Report as of FY2007 for 2006MT86B: "Temporal and spatial changes in the concentration and isotopic composition of nitrate in the upper Silver Bow Creek drainage, Montana."

Publications

Project 2006MT86B has resulted in no reported publications as of FY2007.

Report Follows

Temporal and spatial changes in the concentration and isotopic composition of nitrate in the upper Silver Bow Creek drainage, Montana.

Interim Progress Report

prepared for

The Montana Water Center and the U.S. Geological Survey

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Background

The upper Clark Fork River, Montana, is currently undergoing extensive and costly reclamation activities that are unprecedented in scope within the US. Whereas much progress continues to be made removing sources of heavy metal and arsenic contamination stemming from historic mining and smelting activities in the Butte-Anaconda area, a new problem has emerged that seriously threatens the water quality of the watershed: too many nutrients. As early as the 1990s the Tri-State Water Quality Council examined this problem and made detailed recommendations for the institution of a Voluntary Nutrient Reduction Program that would involve several municipal centers and industrial users in the Clark Fork watershed. Specific targets were set for standing algae crops (measured in terms of mg/m^2 of chlorophyll a), total P (20 µg/L upstream of Missoula), and total N (300 µg/L). Nuisance algae is known to be a major problem in the upper Clark Fork River between Deer Lodge and Missoula, and there are concerns about nutrient loads to Lake Pend Oreille in Idaho. However, the scope of the nutrient problem in Silver Bow Creek, the main headwater stream of the upper Clark Fork River, has largely gone unnoticed.

In Year 1 of this project, our research group has documented numerous sources of nutrient (nitrate, ammonia, phosphate) loading in the upper Silver Bow Creek watershed, focusing on the area upstream of the town of Rocker. The situation is worse than this writer realized when our Year 1 proposal was written. The Butte waste water treatment plant (WWTP) is the largest point source polluter of upper Silver Bow Creek. Based on our work to date, the nutrient species of greatest concern is not nitrate, but rather ammonia (NH_3 or NH_4^+, depending on pH). Ammonia is toxic to fish, is a potential source of chemical oxygen demand (leading to lethal drops in dissolved oxygen during summer nights), and also is highly bio-available, promoting extreme summertime blooms of algae and aquatic macrophytes. The ultimate goal of the ongoing cleanup of Silver Bow Creek is to restore the stream to fully-functioning status in terms of its ability to support aquatic life and ideally a trout fishery that would have recreational and economic benefits to local communities. However, because Silver Bow Creek is a small stream (typical baseflow is < 30 cfs), the quantity of clean water coming from mountain runoff is insufficient to dilute the nutrient loads from the Butte WWTP and other sources. Consequently, despite 100's of millions of dollars in lawsuits and restoration efforts, upper Silver Bow Creek remains much too polluted to support a trout fishery.

Site Description

The city of Butte (pop. 33,000) is located in the Summit Valley, a 60-square mile alluvial-filled intermontane basin at the head of the Clark Fork River watershed (Fig. 1). The main streams flowing north through the valley are Blacktail Creek and the smaller Basin Creek. The upper reaches of Silver Bow Creek coming into the valley from the north are diverted by active mining operations. The ancestral uppermost Silver Bow Creek channel in the study area is now occupied by a much-diminished flow termed the Metro Storm Drain (MSD, Fig. 1). The recently re-engineered MSD has virtually no surface flow during the cold months, and receives less than 1 cfs of clean imported water from Silver Lake (west of Anaconda, MT) during the summer to enhance the esthetics of the area which includes walking trails and interpretative signs explaining some of the reclamation activities that have taken place. Our Year 1 monitoring indicates that the MSD is a very minor source of nutrient loading to Silver Bow Creek. More importantly, three point sources enter Silver Bow Creek before it exits the Summit Valley to the west. These include shallow groundwater collected and treated from the south (Montana Pole) and north

(Lower Area One) sides of Silver Bow Creek, as well as the effluent from the Butte waste water treatment plant (WWTP) (Fig. 1). The discharge from the Montana Pole and LAO facilities averages around 1 cfs during normal baseflow conditions. The volume of the WWTP effluent typically falls in the range of 3 to 10 cfs, and tends to crest in the late morning and afternoon hours in response to patterns of water use by the residents of Butte.

