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Date: JUL 28 2015
Symbol: ENV-DO-15-0216
LA-UR: 15-25449
Locates Action No.: NA

Ms. Michelle Hunter, Acting Chief
Ground Water Quality Bureau
New Mexico Environment Department
Harold Runnels Building, Room N2250
1190 St. Francis Drive
P.O. Box 26110
Santa Fe, NM 87502

Dear Ms. Hunter:

Subject: Notice of Intent to Conduct a Tracer Test at Los Alamos National Laboratory, Technical Area 16

In accordance with Subsection A of 20.6.2.1201 New Mexico Administrative Code, the U.S. Department of Energy and Los Alamos National Security, LLC (DOE/LANS) are filing this notice of intent (NOI) to conduct a tracer test at Technical Area (TA)-16. The tracer test is being conducted to test connectivity of various parts of the TA-16 hydrological system and to support the future assessment of potential remedial alternatives for groundwater contaminated with high explosives (HE). Enclosure 1 contains a completed NMED NOI form. Enclosures 2, 3, and 4 provide information to support this notice.

Please contact Robert S. Beers by telephone at (505) 667-7969 or by email at bbeers@lanl.gov if you have questions regarding this NOI.

Sincerely,

Alison M. Dorries
Division Leader
Environmental Protection Division
Los Alamos National Security, LLC

Sincerely,

Gene E. Turner
Environmental Permitting Manager
National Security Missions
Los Alamos Field Office
U.S. Department of Energy

37235

AMD:GET:MTS:RSB/lm

Enclosures: (1) Completed NMED GWQB Notice of Intent to Discharge Form
(2) *Work Plan for a Tracer Test at Consolidated Unit 16-021(c)-99, Technical Area 16, Revision 1*
(3) Safety Data Sheet (SDS) for tracers sodium naphthalene disulfonate and sodium bromide
(4) Supplemental Information and Publications RE: sodium naphthalene disulfonate

Cy: James Hogan, NMED/SWQB, Santa Fe, NM, (E-File)
John E. Kieling, NMED/HWB, Santa Fe, NM, (E-File)
Stephen M. Yanicak, NMED/DOE/OB, (E-File)
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env-correspondence@lanl.gov, (E-File)

ENCLOSURE 1

Completed NMED GWQB Notice of Intent
to Discharge Form

ENV-DO-15-0216

LA-UR-15-25449

Date: JUL 28 2015

1. **Name and mailing address of person proposing to discharge:**
Stephani F. Swickley
Los Alamos National Security, LLC
P.O. Box 1663, Mail Stop M992
Los Alamos, NM 87544
Work Phone: 505-606-1628
Email: sfuller@lanl.gov
Point of Contact: Robert S. Beers, 505-667-7969, bbeers@lanl.gov

2. **Name of facility:** Los Alamos National Laboratory (LANL).

3. **Physical location of discharge (if applicable, give street address, township, range, section, distance from closest town or landmark, directions to facility, location map):** LANL Technical Area (TA)-16 in Township 19N, Range 6E, Section 29. **Enclosure 2** contains a location map of the project site.

4. **Type of operation generating the discharge (e.g., truck wash, food processing plant, restaurant, etc.):** This tracer study is being conducted to test connectivity of various parts of the TA-16 hydrological system and to support the future assessment of potential remedial alternatives for contaminated groundwater associated with the 260 Outfall. See **Enclosure 2,** *Work Plan for a Tracer Test at Consolidated Unit 16-021(c)-99, Technical Area 16, Revision 1.*

5. **Source(s) of the discharge. Describe how the wastewater, sludge, or other discharges processed and/or disposed at your facility are generated. Identify all sources. Attach additional pages if needed:** Multiple, nonreactive tracers will be deployed to the perched-intermediate groundwater zone. The principal tracer types belong to the group of naphthalene sulfonates (NS). Sodium bromide may also be used depending on dilution test results. See Table 1 below.

Table 1. Summary of the proposed tracers, locations, and quantities.

Locale	Unit	Tracer(s)	Quantity Injecte	Volume of Tracer Solution Injected[a]	Notes
R-25b	Perched	Na-1 NS	2 g	<300 gal. (1 casing volume [CV])	Dilution test. Anticipated recovery: <2%
CdV-9-1(i) Screen 2	Perched	Na-1 NS	2 g	<300 gal. (1 CV)	Dilution test. Anticipated recovery: <2%
CdV-16-1(i)	Perched	Na-2 NS	2 g	<300 gal. (1 CV)	Dilution test. Anticipated recovery: <2%
R-25b	Perched	Na-1,6-NDS[b] NaBr[c]	40 kg 150 kg	12,000 gal. Flush with a small amount of water (wellbore volume or less) after tracer deployment.	Long-term/large-scale natural-gradient test. Anticipated recovery: <2%. Primary candidate location for paired tracer (NDS+Br).
CdV-16-1(i)	Perched	Na-1,5-NDS[d]	40 kg	12,000 gal. Flush with a small amount of water (wellbore volume or less) after tracer deployment.	Long-term/large-scale natural gradient test. Anticipated recovery: <2%. Alternative location for paired tracer (NDS+Br).
CdV-9-1(i) Piezometer 1 (662.9–672.4 ft)	Perched	Na-1,3,6-NTS	25 kg	6000 gal. Flush with a small amount of water (wellbore volume or less) after tracer deployment.	Primary objective: determine connectivity of upper and lower perched in CdV-9-1(i). Secondary objective: conduct long- term/large-scale natural gradient test. Anticipated recovery: <2%.

CdV-9-1(i) Piezometer 2 (852.9–862.4 ft)	Perched	Na-1,3,5-NTS	25 kg	6000 gal. Flush with a small amount of water (wellbore volume or less) after tracer deployment.	Primary objective: determine connectivity of upper and lower perched zones in CdV-9-1(i). Secondary objective conduct long-term/large-scale natural gradient test. Anticipated recovery: <2%.
CdV-9-1(i) Screen 1 (937.4–992.4 ft)	Perched	Na-2,6-NDS	40 kg	12,000 gal. Flush with a small amount of water (wellbore volume or less) after tracer deployment.	Long-term/large-scale natural-gradient test. Anticipated recovery: <2%. Alternative location for paired tracer (NDS+Br).

Note: This table presents an approximation of the types and masses of tracers that may be utilized. Final details are subject to NMED-GWQB approval.

[a] Tracer masses and water volumes are selected to minimize density-driven tracer flow.

[b] NDS = Naphthalene disulfonate.

[c] NaBr may be deployed in CdV-16-1(i), CdV-9-1(i), or R-25b, depending on dilution test results.

[d] NTS = Naphthalene trisulfonate.

6. **Expected contaminants in the discharge (e.g., nitrate-nitrogen, metals, organic compounds, salts, etc.) Include estimated concentration if known, and copies of results of laboratory analyses, if available:**

Sodium naphlalene sulfonates (varieties listed in Table 1) and sodium bromide will be introduced at the quantities listed in Table 1. The approximate total mass of tracer used will be as follows.

- ✓ sodium naphthalene sulfonates: 220 kg
- ✓ sodium bromide: 150 kg

Enclosure 3 provides the Safety Data Sheet (SDS) for the two proposed tracers.

Enclosure 4 provides supplemental information on sodium naphthalene sulfonates.

7. **Describe all components of wastewater processing, treatment, storage, and disposal system (e.g., grease interceptor, lagoon, septic tank/leachfield, etc.) Include sizes, site layout map, plans and specifications, etc. if available:**

See **Enclosure 2**, *Work Plan for a Tracer Test at Consolidated Unit 16-021(c)-99, Technical Area 16, Revision 1.*

8. **Estimated maximum daily discharge volume in gallons per day (or other units):**

Total discharge is approximately 50,000 gallons. Daily maximum discharge is approximately 12,000 gallons.

9. **Estimated depth to ground water (ft):** Approximately 850-900 ft bgs.

Signature: Stephani Swickley **Date:** 7/23/15

Printed name: Stephani Swickley **Title:** Program Manager

Please return this form to:
NMED Ground Water Quality Bureau
P.O. Box 5469
Santa Fe, New Mexico 87502-5469

Telephone: 505-827-2900
Fax: 505-827-2965

ENCLOSURE 2

Work Plan for a Tracer Test at Consolidated Unit 16-021(c)-99, Technical Area 16, Revision 1.

ENV-DO-15-0216

LA-UR-15-25449

Date: JUL 2 8 2015

LA-UR-15-24089
July 2015
EP2015-0105

Work Plan for a Tracer Test at Consolidated Unit 16-021(c)-99, Technical Area 16, Revision 1

Los Alamos
NATIONAL LABORATORY
EST. 1943

Prepared by the Environmental Programs Directorate

Los Alamos National Laboratory, operated by Los Alamos National Security, LLC, for the U.S. Department of Energy under Contract No. DE-AC52-06NA25396, has prepared this document pursuant to the Compliance Order on Consent, signed March 1, 2005. The Compliance Order on Consent contains requirements for the investigation and cleanup, including corrective action, of contamination at Los Alamos National Laboratory. The U.S. government has rights to use, reproduce, and distribute this document. The public may copy and use this document without charge, provided that this notice and any statement of authorship are reproduced on all copies.

EP2015-0105

Work Plan for a Tracer Test at Consolidated Unit 16-021(c)-99, Technical Area 16, Revision 1

July 2015

Responsible project manager:

Printed Name	Signature	Title	Organization	Date
Kent Rich		Project Manager	Environmental Remediation Program	6/24/15

Responsible LANS representative:

Printed Name	Signature	Title	Organization	Date
Randall Erickson	for R. Erickson	Acting Associate Director	Environmental Programs	6/26/15

Responsible DOE representative:

Printed Name	Signature	Title	Organization	Date
Christine Gelles		Acting Manager	DOE-~~LASO~~ EM-LA	7-10-2015

CONTENTS

1.0 BACKGROUND 1
2.0 RATIONALE FOR TRACER TEST 1
3.0 IMPLEMENTATION PLAN 2
4.0 SCHEDULE AND REPORTING 3
5.0 SUMMARY OF MODIFICATIONS FROM THE ORIGINAL TRACER PLAN 4
6.0 MANAGEMENT OF INVESTIGATION-DERIVED WASTE 4
7.0 REFERENCES 4

Figures

Figure 1.0-1 Location of wells and other hydrologic features within the Cañon de Valle watershed 7
Figure 1.0-2 Annotated cross-section illustrating the hydrologic conceptual model for the deep-perched aquifer at TA-16 (after LANL 2011, 207069) 8

Table

Table 3.0-1 Tracer Deployment Parameters 9

1.0 BACKGROUND

Consolidated Unit 16-021(c)-99 (the 260 Outfall) at Technical Area 16 (TA-16) at Los Alamos National Laboratory (LANL or the Laboratory) is currently subject to corrective action for high explosives– (HE-) contaminated groundwater under the Compliance Order on Consent (the Consent Order) (LANL 2007, 098734). Details concerning the site and its groundwater are provided in a series of regulatory documents (LANL 1998, 059891; LANL 2003, 077965; LANL 2007, 098734; LANL 2011, 203711; LANL 2011, 207069, and references therein). Both deep perched-intermediate groundwater (700–1200 ft below ground surface [bgs]) and regional groundwater (>1200 ft bgs) are contaminated with HE, particularly RDX (hexahydro-1,3,5-trinitro-1,3,5 triazine), and other related constituents (LANL 2011, 207069). RDX levels are consistently above the risk-based screening level of 7 µg/L in deep perched-intermediate groundwater in multiple groundwater wells [R-25, R-25b, CdV-16-1(i), CdV-16-2ir, CdV-16-4ip, CdV-16-9(i)]. (Figure 1.0-1). Currently, regional groundwater wells show RDX at levels below the screening level. The extent of the upper perched zone and of RDX contamination within this zone is also shown in Figure 1.0-1, and the curved water-level contours in the vicinity of Cañon de Valle suggest groundwater mounding below the canyon axis.

The hydrogeologic framework for the contaminated deep perched-intermediate zone and regional aquifer is complex (LANL 2011, 207069). A wide range of hydrologic, geochemical, and geophysical data suggest these groundwater zones are quite heterogeneous. In a broad sense, the deep perched-intermediate zone is divided into an upper zone and a lower zone, with the upper zone consistently more contaminated than the lower zone; this is expected conceptually because the contaminant source is located at the ground surface. Conservative geochemical signatures vary both spatially and, to a lesser degree, temporally (LANL 2011, 207069). Hydrologic data, including water levels, pump-test results, and drilling observations, demonstrate the deep perched-intermediate zones are hydrogeologically complex, with localized hydrogeologic regimes (LANL 2011, 207069). Hydraulic connectivity appears to be weaker vertically than horizontally. A recent version of the hydrologic conceptual model for the TA-16 area is shown in Figure 1.0-2.

This plan is a revision of a previously approved tracer test plan for TA-16 (LANL 2012, 210352). Key reasons for the revision include (1) availability of a new well, CdV-9-1(i), which is at a good location to introduce the tracer into both the upper and lower perched-intermediate zone; (2) availability of alternative tracers (napthlalene sulfonates) that have substantially lower analytical detection limits and per weight costs than the previously proposed fluorinated benzoates (FBAs); and (3) changes in the surface water distribution in Cañon de Valle (see section 3.0).

