Desorption Isotherms for Toluene and Karstic Materials and Implications for Transport in Karst Aquifers

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ABSTRACT

Karst aquifers dominated by conduit flow are extremely vulnerable to fuel contamination such as from leaky underground storage tanks or spills. Direct flow paths through fractures and sinkholes often allow contaminants to move rapidly into the conduit system. Not much is known about how the fuel will interact with the carbonate rock in the conduit system. The objective of this research was to bridge this information gap by measuring sorption and desorption of fuels to karst materials. The first phase of this study involved the dissolution and desorption processes. Initial experiments (n=5) used karst bedrock fragments of known size soaked in toluene for 24 hours. Then the sterile toluene-soaked rocks were placed in sterile distilled water. The concentration of toluene dissolved in the water was measured over increasing time periods. These data were used to derive a first-order exponential rate of desorption [$C_w(t)=C_ie^{kt}$]. The empirical value for k was 0.8958. The toluene concentration in the water reached a maximum carrying capacity in approximately 3 weeks. The second phase of this project involved sorption studies using limestone fragments of known size and water containing a known concentration of dissolved toluene. The empirical value for the sorption k was 1.006. These results show that sorption is faster than desorption and have implications for designing a model that predicts the fate and transport of fuels in karst aquifers.

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A Computer Program that Uses Residence-Time Distribution and First-Order Biodegradation to Predict BTEX Fate in Karst Aquifers

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ABSTRACT

Approximately 40 percent of the United States east of the Mississippi River is underlain by karst aquifers. Karst ground-water systems are extremely vulnerable to contamination; however, the fate and transport of contaminants in karst areas are poorly understood because of the complex hydraulic characteristics of karst aquifers. Ground-water models developed using Darcy’s Law coupled to rates of biodegradation are useful for predicting the fate of fuels in unconsolidated aquifers, but have little utility in karst conduits. Conceptual models developed for karst aquifers have a consistent theme of non-ideal flow, storage, and active flow components. This research used a residence-time distribution (RTD) model approach that integrated residence times of contaminants isolated in storage areas with the residence time of contaminants moving through conduits coupled to a pseudo-first order rate of biodegradation. The microcosms consisted of four 1-liter chambers connected with small glass tubing. A peristaltic pump provided a consistent flow of karst water from a 10-gallon reservoir. First, a quantitative dye study was done to establish the residence-time distribution of the three systems. This was followed by a sterile toluene run to measure sorption of toluene to the microcosm systems. The third microcosm run incorporated karst bacteria and toluene. The removal of toluene predicted by the RTD-biodegradation model and the experiment were within 2 percent agreement (n=3). The RTD-biodegradation model was transformed into a user-friendly program that utilizes MS Excel® with Visual Basic interfaces. The input sheet of this prototype program requires site information, a biodegradation rate, and the results of a quantitative tracer study. The results, or output pages, provide residence-time distribution graphs and various statistical calculations. The output pages also report the calculated amount of BTEX removed during transport through the karst aquifer based on RTD and biodegradation. Additional work is needed to incorporate dilution into the model.

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Lactate Induction of Ammonia-Oxidizing Bacteria and PCE Cometabolism