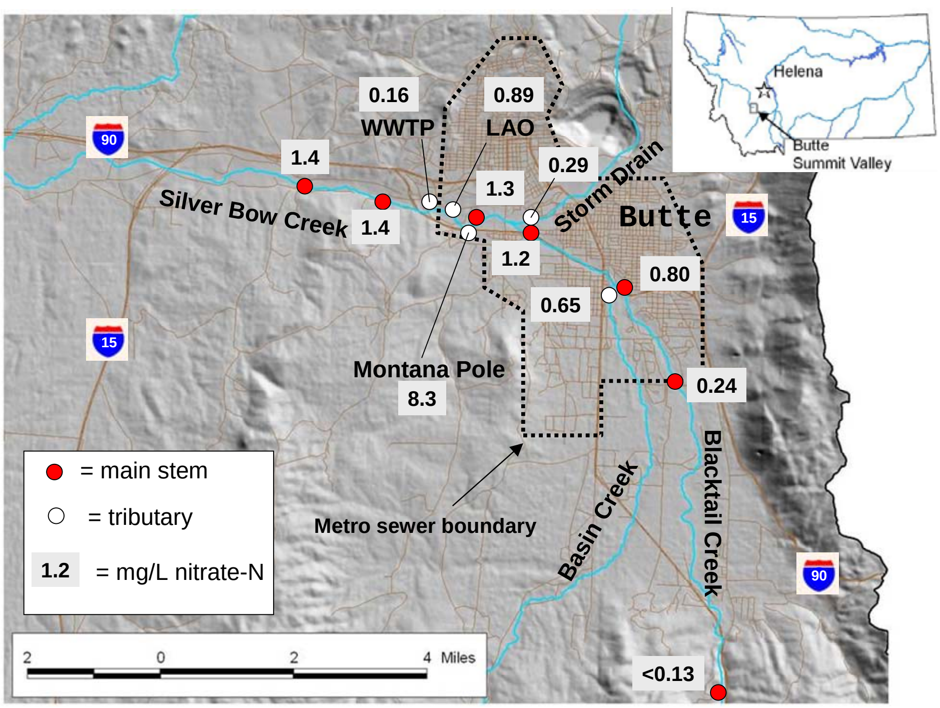

Fig. 1. Map of the Butte Summit Valley, showing sampling locations used in this study. Data next to each sample site are dissolved nitrate results (mg/L as N) obtained by our group in October, 2006. Abbreviations: WWTP = Waste Water Treatment Plant discharge; LAO = Lower Area One discharge.

The flow of Silver Bow Creek immediately below the WWTP discharge point is continuously monitored by a USGS gaging station. Another USGS gaging station is located near the mouth of Blacktail Creek, just upstream of the confluence with the Metro Storm Drain. Streamflows in Silver Bow Creek typically fall in the 20 to 30 cfs range under baseflow conditions, but can show sharp increases to several hundred cfs after heavy rain or snowmelt events. Because of the aforementioned diurnal pattern in the WWTP discharge, the flow of Silver Bow Creek below the WWTP also shows a diurnal cycle under baseflow conditions.

Land use varies from urban/mining/residential in the north part of the valley to lower density residential sub-divisions in the southern part of the valley, with the usual recreational amenities such as golf courses and horses. All residences outside of the municipal water and sewer district (Fig. 1) rely on individual well and septic systems. Like many intermontane valleys in the West, the Summit Valley is expanding, with dozens of new homes constructed each year, mostly in areas outside of the Butte sewer district. The Montana Bureau of Mines and Geology (MBMG) has documented chronically high levels of nitrate in groundwater wells throughout the Butte Summit Valley (Carstarphen et al., 2004), and high nitrate levels in the shallow aquifer were recently responsible for stalling the permitting process for a new sub-division in the southern part of the valley (see "Septic Shock", The Montana Standard, Sept. 17, 2006). However, prior to the current study, little published information existed on nutrient concentrations in surface water. A large amount of information on nutrient concentrations in Silver Bow Creek does exist in the "gray literature" of government and consultant reports, and one of the activities during Year 1 of this study has been to assemble this information. Although not reported here, the results of this synthesis will be included in the final deliverable of the project, which will constitute the MS thesis of Beverly Plumb.