2.0 RATIONALE FOR TRACER TEST

The rationale for the tracer test has not changed since the original plan was approved by the New Mexico Environment Department (NMED) (LANL 2012, 210352; NMED 2012, 210098). This tracer study is being conducted to test connectivity of various parts of the TA-16 hydrological system and to support the future assessment of potential remedial alternatives for contaminated groundwater associated with the 260 Outfall. A remedial alternatives analysis would benefit from an improved understanding of (1) local hydraulic gradients and groundwater velocities/fluxes within the perched-intermediate zone; (2) lateral advective travel times and associated hydrologic parameters within the Otowi Member of the Bandelier Tuff Formation and the Puye Formation; and (3) vertical advective travel times, particularly between the upper perched zone and lower perched zone and between the lower perched zone and the regional aquifer. Pathways, groundwater velocities/fluxes, and travel times from near-surface alluvial aquifers to

the deep-perched zone are also poorly constrained. All these questions may potentially be addressed through a multiple-constituent tracer test.

3.0 IMPLEMENTATION PLAN

To address the uncertainties delineated in section 2.0, the Laboratory proposes the following actions (a pframework for the tracer deployments is provided in Table 3.0-1).

1. *Single Dilution Tracer Test.* For the initial investigation phase, a single-dilution tracer test will be conducted in each of the following wells: CdV-16-1(i), CdV-9-1(i), and R-25b. A small quantity of tracer will be introduced at the well screen and allowed to disperse into the groundwater under natural flow conditions (i.e., no pumping). The reduction in tracer concentration over the following week or two will be monitored. The dilution time series results will be used to quantify local flow velocities around the borehole screens. These tests will also serve to identify the best well to deploy sodium bromide (see item 2).

2. *Deployment of Multiple Nonreactive Tracers.* For the longer term, natural gradient phase of the plan, passive deployment of multiple nonreactive tracers in wells CdV-16-1(i), CdV-9-1(i), and R-25b will be made. These wells are within the perched-intermediate zone, are located farthest upgradient within the contaminated perched zone, and form a transect across Cañon de Valle. Different, chemically distinct tracers will be deployed at each location. The principal tracer types belong to a group of naphthalene sulfonates (NSs) (Nimmo et al. 2002, 210314; Wright and Hull 2004, 209698). Sodium bromide will be deployed along with an NS at one location to examine the effects of dual porosity/dual permeability. To examine the connection between the upper and lower perched-intermediate zone, two other NSs will be deployed in the shallow piezometers in CdV-9-1(i). The NSs can be easily measured using in-house laboratory methods (fluorescence detection) with detection limits <1 ppb. These tracers are nontoxic, should not interfere with sampling of regulated constituents in the aquifer, and are inexpensive. In the original plan, NSs alone were not proposed because at that time they were considered experimental and no testing of their conservative behavior for local TA-16 conditions had been done. Subsequently, a series of laboratory tests were conducted using water and Otowi and Puye material from TA-16 and NSs (LANL 2012, 232277). The results indicated that NSs are suitable to deploy at TA-16. They offer superior detection limits (approximately 0.5 ppb) compared with FBAs (10–30 ppb) and thus increase the probability of tracer detection if low breakthrough concentrations are detected. Details of proposed tracer types, tracer masses, and water volumes for each deployment locality are provided in Table 3.0-1. Masses (and other values) in the table are approximate and are based on estimates of the amount of dilution that may occur between release points and sampling points and the NS detection level. Actual deployment amounts will be subject to permitting by the NMED Ground Water Quality Bureau (GWQB). Pressures in all well screens in the vicinity of the tracer deployments will be monitored during the tracer test. An in-situ real-time conductivity probe will be used to monitor dispersal of the tracers into the perched zone.

3. *Initial and Pre-Breakthrough Monitoring.* Periodic sampling for the tracers will be conducted in intermediate wells R-25b, CdV-16-1(i), CdV-16-2(i)r, and CdV-16-4ip, CdV-9-1(i), and R-47i (Figure 1.0-1). Based on the known hydrologic properties of the lithologies sited next to the deployment screens, initial breakthroughs in nearby wells would be anticipated within 2 yr. Calculations suggest sampling intervals of 2 wk, 6 wk, and 12 wk after deployment, followed by continued quarterly sampling, will likely capture the initial breakthrough of the tracers, if breakthrough can be detected. The necessity for continued sampling will be evaluated periodically based on the ongoing observations. If the proposed sampling frequency does not

adequately capture the breakthrough because of rapid travel times, a subsidiary tracer deployment would be considered in consultation with NMED personnel. Sampling will be coordinated with existing ongoing sampling of these wells through the Laboratory's sitewide groundwater monitoring program. The following regional wells will also be sampled in concert with the Laboratory's sitewide groundwater monitoring program following the monitoring program schedule: R-18, R-47, R-48, R-58 (planned for installation in late fiscal year 2015), and R-63. The implied gradients from the water-level contours shown in Figure 1.0-1 illustrate how tracers introduced in the CdV-9-1(i), CdV-16-1(i), and R-25b transect might migrate to the monitoring locations listed above.

4. *Post-Breakthrough Monitoring.* If tracer breakthrough is observed in any of the above wells, tracer monitoring can be modified to a higher sampling frequency if there is concern about properly capturing the breakthrough curve. Following observation of breakthrough in any screen, hydrogeologic analyses will be completed to determine the optimum sampling frequency to define the tracer breakthrough profile; NMED personnel will be included in these discussions. Note that expectations of tracer mass recovery are low (Table 3.0-1) because of (1) uncertainties in flowpath directions, (2) the relatively long-length scales to many of the monitoring wells, and (3) natural gradient conditions.

5. *Deployment of an NS in Cañon de Valle.* An NS tracer will also be deployed within the surface water/alluvial system near the area of Burning Ground Spring (Figure 1.0-1). The original plan indicated deployment in Peter Seep. However, a recent field visit noted the lack of flowing surface water within the canyon above the Burning Ground Spring confluence (which includes the Peter Seep area). Therefore, it is prudent to move the location downcanyon to the head of the continuously flowing reach. This tracer test is not as important as those described in item 1 above; however, since tracers are being sampled in the deep-perched aquifer, this near-surface tracer can opportunistically be deployed at little added cost and may provide information on recharge rates from the alluvial aquifer to the deep perched-intermediate zone. A single NS (different from any deployed in the deeper zones) with a greater input mass than the well deployments is proposed because of anticipated longer travel times and lower breakthrough concentrations at deep-perched zone monitoring locations. Canyon alluvial wells and surface water sampling (e.g., near the E256 gage station) will be used to monitor tracer movement. Any new alluvial well installations may be used to supplement the existing sampling locations. Actual sampling locations will be determined after a site visit and before tracer deployment, so sampling can be optimized for current hydrological conditions in the canyon.

6. *Analysis of Data.* When tracer breakthrough is observed, data will be interpreted using methods outlined in the literature (e.g., Duke et al. 2007, 210313).

4.0 SCHEDULE AND REPORTING

Dilution tests are anticipated to begin in August 2015, and the long-term tracers will be deployed by September 30, 2015. Applicable permits will be obtained from NMED before the tracers are deployed.

Information on tracer breakthroughs will be formally reported in the biannual corrective measures evaluation progress reports. These reports will describe any tracer breakthroughs observed and will propose any changes to sampling frequencies or other details associated with the tests. All tracer-monitoring data will also be included in the periodic monitoring reports for the TA-16 260 monitoring

group. The NMED will be notified at least fifteen (15) calendar days before the tracer is deployed and will also be notified informally of tracer breakthrough by email or phone.

5.0 SUMMARY OF MODIFICATIONS FROM THE ORIGINAL TRACER PLAN

The following modifications were made to the original tracer test work plan:

- Addition of three dilution tests for characterization of local flow conditions in CdV-16-1(i), CdV-9-1(i), and R-25b using NSs.
- Addition of three new NS tracer deployments in well CdV-9-1(i) for larger-scale perched-zone investigations [CdV-9-1(i) had not been drilled at the time the original plan was submitted].
- Replacement of all previously suggested FBA long-term/natural-gradient deployments with NSs (lower detection limits and lower cost).
- Elimination of R-25 ports for monitoring the tracer from R-25b (R-25 is planned to be plugged and abandoned).
- Deployment of the Cañon de Valle tracer near the Burning Ground Spring confluence instead of Peter Seep (because of reduced continuous flow in the stream in Cañon de Valle).

6.0 MANAGEMENT OF INVESTIGATION-DERIVED WASTE

Investigation-derived waste will be managed in accordance with EP-DIR-SOP-10021, Characterization and Management of Environmental Programs Waste. This standard operating procedure incorporates the requirements of applicable U.S. Environmental Protection Agency and NMED regulations, U.S. Department of Energy orders, and Laboratory requirements.

7.0 REFERENCES

The following list includes all documents cited in this plan. Parenthetical information following each reference provides the author(s), publication date, and ER ID or ESH ID. This information is also included in text citations. ER IDs were assigned by the Environmental Programs Directorate's Records Processing Facility (IDs through 599999), and ESH IDs are assigned by the Environment, Safety, and Health (ESH) Directorate (IDs 600000 and above). IDs are used to locate documents in the Laboratory's Electronic Document Management System and, where applicable, in the master reference set.

Copies of the master reference set are maintained at the NMED Hazardous Waste Bureau and the ESH Directorate. The set was developed to ensure that the administrative authority has all material needed to review this document, and it is updated with every document submitted to the administrative authority. Documents previously submitted to the administrative authority are not included.

Duke, C.L., R.C. Roback, P.W. Reimus, R.S. Bowman, T.L. McLing, K.E. Baker, and L.C. Hull, November 2007. "Elucidation of Flow and Transport Processes in a Variably Saturated System of Interlayered Sediment and Fractured Rock Using Tracer Tests," *Vadose Zone Journal,* Vol. 6, No. 4, pp. 855–867. (Duke et al. 2007, 210313)

LANL (Los Alamos National Laboratory), September 1998. "RFI Report for Potential Release Site 16-021(c)," Los Alamos National Laboratory document LA-UR-98-4101, Los Alamos, New Mexico. (LANL 1998, 059891)

LANL (Los Alamos National Laboratory), September 2003. "Phase III RFI Report for Solid Waste Management Unit 16-021(c)-99," Los Alamos National Laboratory document LA-UR-03-5248, Los Alamos, New Mexico. (LANL 2003, 077965)

LANL (Los Alamos National Laboratory), August 2007. "Corrective Measures Evaluation Report, Intermediate and Regional Groundwater, Consolidated Unit 16-021(c)-99," Los Alamos National Laboratory document LA-UR-07-5426, Los Alamos, New Mexico. (LANL 2007, 098734)

LANL (Los Alamos National Laboratory), June 2011. "Hydrologic Testing Report for Consolidated Unit 16-021(c)-99," Los Alamos National Laboratory document LA-UR-11-3072, Los Alamos, New Mexico. (LANL 2011, 203711)

LANL (Los Alamos National Laboratory), September 2011. "Investigation Report for Water Canyon/Cañon de Valle," Los Alamos National Laboratory document LA-UR-11-5478, Los Alamos, New Mexico. (LANL 2011, 207069)

LANL (Los Alamos National Laboratory), January 2012. "Work Plan for a Tracer Test at Consolidated Unit 16-021(c)-99, Technical Area 16," Los Alamos National Laboratory document LA-UR-12-0440, Los Alamos, New Mexico. (LANL 2012, 210352)

LANL (Los Alamos National Laboratory), November 2012. "Report on the Results of Laboratory Tests of Tracer Compounds at Consolidated Unit 16-021(c)-99," Los Alamos National Laboratory document LA-UR-12-26448, Los Alamos, New Mexico. (LANL 2012, 232277)

Nimmo, J.R., K.S. Perkins, P.E. Rose, J.P. Rousseau, B.R. Orr, B.V. Twining, and S.R. Anderson, August 2002. "Kilometer-Scale Rapid Transport of Naphthalene Sulfonate Tracer in the Unsaturated Zone at the Idaho National Engineering and Environmental Laboratory," *Vadose Zone Journal,* Vol. 1, No. 1, pp. 89–101. (Nimmo et al. 2002, 210314)

NMED (New Mexico Environment Department), February 7, 2012. "Approval with Modification, Work Plan for a Tracer Test at Consolidated Unit 16-021(c)-99, Technical Area 16," New Mexico Environment Department letter to G.J. Rael (DOE-LASO) and M.J. Graham (LANL) from J.E. Kieling (NMED-HWB), Santa Fe, New Mexico. (NMED 2012, 210098)

Wright, K.E., and L.C. Hull, July 2004. "An Evaluation of Tracers for Use in Vadose Zone Investigations at the Idaho National Engineering and Environmental Laboratory," report no. ICP/EXT-04-00334, prepared for the U.S. Department of Energy Idaho Operations Office, Idaho Completion Project, Idaho Falls, Idaho. (Wright and Hull 2004, 209698)

