PROGRESS REPORT

NATIONAL POLLUTION DISCHARGE ELIMINATION SYSTEM

POTENTIAL TOXICITY OF THE MAJOR SALT (SODIUM BICARBONATE) FROM COALBED NATURAL GAS DISCHARGE WATER TO AQUATIC LIFE OF THE TONGUE AND POWDER RIVER DRAINAGES IN MONTANA AND WYOMING

Prepared by:

AIDA FARAG and DAVID HARPER
U.S. GEOLOGICAL SURVEY

And

DON SKAAR
MONTANA FISH, WILDLIFE AND PARKS

Prepared for:

U.S. ENVIRONMENTAL PROTECTION AGENCY
TINA LAIDLAW, PROJECT OFFICER
Project: IAG #14-953964010

And

U.S. BUREAU OF LAND MANAGEMENT
JOE PLATZ, PROJECT OFFICER
Project: Agreement #KAI061019

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Summary

The purpose of this project is to evaluate the sensitivity of aquatic life in the Tongue and Powder River drainages to sodium bicarbonate. This salt is a major constituent of coalbed natural gas (CBNG) discharge water. The level of sodium bicarbonate in CBNG wastewater discharge can be over 1,000 mg/L, and has been shown to be acutely toxic to fishes native to these drainages.

This project was initiated in 2003 and this administrative progress report describes the activities of Montana Fish, Wildlife and Parks (MFWP) and U.S. Geological Survey (USGS) during the period of October 2005-October 2006. All data included in this report is considered provisional, pending completion of the quality assurance and technical review process of the USGS, Columbia Environmental Research Center.

During this time, MFWP and USGS personnel attended two Aquatic Task Force meetings to present progress and participate in the Aquatic Task Force meetings. Personnel also participated in sub-group discussions by phone and e-mail throughout the winter and spring. A fact sheet, **FS 2006-3092:** Toxicity of Sodium Bicarbonate to Fish from Coal-Bed Natural Gas Production in the Tongue and Powder River Drainages, Montana and Wyoming (http://pubs.usgs.gov/fs/2006/3092/) was finalized, and can be downloaded from the internet or is available in print upon request. Funding was provided in June and July 2006, for additional laboratory and field studies. To fulfill obligations for that funding MFWP and USGS are working to complete the following two tasks.

1.) Laboratory toxicity experiments to provide the technical data necessary for the development of a water quality standard for sodium bicarbonate.

2.) *In-situ* toxicity experiments to assess the potential toxicity of current ambient waters in the Tongue and Powder watersheds to aquatic life.

Progress Task 1

Laboratory experiments. Because it was necessary to complete the field study during the summer, Task 2 was initiated immediately upon arrival of the funds. Therefore, we are currently in the process of completing the designs and planning the laboratory experiments scheduled to be performed winter and spring 2007.

Progress Task 2

Two *in-situ* toxicity experiments were conducted with fathead minnows (*Pimephales promelas*; FHM) received from Aquatic Biosystems, Fort Collins, CO. The brood stock were deemed free of disease and kept in isolation at the Colorado facility. The proper permits were obtained for importation of the offspring. Preliminary water quality measurements and site assessments were performed during a reconnaissance trip to the

field, July 5–7, 2006. Six sites were chosen and access approval was obtained before the experiments were initiated. A description of each experiment follows:

Experiment 1: Initiated with FHM < 48-hrs old (2-day old). The experiment was performed at six sites in the Powder River drainage. Two reference sites were used, Powder River at Moorhead, MT and Clear Creek near Buffalo, WY. Four test sites were used; SA Creek, Upper Beaver Creek, Lower Beaver Creek, and Burger Draw, all in Wyoming. The FHM were received from Aquatic Biosystems via FedEx in a cooler. Fish were placed in large plastic bags in a cooler and driven to the test and reference sites. Temperature, DO, and conductivity were monitored in the holding water during travel and at each site. Care was taken at each site to acclimatize fish to increments of changing water quality before fish were placed in the site water. The experimental chambers were 12.7 cm long, cylindrical Butyrate containers with a 6.67-cm diameter. Two rectangular 74-80 µm mesh windows covered approximately 2/3 of the area of the chambers. Each experimental chamber was submerged in a holding pan filled with a mixture of site and culture water. Fish were placed in the open end of the experimental chamber and closed. The experimental chambers were then placed on site, submerged, and secured. Ten fish were placed in each of four experimental chambers for a total of 40 experimental fish at each site. Survival was monitored daily when containers were opened inside of a holding pan and the number of alive and dead fish was noted. Fish were considered dead when they were opaque and did not respond to stimulus.