Summary of Progress from Year 1 Funding

Field sampling in Year 1 of this project began in May 2006, and continued through April of 2007. Because this project was recently granted a 2nd year of funding from the Water Center, what follows is a brief summary of Year 1 activities and results only. A complete interpretation of the data will be given at a later date. Some of the results that follow were presented by MS student Beverly Plumb at the 2006 Montana AWRA conference in Polson, MT (Plumb and Gammons, 2006).

1. Synoptic sampling was performed along the course of upper Silver Bow Creek and its tributaries in May, June, August, October, December 2006, and January, March, April 2007. These data show a moderate increase in nitrate and phosphate concentrations and loads from non-point source pollution as surface water of Blacktail and Basin Creeks makes its way through the Butte Summit Valley (Fig. 1, Fig. 2a). Concentrations of nitrate at the mouth of Blacktail Creek (USGS gaging station 12323240) average near 1 mg/L (as N) during normal flows, which is quite high for a Montana stream, showing clear evidence of nutrient impairment. Blacktail Creek is a gaining stream through its lower reaches, and the majority of the nitrate in lower Blacktail Creek most likely comes from contaminated shallow groundwater in the Butte valley. The source of the nitrate in the shallow aquifer is believed to be a combination of septic tank leachate from non-sewered homes and subdivisions, animal waste, and organic or chemical fertilizers. This hypothesis is consistent with preliminary stable isotope results discussed below.

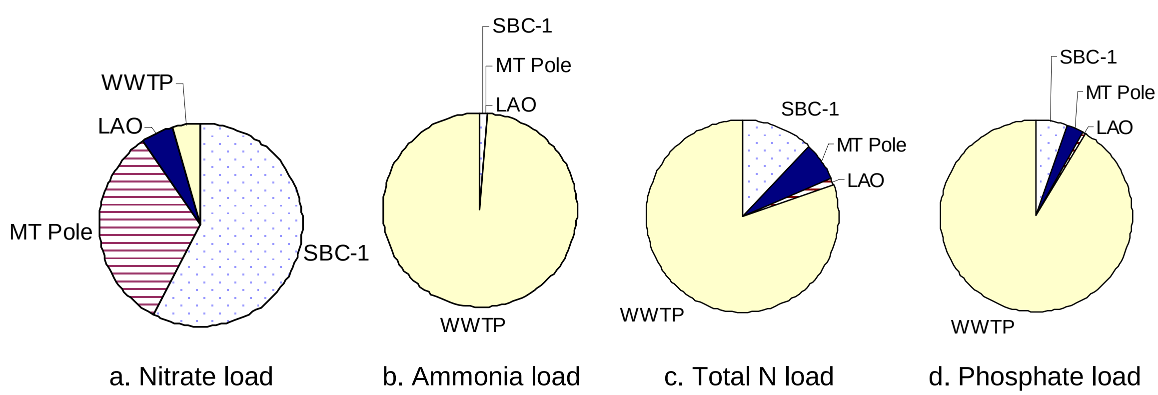

Figure 2. Comparison of nutrient loads in October, 2006. SBC-1 represents the total load in Silver Bow Creek upstream of the three identified point sources.

2. In addition to the chronically elevated nitrate levels in the tributaries to Silver Bow Creek (represented by SBC-1 in Fig. 2), significant increases in nitrate load come from treated groundwater from the Montana Pole Superfund Site (MT Pole), with lesser contributions from treated groundwater from the Lower Area One lime treatment plant (LAO), and effluent water from the Butte Waste Water Treatment Plant (WWTP). It is important to stress that no nutrients

are added to the groundwater that is treated at MT Pole and LAO. The MT Pole site uses a combination of physical and microbial processes to degrade chlorinated hydrocarbons in a highly contaminated groundwater plume on the south side of Silver Bow Creek, whereas LAO uses lime addition to treat metal-contaminated groundwater from the north side of Silver Bow Creek. The WWTP effluent has little nitrate, but very high concentrations and loads of dissolved phosphate and ammonia (Fig. 2b), which together severely degrade the water quality of Silver Bow Creek for many miles downstream (see below).

