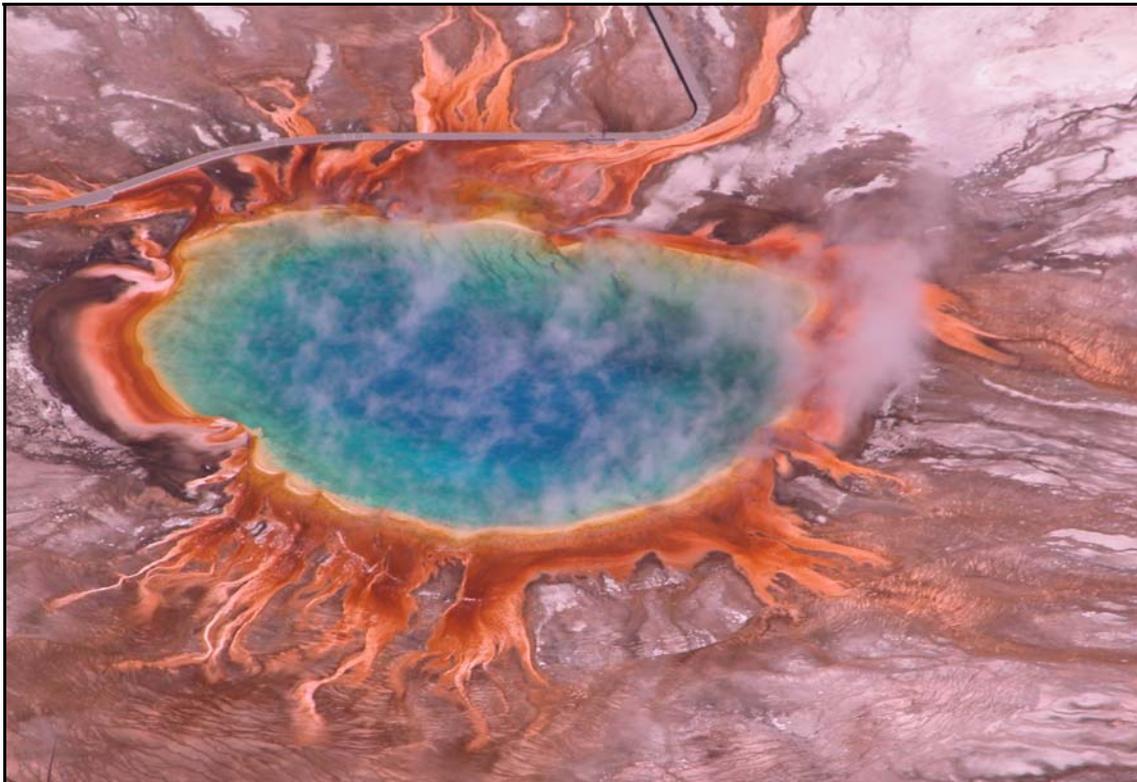


Hydrogeochemistry and Remote Sensing Yellowstone National Park

Preliminary scientific research status report for the field trips
June, 5th to July, 16th, 2003 and
September, 2nd to October, 10th, 2003

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Grand Prismatic Spring, Midway Geyser Basin (fly-over September, 30th, 2003)

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Introduction

From June, 5th to July, 16th, 2003 and September, 2nd to October, 10th, 2003 two field trips to Yellowstone National Park were organized within the course of my PhD project on volatile metal(loid)s in aquatic environments. Both field trips were conducted in cooperation with the research group of Kirk Nordstrom, USGS (United States Geological Survey) Colorado. During the first field trip Manja Seidel (geologist) accompanied me doing a practical training at the USGS. During the second field trip Juliane Becker (geology student) and Beate Böhme (B.Sc., geocology student) accompanied me for a master thesis, and a practical training respectively. Broder Merkel (Dean of the Faculty Geoscience, Geotechnique and Mining) joined the second field trip for one week for the remote sensing project.

