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Biogeosciences Discussions

Interactive comment on "Use of argon to measure gas exchange in turbulent mountain streams" *by* Robert O. Hall Jr. and Hilary L. Madinger

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Response to reviews, Hall and Madinger "Use of argon..."

Reviewer text in black
Author response in blue

Reviewer 1 This is a well produced manuscript that introduces an important and new methodological approach to measuring reaeration in high-gradient streams. The study was well executed and comprehensive. Because the methods and results are

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Discussion paper

relatively straight- forward and the design of the study relatively simple, I have no further comments for improvement.

Thank you.

Reviewer 2, D. McGinnis "Use of argon to measure gas exchange in turbulent mountain streams", by Robert O. Hall and Hilary L. Madinger. In their manuscript, the authors use Argon and SF6 to determine the gas exchange rate in streams of varying slopes. The manuscript it straight forward, concise and convincing, and the topic is certainly timely. The manuscript is a very nice contribution.

My only concern is the effect of the introduced bubbles on the dissolved N2 concentrations. Since the authors use the Ar/N2 ratio, this may have consequences for their calculations. I performed some bubble simulations on shallow streams using various bubbles (pure Ar, O2, etc) and according to the results, a 1 mm diameter Ar bubble will strip as much N2 out of the water as the Ar that is dissolved. If this has a relevant impact on dissolved N2 concentrations, then it would translate to artificially high K values using the Ar/N2 ratio and might explain their higher reported ratio of gas exchange of Ar to SF6. Perhaps the authors can provide additional information if the N2 stripping by bubble addition is truly negligible for their k calculations? A simple test with measuring N2 (or even O2 as it should scale) immediately upstream and downstream of their bubble addition would be compelling.

We completely agree with the reviewer that Ar will strip some of the N_2 from the stream. We briefly mentioned this point in the paper, and we now have added text to the discussion to quantify the worst case scenario of how much N_2 was stripped out. The short answer is very little because we added small quantities of Ar and the Ar pool is much smaller than the N_2 pool . Indeed the amount of N_2 stripped would be so small that it would be difficult to measure using MIMS to estimate concentrations, as opposed to ratios.

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Here is a an example. We enriched Ar from 1.01 to 1.18 of its ambient concentration. Choosing the high value of 1.18 corresponds to in an increase in the dissolved Ar from 0.476 mg L^{-1} to 0.561 mg L^{-1}. This difference corresponds to an enrichment of 0.00214 mmol Ar L^{-1}. Assuming a mole for mole exchange with N_2 gas, there would be a 0.00214 mmol L^{-1} decline in N_2 from its saturation concentration of 0.455 mmol L^{-1}. This value represents a 0.47% decline in dissolved N_2. This decline would not be measurable if we measured N_2 concentrations alone (the MIMS is much more precise with ratios than concentrations). Our standard deviation of replicate measures of N_2 is 0.6% of saturation concentration.

We do recognize that going gung-ho with a huge tank of Ar and big diffusing stones could enrich the stream to e.g., 10$\times$ the Ar concentration. Such enrichment would cause about a 23% decline in N_2. In this situation, one would need to model the N_2 invasion.

The results section includes the level of enrichment of Ar above it saturation concentration, but we will clarify the discussion to explicitly decline the potential N_2 stripping. We will add the following text to the discussion:

" A potential concern when conducting these experiments is excess Ar bubbled to the stream will strip N_2 as Ar diffuses from bubbles and N_2 diffuses in. If this N_2 flux is large, one would need to model the concomitant invasion of N_2 as well as the evasion of Ar. How much N_2 did the Ar strip? We averaged an enrichment of 7% of ambient Ar concentration with a high of 18%. This high value corresponds to in an increase in dissolved Ar from 0.476 mg L^{-1} to 0.561 mg L^{-1}, which is an enrichment of 0.00214 mmol Ar L^{-1}. Assuming a mole for mole exchange with N_2 gas, there would be a 0.00214 mmol L^{-1} decline in N_2 from its saturation concentration of 0.455 mmol L^{-1}. This value represents a 0.47% decline in dissolved N_2, a small amount relative to the 18% increase in Ar."

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Minor comment: Pg 4, line 25. Last sentence of that paragraph is a bit unclear.

We will revise this long sentence into 3 shorter ones “Based on the small enrichment of Ar, we assumed that N_2 concentration changed little during the injection due to bubble exchange with Ar. In addition we assumed no biologically driven N_2 fluxes. Denitrification would cause a uniform and small increase to the N_2 concentration compared to saturation throughout the reach.”