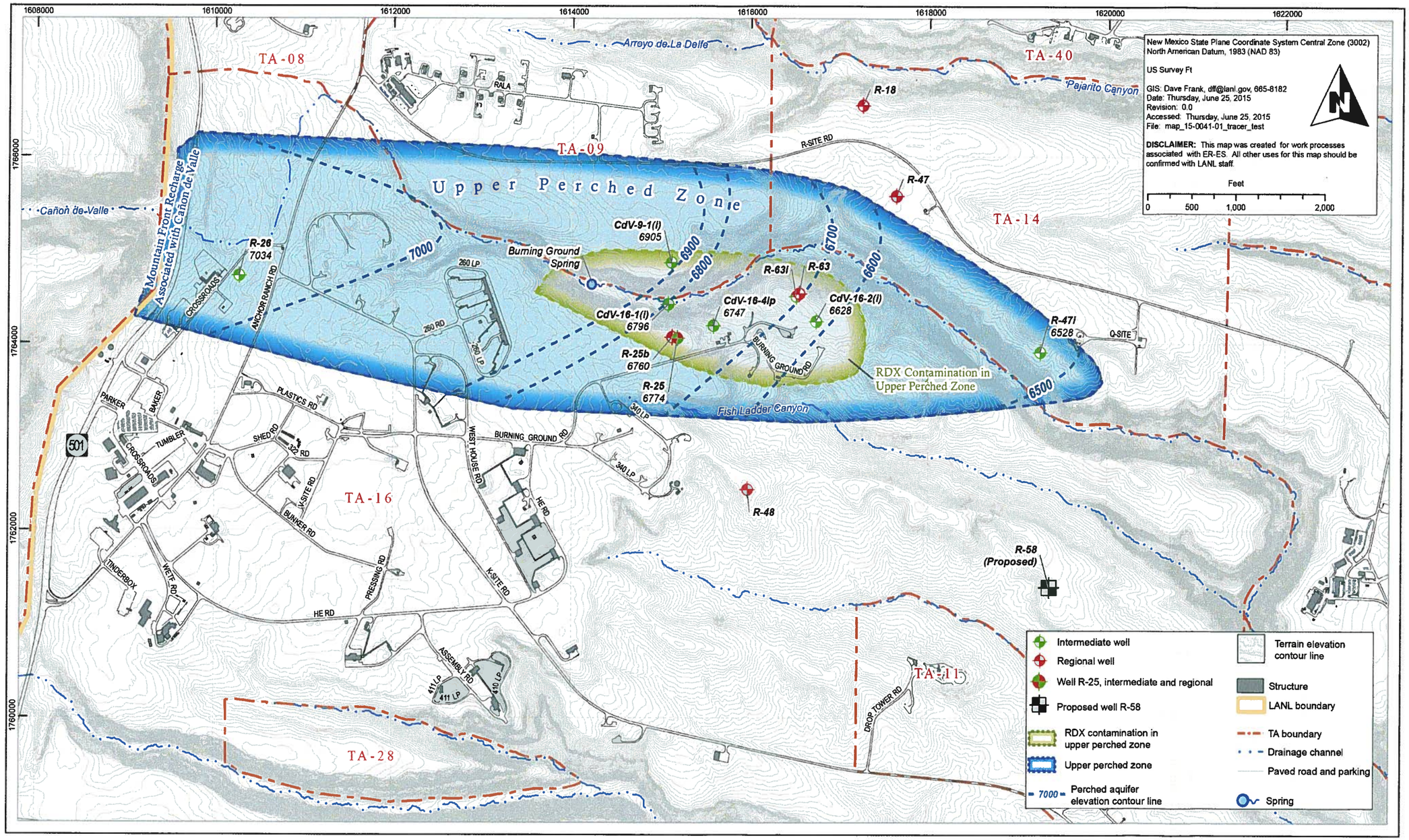

Figure 1.0-1 **Location of wells and other hydrologic features within the Cañon de Valle watershed. The extent of the upper perched zone (with water-elevation contour lines) and the extent of RDX contamination in this zone are shown as an example of the subsurface conditions at TA-16.**

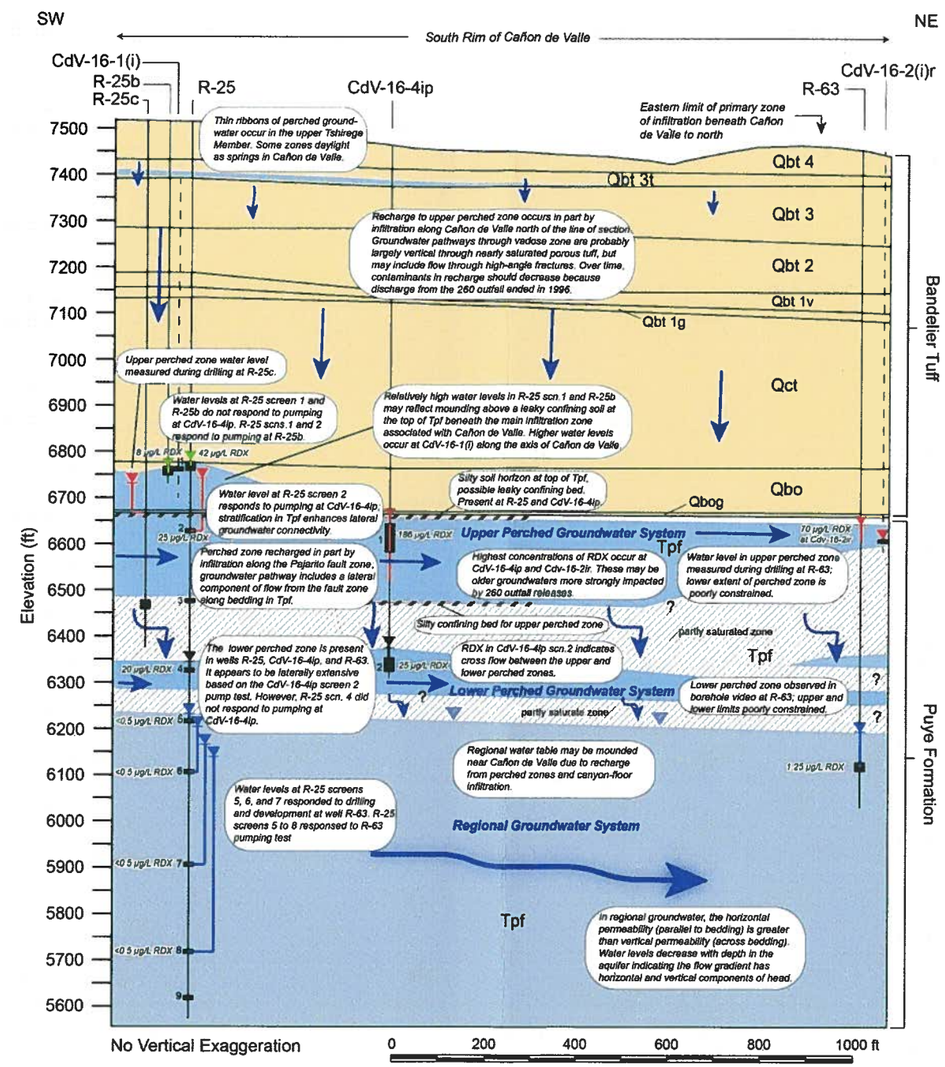

Figure 1.0-2 **Annotated cross-section illustrating the hydrologic conceptual model for the deep-perched aquifer at TA-16 (after LANL 2011, 207069)**

Table 3.0-1
Tracer Deployment Parameters

Locale	Unit	Tracer(s)	Quantity Injected	Volume of Tracer Solution Injected[a]	Notes
R-25b	Perched	Na-1 NS	2 g	<300 gal. (1 casing volume [CV])	Dilution test. Anticipated recovery: <2%
CdV-9-1(i) Screen 2	Perched	Na-1 NS	2 g	<300 gal. (1 CV)	Dilution test. Anticipated recovery: <2%
CdV-16-1(i)	Perched	Na-2 NS	2 g	<300 gal. (1 CV)	Dilution test. Anticipated recovery: <2%
R-25b	Perched	Na-1,6-NDS[b] NaBr[c]	40 kg 150 kg	12,000 gal. Flush with a small amount of water (wellbore volume or less) after tracer deployment.	Long-term/large-scale natural-gradient test. Anticipated recovery: <2%. Primary candidate location for paired tracer (NDS+Br).
CdV-16-1(i)	Perched	Na-1,5-NDS[d]	40 kg	12,000 gal. Flush with a small amount of water (wellbore volume or less) after tracer deployment.	Long-term/large-scale natural gradient test. Anticipated recovery: <2%. Alternative location for paired tracer (NDS+Br).
CdV-9-1(i) Piezometer 1 (662.9–672.4 ft)	Perched	Na-1,3,6-NTS	25 kg	6000 gal. Flush with a small amount of water (wellbore volume or less) after tracer deployment.	Primary objective: determine connectivity of upper and lower perched in CdV-9-1(i). Secondary objective: conduct long-term/large-scale natural gradient test. Anticipated recovery: <2%.
CdV-9-1(i) Piezometer 2 (852.9–862.4 ft)	Perched	Na-1,3,5-NTS	25 kg	6000 gal. Flush with a small amount of water (wellbore volume or less) after tracer deployment.	Primary objective: determine connectivity of upper and lower perched zones in CdV-9-1(i). Secondary objective conduct long-term/large-scale natural gradient test. Anticipated recovery: <2%.
CdV-9-1(i) Screen 1 (937.4–992.4 ft)	Perched	Na-2,6-NDS	40 kg	12,000 gal. Flush with a small amount of water (wellbore volume or less) after tracer deployment.	Long-term/large-scale natural-gradient test. Anticipated recovery: <2%. Alternative location for paired tracer (NDS+Br).
CdV near Burning Ground Spring	Alluvial	Na-2,7-NDS	50 kg	12,000 gal. Flush with 1000–2000 gal. clean water after tracer deployment.	Alluvial aquifer transport and long-term/large-scale natural-gradient test. Anticipated recovery: <2%

Note: This table presents an approximation of the types and masses of tracers that may be utilized. Final details are subject to NMED-GWQB approval.

[a] Tracer masses and water volumes are selected to minimize density-driven tracer flow.

[b] NDS = Naphthalene disulfonate.

[c] NaBr may be deployed in CdV-16-1(i), CdV-9-1(i), or R-25b, depending on dilution test results.

[d] NTS = Naphthalene trisulfonate.

ENCLOSURE 3

Safety Data Sheet (SDS) for tracers
sodium naphthalene disulfonate
and sodium bromide

ENV-DO-15-0216

LA-UR-15-25449

Date: JUL 2 8 2015

SIGMA-ALDRICH

sigma-aldrich.com

SAFETY DATA SHEET

Version 3.3
Revision Date 06/25/2014
Print Date 08/28/2014

1. PRODUCT AND COMPANY IDENTIFICATION

1.1 Product identifiers

Product name : Sodium 1,5-naphthalenedisulfonate dibasic

Product Number : 70240
Brand : Aldrich

CAS-No. : 1655-29-4

1.2 Relevant identified uses of the substance or mixture and uses advised against

Identified uses : Laboratory chemicals, Manufacture of substances

1.3 Details of the supplier of the safety data sheet

Company : Sigma-Aldrich
3050 Spruce Street
SAINT LOUIS MO 63103
USA

Telephone : +1 800-325-5832
Fax : +1 800-325-5052

1.4 Emergency telephone number

Emergency Phone # : (314) 776-6555

2. HAZARDS IDENTIFICATION

2.1 Classification of the substance or mixture

Not a hazardous substance or mixture.

2.2 GHS Label elements, including precautionary statements

Not a hazardous substance or mixture.

2.3 Hazards not otherwise classified (HNOC) or not covered by GHS - none

3. COMPOSITION/INFORMATION ON INGREDIENTS

3.1 Substances

Synonyms : 1,5-Naphthalenedisulfonic aciddisodium salt

Formula : $C_{10}H_6Na_2O_6S_2$
Molecular Weight : 332.26 g/mol
CAS-No. : 1655-29-4
EC-No. : 216-732-0

No ingredients are hazardous according to OSHA criteria.
No components need to be disclosed according to the applicable regulations.

4. FIRST AID MEASURES

4.1 Description of first aid measures

If inhaled
If breathed in, move person into fresh air. If not breathing, give artificial respiration.

In case of skin contact
Wash off with soap and plenty of water.

In case of eye contact
Flush eyes with water as a precaution.

If swallowed
Never give anything by mouth to an unconscious person. Rinse mouth with water.

4.2 Most important symptoms and effects, both acute and delayed
The most important known symptoms and effects are described in the labelling (see section 2.2) and/or in section 11

4.3 Indication of any immediate medical attention and special treatment needed
no data available

5. FIREFIGHTING MEASURES

5.1 Extinguishing media

Suitable extinguishing media
Use water spray, alcohol-resistant foam, dry chemical or carbon dioxide.

5.2 Special hazards arising from the substance or mixture
Carbon oxides, Sulphur oxides, Sodium oxides

5.3 Advice for firefighters
Wear self contained breathing apparatus for fire fighting if necessary.

5.4 Further information
no data available

6. ACCIDENTAL RELEASE MEASURES

6.1 Personal precautions, protective equipment and emergency procedures
Avoid dust formation. Avoid breathing vapours, mist or gas.
For personal protection see section 8.