3. In August of 2006, a 4 mile long "dead zone" was documented below the confluence of the WWTP effluent and Silver Bow Creek. In this reach, the concentration of dissolved oxygen was observed to drop below 5 mg/L for an extended period (> 6 hours) during the night (Fig. 3). Such low levels are lethal to trout, especially if combined with other stresses (such as high ammonia, high nitrite, high pH, or high temperature). In the middle of the dead zone, the concentration of DO dropped below 1 mg/L for over 12 hours between 6 PM and 8 AM (Fig. 4). The unusual DO consumption is believed to be due to addition of nutrients, as well as biological and chemical oxygen demand, from the WWTP. From early July to late August, the streambed through this reach of Silver Bow Creek was choked with a 2 foot thick standing crop of algae and aquatic macrophytes (Fig. 4). This biomass was not apparent in April and May, and also had sloughed out of the stream bed by late September. Monitoring of DO levels in the dead zone in October 2006 showed that DO concentrations did not drop below 5 mg/L at any time during the day or night. This suggests a much lower level of biological and/or chemical oxygen consumption in the colder seasons. Whereas this is good news from the point of view of trout, on the flip side we also observed a further downstream persistence of elevated ammonia concentrations in October. Ammonia at levels we have measured in Silver Bow Creek below the WWTP (up to 5-6 mg/L as N) is toxic to trout (ammonia toxicity depends on water temperature and pH).

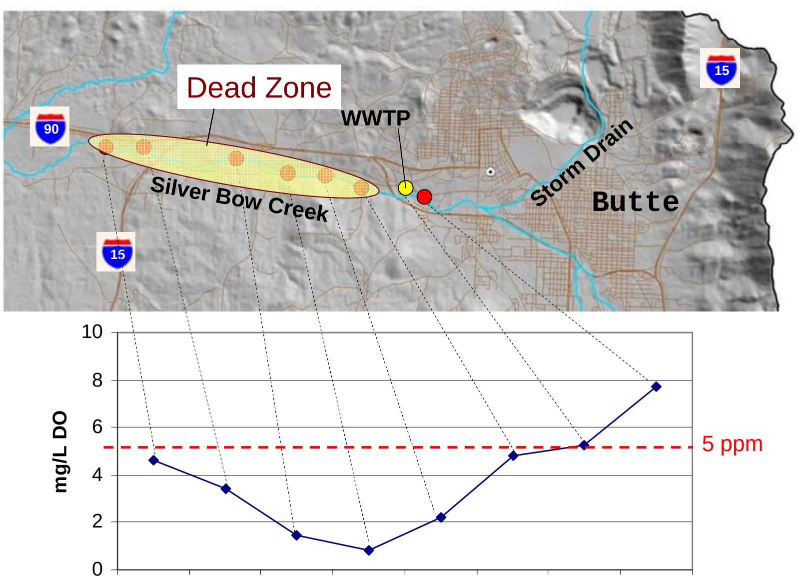

Fig. 3. Dissolved oxygen in Silver Bow Creek measured manually between 4 AM and 6 AM on August 30, 2006 by undergraduate students Stacy Wilcox and Ericka Sholey. The circled area has been termed a "dead zone", by analogy with similar hyper-eutrophic zones found in lakes or oceans.

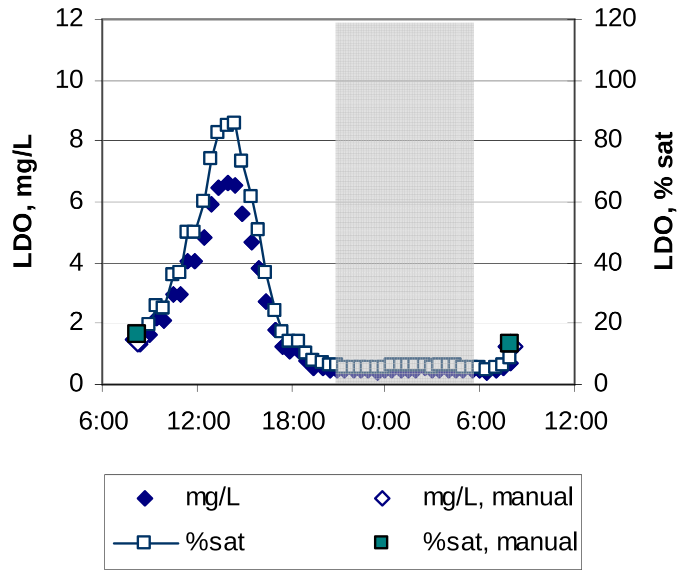

Fig. 4. Biomass (mainly vascular aquatic plants) in upper Silver Bow Creek about 2 miles below the WWTP discharge point (August, 2006). The diagram on the right shows the 24-hour cycle in dissolved oxygen concentration at this site. Continuous data were collected by a Hydrolab Minisonde with luminescent DO probe (LDO), whereas the green squares at either end were collected using a hand-held instrument. The shaded area denotes night-time. DO levels dropped below 1 mg/L for roughly 12 hours on this date.