Two main projects were undertaken: Hydrogeochemical investigations including standard water chemistry but with the main objective of detecting volatile metal(loid)s in the gas phase of the geothermal waters, and, during the second field trip, a remote sensing project for gathering data on the geometry of geothermal structures in an area where volatile metal(loid)s were detected previously.

The formation of volatile metal(oid)s is restricted to elements with either a high affinity for hydrogen or carbon, and halogen compounds. Hydride forming metal(loid)s are B, Si, Ge, Sn, Pb, P, As, Sb, Bi, S, Se, Te. Metal(loid)s with a high affinity for carbon, mostly for a methyl group (CH₃) are additionally to the afore mentioned Zn, Cd, Hg, Al, Ga, In, Tl, I. Methylation most commonly is enzymatically catalysed, e.g., by algae, fungi, yeast, or bacteria and correlates with microbial activity, that is highest at temperatures between 30 and 70°C. Most commonly volatile methylated compounds occur in reducing environments, even though exceptions are known. Additionally metal(loid)s can react in acidic, high-salinity waters with free halide ions, forming semi-volatile metal(loid) halides. Yellowstone geothermal waters provide excellent conditions for the detection of any of those species. Special focus was laid on arsenic determinations. The remote sensing project was used as an additional source of information for possible local distribution patterns of the volatile metal(loid)s.

Final analysis and data interpretation is yet under way and will be published in Juliane Becker's master thesis (mapping part), in my PhD thesis, as well as some peer reviewed papers. First results from the June / July sampling campaign are already submitted and accepted for publication in the Journal of Molecular Structures together with Alfred Hirner's research group in Essen, Germany (1).

Hydrogeochemistry

Five areas were investigated for hydrogeochemistry, especially volatile metal(loid)s: Nymph Lake up to Frying Pan Spring (6 locations (1 for gas only), total of 12 water samples), Hazle Lake (south of Nymph Lake, 2 locations, total of 5 water samples), Ragged Hills at Norris Geyser Basin (28 locations (4 for gas only), total of 30 water samples), Gibbon Geyser Group (8 locations (2 for gas only), total of 10 water samples), Lower Geyser Basin (3 locations, total of 3 water samples). Study areas were chosen based on previously reported (2, 3, 4, 5, 6, 7) high arsenic concentrations in water, since arsenic was the main target element for the volatile metal(loid) investigation, and own pre-investigations in 2002. Lower Geyser Basin was not sampled during the second field trip due to low concentrations and theft of sampling equipment in July 2003. Main focus of the second sampling trip was Ragged Hills.



Ragged Hills area west of The Gap with Titanic hot spring (left) and Milky Way (right) in September 2003

Standard water sampling included determination of pH, temperature, conductivity, redox potential, and oxygen, field photometry (total Fe, Fe(II), SiO₂, S²⁻), and taking samples for IC (ion chromatography), TOC/TIC (total organic / inorganic carbon), AAS (for arsenic), and ICP-MS, the latter two filtered (200nm) and acidified (HNO₃). Photometry of N-species, and Phosphate done during the first sampling trip was abandoned for the second due to bad results caused by interferences (e.g. by arsenate for the phosphate determination). Titration of alkalinity and acidity done during the first field trip was replaced by taking TIC samples. Ion balances for the first sampling campaign worked out much better based on TIC, instead of titrations.

For arsenic speciation the method by Le et al. (8) based on separation of Dimethylarsenate (DMA), Monomethylarsenate (MMA), Arsenate (As(V)) and Arsenite (As(III)) by ion exchangers was used. While DMA is sorbed on a cation exchanger and As(V) and MMA on an anion exchanger, As(III) as zero-valent H₃AsO₃⁰ complex passes through both exchangers and is collected in solution. In the field, the exchangers were wrapped in aluminium foil and stored cool together with the flow through solution containing the As(III) species. In the laboratory the cation exchanger is eluted with 1N HCl, the anion exchanger first with acetic acid to elute MMA, then with 1N HCl for the As(V) fraction.

