USE OF TRACERS TO QUANTIFY SUBSURFACE FLOW THROUGH A MINING PIT

S. Geoffrey Schladow[1,2,4] and Jordan F. Clark[3]

[1]*Department of Civil and Environmental Engineering, University of California, Davis, California 95616 USA*
[2]*University of California, Tahoe Environmental Research Center, Davis, California 95616 USA*
[3]*Department of Geological Sciences, University of California, Santa Barbara, California 93106 USA*

Abstract. Three independent tracer experiments were conducted to quantify the through-flow of water from Herman Pit, an abandoned mercury (Hg) mine pit adjacent to Clear Lake, California, USA. The tracers used were Rhodamine-WT, sulfur hexafluoride, and a mixture of sulfur hexafluoride and neon-22. The tracers were injected into Herman Pit, a generally well-mixed water body of ~81 000 m^2, and the concentrations were monitored in the mine pit, observation wells, and the lake for 2–3 months following each injection. The results for all three experiments showed that the tracer arrived at certain observation wells within days of injection. Comparing all the well data showed a highly heterogeneous response, with a small number of wells showing this near-instantaneous response and others taking months before the tracer was detectable. Tracer was also found in the lake on four occasions over a one-month period, too few to infer any pattern but sufficient to confirm the connection of the two water bodies. Using a simple mass balance model it was possible to determine the effective loss rate through advection for each of the tracers and with this to estimate the through-flow rate. The through-flow rate for all three experiments was ~630 L/s, at least 1–2 orders of magnitude larger than previous estimates, all of which had been based on geochemical inferences or other indirect measures of the pit through-flow.

Key words: Clear Lake, California, USA; mine pit; neon-22; Rhodamine-WT; Sulphur Bank Mercury Mine; sulfur hexafluoride; tracer.

INTRODUCTION

In May 1995, a wide area of flocculent material with high concentrations of sulfate, total mercury, and methylmercury was observed floating in the water column and blanketing the sediment of a portion of Clear Lake, California, USA (Suchanek et al. 1997). The affected area was adjacent to the abandoned Herman Pit, a low-pH (~3.0) flooded mine pit remaining from the Sulphur Bank Mercury Mine (see Suchanek et al. 2008c). As no rain had occurred for over one month this chance observation led to speculation on possible large-magnitude, subsurface flows from the mine pit. The contention was strengthened through subsequent findings that when acidic mine fluids, high in dissolved Hg, mix with pH 8 lake water, a white alumino-silicate flocculent precipitate (floc) of near-neutral density forms in the mixing zone (Suchanek et al. 2000a, b).

To confirm and quantify the subsurface flows into and out of Herman Pit, a series of tracer experiments was conducted. Tracer studies are frequently undertaken to quantify groundwater flow (e.g., Sutton et al. 2001), contaminant flux (e.g., Paul et al. 1995), and diffusivity

of the subsurface matrix (e.g., Jardine et al. 1999), but rarely to assess flows between two standing surface water bodies. Tracer studies in lakes and impoundments are usually targeted at describing flow patterns and mixing rates (see for example Rueda et al. 2008). The study of mining lakes and their associated environmental impacts is a relatively recent, but rapidly growing area of interest (see for example von Rohden and Ilmberger 2001, Karakas et al. 2003, Kamjunke et al. 2005). In this case, the flux from the mine to the lake had the potential to dominate the Hg flux.

Herman Pit is the larger of two mine pits excavated at the Sulphur Bank Mercury Mine. The pit is located adjacent to the end of the Oaks Arm of Clear Lake, California (Fig. 1). When mining operations (and concurrent dewatering) ceased in the 1950s, the pit filled with water. The source of this water is overland flow from the surrounding watershed during storms, meteoric groundwater flow throughout the year, surface seeps, subterranean streams, and geothermal springs at the bottom of the pit (Shipp and Zierenberg 2008). The subsurface characteristics between Herman Pit and Clear Lake are extremely heterogeneous. The subsurface is known to comprise regions of native material, former open pits, mine tailings, and waste rock and is punctuated by an indeterminate network of abandoned mine shafts and davits developed since mining commenced originally as a sulfur mine in 1865 and then as a
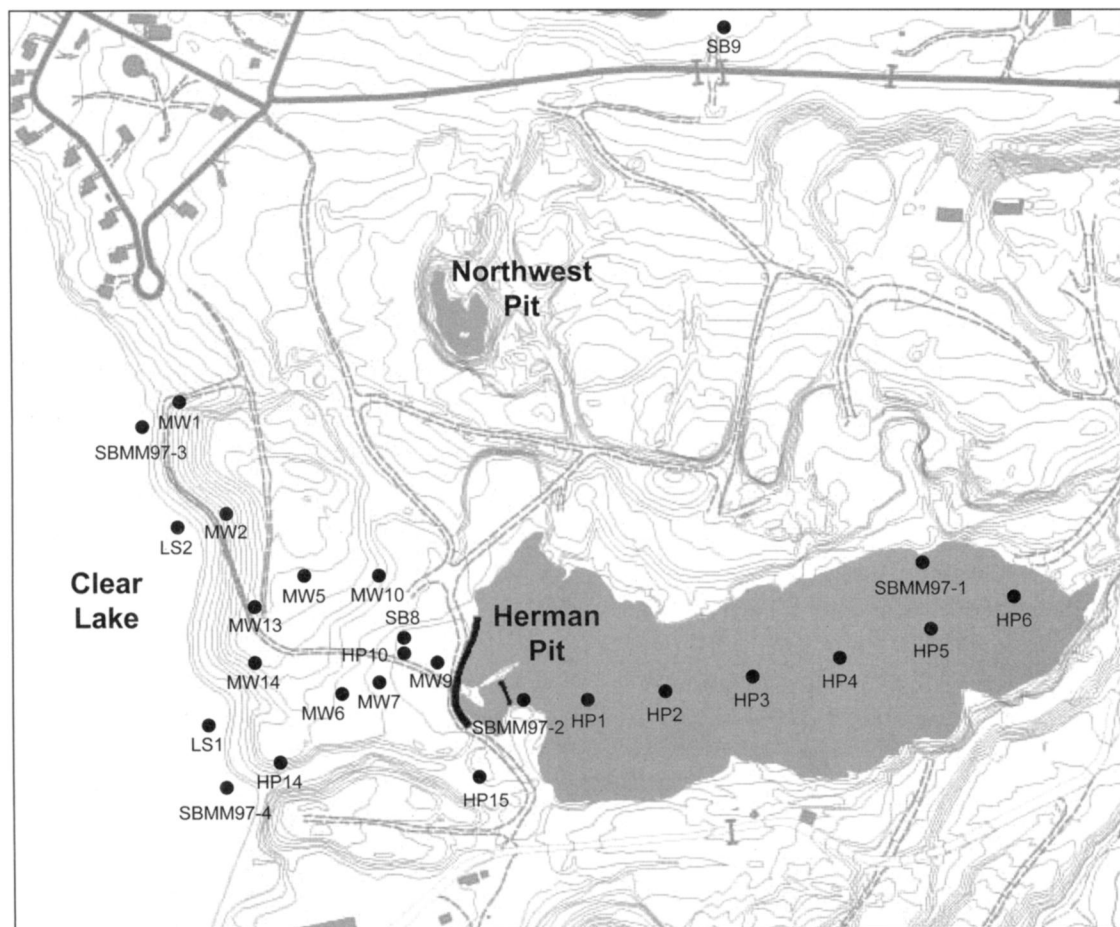
FIG. 1. Map of the Sulphur Bank Mercury Mine Site, California, USA, showing Herman Pit and the Northwest Pit. Clear Lake is to the west. Marked locations (HP1–HP6) within Herman Pit are sampling sites. Existing observations wells are indicated with prefixes HP, MW, or SB. Lake sampling sites are LS1 and LS2. Topographic contours are at 7.6-m (25-feet) intervals.

mercury mine in 1873 (Suchanek et al. 2008c). Herman Pit was created from massive open-pit mining that was initiated ca. 1927. The region is also geothermally very active, with hot springs being recorded in the exact location of the ore body (Veatch 1883) and the largest of the geothermal springs being buried beneath a large waste rock dam that creates a barrier between Herman Pit and Clear Lake (White and Roberson 1962). The water table level when first encountered in mining was unknown but hot water and gases were encountered at relatively shallow depth, presenting a problem for the underground mining activities (White and Roberson 1962).

Prior studies have made estimates of the subsurface flows from Herman Pit. White and Roberson (1962) established that Herman Pit filled with water and first overflowed into Clear Lake in March 1954. Such overflows are rare, occurring only after very wet years. One such overflow event that was documented in 1995 was demonstrated to produce temporarily elevated concentrations of Hg in water, sediments, and biota in Clear Lake (Suchanek et al. 2008a, b). Mine site

drainage remediation, completed in 1998, has almost totally eliminated this possibility in future years (Suchanek et al. 2008c). Veatch (1883) estimated a discharge from the springs of 19 L/s. White and Roberson (1962) concluded, based on the chloride and boron content of a set of springs, that the average net rate of accumulation of water ranged from 3 to 6 L/s. They also concluded that a discharge of 30 L/s is possible but a discharge of as much as 300 L/s is not probable since there are few high-temperature, low-salinity, mainly meteoric water springs discharging at this rate. Goff and Janik (1993) have estimated the spring discharge over time to range from 2.5 to 19 L/s. The most recent study (Jewett et al. 2000) was based on the equipotential surfaces produced from a new set of 33 screened wells installed subsequent to the studies described in this paper. Those results indicated a value of ~1.3 L/s flowing through the soil matrix between Herman Pit and Clear Lake.