YSI Data Sonde units were deployed at four sites; Clear Creek, Lower Beaver Creek, Powder River at Moorhead, and SA Creek to automatically monitor conductivity, DO, pH, and temperature every 30 minutes for the duration of the experiment. Fish survival was monitored daily at every site. Conductivity, dissolved oxygen (DO), pH, and temperature were manually measured on-site each day and samples were collected for daily analyses of alkalinity, ammonia, and hardness. Samples were also collected and filtered into 125 ml acid-washed plastic vials for cation measurements and HCO_3 rinsed plastic vials for anion measurements.

Experiment 2: The experimental design for Experiment 2 was identical to Experiment 1 with the following exceptions. Six day old FHM were used at four sites; Clear Creek, Upper Beaver, Lower Beaver, and Burger Draw. The YSI Data Sonde units continued to monitor at Clear Creek and Lower Beaver Creek during Experiment 2.

For both experiments, the survival data were analyzed with Toxstat software package. A t-test was performed between the reference sites (Experiment 1). Because no difference was observed, the data were pooled and a one-way ANOVA was performed followed by a Bonferroni means comparison. Because one reference site was used during experiment 2, no pooling was necessary. T-tests were used to compare the survival of 2-day old vs 6-day old FHM at each site. All data met homogeneity and normality assumptions without transformations.

Significant reductions in survival were noted at all test sites compared to the pooled reference sites during Experiment 1 (Table 1, Figure 2). No significant reductions in

survival of 6-day old fish were observed at any of the test sites compared to the reference site in Experiment 2. There was no significant difference in survival between 2-day old and 6 day-old fish at Clear Creek, Lower Beaver, or Upper Beaver Creek. There was a significant difference in survival between experiments initiated with 2-day old and 6-day old FHM at Burger Draw. Mean concentrations of total ammonia were 1.5 and 2.0 mg/L at Burger Draw during the Experiment 1 and Experiment 2 respectively (Figure 2). The potential influence that ammonia may have played in survival at this and other sites will be investigated. Temperature, conductivity, dissolved oxygen, and pH measured with the hand-held units and automatic units are presented in Table 2. Principle cation and anion concentrations are presented in Table 3. Because the water chemistry measurements were similar between Experiment 1 and Experiment 2, the data are not presented separately.

Future Plans

Planning of research related to Task 1 has been initiated and the work will be conducted during winter/spring 2007. Additional *in-situ* experiments with pallid or shovelnose sturgeon (or another suitable species) will be conducted during summer 2007.

Table 1. Percent survival of fathead minnow (FHM) during *in-situ* experiments at six sites in the Powder River Drainage, July – August 2006.

A.) Comparisons of survival among sites, within an experiment.

Site Name	Age at start	Percent Survival at 96 h
Experiment 1		
PR @ Moorhead	2 day	77
Clear Creek	2 day	78
Pooled Reference		78
SA Creek	2 day	24*
Upper Beaver	2 day	37*
Lower Beaver	2 day	49*
Burger Draw	2 day	11*
Experiment 2		
Clear Creek	6 day	90
Upper Beaver	6 day	75
Lower Beaver	6 day	75
Burger Draw	6 day	73

* Significantly different from Pooled Reference at P > 0.05

B.) Comparisons of survival within a site, between experiments.

Site Name	Age at start	Percent Survival at 96 h
Clear Creek	2 day	78
Clear Creek	6 day	90
Upper Beaver	2 day	37
Upper Beaver	6 day	75
Lower Beaver	2 day	49
Lower Beaver	6 day	75
Burger Draw	2 day	11**
Burger Draw	6 day	73

**Significantly different from FHM same site but started at 6-days old

Table 2. General water chemistry at the six study sites during *in-situ* exposures of fathead minnow conducted in the Powder River Drainage, July – August 2006.

A.) Measurements performed with hand-held meters. Data are means with standard deviation in parentheses.