4. Concentrations and loads of total dissolved ammonia (NH_4^+ and organic-NH_3) from the WWTP are very high, and overwhelm all other inputs of bio-available nitrogen in the rest of the watershed (Fig. 2b, 2c). Detailed synoptic investigations in August showed that oxidation of ammonia – most likely catalyzed by microbes – resulted in an increase in dissolved nitrite and nitrate concentration with distance below the WWTP confluence (Fig. 5). Once ammonia levels reached background (roughly 1.5 miles below the WWTP), nitrite levels also dropped to background (near or below detection limit). This is explained by the fact that nitrite is most often formed as an intermediate step in the conversion of ammonia to nitrate. Because the most bio-available form of nitrogen for plants is ammonia, it is the addition of ammonia (and also phosphate) from the WWTP that is believed to be primarily responsible for the incredible build-up of plants and algae in the "dead zone" during the summer.

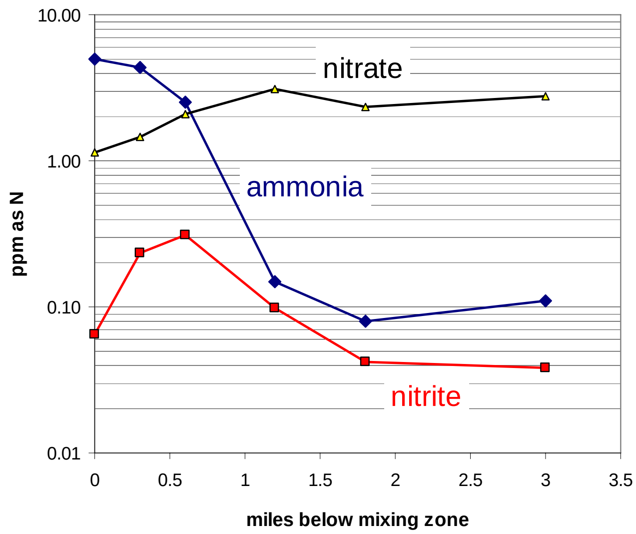

Fig. 5. Changes in concentration and speciation of dissolved N below the WWTP effluent, measured on August 9, 2006. The increase in nitrate concentration in the first 1.5 miles below the WWTP is believed to be due to oxidation of ammonia, first to nitrite, and then to nitrate.

5. A diel (24-h) study was conducted in July 2006 at monitoring stations above and below the WWTP effluent. At the downgradient station along Silver Bow Creek, concentrations and loads of ammonia increased at night and decreased during the day (data not shown). However, it is not known with confidence whether this cycle represents changes in the rate of ammonia breakdown (e.g., due to daytime uptake by photosynthetic plants or increased rate of ammonia oxidation in warm temperatures), or is due to diel changes in ammonia loading from the WWTP point source. The WWTP effluent decreased in flow during the night, as did the loading of total dissolved ammonia. Additional diel work is planned for the summer of 2007. An important objective of this work will be to confirm whether or not the diel changes in ammonia concentration are due to in-stream phenomena or to mixing of up-gradient waters.