We conducted three tracer studies in Herman Pit in order to calculate the rate of dilution of tracer in the pit and thereby estimate the net through-flow of subsurface
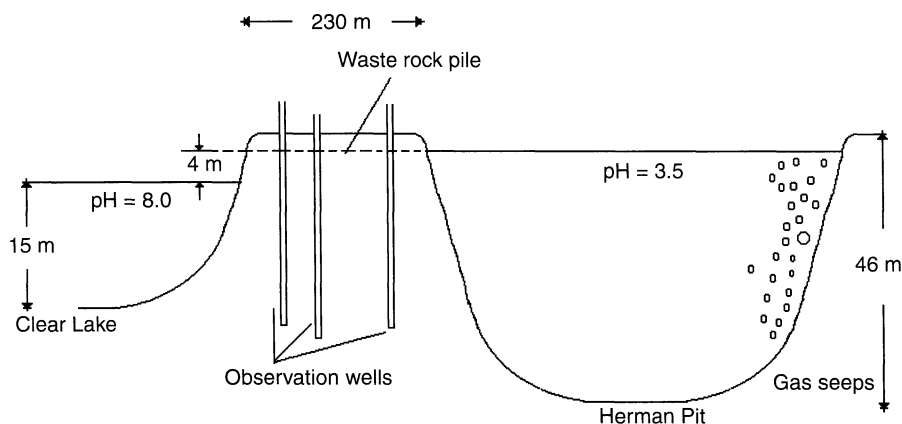
FIG. 2. Schematic cross section of Herman Pit and Clear Lake (not to scale).

water. The tracers used were Rhodamine-WT (Abbey Color, Philadelphia, Pennsylvania, USA), sulfur hexafluoride (SF_6), and a mixture of SF_6 and neon-22 (^{22}Ne). In addition, existing observation wells and the lake shoreline were sampled to independently confirm the loss of tracer from the mine pit and for evidence of preferred pathways.

SITE DESCRIPTION

Herman Pit covers ~81 000 m^2, is filled with water to a depth of 46 m, and is 229 m up gradient of Clear Lake, with an approximate 4-m head above the Clear Lake water level (U.S. Environmental Protection Agency [U.S. EPA], data *available online*).[5] A map of the mine site, sampling sites, and the surrounding area is shown in Fig. 1. Approximately 486 000 m^2 of tailings extend into the Oaks Arm of Clear Lake along 400 m of shoreline. Fig. 2 shows a schematic cross section of Herman Pit. Bubble seeps in the pit, thought to be associated with the geothermal nature of the area, are visible from the ground and are concentrated at the northern and southeastern shores. In August 1990 the Sulphur Bank Mercury Mine site was listed on the U.S. EPA Superfund's National Priority List.

The water chemistry of the pit is highly complex (Shipp and Zierenberg 2008). F. Goff and D. Bergfeld (*unpublished manuscript*) evaluated the chemistry at two locations at opposite ends of Herman Pit and of Clear Lake from two locations adjacent to the mine at the north and south ends of the rip-rapped shoreline. Table 1 summarizes these results. There are several orders of magnitude difference among the values of all the parameters shown. However, both pit locations are quite similar for all parameters measured, suggesting that Herman Pit is a well-mixed system. The values from the two lake sites adjacent to Herman Pit are up to a factor of four different from one another, consistent

with the possibility of discrete point inputs and incomplete mixing in a large lake.

METHODS

Rhodamine-WT tracer experiment

Rhodamine-WT is a widely used hydrologic tracer, detectable fluorometrically in water at concentrations as low as 0.01 ppb under ideal conditions (Keefe et al. 2004, Dierberg and DeBusk 2005). It has previously been used as a tracer in acidic mining environments (see for example Bencala et al. 1986). In the work presented, all measurements of Rhodamine-WT concentration were obtained using two Turner 10-AU fluorometers (Turner Designs, Sunnyvale, California, USA). The instrument used for all laboratory, pit, and lake measurements was equipped with a thermistor to allow for temperature-compensated measurements (standardized to 20°C). The second instrument, used primarily for well measurements, did not have temperature compensation. The fluorometers were calibrated against standard solutions of Rhodamine-WT in deionized water immediately prior to each sampling day. Prior to the injection of Rhodamine-WT, background concentrations were measured in Herman Pit, the observation wells, and Clear Lake.

The injection of Rhodamine-WT into Herman Pit was performed in two stages. Slightly more than half the tracer was injected on one day. The injection commenced on 11 April 1997. A 12.6-L/s trash pump was towed in a dinghy behind an inflatable boat. The screened, 7.5 cm diameter intake hose of the pump was 25 m long; however, with the movement of the dinghy it tended to rise up to a depth of ~15 m. Rhodamine-WT was drawn into the suction side of the pump through a small nozzle attached to the intake mounting, at a rate of ~5.6 mL/s. The original 20% solution had been diluted to ~4% to enable the injection time to be extended. The pump discharged above the pit water surface. The pump was towed randomly across the pit surface, in an effort to distribute the dye as widely as

[5] ⟨http://www.epa.gov/superfund/sites/npl/nar1136.htm⟩

TABLE 1. Water analysis results for Herman Pit (HP) and Clear Lake (CL) water samples (after F. Goff and D. Bergfeld, *unpublished manuscript*).

Sampling site	Temperature (°C)	Concentration (ppm)							
		B	Br	Ca	Cl	Fe	SO$_4$	Li	Na
SBMM97-1 (HP)	17.2	279	2.28	157	324	24.1	2730	2.23	482
SBMM97-2 (HP)	17.6	286	2.11	158	318	24.5	2650	2.3	466
SBMM97-3 (CL)	15.9	1.03	<0.02	22.5	5.7	0.03	8.12	0.02	11.8
SBMM97-4 (CL)	15.6	3.7	<0.02	23.3	8.42	0.07	35.4	0.04	16.4

Notes: The sampling date was 11 November 1997 and sampling sites are shown in Fig. 1.

possible. The injection of 100 L of dilute Rhodamine-WT took five hours. Profiles of Rhodamine-WT concentration at three locations in Herman Pit on 15 April indicated that the tracer was uniformly distributed throughout the pit, so the remainder of the tracer (80 L) was injected in the identical manner on that day.

Rhodamine-WT measurements in Herman Pit and within the Oaks Arm of Clear Lake were taken with the temperature-compensated Turner 10-AU-005 fluorometer at approximately weekly intervals. The instrument was used from an inflatable boat at both locations. A two-stage, 12-V, submersible centrifugal pump, located on the intake side of the fluorometer, drew water through a 1.9-cm nylon garden hose. Water was pumped from discrete depths until the fluorometer reading had stabilized (typically <30 s). In the mine pit, samples were taken at 1–3 m intervals at locations HP1, HP3, and HP5, indicated in Fig. 1. In the lake, the hose intake was moved up and down through the water column as the boat traversed along the shoreline in front of the mine site. The digital readout of the fluorometer was constantly checked for readings above background concentrations.

The 11 mine site test wells were sampled before and after the tracer injection in Herman Pit, using the same type of pump as was used in the pit and lake sampling and at the same intervals. The locations of the wells are indicated in Fig. 1. The 5 cm diameter pumps were lowered down each well, and water pumped through a 1.9-cm nylon garden hose. Extreme care was taken to keep the pit and well sampling pumps and hoses separate, so as to avoid any inadvertent contamination. Each well was pumped until a volume corresponding to three well casings had been discharged or the water ran clear. The discharge was continuously passed through the fluorometer, and readings were recorded at ~2-min intervals. Generally the fluorometer without temperature compensation was used for the well sampling. Each well test took between 6 and 60 min to complete.

Profiles of temperature, conductivity, dissolved oxygen concentration, and pH were also measured in Herman Pit using a YSI 6000 profiler (Yellow Springs Instruments, Yellow Springs, Ohio, USA). When this instrument was not available, temperature profiles were obtained from the fluorometer.

The effect of light on the fluorescence response of Rhodamine-WT was examined by suspending a series of

clear and dark quartz bottles from a buoy in Herman Pit. Each bottle was filled with Herman Pit water spiked with Rhodamine-WT. The bottles were suspended at depths of 1, 2, 4, 6, and 8 m. Rhodamine-WT concentration in each sample bottle was measured with a Turner 10-AU-005 fluorometer at the time the bottles were first deployed on 17 June 1997 and when they were retrieved, 30 d later on 17 July 1997.