6.2 Environmental precautions
Do not let product enter drains.

6.3 Methods and materials for containment and cleaning up
Sweep up and shovel. Keep in suitable, closed containers for disposal.

6.4 Reference to other sections
For disposal see section 13.

7. HANDLING AND STORAGE

7.1 Precautions for safe handling
Provide appropriate exhaust ventilation at places where dust is formed.Normal measures for preventive fire protection.
For precautions see section 2.2.

7.2 Conditions for safe storage, including any incompatibilities
Keep container tightly closed in a dry and well-ventilated place.

hygroscopic Keep in a dry place.

7.3 Specific end use(s)
Apart from the uses mentioned in section 1.2 no other specific uses are stipulated

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

8.1 Control parameters

Components with workplace control parameters
Contains no substances with occupational exposure limit values.

8.2 Exposure controls

Appropriate engineering controls
General industrial hygiene practice.

Personal protective equipment

Eye/face protection
Use equipment for eye protection tested and approved under appropriate government standards such as NIOSH (US) or EN 166(EU).

Skin protection
Handle with gloves. Gloves must be inspected prior to use. Use proper glove removal technique (without touching glove's outer surface) to avoid skin contact with this product. Dispose of contaminated gloves after use in accordance with applicable laws and good laboratory practices. Wash and dry hands.

Body Protection
Choose body protection in relation to its type, to the concentration and amount of dangerous substances, and to the specific work-place., The type of protective equipment must be selected according to the concentration and amount of the dangerous substance at the specific workplace.

Respiratory protection
Respiratory protection is not required. Where protection from nuisance levels of dusts are desired, use type N95 (US) or type P1 (EN 143) dust masks. Use respirators and components tested and approved under appropriate government standards such as NIOSH (US) or CEN (EU).

Control of environmental exposure
Do not let product enter drains.

9. PHYSICAL AND CHEMICAL PROPERTIES

9.1 Information on basic physical and chemical properties

a)	Appearance	Form: powder Colour: beige
b)	Odour	no data available
c)	Odour Threshold	no data available
d)	pH	no data available
e)	Melting point/freezing point	no data available
f)	Initial boiling point and boiling range	no data available
g)	Flash point	no data available
h)	Evapouration rate	no data available
i)	Flammability (solid, gas)	no data available
j)	Upper/lower flammability or explosive limits	no data available
k)	Vapour pressure	no data available
l)	Vapour density	no data available
m)	Relative density	no data available
n)	Water solubility	no data available
o)	Partition coefficient: n-octanol/water	no data available
p)	Auto-ignition temperature	no data available
q)	Decomposition temperature	no data available
r)	Viscosity	no data available
s)	Explosive properties	no data available

t) Oxidizing properties no data available

9.2 Other safety information
no data available

10. STABILITY AND REACTIVITY

10.1 Reactivity
no data available

10.2 Chemical stability
Stable under recommended storage conditions.

10.3 Possibility of hazardous reactions
no data available

10.4 Conditions to avoid
no data available

10.5 Incompatible materials
Strong oxidizing agents

10.6 Hazardous decomposition products
Other decomposition products - no data available
In the event of fire: see section 5

11. TOXICOLOGICAL INFORMATION

11.1 Information on toxicological effects

Acute toxicity
no data available

Inhalation: no data available

Dermal: no data available

no data available

Skin corrosion/irritation
no data available

Serious eye damage/eye irritation
no data available

Respiratory or skin sensitisation
no data available

Germ cell mutagenicity
no data available

Carcinogenicity

IARC: No component of this product present at levels greater than or equal to 0.1% is identified as probable, possible or confirmed human carcinogen by IARC.

ACGIH: No component of this product present at levels greater than or equal to 0.1% is identified as a carcinogen or potential carcinogen by ACGIH.

NTP: No component of this product present at levels greater than or equal to 0.1% is identified as a known or anticipated carcinogen by NTP.

OSHA: No component of this product present at levels greater than or equal to 0.1% is identified as a carcinogen or potential carcinogen by OSHA.

Reproductive toxicity
no data available

no data available

Specific target organ toxicity - single exposure
no data available

Specific target organ toxicity - repeated exposure
no data available

Aspiration hazard
no data available

Additional Information
RTECS: Not available

To the best of our knowledge, the chemical, physical, and toxicological properties have not been thoroughly investigated.

12. ECOLOGICAL INFORMATION

12.1 Toxicity
no data available

12.2 Persistence and degradability
no data available

12.3 Bioaccumulative potential
no data available

12.4 Mobility in soil
no data available

12.5 Results of PBT and vPvB assessment
PBT/vPvB assessment not available as chemical safety assessment not required/not conducted

12.6 Other adverse effects

no data available

13. DISPOSAL CONSIDERATIONS

13.1 Waste treatment methods

Product
Offer surplus and non-recyclable solutions to a licensed disposal company.

Contaminated packaging
Dispose of as unused product.

14. TRANSPORT INFORMATION

DOT (US)
Not dangerous goods

IMDG
Not dangerous goods

IATA
Not dangerous goods

15. REGULATORY INFORMATION

SARA 302 Components
SARA 302: No chemicals in this material are subject to the reporting requirements of SARA Title III, Section 302.

SARA 313 Components
SARA 313: This material does not contain any chemical components with known CAS numbers that exceed the threshold (De Minimis) reporting levels established by SARA Title III, Section 313.

SARA 311/312 Hazards
No SARA Hazards

Massachusetts Right To Know Components
No components are subject to the Massachusetts Right to Know Act.

Pennsylvania Right To Know Components

	CAS-No.	Revision Date
Disodium naphthalene-1,5-disulphonate	1655-29-4	

New Jersey Right To Know Components

	CAS-No.	Revision Date
Disodium naphthalene-1,5-disulphonate	1655-29-4	

California Prop. 65 Components

This product does not contain any chemicals known to State of California to cause cancer, birth defects, or any other reproductive harm.

16. OTHER INFORMATION

HMIS Rating

Health hazard:	0
Chronic Health Hazard:	
Flammability:	0
Physical Hazard	0

NFPA Rating

Health hazard:	0
Fire Hazard:	0
Reactivity Hazard:	0

Further information

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The above information is believed to be correct but does not purport to be all inclusive and shall be used only as a guide. The information in this document is based on the present state of our knowledge and is applicable to the product with regard to appropriate safety precautions. It does not represent any guarantee of the properties of the product. Sigma-Aldrich Corporation and its Affiliates shall not be held liable for any damage resulting from handling or from contact with the above product. See www.sigma-aldrich.com and/or the reverse side of invoice or packing slip for additional terms and conditions of sale.

Preparation Information

Sigma-Aldrich Corporation
Product Safety – Americas Region
1-800-521-8956

Version: 3.3 Revision Date: 06/25/2014 Print Date: 08/28/2014

SIGMA-ALDRICH

sigma-aldrich.com

Material Safety Data Sheet

Version 3.1
Revision Date 01/17/2012
Print Date 03/20/2012

1. PRODUCT AND COMPANY IDENTIFICATION

Product name	:	Sodium bromide
Product Number	:	S4547
Brand	:	Sigma-Aldrich
Supplier	:	Sigma-Aldrich 3050 Spruce Street SAINT LOUIS MO 63103 USA
Telephone	:	+1 800-325-5832
Fax	:	+1 800-325-5052
Emergency Phone # (For both supplier and manufacturer)	:	(314) 776-6555
Preparation Information	:	Sigma-Aldrich Corporation Product Safety - Americas Region 1-800-521-8956

2. HAZARDS IDENTIFICATION

Emergency Overview

OSHA Hazards
Target Organ Effect

Target Organs

Central nervous system

GHS Classification
Acute toxicity, Dermal (Category 5)
Acute toxicity, Oral (Category 5)
Eye irritation (Category 2B)

GHS Label elements, including precautionary statements

Pictogram	none
Signal word	Warning
Hazard statement(s)	
H303 + H313	May be harmful if swallowed or in contact with skin.
H320	Causes eye irritation.
Precautionary statement(s)	
P305 + P351 + P338	IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.

HMIS Classification

Health hazard:	1
Chronic Health Hazard:	*
Flammability:	0
Physical hazards:	0

NFPA Rating

Health hazard:	0
Fire:	0
Reactivity Hazard:	0

Potential Health Effects

Inhalation	May be harmful if inhaled. May cause respiratory tract irritation.
Skin	May be harmful if absorbed through skin. May cause skin irritation.
Eyes	May cause eye irritation.
Ingestion	May be harmful if swallowed.

3. COMPOSITION/INFORMATION ON INGREDIENTS

Formula : BrNa
Molecular Weight : 102.89 g/mol

Component		Concentration
Sodium bromide		
CAS-No.	7647-15-6	-
EC-No.	231-599-9	

4. FIRST AID MEASURES

General advice
Consult a physician. Show this safety data sheet to the doctor in attendance.Move out of dangerous area.

If inhaled
If breathed in, move person into fresh air. If not breathing, give artificial respiration. Consult a physician.

In case of skin contact
Wash off with soap and plenty of water. Consult a physician.

In case of eye contact
Rinse thoroughly with plenty of water for at least 15 minutes and consult a physician.

If swallowed
Never give anything by mouth to an unconscious person. Rinse mouth with water. Consult a physician.

5. FIREFIGHTING MEASURES

Conditions of flammability
Not flammable or combustible.

Suitable extinguishing media
Use water spray, alcohol-resistant foam, dry chemical or carbon dioxide.

Special protective equipment for firefighters
Wear self contained breathing apparatus for fire fighting if necessary.

Hazardous combustion products
Hazardous decomposition products formed under fire conditions. - Hydrogen bromide gas, Sodium oxides

6. ACCIDENTAL RELEASE MEASURES

Personal precautions
Use personal protective equipment. Avoid dust formation. Avoid breathing vapors, mist or gas. Ensure adequate ventilation. Avoid breathing dust.

Environmental precautions
Do not let product enter drains.

Methods and materials for containment and cleaning up
Pick up and arrange disposal without creating dust. Sweep up and shovel. Keep in suitable, closed containers for disposal.

7. HANDLING AND STORAGE

Precautions for safe handling
Avoid contact with skin and eyes. Avoid formation of dust and aerosols.
Provide appropriate exhaust ventilation at places where dust is formed.

Conditions for safe storage
Keep container tightly closed in a dry and well-ventilated place.

Hygroscopic.

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Contains no substances with occupational exposure limit values.

Personal protective equipment

Respiratory protection
For nuisance exposures use type P95 (US) or type P1 (EU EN 143) particle respirator.For higher level protection use type OV/AG/P99 (US) or type ABEK-P2 (EU EN 143) respirator cartridges. Use respirators and components tested and approved under appropriate government standards such as NIOSH (US) or CEN (EU).

Hand protection
Handle with gloves. Gloves must be inspected prior to use. Use proper glove removal technique (without touching glove's outer surface) to avoid skin contact with this product. Dispose of contaminated gloves after use in accordance with applicable laws and good laboratory practices. Wash and dry hands.

Eye protection
Safety glasses with side-shields conforming to EN166 Use equipment for eye protection tested and approved under appropriate government standards such as NIOSH (US) or EN 166(EU).

Skin and body protection
impervious clothing, The type of protective equipment must be selected according to the concentration and amount of the dangerous substance at the specific workplace.

Hygiene measures
Handle in accordance with good industrial hygiene and safety practice. Wash hands before breaks and at the end of workday.

9. PHYSICAL AND CHEMICAL PROPERTIES

Appearance

Form	crystalline
Colour	colourless

Safety data

pH	5.4 at 50 g/l at 20 °C (68 °F)
Melting point/freezing point	Melting point/range: 755 °C (1,391 °F) - lit.
Boiling point	1,393 °C (2,539 °F) at 1,013 hPa (760 mmHg)
Flash point	not applicable
Ignition temperature	no data available
Autoignition temperature	no data available
Lower explosion limit	no data available
Upper explosion limit	no data available
Vapour pressure	1 hPa (1 mmHg) at 806 °C (1,483 °F)
Density	no data available
Water solubility	soluble
Partition coefficient: n-octanol/water	no data available
Relative vapour density	no data available

Odour	odourless
Odour Threshold	no data available
Evaporation rate	no data available

10. STABILITY AND REACTIVITY

Chemical stability
Stable under recommended storage conditions.

Possibility of hazardous reactions
no data available

Conditions to avoid
Avoid moisture. Heat.

