



Linking otolith microchemistry and surface water contamination from natural gas mining[☆]

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ABSTRACT

Unconventional natural gas drilling and the use of hydraulic fracturing technology have expanded rapidly in North America. This expansion has raised concerns of surface water contamination by way of spills and leaks, which may be sporadic, small, and therefore difficult to detect. Here we explore the use of otolith microchemistry as a tool for monitoring surface water contamination from generated waters (GW) of unconventional natural gas drilling. We exposed Brook Trout in the laboratory to three volumetric concentrations of surrogate generated water (SGW) representing GW on day five of drilling. Transects across otolith cross-sections were analyzed for a suite of elements by LA-ICP-MS. Brook Trout exposed to a 0.01–1.0% concentration of SGW for 2, 15, and 30 days showed a significant ($p < 0.05$) relationship of increasing Sr and Ba concentrations in all but one treatment. Analyses indicate lesser concentrations than used in this experiment could be detectable in surface waters and provide support for the use of this technique in natural habitats. To our knowledge, this is the first demonstration of how trace elements in fish otoliths may be used to monitor for surface water contamination from GW.

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1. Introduction

Worldwide unconventional natural gas deposits are estimated to be 83,400–184,200 trillion cubic feet (Tcf) (Dong et al., 2012). A major shale play in North America, the Marcellus Shale formation is located in the Appalachian Mountains (Vengosh et al., 2014) and contains an estimated 410 Tcf of technically recoverable gas (US EIA, 2011). With over 7000 unconventional gas wells drilled in the Pennsylvania portion of the Marcellus from 2004 to 2013 (Brantley et al., 2014), the vast and rapid expansion has come with environmental concerns.

Mining of natural gas has expanded over the past 20 years due to the development and improvement of hydraulic fracturing technology that allows for better extraction of gas from unconventional shale and tight sand formations (Entrekin et al., 2011; Kargbo et al., 2010; Vengosh et al., 2014). During hydraulic

fracturing, large volumes of water mixed with sand and chemical additives are injected into well holes (Kargbo et al., 2010; Weltman-Fahs and Taylor, 2013). The increase in pressure fractures the surrounding rock, freeing the trapped natural gas (Gallegos and Varela, 2015). Freed natural gas is collected at the wellhead along with flow-back and produced waters (Kargbo et al., 2010), collectively referred to as generated waters (GW; from this point forward).

There are many environmental concerns associated with hydraulic fracturing. The main concerns include changes in land cover and fragmentation from wellpads, pipeline and road development, aerial and groundwater contamination, and spills of GW from wellpads, storage lagoons, and during transportation (Entrekin et al., 2011; Keller et al., 2017; Weltman-Fahs and Taylor, 2013). Spills are of concern because GW contain a variety of potentially toxic chemicals and high concentrations of many salts (Entrekin et al., 2011). Although the composition of supply water (water injected into the bore hole) varies across drilling operations and regions, GW typically contains a combination of salts, acids, corrosion inhibitors, biocides, and lubricants (Hayes, 2009). The GW from the Marcellus shale in central and northeastern

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Pennsylvania contains high Sr and Ba concentrations (Hayes, 2009; Vengosh et al., 2014). Typical concentrations of Sr and Ba in GW from the region vary temporally, (0.2–130,000 mg/L and 59–5000 mg/L over a 90-day span) generally increasing with time (Hayes, 2009). In contrast, low dissolved Sr and Ba concentrations characterize ambient water chemistry for this region, < 0.1 mg/L (this paper).

It has been difficult to detect contamination that was sporadic, relatively small in effect, occurred in low concentrations, or was not reported. Thus, it is difficult to assess the actual frequency and magnitude of aquatic contamination by GW and to investigate effects of GW contaminants that are not associated with known spills. In these scenarios, otolith microchemistry may serve as a useful tool for monitoring elemental changes in water chemistry indicative of past GW contamination. Fish incorporate trace elements such as Sr and Ba from the ambient water into their otoliths, small ear bones inside a fish's skull (Campana, 1999). Changes in the concentrations of these and other elements in fish otoliths could be used to indicate past surface water contamination due to natural gas mining. The feasibility of this technique depends on the sensitivity of otolith uptake to Sr and Ba concentrations and the length of exposure necessary to detect a change in otolith microchemistry.

A few studies have used otolith microchemistry to document contamination from oil and gas development. These studies have shown otolith microchemistry to be a useful tool for identifying fish that ingested oil-contaminated food (Morales-Nin et al., 2007), and for discriminating between marine fish which inhabit locations near oil and gas platforms from conspecifics which inhabit other, more distant locations from these industrial practices (Nowling et al., 2011). However, we are unaware of analogous studies that have used otolith chemistry to document surface water contamination from GW in freshwater systems.