Sulfur hexafluoride tracer experiment

Sulfur hexafluoride is an inorganic, artificial tracer that has been used as a deliberate tracer in continental aquatic systems for more than a decade (e.g., Wanninkhof et al. 1985, 1987, Clark et al. 1994, 1996, 2004, Maiss et al. 1994, Gamlin et al. 2001). Sulfur hexafluoride differs from ionic tracers in that it is a low-solubility gas and is lost from the system at the air–water interface. It is chemically and biologically inert, it is not present in nature (atmospheric concentration <1.9 parts per trillion per volume [pptv]), it can be quantified easily and precisely to very small concentrations ($<10^{-16}$ mol/L) using simple chromatographic methods, it is relatively inexpensive and available from different suppliers, and it does not change the density of the tagged water at the low concentrations needed for easy detection (Hibbs et al. 1998).

Sulfur hexafluoride was injected in the pit by bubbling it through a pair of diffusion stones. Approximately 0.5 kg of 99.8% pure SF$_6$ was injected over a period of 1 h on 22 June 1998 from a small boat that slowly motored along the east–west axis of Herman Pit. The motion of the boat caused the stones to deflect upwards, so the exact injection depth was unknown. However the boat speed was varied in an effort to move the diffusion stones up and down so as to distribute the gas. As gas pressure decreased, the diffuser stones had to be raised to overcome the hydrostatic pressure. The advantage of this method is that large quantities of the tracer can be injected rapidly throughout the water column. Because the gas bubbles do not completely dissolve during their rise, an unknown fraction of gas escapes to the atmosphere. The experience with the previous Rhodamine-WT study suggested that whatever SF$_6$ remained dissolved in the water would rapidly be distributed throughout Herman Pit.

Water samples for SF$_6$ analysis in Herman Pit were taken with a 12-V MasterFlex portable peristaltic

TABLE 2. Physical characteristics of the monitoring wells sampled.

Well	Age	Diameter (cm)	Pump type	Hose diameter (cm)	Total depth (m)†	Depth to water (m)
HP10	new	1.9	peristaltic	0.95	3.0	2.4
HP14	new	1.9	peristaltic	0.95	4.6	2.8
HP15	new	1.9	peristaltic	0.95	2.4	1.3
MW10	new	5.1	submersible	0.64	11.9	6.8
MW11	new	5.1	submersible	0.95	22.9	‡
MW13	new	5.1	submersible	0.95	20.5	15.2
MW14	new	5.1	submersible	0.95	14.4	12.4
MW2	old	5.1	peristaltic	0.95	10.9	4.5
MW5	old	5.1	submersible	0.95	19.7	14.8

† Depth to water was measured on 22 June 1998.
‡ Well MW11 was sampled only once due to difficulties in pumping water.

sampling pump (Cole-Parmer, Vernon Hills, Illinois, USA) from sites HP1–HP6 (Fig. 1) at depths of 3, 15, and 23 m at approximately weekly intervals. Samples were collected in tapered-neck 300-mL biological oxygen demand (BOD) bottles and covered with glass stoppers and Teflon-faced rubber septa. The pump was used from an inflatable boat using a 1.9-cm black nylon hose of 33 m length. Before any water sample was taken the hose was purged for 1 min to avoid cross-contamination from the previous sample. The end of the hose always remained in the water as the boat moved along the axis to the next point. The BOD bottles were rinsed before taking the sample and filled to overflowing with special care to avoid bubble formation in the sample prior to analysis, as this would affect SF_6 concentration in solution. Bottles were stored in a cooler, transported to the University of California at Davis, and inspected for formation of bubbles on the walls of the bottles.

The SF_6 concentration of bubbles associated with gas seeps in the pit was measured twice during the experiment using a 20-cm diameter plastic funnel and 2 cm diameter Teflon hose with a valve at the end. The funnel and hose were filled with water and submerged in the pit over a bubble seep. As bubbles were collected, they displaced the water and gas accumulated near the valve. A 50-mL glass syringe was connected to the valve, and the gas was transferred to the syringe. A sample of this gas was injected into 10-mL vacuum tubes (vacutainers).

A series of nine wells located between Herman Pit and the lake (Fig. 1) were sampled before and after the tracer injection, usually on the same days the pit was sampled. Monitoring wells are divided into old wells, installed before 1998, and new wells, installed in 1998. The condition of the packing material and the casings in the old wells was unknown. Table 2 shows information on each of the wells sampled. Black nylon hoses (0.95 cm diameter), characterized by low reactivity and low adsorption, were connected to the peristaltic pump for the 1.9-cm wells and in the old 5-cm MW2 well. Four submersible pumps were connected in series for each new 5.1-cm well and MW5 well, and water was pumped through 0.95-cm black nylon hose. Hoses used in the wells, Herman Pit, and the lake were not interchanged

and were stored in plastic bags. Before samples were taken, submersible and peristaltic pumps operated in the flow range of 1.1–3.8 L/min until a volume corresponding to three well casings was discharged. The wells generally ran turbid at the beginning but were clear by the time the samples were taken, with no evident suspended solids.

A low-flow submersible pump was used in the two sampling points in the lake shoreline (Fig. 1). The pump was submerged ~0.5 m from the surface, and samples were taken after the hose and pump were flushed for 1 min.

Headspace analysis was used to analyze the concentration of SF_6 in each sample. The SF_6 gas was extracted from each sample by filling a 50-mL glass syringe with a known volume of the sample (10 mL or 30 mL, depending on the assumed SF_6 concentration in the sample) and a high-purity nitrogen head space (40 mL or 20 mL, respectively). Care was taken not to alter the concentration of SF_6 in the sample while creating the headspace. Precautions included taking the water sample with a long needle from the bottom of the BOD bottle and using syringes equipped with a three-way valve to avoid the entry of air while creating the nitrogen headspace (Thene 1990). Syringes were shaken for 3 min until the headspace and the water achieved equilibrium. The headspace gas was injected into vacutainers (Wanninkhof et al. 1987, Wanninkhof and Ledwell 1991).

The gas from the vacutainers was injected through a column of $Mg(ClO_4)_2$ (to remove water vapor) and into a small sample loop of known volume (~0.5 or ~1.2 mL). Subsequently the sample was transported with an ultra-high-purity N_2 carrier gas into a gas chromatograph (GC) equipped with an electron capture detector. The SF_6 was separated from other gases with a molecular sieve 5a column (~1 m long) held at room temperature. The detector response was calibrated every 30 min with SF_6 standards (~148.1 pptv and ~1947 pptv) certified by Scott-Marrin (Riverside, California, USA). The precision (determined by replicates) and detection limit of this method was ±6% and 0.1 pmol/L, respectively.
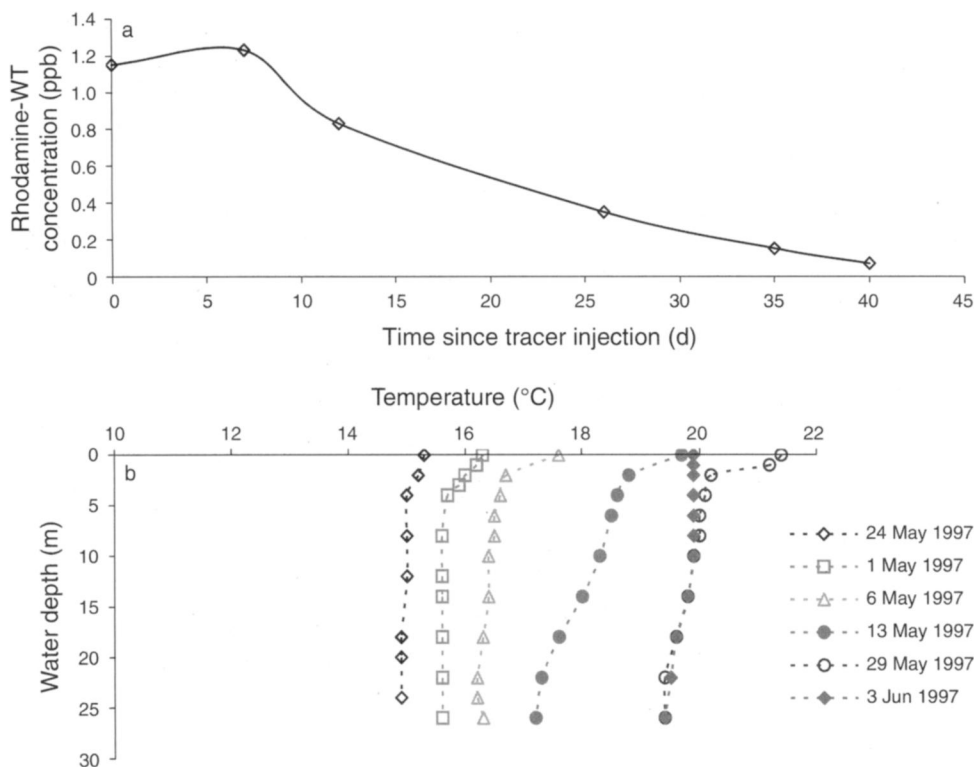
FIG. 3.   (a) Concentration of Rhodamine-WT in Herman Pit at a depth of 8 m. Initial tracer injection commenced on 11 April 1997. (b) Temperature distribution in Herman Pit during the time of the experiment.

To estimate the concentration of SF_6 in the water sample, C_{SF_6}, Henry's Law is combined with a mass balance of the tracer in the sample containers:

$$C_{SF_6} = C_{head}\left(\frac{V_{head}}{V_{water}} + \frac{1}{H}\right). \qquad (1)$$

Here V_{head} is the volume of the headspace (volume of nitrogen injected), V_{water} is the volume of the water sample, C_{head} is the SF_6 concentration in the headspace in units of peak area counts per volume of headspace injected, and H is the Henry's law constant.

