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A COMPARISON BETWEEN FLUORESCEIN DYE AND AMORPHOUS SILICA FOR GROUNDWATER TRACING

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Two hydrologically different localities were chosen to compare the tracing capability of fluorescein dye to amorphous silica, a potentially new, groundwater tracer. Amorphous silica is commercially produced and is non-toxic, colorless, stable, and not easily filtered or absorbed. Although the amorphous silica was not detected in either test case, it is felt that in the more common, hydrologic karst systems with low water storage and single conduit transport, that the silica would be detectable over background. The silica should also prove useful in tracing between two wells in a low to medium storage, karstic aquifer.

INTRODUCTION

Often in groundwater tracing studies, it is absolutely essential that the water supply is not colored by the tracing material. Two hydrologically different study sites in Texas were chosen to test the theory that amorphous silica, a colorless, non-toxic substance, could be used as such as tracer. In order to better quantify the success or failure of the material, fluorescein green dye was simultaneously injected at each site. The purposes of this paper are to review the properties of amorphous silica and to compare the effect of the two different ground materials on the tracers.

PROPERTIES OF AMORPHOUS SILICA: TRACER POTENTIAL

Amorphous silica (fumed silica) is produced by several companies in the United States and is used in a wide range of applications in industry. The silica utilized in this experiment was manufactured by Cabot Corporation in Tuscola, Illinois. The Cab-O-Sil brand of amorphous silica is non-toxic and has been approved by the United States Food and Drug Administration as a food additive at levels up to 2 percent by weight. Example foods using amorphous silica include: chocolate powders, dessert mixes, dried dairy products, flour, instant coffee, instant soup mixes, sugar and many others.

Toxicological studies conducted with Cab-O-Sil indicate that for acute oral toxicity, Oral LD 50 is greater than 5 g/kg (Cabot Corporation, undated). Ingestion of water carrying 1 percent silica as a tracer would require the ingestion of greater than one-half of the body weight of an individual to exceed the 5 g/kg test concentration. Therefore, a 68 kg person would have to drink 34 kg of water with 10,000 mg/1 SiO_2 per day to exceed the test concentration. This equals approximately 34 liters of water per day.

The silica is formed by the hydrolysis of chlorosilanes in a flame of hydrogen and oxygen. The chlorosilane utilized is silicon tetrachloride vapor and the reaction is:

$$SiCl_4 + 2H_2 + 02 \xrightarrow{1800^\circ C} SiO_2 \downarrow + 4HC1 \uparrow$$

(Cabot Corporation, undated). This produces spheres of silica which, by controlling process parameters, range from 7 to 21 millimicrons in diameter with surface areas ranging from 130 to 400 square meters per gram. During cooling, the spheres may collide and form aggregate chains, which vary in size but generally remain in the submicron range.

The small size of the silica spheres (14 millimicrons for this experiment) and the sub-micron size of aggregate chains can be compared to the 30 micron diameter of *Lycopodium* spores. Amorphous silica, when properly dispersed in water, should move with flowing water very well. This is because the very small size of the particles easily allows transport, and because the surface of the silica is hydrophilic and hydrogen bonds to water molecules as well as other hydrogen bonding liquids (Cabot Corporation, undated).

It is believed that filtration of amorphous silica does not occur to any significant degree in limestone aquifers where groundwater may flow through conduits. Filtration of the amorphous silica may occur in very fine-grained porous media such as alluvium or sandstone. Sorbtion of amorphous silica is also not believed to be a problem since the manufacturer considers the material to be "chemically inert" (Cabot Corporation, undated).

The stability of silica over the duration of a trace is certainly not a problem. Silica is one of the most abundant compounds known and is considered completely stable. Amorphous silica is approximately 99.8 percent pure SiO_2 and does not undergo chemical alteration under natural conditions.

Amorphous silica is relatively expensive when compared to some other tracers. For this experiment, a chemical supplier charged $3.60 per pound. However, much more silica must be utilized for a trace than fluorescent dye because the detection limit of fluorescent dye is much lower than the detection limit of silica, detection limits being controlled by background concentrations.