Materials to avoid
Strong acids, Strong oxidizing agents, Alkali metals, Halogens

Hazardous decomposition products
Hazardous decomposition products formed under fire conditions. - Hydrogen bromide gas, Sodium oxides
Other decomposition products - no data available

11. TOXICOLOGICAL INFORMATION

Acute toxicity

Oral LD50
LD50 Oral - rat - 3,500 mg/kg

Inhalation LC50
no data available

Dermal LD50
LD50 Dermal - rabbit - > 2,000 mg/kg

Other information on acute toxicity
no data available

Skin corrosion/irritation
Skin - rabbit - No skin irritation

Serious eye damage/eye irritation
Eyes - rabbit - Mild eye irritation

Respiratory or skin sensitization
no data available

Germ cell mutagenicity
no data available

Carcinogenicity

IARC:	No component of this product present at levels greater than or equal to 0.1% is identified as probable, possible or confirmed human carcinogen by IARC.
ACGIH:	No component of this product present at levels greater than or equal to 0.1% is identified as a carcinogen or potential carcinogen by ACGIH.
NTP:	No component of this product present at levels greater than or equal to 0.1% is identified as a known or anticipated carcinogen by NTP.
OSHA:	No component of this product present at levels greater than or equal to 0.1% is identified as a carcinogen or potential carcinogen by OSHA.

Reproductive toxicity
Reproductive toxicity - rat - Oral
Paternal Effects: Testes, epididymis, sperm duct.
Reproductive toxicity - rat - Oral

Effects on Fertility: Mating performance (e.g., # sperm positive females per # females mated; # copulations per # estrus cycles). Effects on Newborn: Viability index (e.g., # alive at day 4 per # born alive). Effects on Newborn: Weaning or lactation index (e.g., # alive at weaning per # alive at day 4).

no data available

Teratogenicity

no data available

Specific target organ toxicity - single exposure (Globally Harmonized System)
no data available

Specific target organ toxicity - repeated exposure (Globally Harmonized System)
no data available

Aspiration hazard
no data available

Potential health effects

Inhalation	May be harmful if inhaled. May cause respiratory tract irritation.
Ingestion	May be harmful if swallowed.
Skin	May be harmful if absorbed through skin. May cause skin irritation.
Eyes	May cause eye irritation.

Signs and Symptoms of Exposure
Effects due to ingestion may include:, sedation

Synergistic effects
no data available

Additional Information
RTECS: VZ3150000

12. ECOLOGICAL INFORMATION

Toxicity

Toxicity to fish	mortality NOEC - Oryzias latipes - 7,800 mg/l - 96 h
	LC50 - Poecilia reticulata (guppy) - 160,000 mg/l - 96 h
Toxicity to daphnia and other aquatic invertebrates	mortality NOEC - Daphnia magna (Water flea) - 7,800 mg/l - 48 h
	EC50 - Daphnia magna (Water flea) - 5,800 mg/l - 48 h

Persistence and degradability
no data available

Bioaccumulative potential
no data available

Mobility in soil
no data available

PBT and vPvB assessment
no data available

Other adverse effects

no data available

13. DISPOSAL CONSIDERATIONS

Product
Offer surplus and non-recyclable solutions to a licensed disposal company.

Contaminated packaging
Dispose of as unused product.

14. TRANSPORT INFORMATION

DOT (US)
Not dangerous goods

IMDG
Not dangerous goods

IATA
Not dangerous goods

15. REGULATORY INFORMATION

OSHA Hazards
Target Organ Effect

SARA 302 Components
SARA 302: No chemicals in this material are subject to the reporting requirements of SARA Title III, Section 302.

SARA 313 Components
SARA 313: This material does not contain any chemical components with known CAS numbers that exceed the threshold (De Minimis) reporting levels established by SARA Title III, Section 313.

SARA 311/312 Hazards
Chronic Health Hazard

Massachusetts Right To Know Components
No components are subject to the Massachusetts Right to Know Act.

Pennsylvania Right To Know Components

	CAS-No.	Revision Date
Sodium bromide	7647-15-6	

New Jersey Right To Know Components

	CAS-No.	Revision Date
Sodium bromide	7647-15-6	

California Prop. 65 Components
This product does not contain any chemicals known to State of California to cause cancer, birth defects, or any other reproductive harm.

16. OTHER INFORMATION

Further information
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The above information is believed to be correct but does not purport to be all inclusive and shall be used only as a guide. The information in this document is based on the present state of our knowledge and is applicable to the product with regard to appropriate safety precautions. It does not represent any guarantee of the properties of the product. Sigma-Aldrich Corporation and its Affiliates shall not be held liable for any damage resulting from handling or from contact with the above product. See www.sigma-aldrich.com and/or the reverse side of invoice or packing slip for additional terms and conditions of sale.

ENCLOSURE 4

Supplemental Information & Publications RE:
sodium naphthalene disulfonate

ENV-DO-15-0216

LA-UR-15-25449

Date: JUL 28 2015

NOI Supplemental Information RE: Sodium 1,5-naphthalene disulfonate

After careful consideration of many factors, LANL has concluded that sodium 1,5-naphthalene disulfonate is the preferred tracer to use in the proposed dilution tracer tests both from a technical standpoint and from an environmental standpoint. Technically, it is the preferred tracer because it was used successfully in 5 dilution tracer tests in Mortandad and Sandia Canyons in 2014 for the LANL Chromium project under the temporary discharge permit that was in place at the time. It is always good scientific practice to use tracers that have previously produced good results and to be consistent in tracer usage when a goal is to compare results from different tracer tests in the same aquifer.

Environmentally, we consider sodium 1,5-naphthalene sulfonate to be among the most benign of tracers that could be used in dilution tracer tests. One of its sister compounds (sodium 2-naphthalene sulfonate) has been documented to have lower toxicity than other potential tracers such as NaBr and Na-Fluorescein. Furthermore, it has a very low detection limit of around 0.1 ppb, which means that much less of it is needed to achieve a successful tracer test than a salt such as NaBr, which has a detection limit of 10 ppb at best. Sodium 1,5-naphthalene sulfonate has the precedent of being used by the USGS in a tracer test involving the injection of 650 kg of this compound into high-quality surface and ground water in Idaho (Nimmo et al., 2002). It has also been used in tracer tests in geothermal systems in Oregon, Nevada and California, as well as in many places around the world. The entire naphthalene sulfonate family of compounds serve as good geothermal tracers because they are accepted as being environmentally benign and they have excellent thermal stability (Rose et al., 2001). Their superior thermal stability compared to other fluorescent dyes such as fluorescein or rhodamine-WT speaks to their tendency to not degrade into products that might be a concern for these other organic compounds that are commonly used as water tracers. Both Nimmo et al. (2002) and Rose et al. (2001) cite Greim et al. (1994) for toxicity information on naphthalene sulfonates.

Cited references are attached.

Kilometer-Scale Rapid Transport of Naphthalene Sulfonate Tracer in the Unsaturated Zone at the Idaho National Engineering and Environmental Laboratory

John R. Nimmo,* Kim S. Perkins, Peter E. Rose, Joseph P. Rousseau, Brennon R. Orr, Brian V. Twining, and Steven R. Anderson

ABSTRACT

To investigate possible long-range flow paths through the interbedded basalts and sediments of a 200-m-thick unsaturated zone, we applied a chemical tracer to seasonally filled infiltration ponds on the Snake River Plain in Idaho. This site is near the Subsurface Disposal Area for radioactive and other hazardous waste at the Idaho National Engineering and Environmental Laboratory. Within 4 mo, we detected tracer in one of 13 sampled aquifer wells, and in eight of 11 sampled perched-water wells as far as 1.3 km away. These detections show that (i) low-permeability layers in the unsaturated zone divert some flow horizontally, but do not prevent rapid transport to the aquifer; (ii) horizontal convective transport rates within the unsaturated zone may exceed 14 m d^{-1}, perhaps through essentially saturated basalt fractures, tension cracks, lava tubes, or rubble zones; and (iii) some perched water beneath the Subsurface Disposal Area derives from episodic surface water more than 1 km away. Such rapid and far-reaching flow may be common throughout the Snake River Plain, and possibly occurs in other locations that have a geologically complex unsaturated zone and comparable sources of infiltrating water.

Large-scale transport in the unsaturated zone is commonly assumed to be slow (a few meters per year or less) and predominantly vertical. Slow transport is likely if the flow proceeds in classic diffuse fashion, limited by low unsaturated hydraulic conductivity. Vertical transport is likely if the main transport mechanisms are dominated by gravity, as opposed to pressure or concentration gradients, and if the subsurface is effectively homogeneous within each horizontal plane.

The slow-flow generalization may not hold for geologically diverse unsaturated zones or for large, nonuniform inputs of water over the land surface. Preferential flow paths can transport water and contaminants horizontally to adjacent regions or vertically to the aquifer far sooner than might be predicted based on bulk medium properties and Richards' equation. Another important effect of preferential flow is that a relatively small fraction of the subsurface medium interacts with the contaminants, which limits adsorption and other attenuating processes.

Fluid transport that is difficult to explain by common unsaturated-flow concepts is suggested in several recent cases of contaminant detections in the unsaturated zone at substantial horizontal distances from the source of contamination. At a location about 100 m away from a waste burial site in the Amargosa Desert of Nevada, tritium has been detected in plants and in boreholes within the 108-m-thick unsaturated zone at much greater than ambient concentrations (Prudic and Striegl, 1995). Horizontal liquid movement along hypothetical preferential flow paths might plausibly cause such transport (Striegl et al., 1996; Prudic et al., 1997). In the Mojave River Basin of California, Izbicki et al. (1998) found evidence of unsaturated-zone horizontal movement of liquid water 45 m from a stream channel, on the basis of the detection of atmospherically derived tritium presumed to have infiltrated through the channel. At a nearby site, Izbicki (personal communication, 2000) noted evidence of gaseous chlorofluorocarbon transport, horizontally within the unsaturated zone to distances of 400 m from a landfill. On the Snake River Plain in southeastern Idaho near the Idaho National Engineering and Environmental Laboratory (INEEL), detection of chlorofluorocarbons, tritium, carbon-14, and chlorine-36 in the unsaturated zone suggests they may be transported vertically to the water table at about 200 m depth and horizontally as much as several kilometers in a few years (E. Busenberg and L.D. Cecil, personal communication, 1998). Contaminants in groundwater and inferred water recharge temperatures at this location suggest that recharge through the unsaturated zone can be rapid (Busenberg et al., 1993). In another INEEL study, a 1994 field experiment known as the Large-Scale Infiltration Test, water that infiltrated from a 200-m-diameter basin was found to move at a rate of 5 m d^{-1} (Burgess, 1995; Wood and Norrell, 1996; Dunnivant et al., 1998).

At waste-disposal or spill sites, tracer studies are commonly based on detection of contaminants that derive from the pollution source. Conclusions from such studies sometimes raise questions about other possible sources of contamination closer to the point of detection, other possible modes of transport (e.g., through the atmosphere or on contaminated waste-conveying vehicles), the uncertainty of timing, and the magnitude of contaminant release. Field experiments with deliberately introduced chemicals as tracers avoid some of these uncertainties and afford fairly precise knowledge of the position and temporal nature of the source.

This paper describes an artificial tracer experiment near the Subsurface Disposal Area of the Radioactive Waste Management Complex at the INEEL (Fig. 1). This facility has a variety of radioactive and hazardous chemical wastes buried at shallow depths on the eastern Snake River Plain. Some contaminants have traveled down to the large and heavily used Snake River Plain aquifer (Laney et al., 1988). At this semiarid location, seasonal streamflow, snowmelt, and local runoff episodically generate large quantities of infiltrating water for

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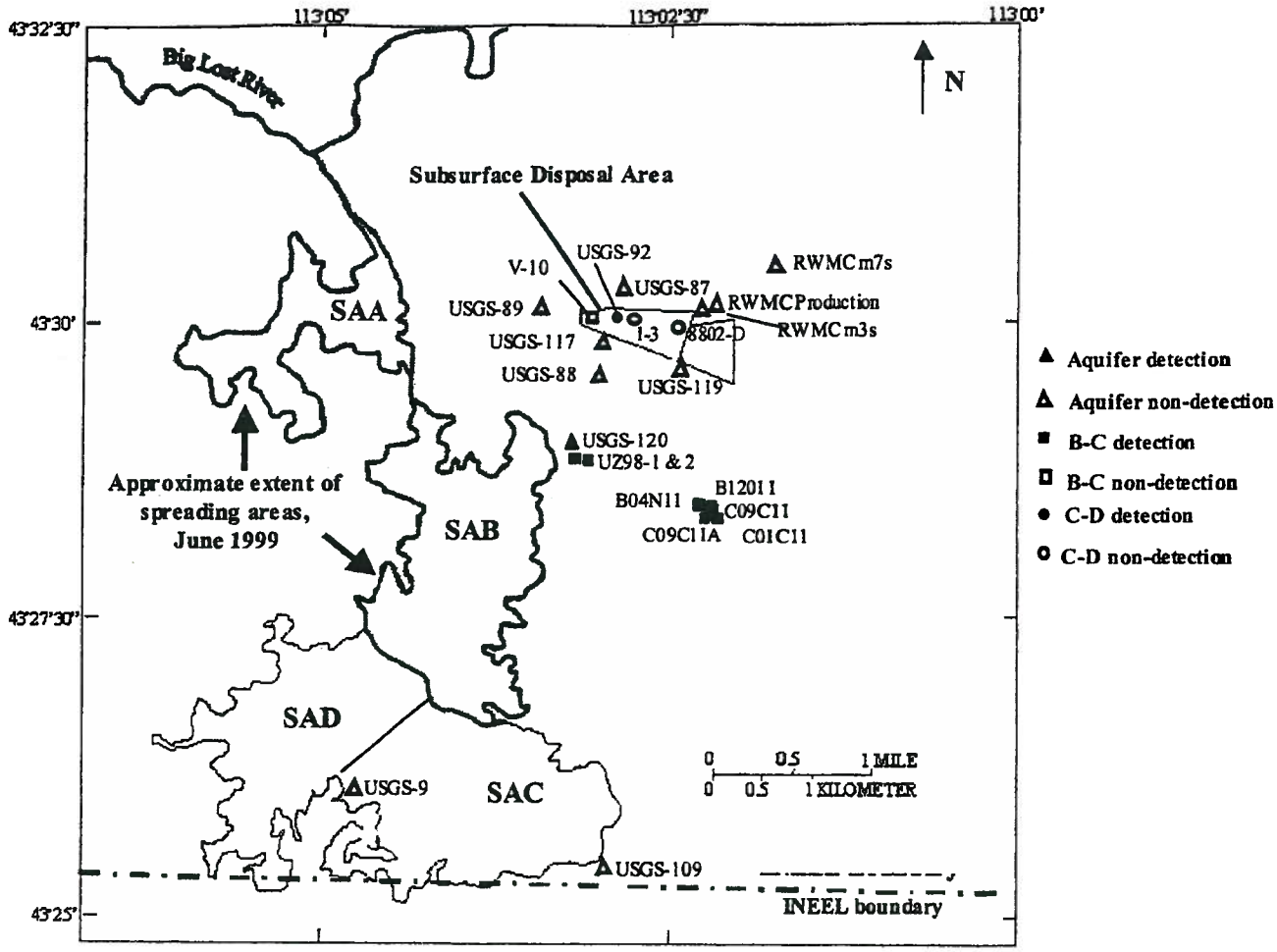