Sulfur hexafluoride/neon-22 tracer experiment

Sulfur hexafluoride and ^{22}Ne were premixed using the method of Clark et al. (1996). The mixture was injected from a boat in a manner similar to the SF_6 experiment on 9 September 1998. Although there was SF_6 from the first injection still in the system, the concentrations added were sufficient to detect the arrival of the new tracer at the observation wells. A sufficient mass of SF_6 and ^{22}Ne was added such that all the concentration measurements taken during the study were well above their respective limits of quantification (LOQ).

The method used to sample SF_6 in this experiment was identical to that used for the SF_6-only experiment. The samples for ^{22}Ne analysis were collected from points HP2, HP4, and HP6 at water depths of 3 and 15 m (Fig. 1) into 0.95-cm copper refrigeration tubing cut to 36-cm lengths. The copper tubing was held between two knife-edge clamps attached to a rigid back plate. The sample hose was connected to one end of the copper tubing, and as water was being pumped, hexagonal bolts on the clamps were tightened little by little and in sequence. This forced the two knife-edges of the clamps together, which crimped the copper tubing, forming a gas-tight seal. The speed of the pump was reduced by the time the tubing was almost clamped, avoiding high pressure in the hose.

The well sampling technique was identical to that used for the SF_6-only experiment. Due to the low cost of the SF_6 analysis relative to ^{22}Ne analysis, only well samples for SF_6 analysis were collected in this experiment. Similarly, lake sampling in this experiment was only for SF_6.

The SF_6 analysis for this experiment was identical to that described previously. The ^{22}Ne samples were analyzed on a VG-5400 Micromass static mass spectrometer (Micromass UK, Manchester, UK) at the Lawrence Livermore National Laboratory (Livermore, California, USA) using methods described by Rademacher et al. (2001). Precision of the measurements was ±2%. A total of 10 samples were analyzed.

RESULTS

Rhodamine-WT

Prior to injection, the observed concentration of Rhodamine-WT in Herman Pit was below the LOQ.
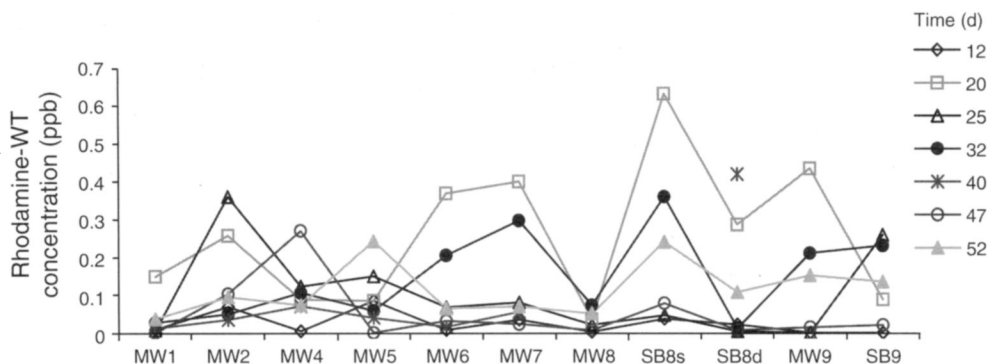
FIG. 4. Concentration of Rhodamine-WT in observation wells at different times since initial injection on 11 April 1997.

Following the injections, the Rhodamine-WT concentration in Herman Pit at a depth of 8 m declined (Fig. 3a). All other measurement depths showed a similar trend. Within approximately one month, an order of magnitude decrease in concentration was observed at all depths. The vertical temperature distribution in Herman Pit over the period of the experiment (Fig. 3b) indicated that the water column was generally well mixed in the vertical profile or only weakly stratified. Given the sheltered location of Herman Pit, it seems possible that the bubble seeps referred to earlier may have been the dominant factor in maintaining this mixed state (see for example Schladow 1992).

Background concentration of Rhodamine-WT in all the wells was below the LOQ. Rhodamine-WT concentrations in the observation wells after injection on 11 April show considerable variation both spatially and over time (Fig. 4). For example, wells SB8s, MW5, and MW2 are all in a direct line in order of increasing distance from Herman Pit, yet their responses are markedly different (Fig. 5). The mid-distance well was the first in which the tracer was detected, and none of the responses appear particularly well correlated in time. The well concentrations were always lower than the pit concentrations (as they should have been), although the concentrations in well SB-8s were only a factor of two lower than pit concentrations. There are several factors that could contribute to this, including the unknown condition of the well casings in this low-pH environment. It is possible that the wells are drawing water from a range of strata and faults, each displaying different concentrations of tracer. Conditions in the subsurface are known to vary considerably. For example, on 23 April, well temperatures ranged from a low of 14°C (SB8s) to a high of 26.4°C (MW8), compared to a pit temperature of ~15°C. All the other wells had unique temperatures within this range. The wells generally ran turbid at first, and the suspended solids would have contributed to some background interference. Laboratory tests in which Herman Pit sediment material was added to water showed only a small change in the fluorescence response. A similarly small effect was observed with the addition of air bubbles to the water.

However, it is inconceivable that the marked response occurred without the presence of some tracer.

Fig. 6 shows the vertical distribution of Rhodamine-WT in the light and dark quartz bottles at the beginning and end of the 30-d test period. Rhodamine-WT concentrations in the dark bottles are essentially unchanged. The clear bottles show an exponential decline in Rhodamine-WT concentration, similar to what might be expected in the ambient light field.

Sulfur hexafluoride

Background SF_6 concentrations prior to injecting the gas tracer were below the detection limit. The gas tracer concentrations at each sampling site in Herman Pit are averaged and plotted over time in Fig. 7a. Variability in the vertical distribution of the SF_6 tracer concentration can be seen. Immediately after injection, the highest SF6 concentrations were found at a depth of 15 m, since injection was centered at this depth, and the lowest concentrations were found at a depth of 23 m. One week after injection the concentrations at the surface were slightly lower than elsewhere in the water column, most likely due to the gas evasion across the air–water interface. The values at 15 and 23 m were almost identical. This was expected due to the generally well-mixed nature of Herman Pit, as evidenced by the temperature distributions shown in Fig. 7b. The pit average concentration curve shows an exponential
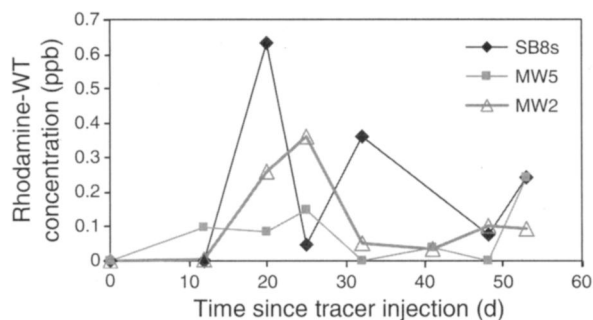

FIG. 5. Time series of concentration of Rhodamine-WT in selected observation wells vs. days since initial injection on 11 April 1997.
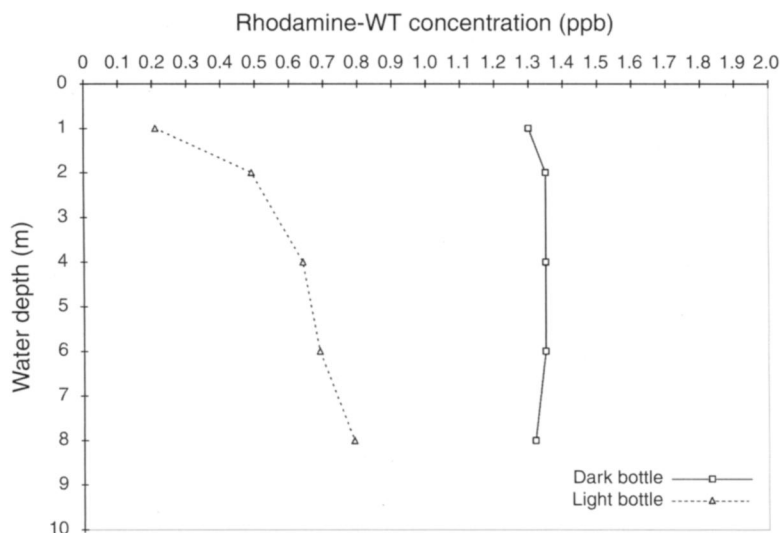
FIG. 6.   Attenuation of Rhodamine-WT in light and dark bottles suspended in Herman Pit.

decay, and the tail approaches the zero concentration level asymptotically.

Fig. 8 shows the pit mean SF_6 concentration on a semilogarithmic plot, showing that a straight line describes the decay of SF_6 after the seventh day (at which time the tracer was uniformly distributed). The equation that best fits the data ($R^2 = 0.99$) is

$$C = 277e^{-0.08t} \qquad (2)$$

where C is the concentration of SF_6 in picomoles per liter and t is time in days. The figure corresponds to the period given by days 7–28 after injection with initial and final SF_6 concentrations values of 146.6 and 27.8 pmol/L, respectively.