The duration of exposure needed for detection in the otolith depends on the concentration of the element(s) in the water and the vital effects of the species – effects encompassing physiological and behavioral interactions with the environment which influence the incorporation of elements into a biological structure (Kalish, 1991; Melancon et al., 2009), in this case the otolith. Although vital effects account for some amount of variability in incorporation rates among fishes, this variability is typically small in relation to the variability caused by the environment. For example, Elsdon and Gillanders (2006) documented significant differences in otolith Sr, Ca, Ba, and Mn among tides in one estuary location. The potential for detection of short-term exposure from fracking related spills presents an excellent case study, because: 1) detection of exposure to spills is important for protecting water quality; and 2) spills are likely to have high concentrations of the same elements (Sr, Ba) already shown to be detectable in otoliths.

The incorporation of Ba and Sr into the otolith depends partly on the crystalline form of calcium carbonate comprising the otolith (Gauldie, 1986; Morat et al., 2008). Sagittal otoliths (the otolith used in this study) are normally aragonitic, but vateritic polymorphs of CaCO₃ also occur (Campana, 1999). Vateritic sagittal otoliths occur more commonly in salmonids (Gauldie, 1986), particularly in fish under stress (e.g., while held in hatcheries) (Morat et al., 2008). Vateritic sagittal otoliths have a characteristic transparent appearance (Morat et al., 2008). Specific elements partition differently into the various polymorphs of calcium carbonate, rendering disproportionate element concentration partitioning in vateritic and aragonitic sagittal otoliths or regions of otoliths with different polymorphs (Melancon et al., 2005). Thus, direct comparisons between these two types of polymorphs are inappropriate. This necessitates excluding vateritic sagittal otoliths from analyses or adjusting for differences in incorporation rates (i.e., different partition coefficients) between vateritic and aragonitic matrices.

Brook Trout (*Salvelinus fontinalis*) are native to North America and common in the Appalachian Mountains where hydraulic fracturing practices occur (Stauffer et al., 2016). Brook Trout prefer clear, cold waters of good quality (Stauffer et al., 2016), and therefore may be used as bioindicators of water quality and ecosystem health. Although Brook Trout are tolerant of high salinities and adult individuals are known to migrate between fresh and marine waters in coastal areas, Brook Trout do not have access to marine waters in the Appalachian Mountains of Pennsylvania. Considering this and the ability of Brook Trout to tolerate high salinities, Brook Trout otoliths have high potential as a tool to monitor Sr and Ba concentrations in headwater streams in the vicinity or downstream of Marcellus shale mining operations.

The purpose of this study was to test our hypothesis that the concentration of GW that a fish is exposed to is a significant predictor of elemental concentrations in the otolith. To test our hypothesis, we established the following objectives: 1) demonstrate that Brook Trout can incorporate elements from GW into the otolith, 2) identify the GW microchemical signature in the otolith, 3) relate GW otolith signatures to treatment concentrations, and 4) determine the ability to detect incorporation after relatively short periods of exposure. Ideally, relationships between element concentrations in water and otoliths could be used to determine threshold values diagnostic of Brook Trout that have been exposed to GW. To put the findings of this work into a real-world context, we provide values for ambient elemental concentrations and discuss the applicability to wild fish. To our knowledge, this is the first demonstration of how trace elements in fish otoliths may be used to monitor for surface water contamination from GW.

2. Methods

2.1. Surrogate generated water (SGW)

We were unsuccessful in obtaining a GW sample being used at an active fracking site for use in exposure studies, and therefore, a surrogate (henceforth called SGW) was created for use in this study. Averaged elemental concentrations from a referenced GW sample (collected on the fifth day of an active drill operation in north-eastern Pennsylvania; Hayes, 2009) was used to create our SGW (Table 1). Main constituents included NaCl, KBr, CaSO₄, BaCl₂, CaCl₂, FeCl₂, MgCl₂, SrCl₂, LiCl₂, Mg₂CO₃, and C₄H₆O₆.

2.2. Experimental design

Age-1 Brook Trout (1-year-old; 5–8 cm total length: 3.6–4.3 g)

Table 1

Concentrations of elements (mg/L) in Generated Water (GW) in Pennsylvania counties (USA) on day 5 of flow back using averages as described in Hayes (2009), Surrogate Generated Water (SGW; made in laboratory to approximate GW), Control (Northern Appalachian Research Laboratory (NARL) well water) and treatments assuming a Low (0.01%), Medium (0.10%), and High (1.0%) dilution of SGW in NARL well water. Control concentrations were determined from the analysis of eight separate tanks prior to treatment. The volume of SGW added to control water was used to volumetrically calculate Low, Medium, and High concentrations. n.a. indicates below detection limit.

Element	GW	SGW	Control	Low 0.01%	Medium 0.10%	High 1.0%
Cl	49,000	44,000	1.7	4.4	44	440
Br	410	400	n.a.	n.a.	0.40	4.0
Ba	3400	3300	0.021	0.33	3.3	33
Ca	4800	4000	12	0.40	4.0	40
Mg	380	430	1.7	0.043	0.43	4.3
K	190	220	1.0	n.a.	n.a.	2.2
Na	20,000	22,000	1.2	2.2	22	220
Sr	1400	1100	0.039	0.11	1.1	11

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