Analyses were done mainly at the USGS labs in Boulder, Colorado (IC, ICP-AES, and AAS). AAS for the arsenic species was done in the lab in Freiberg, determination of total arsenic concentrations was repeated for cross-checks. TIC/ TOC were done in Freiberg.



Left: Arsenic speciation with two ion exchanger cartridges for the separation of DMA, MMA, As(V), and As(III) according to the method by Le et al. (8) done in the field (Ragged Hills)

Below: Water sampling with USGS (Kirk Nordstrom, Jim Ball, Beate Böhme, JoAnn Holloway from left to right) at Cinder Pool



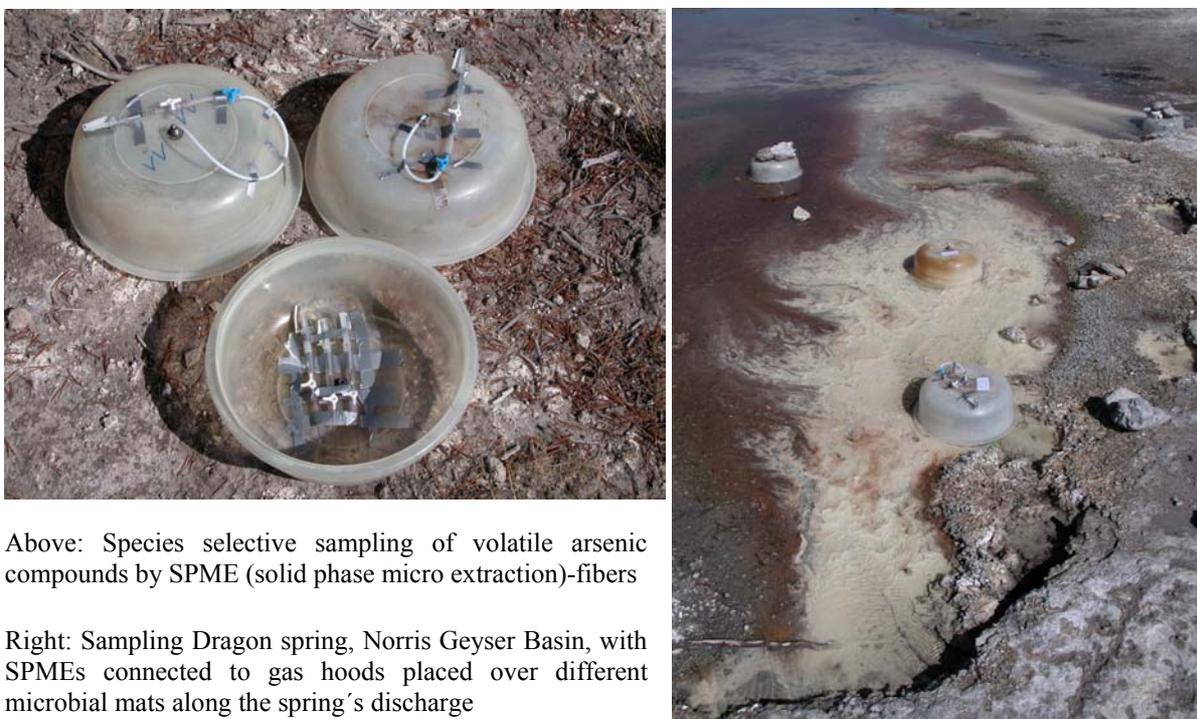
Gas sampling was done both by a screening method for total concentrations of volatile metal(loid)s and by species selective sampling, especially for arsenic. The screening method was developed beforehand (9). Plastic gas hoods were used over the hot spring discharges to collect the geothermal gases. A Teflon bottle containing a liquid oxidizing sorbent (NaOCl solution, diluted 1:100) was attached to the gas hood. Water traps were installed between gas hood and oxidizing bottle to exclude squirt water and condensation from water vapor. The gas sampling equipment was left for 3-5 days in the field to increase concentration enrichment of the volatile metal(loid)s. The NaOCl matrix gas samples were analyzed by AAS and ICP-AES in the lab afterwards with positive results for almost all locations sampled.