Fig. 9 shows the mean concentration of SF_6 at each sampling site in Herman Pit. A horizontal distribution can be observed during the first week after the injection, after which the tracer becomes evenly distributed across
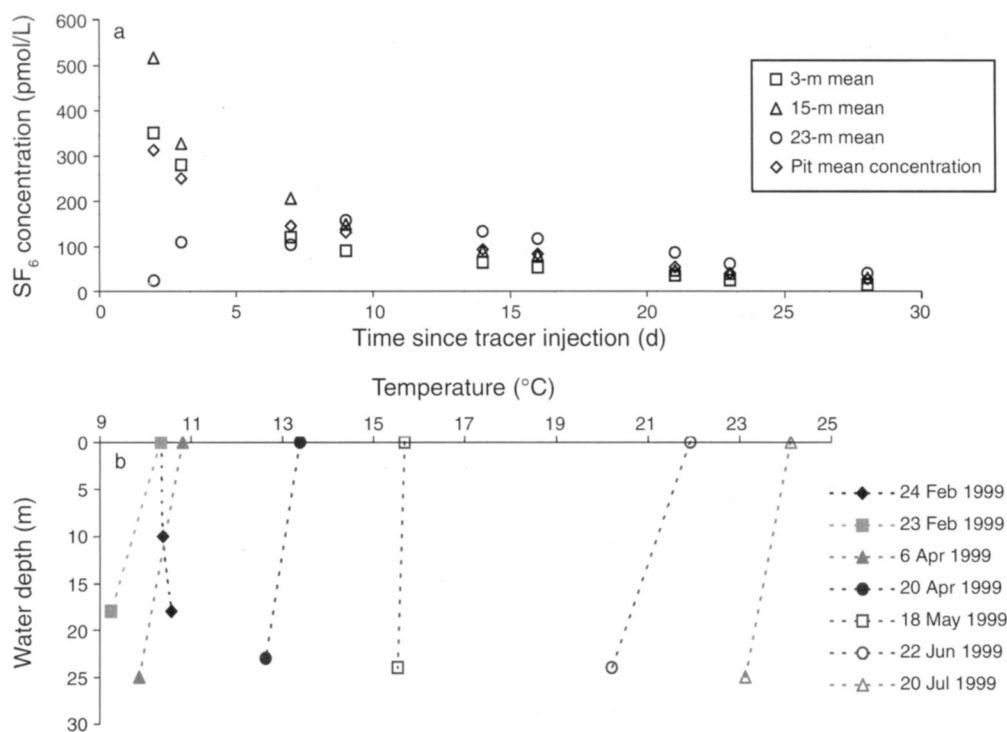
FIG. 7.   (a) Time series of concentration of SF_6 in Herman Pit vs. days since initial injection on 22 June 1998. (b) Temperature variation in Herman Pit (February–July 1998).
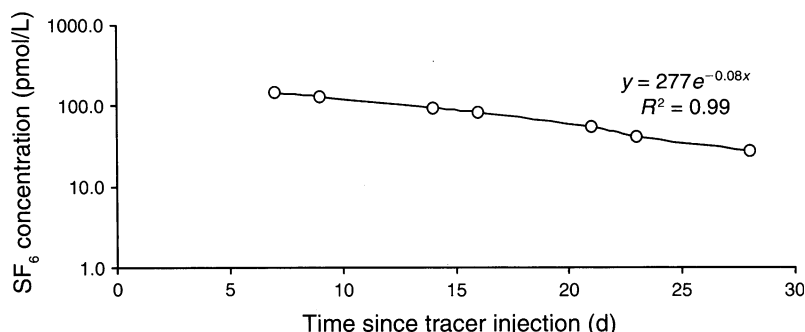
FIG. 8. Mean concentration of SF_6 in Herman Pit as a function of time in days since initial injection on 22 June 1998.

the pit. The lowest concentrations during the first week are present at the sampling points HP4, HP5, and HP6 (Fig. 1). As a horizontal gradient was only evident during the first week, it was probably due to unevenness during the injection. The area around these sites also has a higher presence of subsurface gas seeps and surface water seeps. The SF_6 concentration of the rising bubbles at the northern part of the pit was analyzed and the SF_6 concentration (~2700 pptv) suggests that bubbles are indeed removing part of the gas tracer. However, the fact that no detectable horizontal gradient is present beyond the first seven days suggests that these effects are minor.

Nine wells were monitored for SF_6. Background measurements of SF_6 concentration were below the detection limit. Relatively large concentrations of SF_6 were observed at well HP10 during the first seven days after the injection. Four weeks after injection, the wells that showed presence of SF_6 were HP10, MW13, MW14, MW2, MW10, and MW5 (Fig. 10). The data show a peak in wells HP10 and MW14 three weeks after injection. Wells HP14 (not shown) and HP15, the southernmost sampled wells located near the overflow channel from Herman Pit, showed no detectable SF_6 during this experiment (or at least up until day 28). This suggests that tracer may be traveling along preferred pathways, rather than spreading uniformly between the pit and the lake.

The SF_6 concentrations in the observation wells were lower than concentrations in the pit, as was also observed in the Rhodamine-WT tracer experiment. The observed dilution of the tracer could be explained by the mixing of water from Herman Pit (with tracer) with subsurface water that had not flowed through the pit and therefore contained no tracer. Temperature and pH measurements are shown in Fig. 11a, b. It is evident that many of the wells have temperature and pH signatures that set them clearly apart from Herman Pit water at different times.

Sulfur hexafluoride was not detected in any sample from the lake shoreline sites LS1 and LS2, offshore of the mine face. This could be due to dilution of pit water in the lake reducing concentrations below the detectable limit, discharge points of pit water sufficiently far from the sampling points, or pit water never reaching the lake.

Sulfur hexafluoride/neon-22 tracers experiment

The injection of the combined $SF_6/^{22}Ne$ occurred on 9 September 1998. Background concentration of ^{22}Ne in the pit was at equilibrium with the atmosphere (10^{-7} cm^3 STP/g [STP, at standard temperature and pressure]), so it was used in the second dual-gas tracer injection. Results for the decay of ^{22}Ne after injection are presented in Figs. 12 and 13. By 2 October (23 d after injection), the excess of ^{22}Ne had already been removed so the final measurement was not used in calculating the
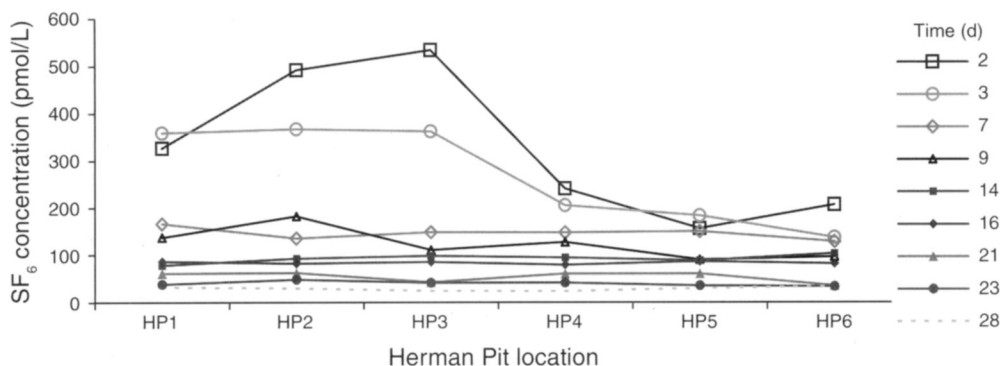

FIG. 9. Mean concentration of SF_6 at each sampling site in Herman Pit as a function of time in days since initial injection on 22 June 1998.
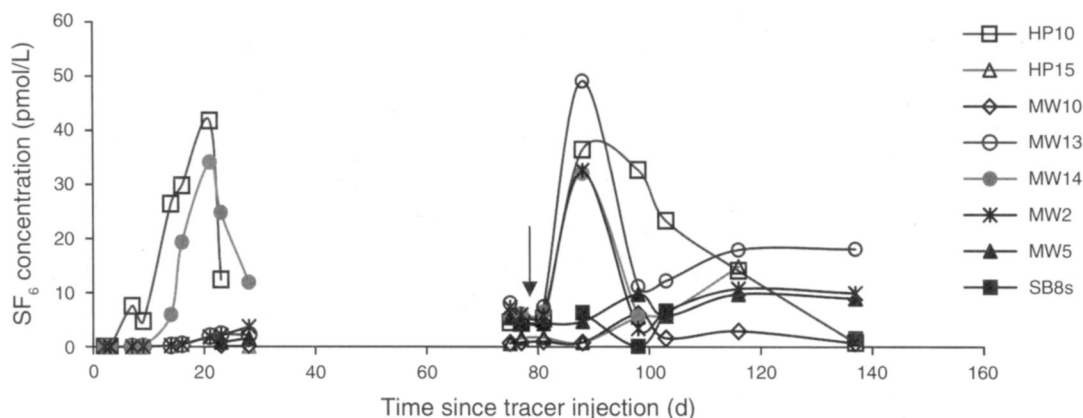
Fig. 10. Concentration of SF_6 in monitoring.wells vs. days since initial injection on 22 June 1998. The arrow at day 79 indicates the date of second injection.

loss rate. The concentration–time data for the first 13 d is well represented ($R^2 = 0.97$) as an exponential decay such that

$$C = 2 \times 10^{-9} e^{-0.27t} \qquad (3)$$

where C is the ^{22}Ne concentration (in cubic centimeters at standard temperature and pressure per gram) and t is time in days.

