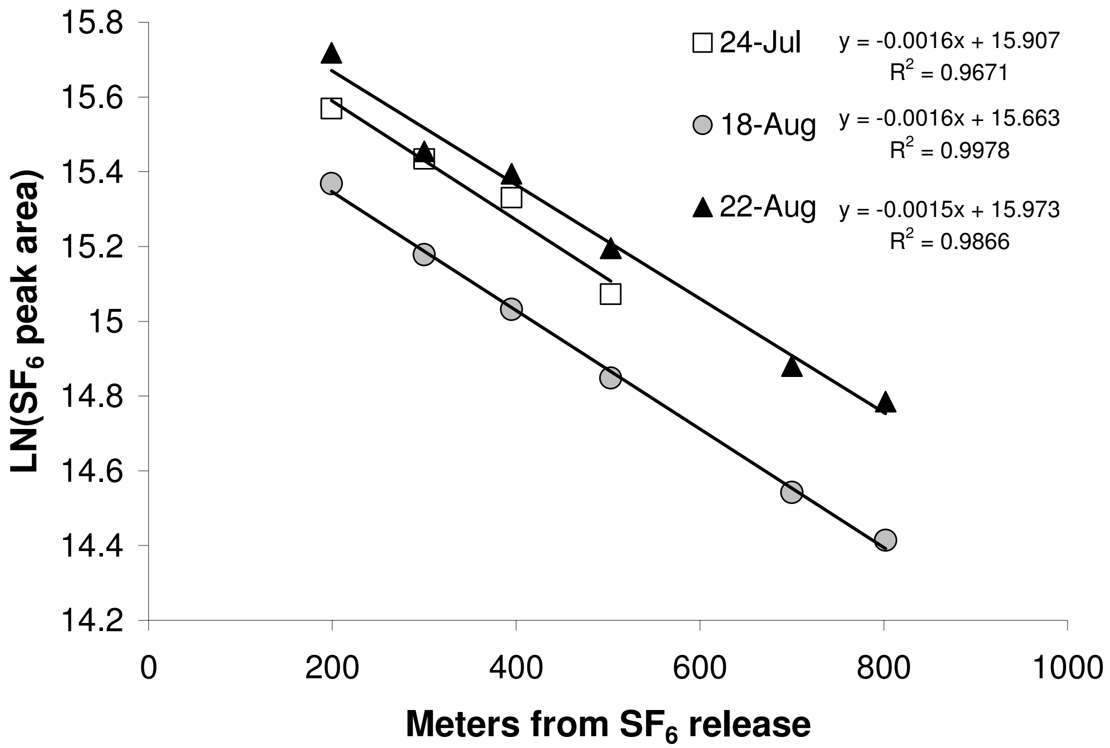

Figure 1. Example of the decline in SF_6 downstream from release site using SF_6 peak areas from three different SF_6 releases during summer 2006 in Kelly Warm Springs, WY. Each point represents an average of peak areas from three samples collected at each site. These data gave a SF_6 loss rate of 0.00155 m^{-1} for Kelly Warm Springs, which was used for reaeration calculations in Hotchkiss & Hall (2010) *Oecologia*.

Table 1. Constants used to calculate Schmidt numbers for SF_6, CO_2 and O_2 (as in Wanninkhof 1992).

Gas	A	B	C	D
SF_6	3255.3	217.13	6.8370	0.086070
CO_2	1911.1	118.11	3.4527	0.041320
O_2	1800.6	120.10	3.7818	0.047608

Relevant Works Cited

Cole, J.J. & N.F. Caraco. 1998. Atmospheric exchange of carbon dioxide in a low wind oligotrophic lake. *Limnology and Oceanography* 43:647-656.

Tobias, C.R., J.K. Böhlke, J.W. Harvey, & E. Busenberg. 2009. A simple technique for continuous measurement of time-variable gas transfer in surface waters. *Limnology and Oceanography: Methods* 7: 185-195.

Wanninkhof, R., P.J. Mulholland, & J.W. Elwood. 1990. Gas exchange rates for a first-order stream determined with deliberate and natural tracers. *Water Resources Research* 26:1621-1630.

Wanninkhof, R. (1992). Relationship between wind speed and gas exchange over the ocean. *Journal of Geophysical Research* 97: 7373-7382.

Sulfur Hexafluoride (SF_6) Analysis on the GC 14A w/ ECD *ERH (9.7.06)*

Starting Up

Replace septa.
Turn on carrier gas (nitrogen high purity).
Turn on the carrier gas at the GC, Carrier (m) ~2kg/cm^2.
Turn on the POWER.
Set DETECTOR to #3; Press [DET] then [3] then [ENT].
Set RANGE to 0 and CURRENT to 0.5.
Set Detector temperature to 320: Press [DET] then “320” [ENT].
Check Detector temperature: Press [MONIT] then [DET-T].
Column temperature should be set to 40 (if not, press [COL] [INIT] and “40” [ENT]).
Check Column temperature: Press [MONIT] then [COL].

Establishing Baseline

Allow the GC to run and warm-up for 6-8 hours or overnight.

Run Settings

Open program DA 1
  Under Data, choose “Show Data Trace” and “Show Report.”
  Under File, choose “Open Method” and choose “SF6.me” saved in Bob’s folder
  Under Control, choose “Run Control.”
    → Start Run → Inject (immediately after injecting your sample).
  To SAVE: “Set Data Name” in Run Control window (should print automatically).

Running Samples

When ready to run samples press the CURRENT button IN.
Inject 0.1 mL of sample.
Retention time is ~2 minutes.
Record peak area.
Make sure that you run all samples from a single release at the same time, as there are no standards that can be used with this SF_6 method.

Shutting Down

Turn off CURRENT.
Set Detector temperature to 31 (so it cools slowly).
Set Column temperature to 20.
Turn off Heater.
Turn off POWER to GC.
Turn off carrier gas (at gas tank).

GC methods edited and updated by Erin R. Hotchkiss (2006) from methods written by:
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