Detection of amorphous silica is, at this time, not particularly easy. The standard method for analysis of silica in water is a colorimetric procedure for dissolved silica, with a working range of 2 to 25 mg/l silica (American Public Health Association, 1975). Because the amorphous silica would exist in significantly higher concentrations and is predominantly in a colloidal suspension, not dissolved, the standard method is not acceptable. For this experiment, detection was accomplished using Inductively Coupled Plasma Emission Spectrometry (ICPES) which analyzes for silicon, and approximately 40 other metals, for both suspended and dissolved species.

It is imperative that the background concentration of a tracer species be low. *Lycopodium* spores and some fluorescent dyes have proved successful primarily because there is essentially no natural background concentration of these materials in groundwater. Amorphous silica can be easily masked by a relatively high background of dissolved silica. This background concentration, controlled by the solubility of natural amorphous silica, not quartz (Garrels and Christ, 1965) varies from one aquifer to another, but appears to be relatively stable in a given aquifer or area. For aquifers, SiO_2 is commonly less than 30 mg/l (Marquardt and Elder, 1979). In the Edwards Aquifer, dissolved silica concentrations range from 10 to 15 mg/l.

In summary, amorphous silica appears to be favorable as a tracer in regard to toxicity, tracer movement, chemical stability, and filtration/sorbtion. The need of a tracer with the properties of amorphous silica may outweigh its higher expense and time associated with having to regularly collect samples. Although background concentrations may at first appear to be a problem, the small variation in silica content in most karst waters allows for even slight changes due to tracer injection, to be detected. The following two case histories test the use of fluorescein and amorphous silica in a high-storage karst system and a low-storage alluvial system.

CASE 1—CAMP WOOD, TEXAS
GEOLOGY AND HYDROLOGY

Old Faithful Spring, the water supply for the town of Camp Wood, Texas, was first briefly described by Long (1958), and discussed in a little more detail by Brune (1975). Brune (1975) states that Old Faithful Spring (Camp Wood Spring) issues through alluvium, but its source is from cavernous strata of the Glen Rose Limestone.

The Camp Wood Creek basin is 74 square kilometers and is underlain primarily by Glen Rose Limestone (Figure 1). Roaring Springs, Cave Springs, and the South Prong Springs are the three largest springs producing the base flow of Camp Wood Creek. The water sinks for short distances in the chert-rich river gravels and reappears on the surface until the final sink point is reached. The stream is normally dry between this point and Old Faithful Spring which is about 7 kilometers away. Only during major storm events does Camp Wood Creek flow all the way to the Nueces River.

Figure 1. **Drainage basin of Camp Wood Creek and Old Faithful Spring.**

METHODS AND RESULTS

In order to establish a connection between the final sinking point of Camp Wood Creek and Old Faithful Spring, fluorescein and the silica were injected into the flowing water. A slurry of silica was mixed by the creek using two electric outboard motors in a 55-gallon drum. A 10% (100,000 mg/l) slurry of silica was placed into the stream and allowed to infiltrate into the streambed. Some of the silica appeared to drop out of suspension soon after injection.

Twenty minutes later, 0.82 kg of concentrated powdered fluorescein was mixed with water and released to the stream which was flowing at 0.068 cms. Quantification of the dye trace was performed using an ISCO automatic water sampler and a Turner Designs fluorometer. The first samples were taken at Old Faithful Springs one and one-half hours after tracer injection. Discharge of the spring was 0.062 cms at that time. The dye began to arrive at the spring about 23 hours after injection (Figure 2). The original dye concentration injected into Camp Wood Creek was 8,500 mg/1. The maximum dye concentration measured at Old Faithful Springs was 0.094 mg/1, so the dye experienced approximately a 5 order magnitude dispersion. Assuming that the silica would be dispersed at the same rate and that the initial silica concentration was 100,000 mg/1 (10%), a silica concentration due to the trace materials of approximately 1 mg/1 was expected. The average background SiO_2 concentration of 13.271 mg/1 would tend to mask a 1 mg/1 maximum increase unless the background SiO_2 concentrations were extremely constant (standard deviation approaching zero). The standard deviation of the silica analyses was 0.365, which would make a 1 mg/1 increase significant (2.74 standard deviations) if observed. During the period of dye arrival, however, the highest silica content (above test average) was 0.350 mg/1. This occurred 9 hours after the dye peak, and could not be construed as a significant increase (Pearce, 1984).