Background concentrations of SF_6 were measured one week prior to injection, and the amount of SF_6 remaining from the first injection was ~0.3 pmol/L. Fig. 14 shows the mean concentration per sampling site

in Herman Pit after the second injection. When comparing Fig. 14 with Fig. 9, it can be concluded that the tracer concentration showed less variability in the second experiment two days after the injection. However, in both injections, the tracer was evenly distributed across the pit one week after the gas was injected.

Fig. 15 shows the exponential decrease in SF_6 concentrations over time following the second injection. The second gas injection was better controlled and executed, and little vertical distribution in the SF_6 immediately after injection was observed. It also shows how well mixed the pit was right after the injection as a consequence of a natural mixing process. Fig. 16 shows
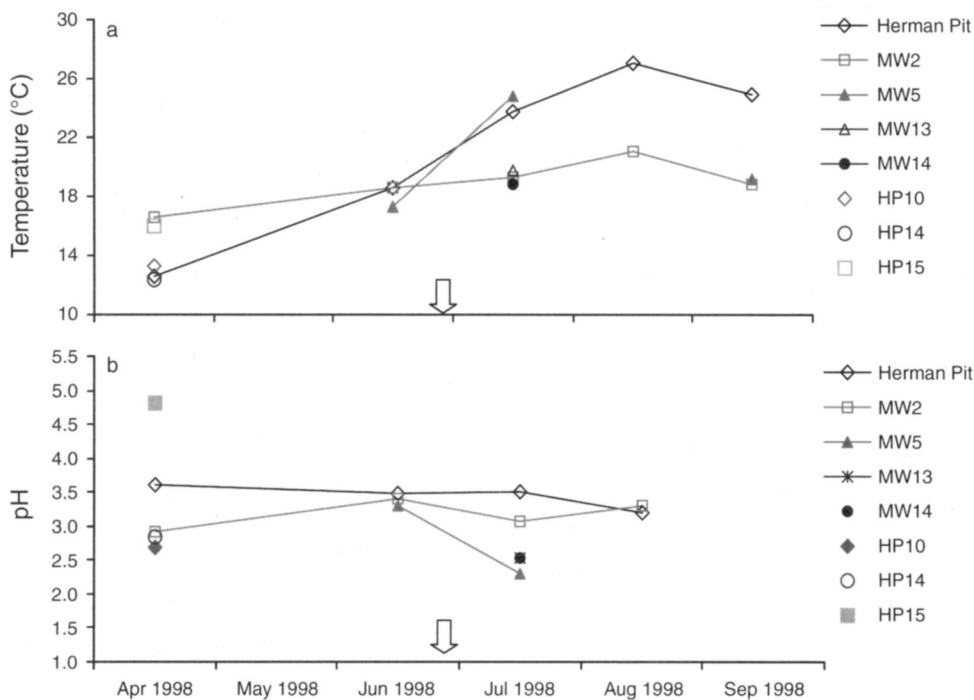

Fig. 11. (a) Temperature and (b) pH of Herman Pit and observation wells. The arrows indicate the date of SF_6 injection on 22 June 1998.
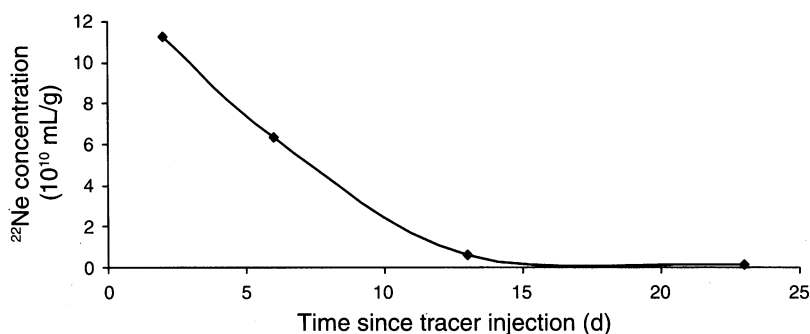
FIG. 12. Exponential decay of ^{22}Ne concentration in Herman Pit as a function of time in days since initial injection on 9 September 1998.

$$y = 2\,10^{-9}e^{-0.27x}$$
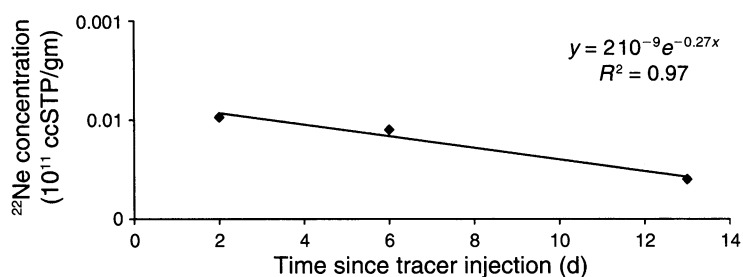$$R^2 = 0.97$$

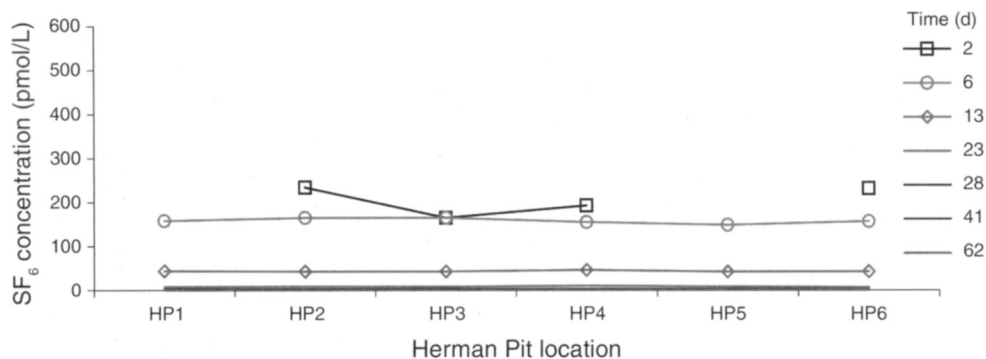FIG. 13. Concentration of ^{22}Ne in Herman Pit as a function of time in days since initial injection on 9 September 1998.

FIG. 14. Mean concentration of SF$_6$ at each sampling site in Herman Pit as a function of time in days since the second injection on 9 September 1998. After day 14, all measured values were near zero and cannot be distinguished at this scale. Data for HP5 from day 2 was lost.

FIG. 15. Time series of SF$_6$ concentration in Herman Pit as a function of time in days since injection on 9 September 1998.
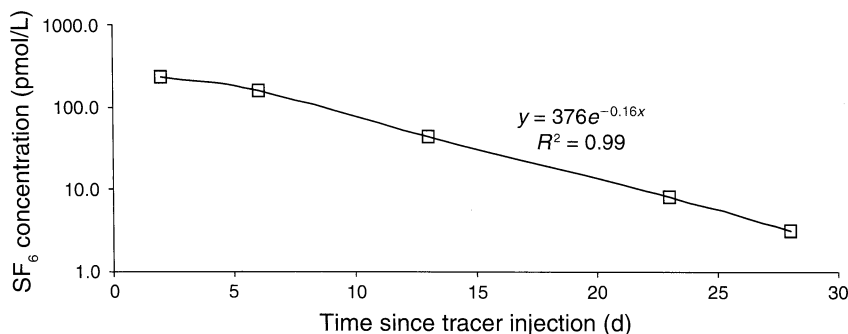
Fig. 16. Mean concentration of SF_6 in Herman Pit as a function of time in days since injection on 9 September 1998.

SF_6 concentrations plotted against time on a semilog scale once the initial mixing period was reached.

Fig. 17 compares the two SF_6 gas-tracer injections conducted during the summer of 1998 by plotting the normalized concentrations against time. The slope is steeper for the second injection, as is evident in the semilog plots of Fig. 18. The ranges of SF_6 concentrations plotted are after the time the tracer is uniformly distributed throughout Herman Pit. The slope of the second experiment is

$$C = 376e^{-0.16t}. \qquad (4)$$

Eight of the monitoring wells sampled showed presence of SF_6 two days after the second injection (83 d after the first injection). The results are shown in Fig. 19. The presence of SF_6 in these samples suggests that water from the pit is flowing through the waste rock piles between the pit and the lake over a large area. However it is likely that the concentration detected in all the wells sampled two days and six days after the injection represents a residual from the first injection. This suggests that as well as following the preferred set of pathways alluded to earlier, the tracer moves through all areas of the waste rock pile albeit over a longer time period.