Fig. 1. The Idaho National Engineering and Environmental Laboratory Subsurface Disposal Area and vicinity, including spreading areas SAA, SAB, SAC, and SAD. The prevailing aquifer flow direction is toward the southwest. The predominant dip direction of the BC and CD interbeds is toward the east. Point symbols indicate wells sampled to determine tracer concentrations. Symbol shape indicates the stratigraphic unit associated with that well. Solid symbols represent wells where there was a significant positive detection of tracer during the experiment, and open symbols represent wells where there was no such detection.

periods of days or weeks. Particular concerns arise from seasonal artificial diversions of the Big Lost River to enhanced depressions called spreading areas, which serve as infiltration ponds. Contaminants from the Subsurface Disposal Area are known to have migrated to considerable depths in the unsaturated zone, so this additional water may enhance their further migration toward the aquifer.

Although several investigators (Robertson et al., 1974, p. 26; Hubbell, 1990; Rightmire and Lewis, 1987b) have hypothesized that water from the Big Lost River and spreading areas may affect flow in the unsaturated zone beneath the Subsurface Disposal Area, the distance (more than 1 km) and the generally expected insignificance of horizontal flow in the unsaturated zone has led to an expectation that such influence would be negligible. Some results support this assumption, for example, those of the Large-Scale Infiltration Test described above. Dunnivant et al. (1998) noted that through fractured basalt above the 55-m depth, water appeared to flow downward "within a cylinder defined by the infiltration basin." On the other hand, these investigators reported perched water and some horizontal movement just above the sediments at this level. Busenberg et al. (1993) noted that fast horizontal transport might account for previously observed horizontal spreading of ^{36}Cl and chlorofluorocarbons at the INEEL.

This evidence is inconclusive on the issue of significant horizontal flow, and on the issue of the ability of contrasting layers to inhibit vertical flow to the aquifer. Our investigation tests both of these issues, with emphasis on the hypothesis that short-term, large-volume infiltration may cause rapid, long-range transport through the unsaturated zone near the INEEL Subsurface Disposal Area.

SITE DESCRIPTION

Geology and Stratigraphy

Because the geologic character of the unsaturated zone near the INEEL Subsurface Disposal Area is critical to the transport phenomena explored in this study, we describe its major transport-related features in significant detail.

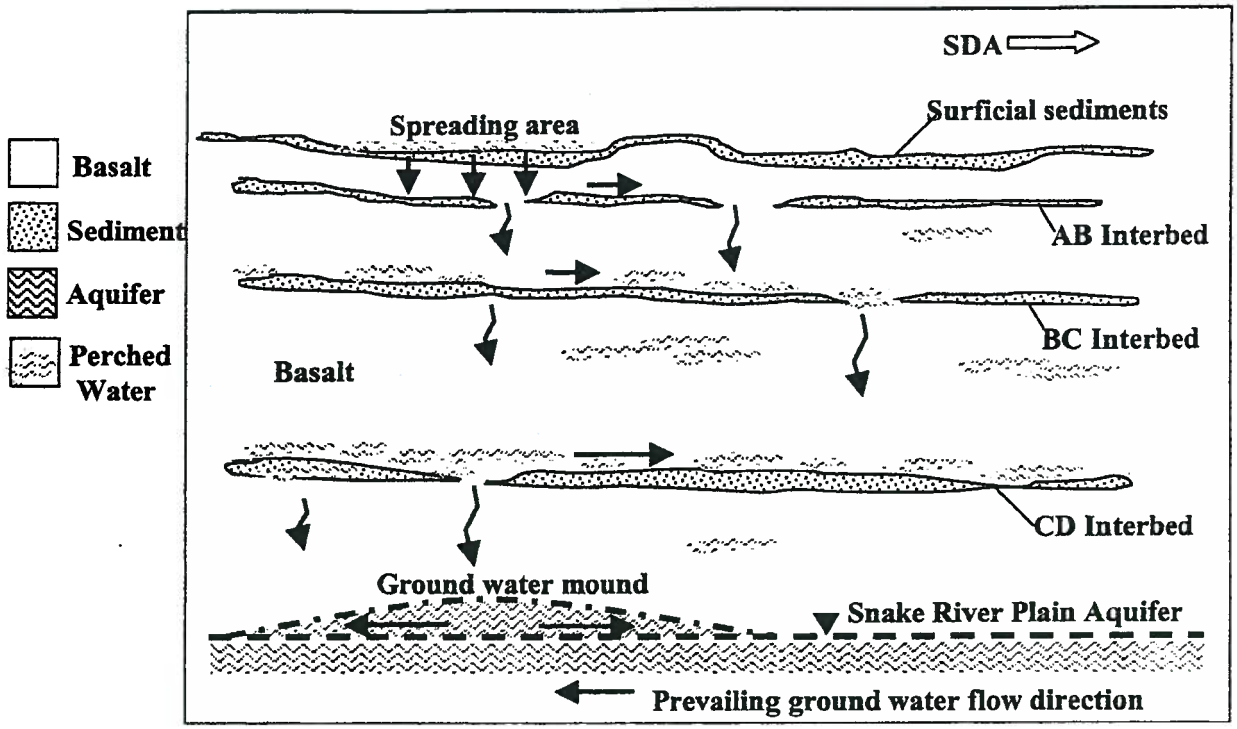


Fig. 2. Diagrammatic cross section illustrating major subsurface features, especially basalt layers, interbeds, and hypothetical perching. Arrows indicate hypothetical flow paths. This figure is not to scale; the actual depth of the BC interbed is about 35 m, of the CD interbed about 70 m, and of the water table about 200 m.

The unsaturated zone near the Subsurface Disposal Area is highly stratified and about 200 m thick, as illustrated in Fig. 2 and 3 (Anderson and Lewis, 1989; Anderson et al., 1996). Additional scale drawings and other stratigraphic information are in the works of Barraclough et al. (1976), Rightmire and Lewis (1987a,b), and Anderson and Liszewski (1997). The unsaturated zone comprises low-permeability layers of fine sediments or dense basalt, and layers of fractured or rubbly basalt that conduct water easily when wet. Depending on the magnitude and prevalence of critical hydraulic processes within these layers, they may accelerate or retard contaminant transport, concentrate or dilute contaminants, and establish the dominant movement as vertical or horizontal.

Individual basalt flows mostly are thin (3–9 m), tube-fed pahoehoe flows similar to those of Hawaii (Anderson et al., 1999). Outcrop exposures indicate that individual basalt flows

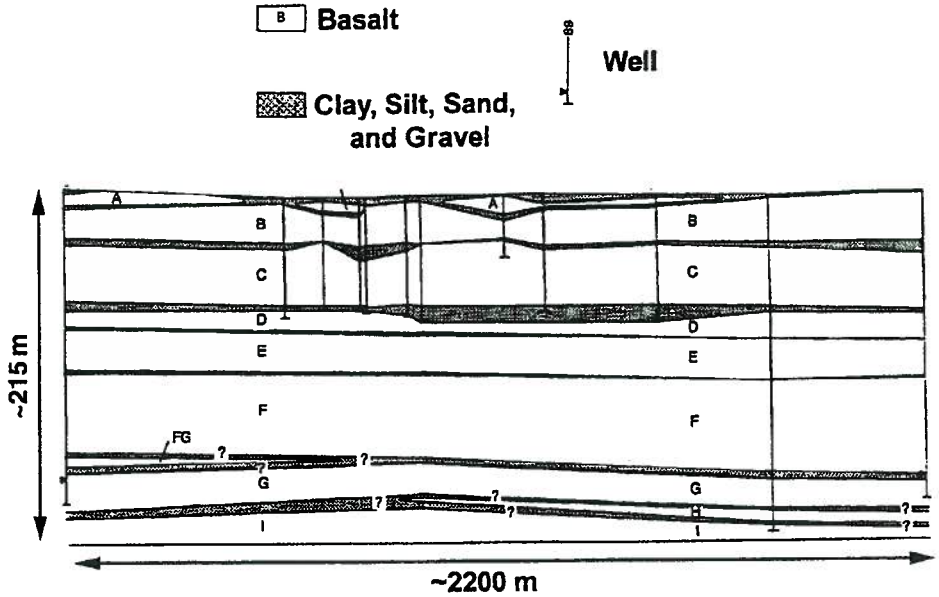


Fig. 3. West to east schematic cross section centered on the Subsurface Disposal Area (modified from Anderson and Lewis, 1989, p. 25). This diagram is based on data from 12 boreholes shown here as vertical lines. The linear interpolations between these indicate less variability in interbed thickness and topography than actually exists.

generally form long, sinuous lobes having median length/width ratios of about 3:1 (Welhan et al., 1997). Some flows are as long as several kilometers (Kuntz et al., 1994). Void spaces in these flows are greatest along their top and bottom surfaces and near volcanic vents. Many of the flows have numerous features such as lava tubes and closely spaced fractures up to a few meters wide and tens of meters long. These may be open or filled with rubble, sediment, or younger lava. In some places, basalt flows are cut by vertical fissures, dikes, and tension cracks associated with northwest-trending volcanic rift zones (Anderson et al., 1999; Hughes et al., 1999). Where they can be observed at the land surface, tension cracks cut vertically through numerous flow groups, are as wide as 2 m, and occur as closely spaced openings along the edges of eruptive fissures over distances of many kilometers.

Basalt flows and other volcanic deposits combine into a basalt flow group, a complex assemblage of overlapping flows and deposits related to a single eruption. Three important basalt flow groups, called A, B, and C, are within about 70 m of the surface at the Subsurface Disposal Area.

Rubble zones are common along the rapidly cooled margins of basalt flows. Basalt rubble and scoria (cinders) have been described in some wells near the Subsurface Disposal Area, but have not been systematically characterized. The potential for scoria is greatest in basalt-flow group C because its vent is thought to be located in this vicinity (Anderson and Liszewski, 1997).

Between some individual basalt flows, and especially between flow groups, sedimentary interbeds consist of well sorted to poorly sorted deposits of clay, silt, sand, and gravel. These interbeds are named after the basalt flow groups they lie between, for example, AB, BC, and CD (Fig. 2). Their depths below land surface vary topographically, but the two most prominent interbeds under the Subsurface Disposal Area, the BC and CD interbeds, are traditionally labeled with depths of 34 and 73 m, respectively. Near the Subsurface Disposal Area, they tend to dip in an easterly direction, the BC interbed about 3.8 m km^{-1} and the CD about 4.7 m km^{-1} on average (Anderson and Lewis, 1989). Their thicknesses vary in accordance with the topography of underlying basalt flows, and in some places they pinch out to zero thickness. Immediately below a particular basalt flow, an interbed is likely to have a baked zone of sedimentary or volcanic material whose properties may have been altered by exposure to the heat of fresh lava.

Barraclough et al. (1976) noted that at the interface between basalt and sedimentary layers, the permeable openings into the basalt are partially filled by sediment, the nature of which has been further investigated by Rightmire (1984). A layer of basalt in which the fractures are filled with fine sediments may be particularly low in effective permeability.