Site	Temperature (^{o}C)	Conductivity (µS/cm)	Dissolved Oxygen (mg/L)	pH
Powder R. Moorhead	27.4 (2.3) N=5	3616 (131) N=5	7.6 (0.5) N=5	8.3 (0.2) N=5
Clear Creek	21.6 (3.2) N=9	857 (49) N=9	8.9 (2.0) N=9	8.5 (0.3) N=8
Lower Beaver	21.9 (3.4) N=9	2843 (82) N=9	8.8 (1.0) N=9	9.3 (0.1) N=4
Upper Beaver	20.3 (2.4) N=9	2612 (38) N=9	8.0 (0.08) N=9	9.0 (0.1) N=4
Burger Draw	21.9 (4.7) N=9	3649 (30) N=9	8.3 (0.6) N=9	9.0 (0.1) N=6
SA Creek	27.6 (2.5) N=6	2620 (91) N=6	9.5 (2.0) N=6	8.9 (0.2) N=6

B.) Minimum and maximum temperature, conductivity, dissolved oxygen, and pH measurements recorded every 30 min at four sites with YSI 5000 Data Sonde units

Site	Temperuature (^{o}C)	Conductivity (µS/cm)	Dissolved oxygen (mg/L)	pH
Powder R. Moorhead	21.34 – 31.20	3280 – 4142	NA	7.74 – 8.38
Clear Creek	15.12 – 29.51	669 – 891	5.59 - 12.33	7.81 – 8.73
Lower Beaver	14.13 – 31.95	2390 – 2644	5.14 - 10.68	9.23 – 9.35
SA Creek	16.21 – 29.97	2095 – 2892	NA	8.50 – 8.97

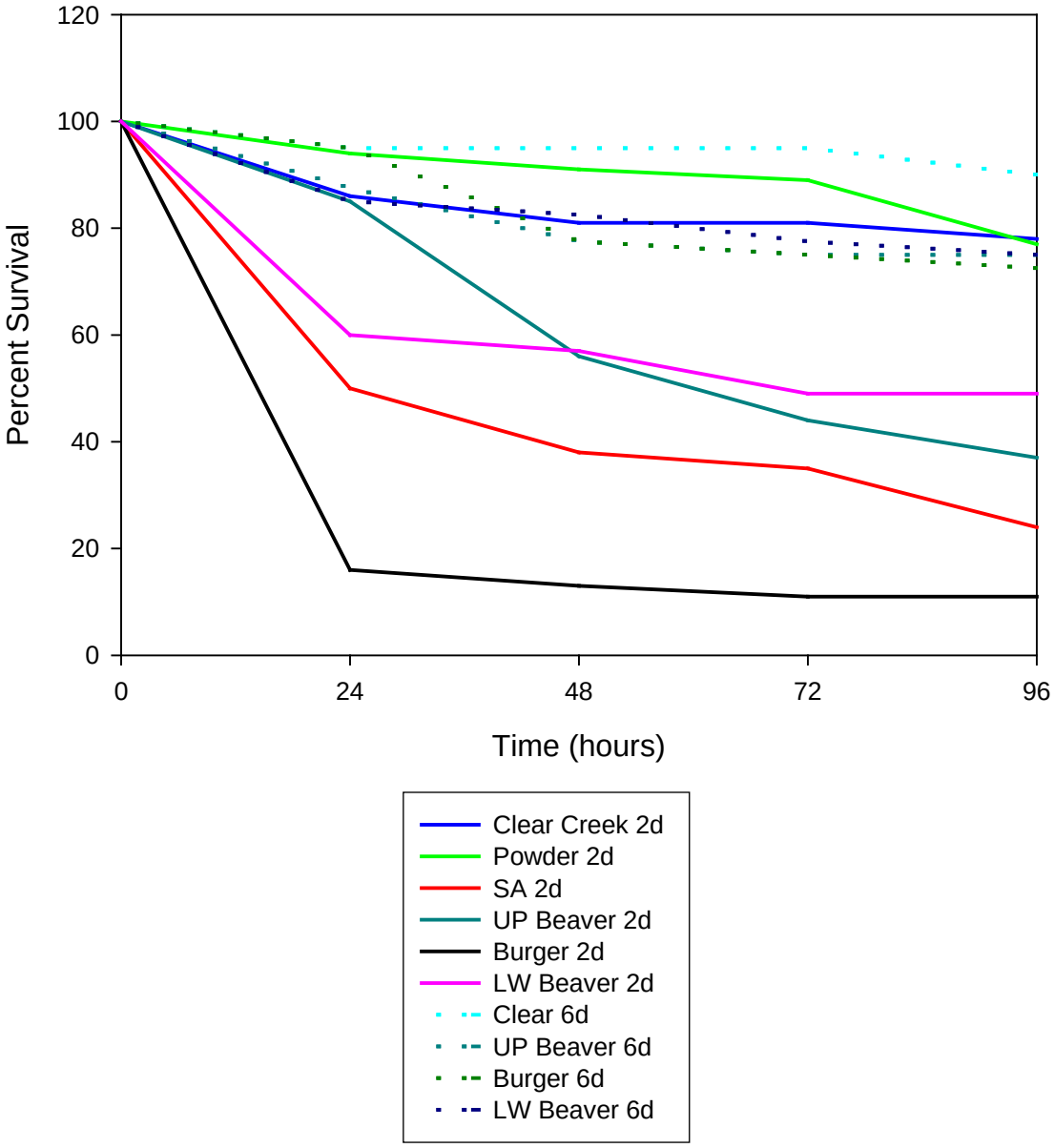
NA = not applicable, probe failed.