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ABSTRACT

Water containing bacteria was collected from a PCE-contaminated karst aquifer in north-central Tennessee to establish liquid, 1-liter microcosms. The microcosms were spiked with known concentrations of perchloroethylene (PCE) and 11 different formulations of lactic acid. The ammonia-lactate formulation caused a rapid removal of PCE and oxygen (O_2). Similar results that were achieved by using a second set of microcosms spiked with ammonia-lactate to re-test the removal rate of PCE and O_2 indicated a possible cometabolic PCE-removal process. Although only one report of PCE-cometabolism was found in the literature, ammonia-oxidizing bacteria indigenous to the karst aquifer were hypothesized to be capable of cometabolizing PCE with the ammonia mono-oxygenase (AMO) pathway. To test this hypothesis, microcosms were established using different forms of ammonia (ammonia-lactate, ammonia-chloride, ammonium plus sodium lactate), reference controls (sterile, live without food, sodium lactate, sterile + ammonia lactate), and ammonia mono-oxygenase inhibitors [2-chloro-6-(trichloromethyl) pyridine, azide, and allylthiourea]. Microcosms treated with ammonia-lactate had the most rapid reduction of PCE and O_2, followed by the ammonium + sodium-lactate treatment. The other live microcosms treated with ammonia also experienced significant drops in PCE and O_2 after 24 hours. The control (sterile and live without food) microcosms did not experience a significant drop in PCE in the same time period. After 24 hours, the rapid PCE removal in all the ammonia-treated microcosms decreased due to the consumption of the oxygen. Tests with the AMO inhibitor in the presence of ammonia-lactate did not prevent the PCE removal or O_2 consumption. Lactate may stimulate AMO or protect the enzyme from inhibition. Additional tests need to be conducted to prove that AMO is responsible for the removal of PCE. These preliminary results provide strong evidence that karst bacteria indigenous to this aquifer can cometabolize PCE.

Biodegradation of Toluene as It Continuously Enters a 5-Liter Laboratory Karst System

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ABSTRACT

Contamination releases can occur as slow, long-term spills rather than as instantaneous spills. These continuous releases can result in a steady state of contaminants that can last months to years. Predicting the fate and transport of these contaminants in a karst aquifer is especially challenging because of the complex hydrogeology and uncertainties in residence time. The objective of this research was to adapt the residence-time distribution (RTD) biodegradation model, which was developed to predict the biotransformation of a single spill in a karst aquifer, for a continuous input of contaminants. Theoretically, the RTD for a karst system calculated from either a pulse- or a continuous-input tracer study would be identical, but mathematical manipulation of the data for the two approaches is quite different. Determination of the RTD from a continuous input requires numerical differentiation of tracer response data as opposed to numerical integration for the pulse approach. Three experimental runs were conducted involving the application of a continuous input: (1) rhodamine dye alone to establish RTDs for the systems, (2) sterile toluene (25 micrograms per liter) to quantify abiotic sorption, and (3) toluene with karst bacteria to quantify biodegradation. The three replicate karst systems were each 5 liters and had a continuous flow rate of 3.3 milliliters per minute. The difference between the RTD-based model prediction and the experimental toluene conversions was 17 percent. The continuous-input approach (numerical differentiation) had the tendency to magnify experimental and random errors in the tracer response data as compared to the pulse-input method (numerical integration).

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Bacteria Induced Dissolution of Limestone in Fuel-Contaminated Karst Wells

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ABSTRACT

Karst landscapes are formed in water-soluble geologic formations, such as limestone, in which dissolution processes have enlarged water-transmitting openings. Approximately 20 percent of the United States is underlain by carbonate rocks and is classified as karst, and 40 percent of the United States east of the Mississippi River is underlain by karst aquifers. Karst ground-water systems are extremely vulnerable to contamination. Many organic contaminants such as fuels can stimulate bacteria biodegradation and the production of carbon dioxide (CO_2). The increased respiration by bacteria in contaminated karsts aquifers can lead to a significant increase in CO_2 production and formation of carbonic acid.

A quantitative study was conducted to determine the effect of elevated concentrations of carbonic acid due to bacteria action on limestone dissolution. Sealed flasks were set up that contained 250 milliliters of distilled water, limestone fragments of known size and weight, and varying concentrations of CO_2. The flasks with elevated CO_2 concentration had a 3-fold increase in the rate of calcium carbonate dissolution. Water with elevated CO_2 concentrations had a slightly lower pH than water with the lower CO_2 concentrations, but the difference in pH was not statistically significant at the 0.05 confidence level. Further tests were done to determine if these lab results applied to field conditions. Water samples were collected from wells completed in karst aquifers. The CO_2 concentrations in water samples collected from fuel-contaminated wells were higher than in samples collected from wells with no fuel contamination. Also, the dissolved calcium was usually two or three times greater in the fuel-contaminated wells. The results have implications for redesigning geochemical models that predict conduit enlargement when fuel contaminants are present in karst aquifers.