Hydrology

Surface Water

The Big Lost River is the principal stream within the INEEL and a major source of recharge to the Snake River Plain aquifer. To minimize the likelihood of floods at INEEL facilities, a diversion was constructed on the river in 1958 and enlarged in 1984. During high flows, water can be diverted into four spreading areas designated SAA, SAB, SAC, and SAD (Fig. 1). The estimated total capacity is 2.8×10^7 m^3. Barraclough et al. (1967) estimated characteristic ponded infiltration rates of 2.5×10^{-6} m s^{-1} (0.22 m d^{-1}) for SAA and

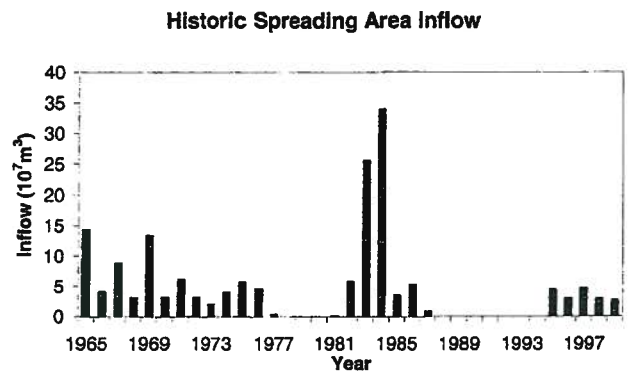


Fig. 4. Total annual inflow to spreading areas, 1965 through 1999. Data are from http://waterdata.usgs.gov/id/nwis, Station 13132513.

9.1×10^{-6} m s^{-1} (0.79 m d^{-1}) for SAB. As Fig. 4 shows, the average annual flow into the spreading areas from 1965 through 1999 was 4.9×10^7 m^3. From 1977 to 1981, the spreading areas received little water, with none at all in 1978 and 1979. There also was no inflow from 1988 to 1994. During the wet years of 1982 through 1985, approximately two-thirds of the Big Lost River flow that entered the INEEL was diverted to the spreading areas (Pittman et al., 1988).

Flow and Perching in the Unsaturated Zone

Water movement in the unsaturated zone at this site may be predominantly vertical, but it is likely to be significantly retarded and diverted by features of the basalts and sediments. Several studies (Barraclough et al., 1976; Rightmire and Lewis, 1987b; Anderson and Lewis, 1989) have shown that water episodically accumulates in perched layers that typically persist for a few months. By analysis of water levels in wells and measured water content profiles, Cecil et al. (1991) showed that perching can take place within both sediments and basalts, and suggested that specific mechanisms for this might include (i) contrasts in vertical hydraulic conductivity between basalt flows and sedimentary interbeds; (ii) reduced hydraulic conductivity in baked zones between basalt flows; (iii) reduced vertical hydraulic conductivity in dense, unfractured basalt; and (iv) reduced vertical hydraulic conductivity from sedimentary and authigenic mineral deposits filling fractures in basalt. Additionally, the interfaces between any adjacent layers, for example sandy and silty layers within interbeds, may retard flow under unsaturated conditions (Miller and Gardner, 1962).

Perched water might enable high-permeability features such as fractures and rubble to divert flow horizontally. Such flow would probably parallel the axis of a basalt flow. Near the Subsurface Disposal Area, this direction would be generally northward because these basalt flows erupted from vents on a volcanic rift zone south of the Subsurface Disposal Area. Lateral flow within or adjacent to sedimentary interbeds is likely to move in the direction of dip of the interbeds. The horizontal continuity and dip of some of the interbeds suggests that perched water derived from the spreading areas could move eastward, toward and beyond the Subsurface Disposal Area.

Beneath the Subsurface Disposal Area, some perched water, possibly nearly all of it, may derive from the spreading areas and the Big Lost River rather than from local precipitation. Rightmire and Lewis (1987b), for example, found relatively light abundances of ^{18}O and ^{2}H in perched water beneath the Subsurface Disposal Area. This suggests a source at higher altitude than the Snake River Plain, consistent with the high-

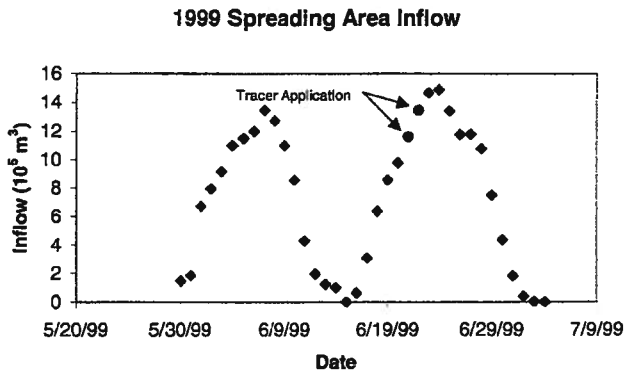


Fig. 5. Inflow to spreading areas, 30 May to 4 July 1999.

altitude streamflow present in the Big Lost River and spreading areas.

Properties and Behavior of the Aquifer

Rubble and fracture zones provide the main conduits for groundwater flow in the saturated zone at the INEEL. Anderson et al. (1999) found the effective hydraulic conductivity to range from about 3×10^{-8} to 8.4×10^{-2} m s^{-1}. They suggested that values less than about 3×10^{-4} m s^{-1} are associated with dikes and thick (>9 m) basalt flows. Greater values are associated with rubble zones and various types of fractures. The prevailing direction of regional flow in the aquifer is toward the southwest.

Fluctuating recharge rates can temporarily alter the flow rate and direction in the aquifer. Barraclough et al. (1976) suggested that periods of high infiltration cause local reversals in water-level gradients near the Subsurface Disposal Area sufficient to move water toward the northeast, against the prevailing direction. They judged infiltration from the spreading areas to be the predominant influence in this process, exceeding the influence of infiltration from local precipitation and the Big Lost River. Rightmire and Lewis (1987a,b) summarized related evidence concerning a fluctuating groundwater mound beneath the spreading areas that alters gradients in the saturated zone. By mapping the rise in water levels that occurred during the unusually wet period between July 1981 and July 1985, Pittman et al. (1988) found further support for this hypothesis.

Expected Behavior of Water from Spreading Areas

Based on available evidence from earlier investigations, and consistent with the understanding of hydrologists knowledgeable about this site, our initial conceptualization of the flow system was as follows (see also Fig. 2). We assumed that when spreading areas become filled, water infiltrates over the course of a few weeks, as long as ponded surface water remains. Initially much of the infiltrating water is taken up by unsaturated-zone pore space, including dead-end fractures. The water percolates downward, continuing for some time after surface water is gone. Vertical flow occurs mainly through highly conductive fractures, taking a few days to reach the water table. Some of the water perches in or on layers of lesser effective vertical conductivity. Most of the water goes down to create a mound, a few meters thick, on top of the aquifer. The mound spreads radially while the spreading areas have standing water, and for a few days or weeks after they empty. The mound dissipates into the aquifer and its water and solutes are carried along with the prevailing Snake River Plain aquifer flow. The perched zones may persist for a few months or longer, until horizontal and vertical flow spreads them enough to leave the porous materials unsaturated.

METHODS

The general plan of the field experiment was to work with expected spring–summer hydrologic behavior in 1999, a year of above-average precipitation. Tracer would be applied to spreading areas while they contained surface water, and samples from perched and aquifer water within several kilometers would be analyzed for tracer. Figure 5 shows the inflow to the spreading areas measured with stream gages during 1999.

Naphthalene Sulfonate Tracers

Naphthalene sulfonate tracers have been successfully tested for tracing in geothermal systems. They are environmentally benign, easily detectable by ultraviolet-fluorescence spectroscopy, and thermally stable. Figure 6 shows various naphthalene sulfonates recently tested in the laboratory and in geothermal fields (Rose et al., 2001). The third column of the figure gives the wavelengths of the peaks of the excitation and emission bands. For this study, we selected 1,5-naphthalene disulfonate as the field tracer.

The adsorption properties of the naphthalene sulfonates in groundwater other than under geothermal conditions have not been reported. Under low-temperature geothermal conditions, however, 1,5-naphthalene disulfonate was shown not to adsorb to negatively charged reservoir rocks or clays (Rose et al., 1999), since the sulfonate groups make these compounds very anionic and soluble in aqueous media. The naphthalene

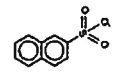
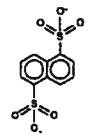
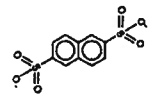
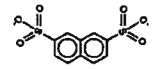
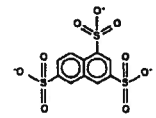
Compound	Structure	Excitation / Emission (nm)
1-naphthalene sulfonate		*217 / 333*
2-naphthalene sulfonate		*220 / 336*
1,5-naphthalene disulfonate		*218 / 334*
2,6-naphthalene disulfonate		*225 / 342*
2,7-naphthalene disulfonate		*226 / 339*
1,3,6-naphthalene trisulfonate		*228 / 342*

Fig. 6. Chemical structures and wavelengths of the excitation–emission spectral peaks of the polyaromatic sulfonates tested in the laboratory and in geothermal reservoirs. The third entry, 1,5-naphthalene disulfonate, was selected for the field experiment presented here.

sulfonates have been shown to be neither mutagenic nor carcinogenic (Greim et al., 1994).

Field Application, Sampling, and Monitoring

The tracer was applied to the spreading areas from a pontoon-type power boat. Fifty-kilogram bags of tracer were partially opened at one end and suspended over the bow of the boat, allowing the material to gradually spill out and the propeller to disperse it as the boat moved forward. The course followed with the boat during this operation was intended to broadly cover the area of ponded water, so that the concentration might be fairly uniform throughout each spreading area. On 21 June 1999, 350 kg of tracer was applied in SAA. The following day, 300 kg was applied in SAB. On 23 June, 83 surface water samples were taken at various locations and depths throughout both spreading areas to assess mixing and approximate concentrations. After the sampling on 23 June, an additional 25 kg of tracer was applied to the northeastern lobe of SAB (Fig. 1), which had filled with water overnight.

A monitoring network of existing wells, both up- and downgradient, was selected to characterize the vertical and horizontal extent of infiltrated spreading-area water. After positive detection of tracer in perched zones, additional wells near the Subsurface Disposal Area were added to the sampling scheme. In December, sampling began at additional Subsurface Disposal Area wells and at monitoring wells (B series and C series wells in Fig. 1) at the location of the Large-Scale Infiltration Test (Wood and Norrell, 1996).

Each well was sampled using a dedicated pump or bailer, or both, following U.S. Geological Survey protocol (Mann, 1996). Extreme precautions were taken in cleaning field equipment to avoid cross-contamination between wells (see Appendix). Samples were collected in clear plastic Nalgene 30-mL bottles, externally rinsed after collection, then labeled and shipped to the analysis lab at the University of Utah. Well conditions were noted in a field logbook.

Initial sampling frequency during June through September 1999 was weekly, biweekly, or monthly, depending on well location, available personnel, and anticipated travel times predicted on the basis of previous studies. After September, sampling was carried out monthly.

RESULTS

Two peaks of inflow to the spreading areas occurred in 1999, on 7 and 24 June (Fig. 5). The total inflow volume for the season was approximately 2.6×10^7 m^3, 40% of which occurred after the introduction of tracer.

Substantial amounts of perched water were found in the unsaturated-zone wells. Those at the Large-Scale Infiltration Test site (south of the Subsurface Disposal Area and east of the spreading areas) were not sampled until 183 d after tracer introduction. Water was encountered in five of the 38 wells that were probed, and water samples were recovered from three of these (C09C11, C09C11A, and B12011). On the following sampling visit, 227 d after tracer introduction, water samples were recovered from all five of the wells with standing water. These five wells were completed in, and above, the base of the BC interbed, which comprises low-permeability silty-clay loam material. Wells that did not yield water were either completed in the basalts above the BC interbed or in the basalts below the BC interbed, so for any water that might cascade in, there was nothing to prevent immediate outflow through basalt fractures. Thus, the presence of standing water in five of the wells is consistent with there being lateral flow in the basalts from the spreading areas.

Measured tracer concentrations in the spreading-area surface-water samples averaged 16.6 μg L^{-1} ($\pm$ 20.6 μg L^{-1} standard deviation, based on 8 samples) in SAA and 180.4 μg L^{-1} ($\pm$ 99.0 μg L^{-1}, based on 18 samples) in SAB. It is likely that concentrations in SAA were lower because of rapid infiltration between the time of application and the surface water sampling, and the fact that the SAA water was sampled 48 rather than 24 h after tracer introduction.

Tracer was detected in nine wells. Figure 7 shows measured concentrations vs. time. In the Snake River Plain aquifer at USGS-120, tracer was detected 9 d after introduction. The preceding sample, taken 6 d after tracer introduction, showed no tracer. The breakthrough curve for USGS-120 has a double peak, as is not uncommon for tracer studies involving preferential flow (e.g., Mohanty et al., 1998). In perched water from basalt immediately above the BC interbed at UZ98-2, tracer was detected 18 d after introduction. It also was detected in perched water from the BC interbed at the nearby well UZ98-1, 65 d after introduction, but in this well the tracer may have been accidentally introduced when the well's casing was temporarily pulled to conduct a cross-hole tomography study, and then reinstalled just before the sample was collected. In the five sampled BC-level wells at the Large-Scale Infiltration Test site, tracer was detected at relatively high concentrations (12–65 μg L^{-1}) in all water samples taken. Limitations of the sampling schedule prevent precise estimates of arrival times at these five wells, but clearly it took less than 183 d to travel this 1.3-km distance.