Table 3. Mean concentrations of principle anions and cations in water at the study sites during in-situ exposures of fathead minnow conducted in the Powder River Drainage, July – August 2006. Standard deviation is in parentheses.

Site	Alkalinity (mg/L as $CaCO_3$)	HCO_3^-* (mg/L)	Sulfate (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	Total Ammonia (mg N/L)
Powder R. Moorhead	202 (21) N=5	196 (20) N=5	1767 (51) N=3	197 (97) N=4	185 (85) N=4	660 (281) N=4	32 (15) N=3	<0.01 N=5
Clear Creek	198 (32) N=8	192 (29) N=8	285 (24) N=5	74 (28) N=6	52 (20) N=6	68 (11) N=6	5 (0.3) N=5	0.05 N=1
Lower Beaver	1926 (191) N=9	1740 (185) N=9	75 (2) N=5	10 (1) N=6	27 (1) N=6	765 (10) N=6	20 (0.3) N=5	0.05 (0.03) N=5
Upper Beaver	1759 (186) N=9	1646 (182) N=9	257 (471) N=5	16 (1) N=6	24 (0.4) N=6	664 (14) N=6	20 (1) N=6	0.5 (0.1) N=5
Burger Draw	2535 (381) N=9	2315 (384) N=9	27 (18) N=5	15 (4) N=5	28 (1) N=5	1003 (13) N=5	41 (2) N=5	1.5 (0.5) N=5
SA Creek	1364 (106) N=5	1245 (87) N=5	395 (36) N=3	17 (2) N=4	45 (1) N=4	605 (31) N=4	16 (3) N=3	0.13 (0.07) N=5

* Speciation calculated on the basis of CO_3/HCO_3 equilibrium equations.

Figure 1. Survival during in-situ experiments initiated with 2-day old or 6-day old fathead minnow in site waters from Powder River Drainage, July - August 2006.