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INTRODUCTION TO THREE FIELD TRIP GUIDES:
Karst Features in the Black Hills, Wyoming and South Dakota-Prepared for the Karst Interest Group Workshop, September 2005

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This years Karst Interest Group (KIG) field trips will demonstrate the varieties of karst to be seen in the semi-arid Black Hills of South Dakota and Wyoming, and will offer comparisons to karst seen in the two previous KIG trips in Florida (Tihansky and Knochenmus, 2001) and Virginia (Orndorff and Harlow, 2002) in the more humid eastern United States.

The Black Hills comprise an irregularly shaped uplift, elongated in a northwest direction, and about 130 miles long and 60 miles wide (figure 1). Erosion, following tectonic uplift in the late Cretaceous, has exposed a core of Precambrian metamorphic and igneous rocks which are in turn rimmed by a series of sediments of Paleozoic and Mesozoic age which generally dip away from the center of the uplift. The homoclinal dips are locally interrupted by monoclines, structural terraces, low-amplitude folds, faults, and igneous intrusions. These rocks are overlapped by Tertiary and Quaternary sediments and have been intruded by scattered Tertiary igneous rocks. The depositional environments of the Paleozoic and Mesozoic sedimentary rocks ranged from shallow marine to near shore-terrestrial. Study of the various sandstones, shales, siltstones, dolomites and limestones indicate that these rocks were deposited in shallow marine environments, tidal flats, sand dunes, carbonate platforms, and by rivers. More than 300 ft (91 m) of gypsum and anhydrite were deposited at various times in evaporite basins.

Erosion of these uplifted rocks produced the landscape we see today. Rocks of the Pahasapa Limestone (Madison of some reports), Minnelusa Formation and older sediments form a limestone plateau that rims the central Precambrian metamorphic core. Erosion of weak red siltstones and shales of the Spearfish Formation has formed the "Red Valley”, the main area of present and proposed future housing and industrial development. White gypsum caps many of the hills in the Spearfish and is a conspicuous landform in the overlying Gypsum Spring Formation. Resistant sandstones that are interbedded with other rocks lie outboard from the Red Valley and form the hogback that encircles the Black Hills and defines its outer physiographic perimeter.

Relatively soluble rocks, including dolomite, limestone, gypsum and anhydrite, comprise about 35 percent of the total stratigraphic section within the topographic Black Hills, that is, the area including and within the “Dakota sandstone hogback” (fig. 1), comprising rocks of the Inyan Kara Group (fig. 2). Karst is significant in many formations in the limestone plateau and Red Valley (fig. 2). World-class caves, sinking streams, and other features are found in the Pahasapa Limestone. Lesser karst features are found in the other carbonate units. Evaporite karst has developed extensively in the anhydrite and gypsum in the Minnelusa, Spearfish, and Gypsum Spring Formations. Solution of soluble evaporate and carbonate rocks at depth has produced collapse in non-soluble bedrock and surficial deposits at the surface, which in several places extends many hundreds of feet above the soluble rocks.