6. Another objective of the Year 1 project was to use stable isotopes as tracers of sources of nutrients into upper Silver Bow Creek. Filtered, one-gallon water samples were collected in early October for isotopic analysis of δ^{15}N-ammonia, as well as δ^{15}N and δ^{18}O of nitrate. The results (Fig. 6) show a range in δ^{15}N-nitrate from +5.0 to +12.5 per mil, with a possible trend of <u>decreasing</u> δ^{15}N with distance downstream, and a range in δ^{15}N-ammonia of +8.9 to +15.7 per mil, with a possible trend of <u>increasing</u> δ^{15}N with distance downstream. In general, the N and O isotopic composition of nitrate for the surface water samples are very similar to results obtained by the Montana Bureau of Mines and Geology (MBMG) and HKM labs for shallow groundwater in the Butte Summit Valley. The LAO sample had an unusually high δ^{18}O-nitrate value, which will be tested by follow-up sampling in 2007. We plan to collect a more detailed synoptic set of samples in the summer of 2007 to see if the inferred trends in δ^{15}N-nitrate and δ^{15}N-ammonia are real. Our hypothesis is that ammonia-oxidizing bacteria in Silver Bow Creek selectively metabolize isotopically light NH_4^+, which then becomes isotopically light NO_3. The result is a lowering of the average δ^{15}N-nitrate of the stream, while enriching the residual ammonia in heavy N. This hypothesis explains the contrasting trends in isotopes of nitrate and ammonia, but needs to be tested by follow-up sampling in 2007.

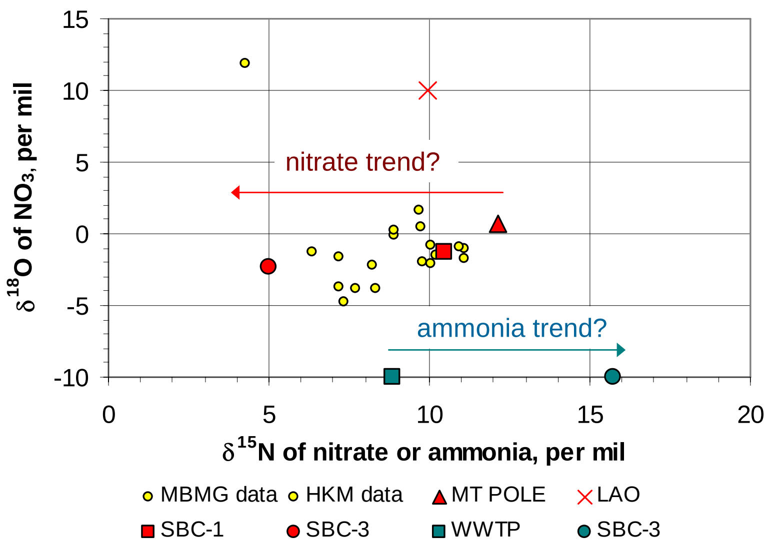

Figure 6. Stable isotope results for surface water samples collected in this study. Data for nitrate are shown in red. Data for ammonia are shown in green (arbitrarily plotted at y = -10). Also shown are isotopic analyses of shallow groundwater wells from the Butte Summit Valley (small open circles).

7. We had also planned to investigate diurnal (24-h) changes in the stable isotopic composition of nitrate and ammonia, as well as dissolved N_2 and O_2 gas. However, because our colleague Simon Poulson – who performs the specialized isotopic analyses of dissolved gas – was on sabbatical in Japan, this activity was not performed in 2006. We intend to do this in the summer of 2007.

Budget

As of this writing the project is well within budget, and the project end date was recently extended through the end of 2007. Much of the budgeted analytical money is set aside for stable isotopic analysis, and we still haven't received the invoice from Waterloo Lab for our preliminary set of isotopic analyses. We anticipate spending quite a bit more money in 2007 for analysis of conventional nitrate and ammonia isotopes, as well as isotopes of dissolved O_2 and N_2 gas. Additional analytical expenses are associated with quantification of dissolved nitrate. Although we had originally planned to use a HACH spectrophotometer for nitrate analysis, we decided during the summer of 2006 that this method gave unreliable results. As a result, all samples are now analyzed for nitrate – along with a complete suite of major anions - by ion chromatography at the Murdock Laboratory, Univ. of Montana (Missoula, MT). This adds to the analytical costs, but the project is still anticipated to be well within budget through 2007 into 2008.

Presentation of Results

Preliminary results were presented by graduate student Beverly Plumb at the 2006 AWRA conference in Polson, MT (Plumb, 2006), and by undergraduate students Ericka Sholey and Stacey Wilcox at the 2007 Montana Tech Undergraduate Research Symposium (Wilcox and Sholey, 2007). Bev Plumb is expected to write her thesis in the Fall of 2007, and defend either in December 2007 or the following semester. This thesis will contain all of our data, and will be the final deliverable for the project. We also anticipate submitting one or more papers for publication in a scientific journal.

References

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