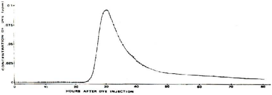

Figure 2. **Fluorescein dye concentration versus time curve at Old Faithful Spring.**

The concentration of dye decreased rapidly and was down to 0.019 mg/1 just 20 hours after peak. Forty percent of the original dye emerged from the spring within the first 100 hours after injection. Probably no more than another 10% emerged after this since the curve was approaching zero concentration. The rest of the dye must have been largely adsorbed by clay minerals and particle surfaces which would be unexpected for flow through an open conduit. Just slightly before the dye reached the spring, a nearby resident complained of her well water turning green. Subsequent discussions with the driller showed that the well had been drilled *only* through river alluvium. This fact, plus the data from the dye-dilution curve, dispel the previously held concept that the groundwater flow was through limestone conduits.

It is our opinion that this trace was a borderline case of silica effectiveness. If the dispersion was slightly less or the initial silica concentration increased, the trace would probably have been successful. It is important to note again that the silica appeared to drop out of suspension along the streambed at the injection site thus lowering the initial concentration. In an open karst system of low storage such as found in West Virginia or Kentucky, the silica concentration would probably remain high enough to be detected at a spring resurgence.

CASE 2—EDWARDS AQUIFER, SAN MARCOS, TEXAS

The Edwards Limestone Aquifer in the Balcones Fault Zone has been well studied and defined as having many cavernous systems that transport water from recharge points to the spring outlets. Although detailed hydrogeologic reports have been published about large areas of the region (Puente, 1969; Reeves, 1976; Maclay and Rappmund, 1979; Klemt et al., 1979; Maclay, 1981) little attention has been drawn to charcterizing the flow conditions between nearby points within the aquifer.

GEOLOGY AND HYDROLOGY

The area around San Marcos is underlain by Cretaceous Aged rocks that have been intensely faulted, causing the Edwards Aquifer to be broken into numerous blocks. The San Marcos Springs issue from the Edwards Limestone Group along the San Marcos Springs Fault (Figure 3) which has created the Balcones Escarpment. On the southeast side of the fault escarpment, quaternary alluvium mantles the flatland areas. Northwest of the escarpment, the hills are underlain by the Del Rio and Buda Formations and the Eagle Ford Group.

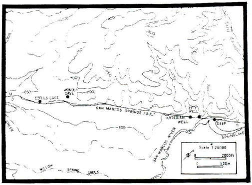

Figure 3. **Location of the San Marcos Springs Fault and points involved with the dye trace.**

The San Marcos Springs is the second largest spring in Texas with an average flow of 4.6 cms (161 cfs) during the period 1965–74 (Guyton et al., 1979). At the time of dye and silica injection, the spring was flowing at 3.0 cms (105 cfs). Estimated transmissivities for the aquifer along the San Marcos Springs Fault are generally over 1 million gpd/ft. This demonstrates the highly-cavernous nature of the aquifer and the great amount of water in storage around the test site. The San Marcos Springs are actually composed of over a dozen individual spring orifices which are beneath ten to forty feet of water due to an impoundment made by a commercial glass-bottom boat tour operation. Prior to this study, only one trace had been performed to the springs (Ogden, 1984), so flow paths, water-velocities, and the degree of interconnection of spring orifices was essentially unknown.