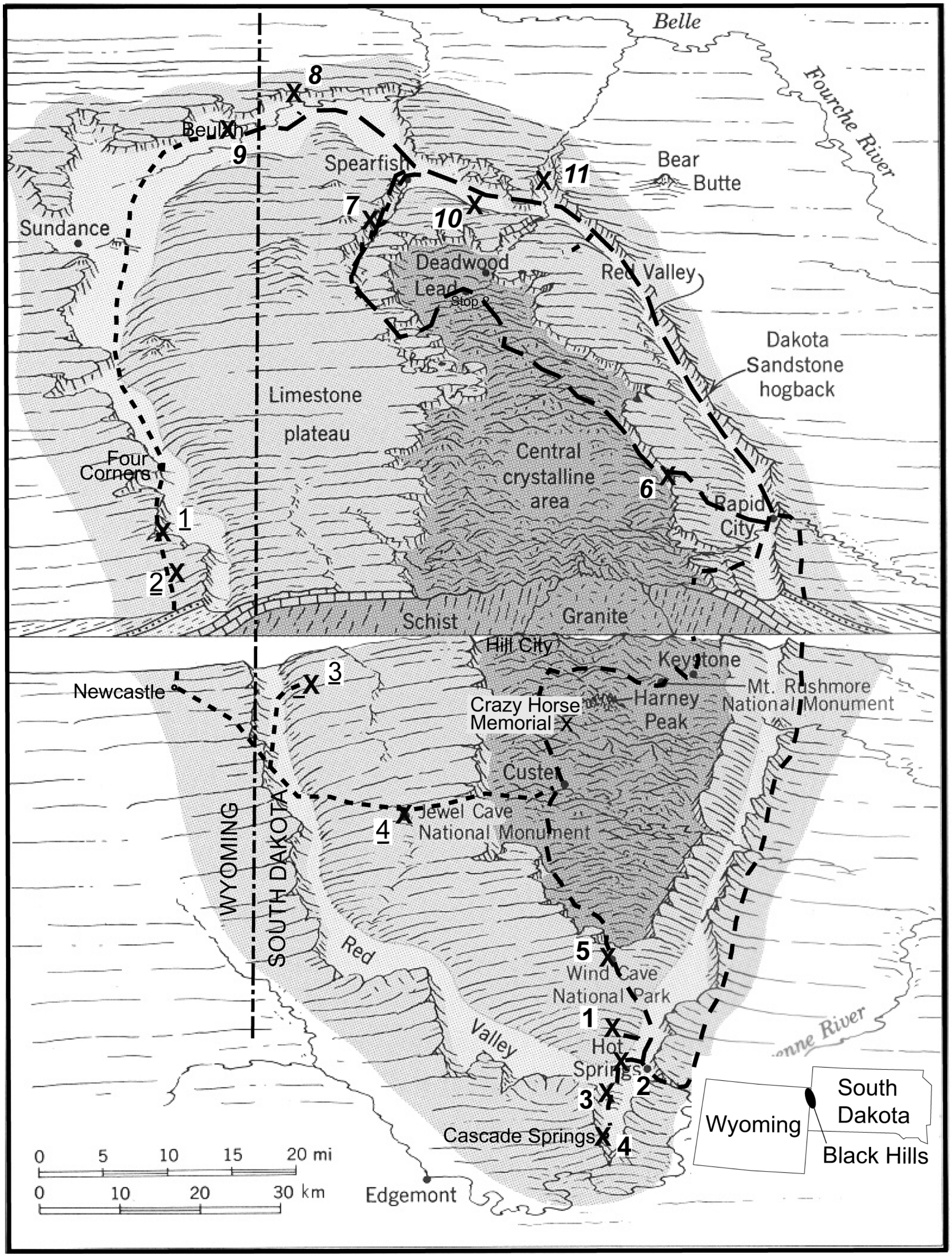

Figure 1. Generalized diagram showing the geology and geomorphology of the Black Hills and route of three 2005 Karst Interest Group field trips (southern trip, regular numbers; Northern trip, italics; western trip, numbers underlined). Most of the urban development and karst features are in the Red Valley, underlain by Triassic red beds and in the lime-