The wells were sampled for a longer period following the second SF_6 injection. Most of the wells show a peak value in the SF_6 concentration. The wells that showed the earliest peaks showed the largest and quickest response to the first injection. Wells MW13 and MW12 showed only a very low concentration of SF_6 during the first injection. Well MW13 showed the highest values during the second injection. A further difference between the two experiments was that after the first injection, the large increase in tracer detection occurred between days 9 and 14 and peaked around day 22. In the second experiment, the large increase occurred between days 6 and 13 and peaked around day 13. The peaks also appeared to be considerably broader (Fig. 10). Thus it appears that while there were some similarities between the two experiments, there were considerable differences. These differences, the earlier arrival time of the gas tracer, the detection of high peaks

at more wells, and the broad extent of the peaks, are all consistent with the more rapid removal of tracer from Herman Pit during the second experiment. The results suggest that subsurface flow conditions at this site may be highly variable, temporally as well as spatially. Although two months separated the experiments, the two injections occurred over the summer during which there was no significant precipitation.

The SF_6 concentrations at the lake shoreline, detected for the first time 77 d after the first injection, were one to two orders of magnitude lower than the peak values in Herman Pit (Fig. 20). Though the values are very low, they confirm that pit water enters the lake because they are still an order of magnitude higher than the detection limit. However, there are too few observations of the tracer in the lake to say anything more definitive about potential flux rates into the lake.

DISCUSSION

Through-flows based on the Rhodamine-WT experiment

Using the data presented above, it is possible to construct a continuous stirred tank reactor (CSTR) model of the fate of Rhodamine-WT in Herman Pit and thereby estimate the groundwater exchange. It is necessary to assume that the pit is in general well mixed, so that fluid at all depths will be exposed to light for some part of the day. The temperature data presented previously support such an assumption.

Applying conservation of mass to the Rhodamine-WT, one can write

$$V\frac{dC}{dt} = Q_i C_i - Q_o C_o - rVC \qquad (5)$$

where t is time, V is the pit volume, C is the concentration of Rhodamine-WT, subscripts i and o refer to the inflow and outflow, respectively, and r is a rate coefficient associated with the breakdown of the Rhodamine-WT due to light. Assuming that the concentration of Rhodamine-WT in the inflow to the pit is zero, that the concentration in the outflow is the same as the concentration in the pit, and that the volume of inflow and outflow are equal, the equation simplifies to:
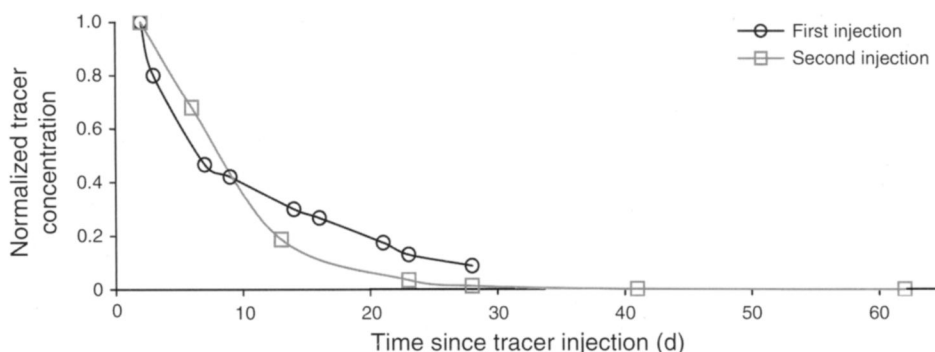
FIG. 17. Normalized Herman Pit SF$_6$ concentration for the two experiments plotted against time since respective injection (first, 22 June 1998; second, 9 September 1998). Each experiment was normalized against the maximum pit mean concentration for that experiment.

$$V\frac{dC}{dt} = -QC_o - rVC \qquad (6)$$

the solution to which is given by

$$C = C_b e^{-t[(Q/V)+r]} \qquad (7)$$

where C_b is the initial concentration of the tracer and $Q = Q_o = Q_i$.

This equation implies that the decrease in concentration is due to a combination of the exchange rate and the decay rate. If we know the decay rate, then we can calculate the flow rate. For the 30 days that the light and dark bottles were hanging in Herman Pit, it is possible to calculate an exponential decay rate for the Rhodamine-WT in each of the sealed bottles. The calculated decay rate varies from 0.061 d^{-1} at 1 m depth to 0.017 d^{-1} at 8 m depth. Herman Pit is 28 m deep, and a depth of 8 m corresponds to a mid-volume point, i.e., half the pit volume is on either side of this depth. This latter decay rate, 0.017 d^{-1}, is similar to the values presented by Lin et al. (2003) and Dierberg and DeBusk (2005).

Assuming that the decay coefficient at this depth is representative of the pit, then using Eq. 7 we can estimate what the corresponding inflow would need to be to account for the observed change in Rhodamine-WT concentration. The pit volume is 10^6 m^3. From Fig.

3a we can obtain both initial and final concentration values and the time between them. Selecting 26 d from 24 April to 20 May, during which time concentration changes from 1.2 ppb to 0.2 ppb, the calculation yields a value of $Q = 5.2 \times 10^4$ m^3/d (600 L/s). This corresponds to a mean detention time of 19.3 d. For comparison, if the 4-m decay rate, $k = 0.025$, was used, then the calculated flow rate would decrease to $Q = 4.4 \times 10^4$ m^3/d (508 L/s). These values are an order of magnitude greater than previous estimates (Veatch 1883, White and Roberson 1962, Goff and Janik 1993).

Through-flows based on the sulfur hexafluoride gas tracer injection

Sulfur hexafluoride gas exchange flux across the air–water interface can be calculated as

$$k = \frac{F}{A(C_{sur} - C_{eq})} = \alpha h \qquad (8)$$

where F is the mass flux of gas across the air–water interface, C_{sur} and C_{eq} are the gas concentrations in the surface water and at equilibrium, respectively, A is the mean surface area, and h is the mean depth.

Assuming that the gas transfer velocity, $k = 3$ cm/h (Clark et al. 1996), then the rate constant $\alpha = k/h = 1.67$
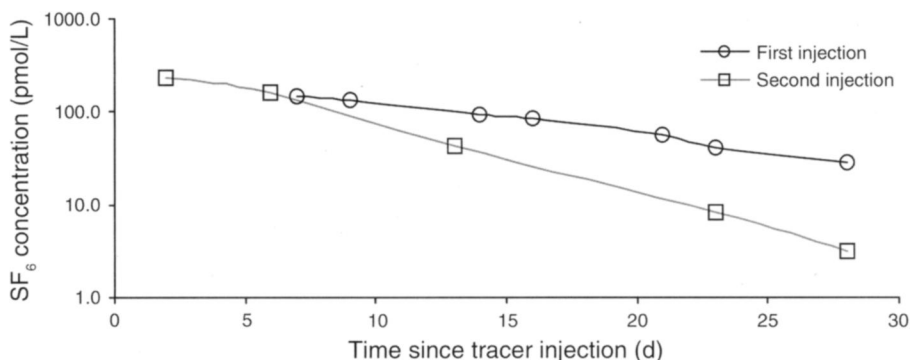

FIG. 18. Concentration of SF$_6$ for the two experiments, with both sets of results plotted against time since respective injection (first, 22 June 1998; second, 9 September 1998).
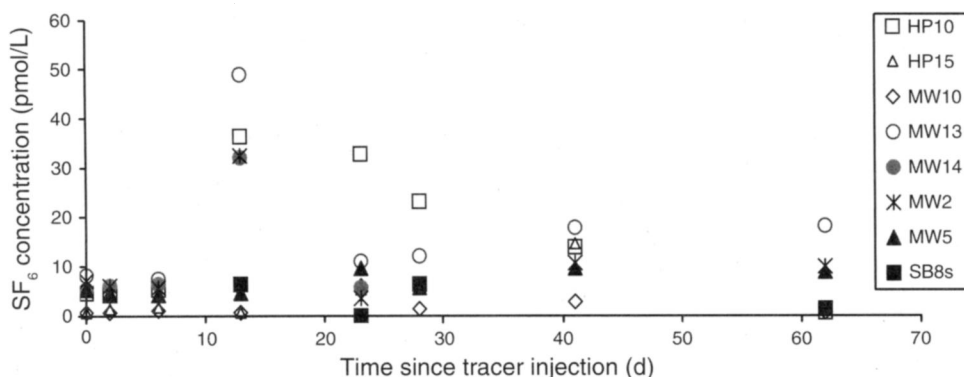
FIG. 19. Concentrations of SF_6 in the observation wells as a function of time since injection on 9 September 1998.

$\times 10^{-5}$ /min for a mean Herman Pit depth, $h = 30$ m. The pit surface area is 81 000 m^2, and soon after the gas tracer injection the concentrations were $C_{sur} = 121$ pmol/L $= 1.2 \times 10^{-13}$ mol/mL and $C_{eq} = 0.0005$ pmol/L $= 5 \times 10^{-17}$ mol/mL. This yields a flux across the air–water interface, F, of 8.44×10^{-6} mol SF_6/s.