METHODS AND RESULTS

Ezell's Cave, located 2.5 km southwest of the springs and on the San Marcos Springs Fault (Figure 3), was chosen as the test site because it has a large, deep lake at the bottom that was assumed to be in hydrologic connection with the springs. Approximately 13.6 kg of silica were mixed with approximately 132 liters of water, yielding an initial concentration of 10% silica (100,000 mg/1). Mixing was again by electric outboard motor in a 55 gallon drum. The slurry was pumped down into the cave pool. At the same time (April 1, 1983), 0.91 kg of fluorescein was added to the pool. The following day sampling was initiated at the university's artesian well (Figure 3) using the automatic sampler. Samples were also taken from one of the city's wells by the city employees (Figure 3). Both sites are located along the San Marcos Springs Fault and were sampled every three hours. Charcoal traps were also placed at the two wells and seven of the spring orifices.

For samples collected at the artesian well, SiO_2 values range from 12.806 mg/1 to 14.265 mg/1 with a mean value of 13.439 mg/1 and a standard deviation of 0.368. Samples collected at the city's well ranged from 13.252 mg/1 to 14.650 mg/1 with a mean value of 13.605 mg/1 and a standard deviation of 0.230. The small variation in silica content was evident that no significant trend of increased silica content occurred. Only small variations exist, which are normal for a natural system (Pearce, 1984).

Each sample collected was also treated for fluorescence using the fluorometer. None of the samples displayed any measurable fluorescence (greater than 1 ppb). The great amount of water in storage had caused the dye to be highly dispersed.

Nine days after injection of the dye (April 10th), the charcoal traps had adsorbed and concentrated enough dye to confirm a hydrologic connection. The next day (April 11), the charcoal trap at the city's well showed the dye's presence. The charcoal traps were retrieved by divers from the seven spring orifices on the following day (April 12th) and surprisingly *only one* orifice (Deep Spring, Figure 4) was positive. The dye continued to emerge from Deep Spring for approximately 40 more days as the May 24th samples were negative. Catfish Spring (Figure 8) showed a slight presence of the dye on May 18th and the dye ceased emerging just one week later. Water from the other five spring orifices never tested positive.

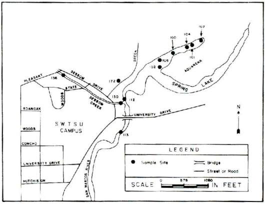

Figure 4. **Location of the San Marcos Springs orifices tested during the dye trace: (100) Divergent Spring, (101) Cabomba Spring, (102) Deep Spring, (104) Johnny W. Spring, (106) Catfish Spring, and (107) Hotel Spring.**

Prior to the dye trace, water samples were taken weekly by divers during the previous year. Close inspection of the water chemistry data demonstrated that the Deep and Catfish Spring orifices of the San Marcos Springs are similar chemically, but quite different from the other spring orifices in temperature level and dissolved oxygen content. This information suggests that there are two flow regimes quite isolated from one another. A postulated fault was shown on Guyton's (1979) map that would separate the two sets of springs. This fault could have significant enough displacement to cause isolation of the two flow systems. The conclusion drawn from this dye trace is that the water emerging from the San Marcos Springs is not from a single aquifer zone.

CONCLUSIONS

The two case studies demonstrate that amorphous silica is not a viable tracer in karst systems with high dispersion or for alluvial aquifers with high filtration and adsorption. Most speleologists perform groundwater tracing in open karst aquifers of low storage in which the water is moving under vadose conditions. In these karst aquifers, small surface streams commonly sink into cave openings and travel through long, air-filled passages to emerge as springs with little increase in water volume. Amorphous silica may be effective in such systems. The major drawback to this material is its expense and the need for sophisticated detection equipment and an automatic sampler. But where a hydrogeologist is working under contract, the necessity of using a non-toxic, colorless, and stable tracer may outweigh expense, and in fact may be less expensive than some other tracers meeting the same requirements. Tracing between municipal wells may be such a situation.

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