AGE			FORMATION	LITHOLOGY (Thickness in feet) (*thicknesses mostly from DeWitt and others, 1989*)	KARST FEATURES	FIELD TRIP STOP
CENOZOIC	QUATERNARY	Holocene/ Pleistocene	Terrace deposits, alluvium, colluvium, landslide deposits, sinkhole fill, spring deposits	Gravel, sand, silt, clay, and calcareous tufa	Collapse sinkholes due to dissolution of evaporites and carbonates in formations below; spring deposits; paleontologic animal traps	2, 8, 9, 11
MESOZOIC	CRETACEOUS	Upper	Hell Creek Formation	Shale and sandstone, lignite (425+)		
			Fox Hills Sandstone	Sandstone (25-200)		
			Pierre Shale	Dark-gray and black shale (1,200-2,700)		
			Niobrara Formation	Calcareous shale and impure chalk (80-300)		
			CarlileShale	Light- to dark-gray shale (325-750)		
			Greenhorn Limestone	Shaly limestone and calcareous shale (225-400)		
			Belle Fourche Shale	Gray shale with limestone concretions and bentonite (150-850)		
			Mowry Shale	Gray siliceous shale (125-250)		
			Newcastle Sandstone	Brown and white sandstone (0-100)		
			Skull Creek Shale	Dark-gray to black shale (150-270)		
		Lower	Fall River Sandstone	Massive to slabby sandstone (10-200)		
			Lakota Formation	Cross-bedded, copnglomeratic sandstone, shale, clay and local impure limestone (35-700)	Breccia pipes extending down to the Minnelusa Formation	
	JURASSIC	Upper	Morrison Formation	Green to maroon shale and thin sandstone (0-220)		
			Unkpapa Sandstone	Fine-grained sandstone (0-275)		
		Middle	Sundance Formation	Greenish-gray shale, yellow sandstone, and reddish sandstone and siltstone (250-475)		
			Gypsum Spring Formation	Gypsum, red siltstone, limestone, dolomite (0-45)	Gypsum karst: sinkholes; contorted gypsum.	11
	TRIASSIC	Lower	Spearfish Formation	Red shale, siltstone, fine-grained sandstone and gypsum (250-900)	Gypsum karst: sinkholes; probable caves at depth in several stratigraphic intervals; contorted gypsum; gypsum stringers; springs.	2, 4, 8, 9
PALEO.	PERMIAN	Upper	Minnekahta Limestone	Laminated, purplish-gray limestone (30-65)	Minor carbonate karst: solution-enlarged fractures; few sinkholes; color leaching in Opeche below.	3, 4, 10

Figure 2. Generalized stratigraphic section showing known karst features in sedimentary rocks in the Black Hills, South Dakota-Wyoming. Numbers indicate formations visited during the formal conference. Underlined numbers indicate stops in the supplementary western field trip.

stone plateau, underlain by a variety of Pennsylvanian and Permian rocks. Modified from Strahler and Strahler (1987) with permission.

PALEOZOIC	PERMIAN	Up.	Opeche Shale	Red shale, siltstone, and fine-grianed sandstone and scattered gypsum (25-150)	Possible minor dissolution of gypsum	10
	PERMIAN PENNSYLVANIAN	Lower Upper	Minnelusa Formation	Yellow, red, cross-bedded sandstone, gray cherty limestone, dolomite, red shale and siltstone, and anhydrite in subsurface that is mostly absent at the surfrface due to dissolution. (350-1,500)	Intrastratal anhydrite karst in upper half: advancing dissolution front at depth; disrupted bedding, caves, collapse breccia; breccia pipes, some extending upwards as much as 1,000 feet into the Lakota Formation; paleokarst sinkhole fill at base.	1
	MISSISSIPPIAN	Lower	Pahasapa Limestone (Madison Limestone)	Massive, gray limestone that is locally dolomitic, with an irregular upper contact due to pre-Pennsylvanian karst weathering. (300-630)	Carbonate karst: world-class caves in upper part; swallow holes; resurgent springs; sinking streams; paleokarst; few surface sinkholes, if any.	5, 6, 7 Evening Cave Trips to Wind and Jewel Caves
	MISSISSIPPIAN DEVONIAN	Lower Upper	Englewood Formation	Gray to lavender limestone with shale at base (30-60)		
	ORDOVICIAN	Upper	Whitewood Formation	Gray dolomite and limestone (0-150)		
	ORDOVICIAN	Upper	Winnipeg Formation	Green shale and siltstone (0-110)		
	ORDOVICIAN CAMBRIAN	Lower Upper Middle	Deadwood Formation	Brown sandstone, green glauconitic shale, basal conglomerate and limestone-pebble conglomerate (4-700)		
PRECAMBRIAN			Precambrian rocks	Schist, slate, quartzite, sandstone, intruded by amphibolite, granite, and pegmatite.		