The amount of SF_6 that leaves the pit because of the bubble seeps, $F_{SF6\,B}$, can be estimated as

$$F_{SF6\,B} = (C_{SF6\,B}) \times F_B \qquad (9)$$

where $(C_{SF6\,B})$ is the concentration of the SF_6 in the bubbles per unit volume of gas and F_B is the flux of the gas bubbles. Based on the field analysis of the gas concentration in the bubbles, it will be assumed that the average $C_{SF6\,B} = 2700$ ppt$_v$. Then,

$$C_{SF6\,B} = 2700 \times 10^{-12} L_{SF6}/L_{gas} \times 1 \text{ mol } SF_6/24.2 L_{SF6}$$
$$= 1.2 \times 10^{-10} \text{mol } SF_6/L_{gas} = 120 \text{ pmol}/L_{gas}.$$

The area of Herman Pit with bubble seeps was observed to be confined to a few patches on the north and southeast of Herman Pit. The pit surface area influenced by the release of bubbles could be assumed to be equal to 1000 m^2. The water surface was barely perturbed by the bubbles, and most of them were only evident when there was no wind. Assuming that the gas seep flux, F_{BUB}, was 10 L/s, then the flux of SF_6 leaving the pit via the bubble seeps would be:

$$F_{SF6\,B} = 120 \text{ pmol}/L_{BUB} \times 10 L_{BUB}/s = 1200 \text{ pmol } SF_6/s$$
$$= 1.2 \times 10^{-11} \text{mol } SF_6/s.$$

This is five orders of magnitude smaller than the flux across the air–water interface ($F = 8.44 \times 10^{-6}$ mol SF_6/s). If the assumed magnitude of the gas seep flux is even one or two orders smaller than is the actual flux, the result would still be that the bubble flux of SF_6 is negligible. Hence, the SF_6 gas transfer via the bubbles will not be considered in further calculations.

Using a similar CSTR model, it is possible to write

$$V\frac{dC}{dt} = -QC - VC\alpha_F \qquad (10)$$

for which the solution is

$$C = C_I e^{-t[(Q/V)+\alpha_F]} \qquad (11)$$

where C and C_1 are the final and initial mean SF_6 concentrations in Herman Pit plotted in Fig. 7a.

Eq. 11 expresses the fact that the decrease in the SF_6 concentration is due to a combination of the inflow/outflow rates of the pit and the transfer across the air–water interface.

Using $C_1 = 146.6$ pmol SF_6/L and $C = 27.8$ pmol SF_6/L after an interval of 21 d yields a value of 637 L/s, remarkably close to the flow obtained from the Rhodamine-WT tracer injection (600 L/s).
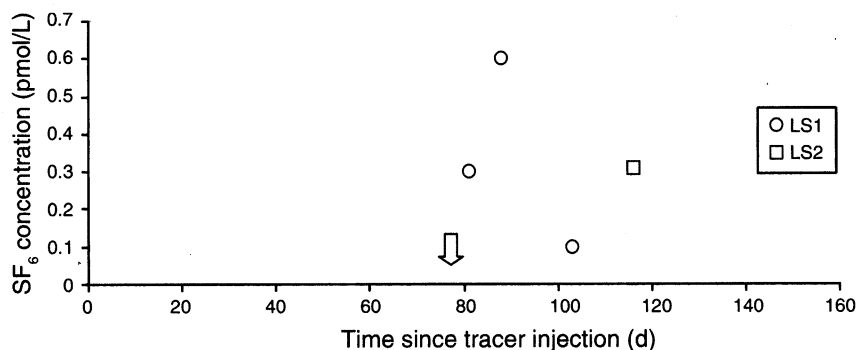

FIG. 20. Lake shoreline concentrations of SF_6 from the monitoring points LS1 and LS2 as a function of time in days since first injection on 22 June 1998. The arrow indicates the date of the second SF_6 injection on 9 September 1998.
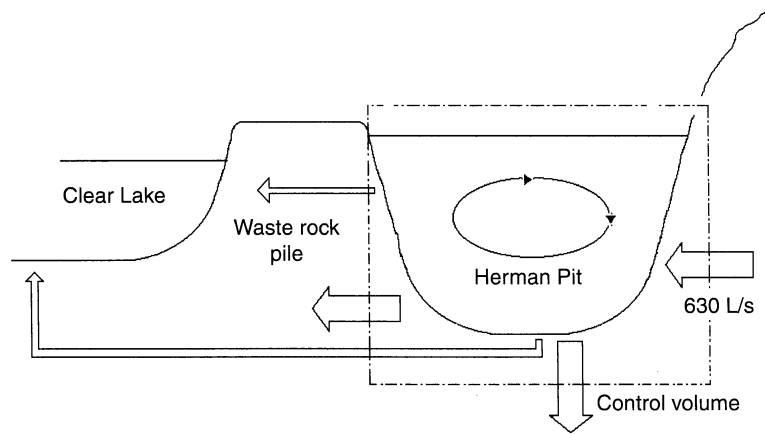
FIG. 21. Conceptual model of the through-flows in Herman Pit. (Note that the sizing of the arrows is arbitrary.)

Through-flows based on the sulfur hexafluoride/neon-22 injection

In a two-gas tracer system, SF$_6$ and ^{22}Ne, the gas transfer velocities are related by their Schmidt numbers, and so a transfer velocity does not have to be estimated. The Schmidt number relationship is

$$\frac{k_{\text{SF6}}}{k_{\text{22Ne}}} = \left[\frac{\text{Sc}(\text{SF}_6)}{\text{Sc}(^{22}\text{Ne})}\right]^{-n}. \qquad (12)$$

The Schmidt numbers are estimated using the polynomial relationship given by Wanninkhof (1990):

$$\text{Sc} = A - Bt + Ct^2 - Dt^3. \qquad (13)$$

For SF$_6$: $A = 3255.3$, $B = 217.3$, $C = 6.837$, $D = 0.086070$, hence Sc $= 1065.9$. For ^{22}Ne: $A = 764$, $B = 42.234$, $C = 1.1581$, $D = 0.013405$, hence Sc $= 314.8$.

Then, using Eq. 12 and assuming a Schmidt coefficient $n = 0.5$ yields

$$\frac{k_{\text{SF6}}}{k_{\text{22Ne}}} = \frac{\alpha_{\text{SF6}}}{\alpha_{\text{22Ne}}}\left[\frac{1065.9}{314.8}\right]^{-0.5} = 0.544.$$

To calculate the through-flows at the mine by using the dual gas tracer data, an equation system given by Eq. 10 for SF$_6$ and ^{22}Ne and Eq. 12 are used. As discussed previously, it is assumed that the influence of the bubble seeps in the tracer transfer is negligible. The concentration values for ^{22}Ne and SF$_6$ tracers are given by Figs. 12 and 15, respectively. For ^{22}Ne the concentration values range from 1.13×10^{-9} mL/g to 6.39×10^{-11} mL/g after 11 d, and for SF$_6$, the values range from 232.3 pmol SF$_6$/L to 3.1 pmol SF$_6$/L after 26 d. These yield $\alpha(^{22}\text{Ne}) = 1.45 \times 10^{-4}$ min^{-1}, $\alpha(\text{SF}_6) = 7.86 \times 10^{-5}$ min^{-1} and $Q = 611$ L/s, very close to the flow estimate produced by the other two experiments.

Conceptual model of the through-flows in Herman Pit

The three sets of experimental results presented all support a through-flow rate in Herman Pit on the order of 630 L/s (Fig. 21). Based on one of the experiments it was absolutely confirmed that some fraction of the water that leaves Herman Pit does reach Clear Lake. Well observations also support this likelihood, as high concentrations of tracer are seen in wells that are only a short distance from the lake. Even though it is known that water from Herman Pit is flowing into Clear Lake, it cannot be estimated from these calculations how much is going into the lake or the precise path the flow is taking. As shown in Fig. 21, of the approximate 630 L/s flowing into and out of Herman Pit, fluid may leave the pit and flow directly into the lake through the waste rock piles, through the native sediment that underlies the waste rock piles, or simply flow elsewhere. These results are totally consistent with Shipp and Zierenberg (2008), indicating sub-sediment flow of acid mine fluids derived from Herman Pit for a substantial distance out into Clear Lake.

CONCLUSIONS

Three tracer experiments have been used to explore the hydraulic communication between Herman Pit, Clear Lake, and the observation wells that lie between the two water bodies. The through-flows in Herman Pit obtained from the three experiments are all on the order of 630 L/s, which is two orders of magnitude higher than historical estimates.

All three experiments indicated that there were preferred pathways along which the tracers were detected within days of injection to Herman Pit. These are presumed to be unidentified conduits or old abandoned shafts beneath the waste rock rubble or the dam or both. The higher concentrations of tracer seen at those wells that indicate these preferred pathways, along with the rapid arrival time (requiring high flow rate), imply that the vast majority of Herman Pit flux occurs along those pathways. The experiments showed that eventually all wells showed signs of the tracers, which supports the fact that there is also a background flux driven by the groundwater equipotential gradient.

These experiments provide the only direct estimates of flow from Herman Pit, and the fact that three independent experiments using three different tracers yielded essentially the same result is compelling evidence of a high through-flow rate. All other estimates are based on geochemical inferences, historical estimates of refilling rates of the mine pit, or, most recently, the groundwater flow in the more consolidated regions of the mine waste rock pile. This latter study (Jewett et al. 2000), while possibly accurate in its estimate of the background equipotential flow, by its strategy of not placing new wells adjacent to the preferred pathways, may have inadvertently missed the majority of the groundwater transport.

Observations from the wells during each of the tracer experiments also suggest that the subsurface flows are highly variable, both spatially and temporally, although the overall through-flow changes little between experiments. Based on order-of-magnitude calculations, the presence of gas seeps in the site seemed not to have a major effect on the concentration of the gas tracers.

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