Recalculation from the obtained concentrations dissolved in the oxidizing solution ($\mu\text{g/L}$) to actual concentrations in the gas phase ($\mu\text{g/m}^3$) will require some more work upon. During gas sampling there was no measurable gas flow. Apparently the small diameter (2 mm) hoses and an about 20 cm high liquid column (NaOCl in the oxidizing bottle) created enough back pressure to prevent active gas flow through the system. Assumption so far is, that the concentrations in the oxidizing solution are due to concentration driven diffusion. That problem has to be modelled yet with a hydrogeochemical modelling program taking into account the gradient between concentrations in the aquatic phase of the geothermal feature and the oxidizing solution, exposure time, as well as species specific parameters.



Sampling volatile metal(loid)s by dissolving and oxidizing them in NaOCl in the white Teflon bottles

Species selective sampling of volatile metal(loid)s was done by sorption on SPME (solid phase micro extraction)-fibers. CAR-PDMS (Carboxen-Polydimethylsiloxane) and DVB-CAR-PDMS (Divinylbenzene) coatings were chosen, since they proved to be most suitable for sorbing volatile arsenic species. The fibers were exposed 2-3 days and analyzed after 1 day of cool storage at the Denver Federal Center, respectively Bozeman University. Results were so far only interpreted for arsenic. Trimethyl-arsine, dimethylchloroarsine, and methylchloroarsine were found. Additionally a volatile arsenic sulphur compound was detected, which was so far only synthesized in the lab (1). These first results are promising. However there were large variations in where and when those volatile arsenic species occurred, which can hopefully at least partly be clarified by the following data interpretation.



Above: Species selective sampling of volatile arsenic compounds by SPME (solid phase micro extraction)-fibers

Right: Sampling Dragon spring, Norris Geyser Basin, with SPMEs connected to gas hoods placed over different microbial mats along the spring's discharge

Remote sensing

Remote sensing was restricted to the Ragged Hills area only. It is supposed to provide a GIS (Geographical Information System) – based database for both detecting possible local distribution patterns of the volatile metal(loid)s analyzed and for registering changes in the geometry of geothermal features in this area of intense hydrothermal activity.

Aerial photography does exist from the study area, however not in the required resolution. Thus, aerial photographs had to be taken during the September / October field trip. The idea was to cut the study area down in several single pictures with sufficient overlap and combine the mosaic afterwards in a GIS program (TNTmips).

Checkpoints on the ground were needed for later georeferencing and georectifying the single pictures. For an area of approximately 300 m by 100 m 114 checkpoints were laid out in a 14 m raster. Points were first surveyed by differential GPS, the raster was checked, single points were slightly moved to better fit the raster, and the whole grid was surveyed again by theodolite relative to one permanent point which was erected by the National Park Service on the hillside over The Gap. All 114 checkpoints were marked temporarily only by red-white plastic stripes.



Right: Surveying the georeference raster by differential GPS



Left: Juliane Becker balancing the reflector on the checkpoints Right: Steve Miller (NPS) on the theodolite

As soon as the raster was set and surveyed, the problem of taking the aerial pictures was addressed. For that, a latex balloon of approximately 450 cm perimeter, and 150 cm diameter was used, filled with 2 m³ technical helium (lifting capacity 1.5 kg maximum). Attached to the balloon were two guiding lines; the second line proved useful not only as a backup system but also to keep the balloon a little bit more stable with changing wind directions.