Figure 2. Generalized stratigraphic section showing known karst features in sedimentary rocks in the Black Hills, South Dakota-Wyoming. Numbers indicate formations visited during the formal conference. Underlined numbers indicate stops in the supplementary western field trip -continued.

Two major aquifers are located in formations that include karstic rocks water in the Black Hills--c-rbonate karst in the Pahasapa Limestone, and evaporite karst in the Minnelusa formation. The Madison and Minnelusa aquifers are two of the most important aquifers in the Black Hills area and are used extensively for water supplies. Headwater springs originating in the limestone plateau, streamflow losses to the Madison and Minnelusa outcrops, and large artesian springs in the Red Valley are important hydrologic features that are associated with karst processes in these aquifers. Locally, secondary porosity has developed in the lower Spearfish formation due to gypsum dissolution. Sinkhole collapse in gypsum-bearing rocks is common. Sinkholes, of the type's common in the eastern United States are rare. Solution in carbonate rocks has produced the third and sixth largest known recreation caves in the world, Jewel Cave and Wind Cave. A sinkhole in Hot Springs is one of the world's greatest vertebrate paleontologic occurrences. Finally, carbonate rocks are the major aggregate resource in the Black Hills.

Three field trips are offered this year. They are not duplicative; each stop has something different to offer, demonstrating the wide variety of evaporite and carbonate karst in the Black Hills. The trip in the Southern Black Hills will examine evaporite karst in the Minnelusa Formation, artesian springs due to both carbonate and evaporite dissolution at depth, sinkholes and fracturing in the Minnekahta raising the question of the definition of karst, a large sinkhole that trapped Pleistocene animals, and a visit to Wind Cave. The northern trip will discuss dye tracing in carbonate rocks, hydrology in Spearfish Canyon that made the famous Black Hills gold mining possible, a variety of collapse features and gypsum intrusion in the lower Spearfish Formation creating a strong secondary porosity, effects of leaching in the Minnekahta, and a proposed sewage lagoon in a precarious area of evaporite karst. A third trip to the western Black Hills is offered for those wishing to do it on their own. Highlights are an overlook of the steeply dipping rocks in flatirons in a major monocline, a sinkhole in non-soluble rocks extending more than 800 feet down to the source of collapse, the most spectacular cliff exposure of caves, sinkholes, brecciation, and disrupted bedding in the Minnelusa formation, and a trip to Jewel Cave. Two guided evening trips are also planned to Jewel and Wind Caves.

Each field trip guide not only has detailed information for driving instructions and text for each stop, but also, provides comments about sites to see from the vehicle window and the text of historic markers and plaques along the way. The total miles and miles between driving directions, comments, markers, and stops have been noted on each field trip guide.

Parts of the field guide itineraries were borrowed freely from many excellent published guides to the Black Hills (Fahrenbach and Fox, 1996; Gries, 1996; Lisenbee and others, 1996; Martin and others, 1996; Rahn and others, 1977; Rahn and Davis, 1996; Redden and Fahrenbach, 1996). Additional sources of information about the Black Hills or engineering geology are found in Darton (1909) and Rahn (1986).

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