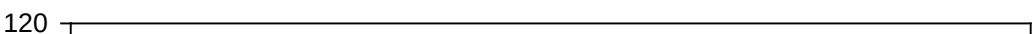
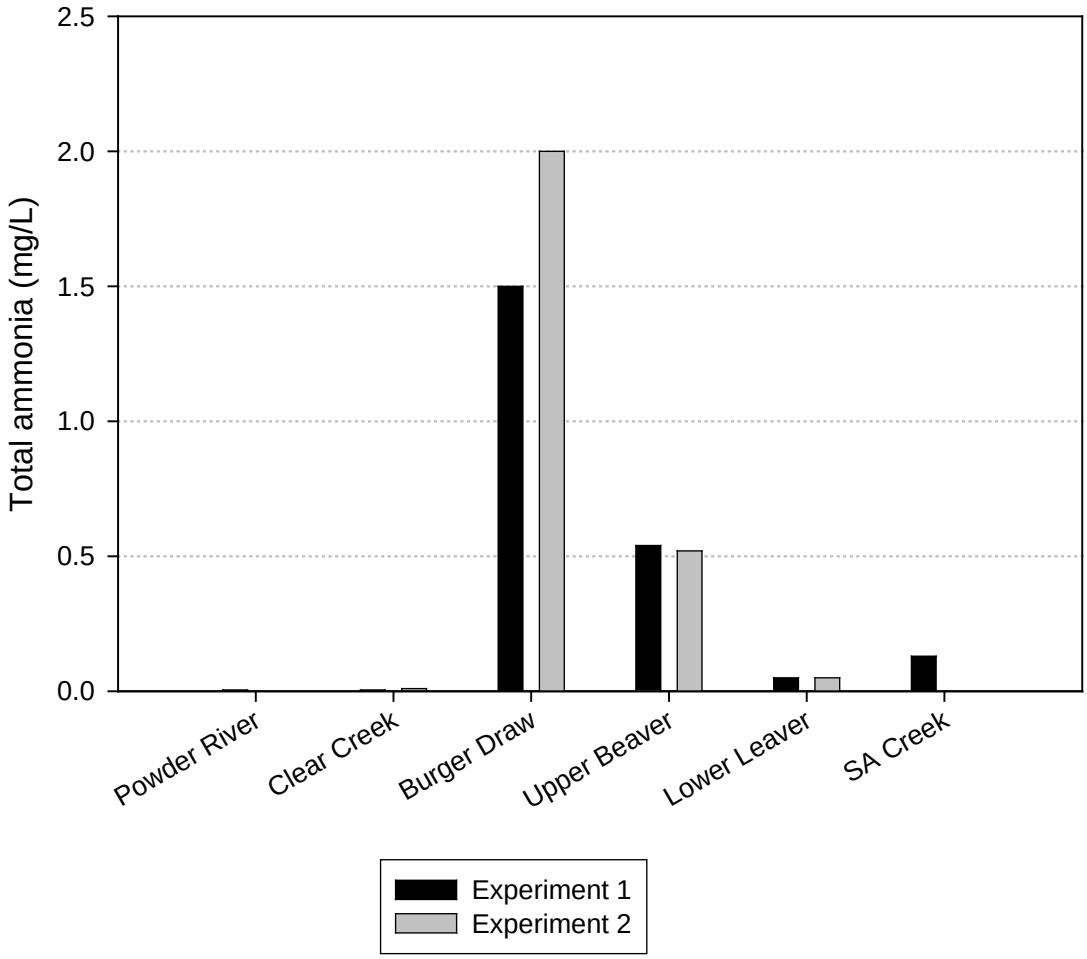


Figure 2. Mean concentrations of total ammonia at sites during *in-situ* experiments conducted in the Powder River Drainage, July - August 2006.



Appendix Table 1. Additional trace metal scans conducted by ICP in water samples collected from experimental sites for *in-situ* study performed Powder River Drainage, July – August 2006. N = 1 for all.

Powder River at Moorhead 7/26/06

		mg/L
Arsenic	<	0.001
Barium		0.063
Beryllium	<	0.002
Calcium		150
Cadmium	<	0.002
Chromium		0.004
Copper		0.004
Iron		0.10
Magnesium		144
Manganese		0.048
Sodium		525
Nickel	<	0.01
Lead	<	0.005
Selenium	<	0.005
Zinc		0.011
Total Hardness as CaCO3		968

Clear Creek 7/27/06

		mg/L
Arsenic		0.001
Barium		0.045
Beryllium	<	0.002
Calcium		88.8
Cadmium	<	0.002
Chromium		0.002
Copper		0.007
Iron		0.10
Magnesium		41.3
Manganese		0.052
Sodium		69.6
Nickel	<	0.01
Lead	<	0.005
Selenium	<	0.005
Zinc		0.052
Total Hardness as CaCO3		392

Lower Beaver Creek 7/27/06

		mg/L
Arsenic		0.004
Barium		0.215
Beryllium	<	0.002
Calcium		10.6
Cadmium	<	0.002
Chromium		0.003
Copper		0.009
Iron		0.38
Magnesium		27.5
Manganese		0.011
Sodium		773
Nickel	<	0.01
Lead	<	0.005
Selenium	<	0.005
Zinc		0.058
Total Hardness as CaCO3		140

Upper Beaver Creek 7/27/06

		mg/L
Arsenic		0.005
Barium		0.079
Beryllium	<	0.002
Calcium		14.6
Cadmium	<	0.002
Chromium		0.011
Copper		0.005
Iron		0.34
Magnesium		44.7
Manganese		0.031
Sodium		599
Nickel	<	0.01
Lead	<	0.005
Selenium	<	0.005
Zinc		0.008
Total Hardness as CaCO3		220