Above: Camera and GPS on the helium balloon

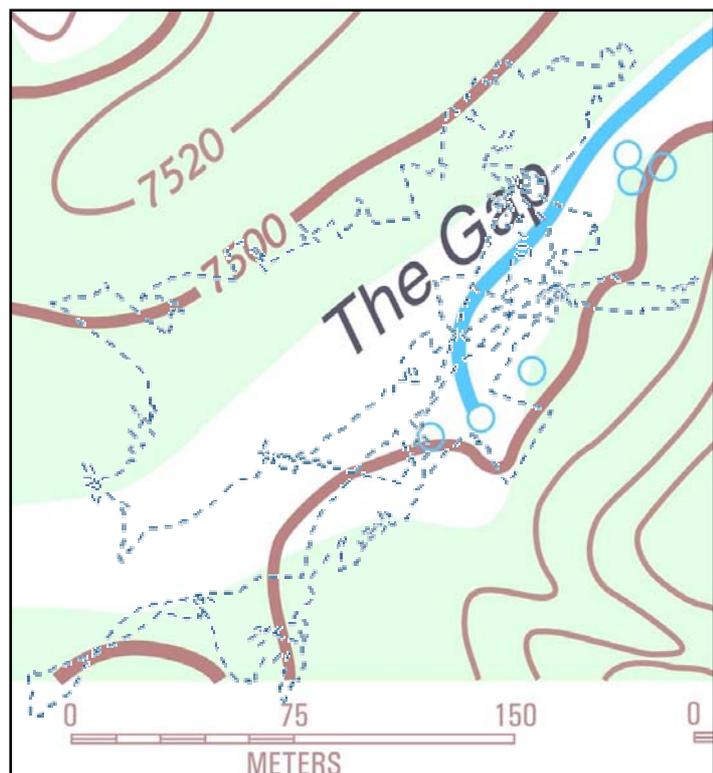
Left: Downloading the digital pictures on the laptop



A Canon G5 Powershot digital camera and a GARMIN GPS were mounted on the balloon. The GPS recorded the track of the balloon, taking position every 30 seconds. The camera was mounted on a cross construction of two 0.75 m long aluminium sticks, stabilized by a wire spun around all four ends of the sticks, tightened, and connected to the balloon. The Powershot camera had an additional function of taking pictures in pre-set time intervals for a pre-set duration. The camera was programmed on the ground to take one picture every minute for 100 minutes. Exposure time was first set to 1/1000, however 1/2000 turned out to produce sharper pictures still light enough.

The balloon was then released to an altitude of about 50 m. Two people, one on each line, walked the balloon over the study area. The picture on the right shows that with changing wind directions it was impossible to keep the balloon on a straight line. However, the overlap between the single pictures was still sufficient to guarantee the creation of the mosaic without missing gaps.

Right: Balloon position tracked by GPS during a 100-minutes-over-fly over the area west of The Gap, Ragged Hills





Above: 3-minutes-sequence of pictures from the helium balloon at 50 m altitude above Titanic hot spring; picture taken every minute, from left to right moving to the west

Additionally to the pictures from the balloon, aerial photographs were taken from a Cessna 172 at 2000 ft altitude. The camera used was the Canon G5 Powershot again. In a designed construction it was attached to the wing strut and operated from the cabin via a pneumatic auto timer. Alternatively it was possible to operate the camera via a USB cable from a laptop using Canon Capture software. Exposure time was 1/2000 again and 4x zoom. Flight routes with shooting points were programmed to a handheld GPS.



Cessna 172 with Canon G5 Powershot camera mounted to the wing strut, remotely operated by a pneumatic auto timer



Besides the colored digital aerial photographs, some thermal pictures were taken in a first spontaneous cooperation with Earl Mattson and Mitch Plummer from Idaho National Engineering & Environmental Laboratory. The digital camera and the thermal camera were mounted on one axis, pictures taken simultaneously. The normal color pictures will be used for georeferencing the thermal pictures. Better resolution will certainly be obtained using the balloon technique for the thermal camera, too. However, a higher lifting capacity of the balloon as well as solving the problem for remote operation of the thermal camera will be necessary for this project in the future.

Besides the described aerial photography detailed ground survey was done. All information on geometry, thermal heat distribution, and hydrogeochemistry from own investigations and previous reports (2-7) will be combined in a GIS atlas in Juliane Becker's master thesis, mapping part including a report with the evaluation of the balloon technique as well as suggestions for further improvements.

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