Directly under the Subsurface Disposal Area in USGS-92, immediately above the CD interbed, tracer was first detected 91 d after introduction. This detection was corroborated by three additional detections on samples taken 122, 147, and 182 d after introduction. Analyses of two archived water samples from this well, from 794 and 83 d before tracer introduction, indicate that 1,5-naphthalene disulfonate was not present in the perched water at this well prior to the start of this test. The pattern of declining concentration in two later detections in USGS-92 (Fig. 7) along with the fact that no samples were taken between the introduction of tracer and the 91-d sampling suggest that tracer may have arrived and peaked at this location in less than 91 d.

Measurements low enough that their difference from zero might not be significant, or where it is not obvious that their measurement uncertainty can be attributed to analytical uncertainty rather than variability in the measured population, may require more formal decision criteria before detections can be confirmed as true positives. Data from USGS-92 and USGS-120 fell into these categories and were evaluated as described in the Appendix.

DISCUSSION

The initial detection of tracer in the aquifer well USGS-120 indicates an average vertical movement of

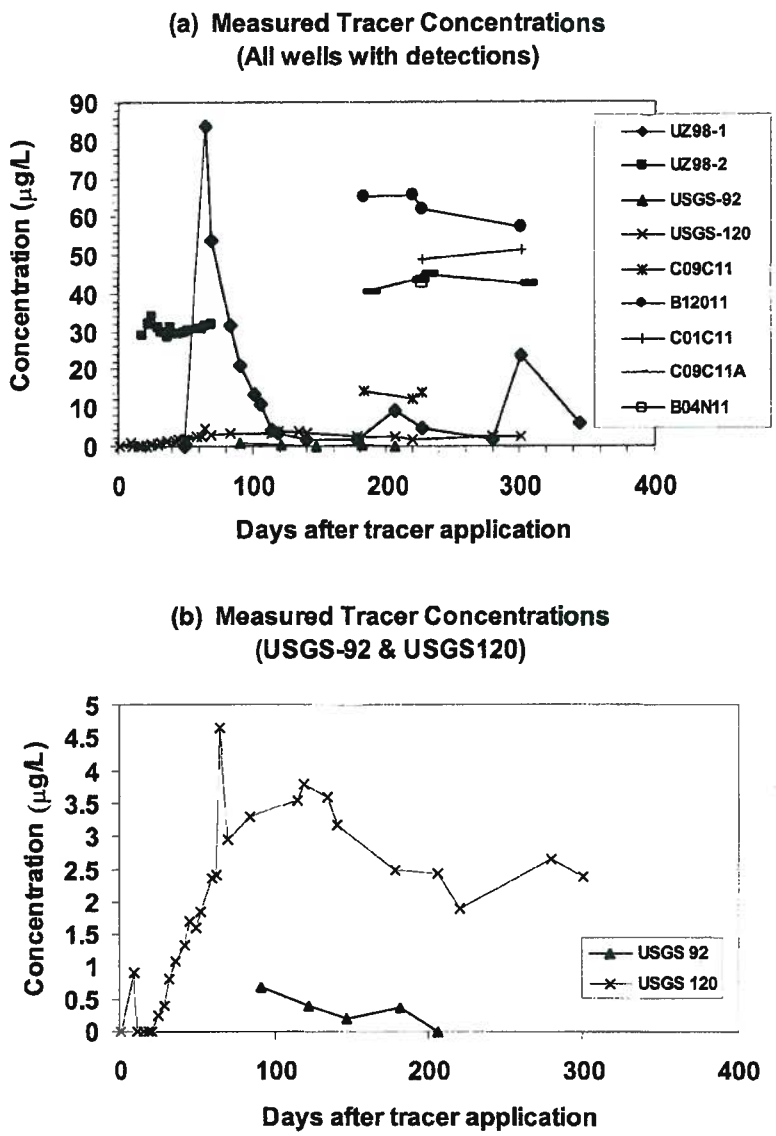


Fig. 7. Measured concentrations in selected wells with positive detections. (a) Concentration vs. time for all nine wells on the same scale. (b) Data for two of the wells on a magnified scale.

at least 22 m d^{-1} at that location. This is about a factor of 4 greater than the average rate through basalt flows A and B in the Large-Scale Infiltration Test (Dunnivant et al., 1998). The measured concentrations as great as 4.7 µg L^{-1} (Fig. 7) suggest that dilution had been modest, consistent with a large amount of tracer-tagged water going all the way through the unsaturated zone and at least 0.2 km horizontally. This indicates that under ponded infiltration, the sedimentary interbeds and any other layers expected to have low hydraulic conductivity are not an effective barrier to vertical flow.

Several hypotheses may account for the tracer's apparent up-gradient (northeastward) movement over the 0.2 km or more to USGS-120 from the spreading areas. First, significant movement of tracer within the unsaturated zone may have provided an up-gradient source to migrate downward and then back down-gradient to the well. Second, highly localized mounding, as previously hypothesized, may have temporarily reversed the prevailing flow at this location. There are not enough nearby aquifer wells to adequately identify small, localized changes in gradient and flow direction.

The lack of positive detections in the other 12 sampled aquifer wells (Table 1) limits the possible generalizations concerning aquifer flow. These 12 points of nondetection are 0.7 to 2.9 km away from the nearest point of tracer introduction. Two of these, USGS-9 and USGS-109, are close to SAC and SAD, which did not contain surface water during the experiment. From SAB, USGS-9 is 1.5 km down-gradient and USGS-109 is 1.8 km across gradient. The other locations of aquifer nondetection are near the Subsurface Disposal Area, and thus are in the direction opposite the prevailing aquifer flow. Therefore, this experiment does not confirm the hypothesized spreading-area-related reversal of groundwater flow (Barraclough et al., 1976) over

Table 1. Basic location and detection information for the 24 wells sampled for measurement of 1,5-naphthalene disulfonate concentration.

Well name	Completion depth (approximate)	Distance to spreading areas (km to nearest point)	Sampling initiated (days after introduction)	Detection
V10	BC	1.3	176	no
B04N11	BC	1.2	227	yes
B12011	BC	1.2	183	yes
C01C11	BC	1.3	227	yes
C09C11	BC	1.3	183	yes
C09C11A	BC	1.3	183	yes
UZ98-1	BC	0.2	2	yes
UZ98-2	BC	0.2	18	yes
USGS-92	CD	1.3	91	yes
8802-D	CD	1.2	176	no
I-3	CD	1.5	176	no
USGS-109	Aquifer	1.8	1	no
USGS-9	Aquifer	1.5	2	no
USGS-86	Aquifer	2.9	16	no
USGS-87	Aquifer	1.7	1	no
USGS-88	Aquifer	0.7	2	no
USGS-89	Aquifer	1.1	1	no
USGS-117	Aquifer	1.1	1	no
USGS-119	Aquifer	1.3	1	no
USGS-120	Aquifer	0.2	2	yes
RWMC prod.	Aquifer	1.7	23	no
RWMC m7s	Aquifer	2.6	21	no
RWMC m1sa	Aquifer	1.0	22	no
RWMC m3s	Aquifer	1.8	22	no

distances >0.2 km. However, the possibility of considerable and rapid dilution of spreading area–derived water within the Snake River Plain aquifer makes for a significant probability that any tracer-tagged water that had traveled 0.7 km or more through the aquifer was diluted to below detection limits. Therefore the observed pattern of aquifer nondetections at horizontal distances >0.2 km does not refute the flow-reversal hypothesis.

At the BC interbed level, positive detections in seven of eight sampled wells confirm that substantial infiltrated spreading-area water is diverted horizontally by this interbed or flow paths within it or above it. Different temporal patterns of tracer concentration between the two nearby BC wells (UZ98-1 and -2, 0.2 km from SAB, Fig. 7) may be influenced in part by the casing replacement in UZ98-1 noted above. Detections in the Large-Scale Infiltration Test wells, 1.3 km east, show that the perched water can move faster than 10 m d^{-1} over considerable distances. There is relatively little dilution here. The rapid lateral flow and minimal dilution suggest a consistently low permeability of the BC interbed, and high permeability of a layer above it, between the spreading areas and the Large-Scale Infiltration Test. The easterly dip of this interbed may also be significant. Of the eight sampled BC-perched wells, the only one that has no detection is V-10. This well may be subject to much different hydrogeologic influences, since it is the only one of these wells that is distant from SAB (1.3 km) in a direction other than east. From SAA, however, its direction is eastward (2.0 km). Plausible reasons for lack of a detection here include (i) an absence of suitable flow paths in this direction, (ii) the dip of the BC interbed not having the required consistency or flow direction, (iii) a discontinuity in the BC interbed that allows perched water to percolate readily into basalt unit C between the spreading areas and the Subsurface Disposal Area, (iv) dilution to below detection limits with perched water from other sources, and (v) travel times shorter or longer than the samplings conducted. The experiment provides no confirmation that BC-perched water travels from spreading areas to the Subsurface Disposal Area. It does demonstrate that at this level in at least one direction, substantial rapid flow occurs to distances of at least 1.3 km.

At the CD interbed level, tracer was detected from one of the three sampled wells, USGS-92, directly under the Subsurface Disposal Area 1.3 km northeast of SAB and 2.2 km east of SAA. The detected concentrations (0.7 $\mu g\ L^{-1}$ and less) are low but significant (see Appendix). Because they declined after the first detection, the concentration may have peaked at this point in <91 d. They suggest an average horizontal flow rate of at least 14 m d^{-1}. This detection may indicate an isolated case of flow through a single channel. The experiment cannot rule out more widespread horizontal spreading at this depth, however, because so few CD wells were available for sampling. The other two CD wells, also under the Subsurface Disposal Area, may also have contained tracer before the sampling of these wells began or at undetectable concentrations. The results from USGS-92 demonstrate that perched water beneath the Subsurface Disposal Area comes in part from subsurface flow of spreading-area water.

Of possible driving forces for flow, if conditions are nearly saturated, gravity would be expected to dominate. Besides the average easterly dip noted above, the pattern of observed unsaturated-zone detections is consistent with the known elevation of interbed contacts at various points (Anderson et al., 1996). The average dip of the interbeds gives a modest driving force, being a component 0.004 times vertical gravity. Thus, if the component of gravity parallel to the interbeds is the chief driving force, the observed long-range horizontal transport suggests an overwhelming effective anisotropy in unsaturated-zone properties.

It is unlikely that horizontal convective transport rates >10 m d^{-1} in the unsaturated zone occurred directly through the fine-textured portions of the interbeds be-

cause of the low saturated hydraulic conductivity of these materials (ranging from 10^{-7} to 10^{-4} cm s^{-1}, Perkins and Nimmo, 2000). It is more likely that the interbeds caused perching that extended upward into some portion of the overlying basalt. Rapid transport may be possible through interconnected rubble zones, tension cracks, or similar features if they are nearly saturated. There must also be substantial impediments to vertical flow, such as interbeds or dense basalt that cause perching that extends upward into the highly conductive layer or flow path. Given the observed lengths of individual basalt flows and volcanic rift zones, such horizontal movement of water over distances of a kilometer or more is plausible.

This evidence as a whole supports several particular hydrologic phenomena.

1. There can be rapid vertical transport under the spreading areas.
2. Substantial perching of water in the unsaturated zone results directly from the percolation of water from the spreading areas.
3. Over distances of a few kilometers and durations of a few months, horizontal transport occurs in perched water in or above both the BC and CD interbeds.
4. The horizontal spreading in perched zones is not uniform with direction.

These hydrologic phenomena suggest certain subsurface features that determine the character of flow. Sedimentary interbeds and impeding features of the basalts are imperfect barriers that permit substantial vertical flow, possibly because of interbed discontinuities and basalt fractures. This is consistent with earlier evidence showing that the interbeds impede vertical flow where they are continuous, for example, the Large-Scale Infiltration Test (Wood and Norrell, 1996c; Dunnivant et al., 1998). In spite of existing vertical fast flow mechanisms, at least some of the flow-impeding features are sufficiently effective and continuous that they divert substantial flow horizontally for considerable distances. Nonuniformities in both basalt and interbed topography are likely causes of the irregular spatial patterns of tracer detection.

The long-range horizontal flow inferred from unsaturated-zone tracer detections requires alteration of previous conceptualizations of subsurface contaminant transport that did not include this sort of flow. Horizontal movement by itself does not necessarily imply a greater likelihood that water-borne contaminants will be transported to the aquifer. However, it does put more water under the Subsurface Disposal Area than would occur without spreading-area input. This water may facilitate contaminant transport to the Snake River Plain aquifer by intercepting water-borne contaminants that would otherwise percolate into and be absorbed by the underlying sedimentary interbeds; it may also transport them downward through preferential flow paths that are active because of the greater amount of water present. The horizontal flow is likely to dilute contaminants and disperse them over wider regions of the unsaturated zone. This could provide greater opportunity for sorption, especially within the sedimentary interbeds, by reducing competition for sorption sites, increasing the availability of sorption sites, and changing solution chemistry to favor sorption. Therefore some effects of the inferred horizontal and nonuniform flow are likely to enhance and others to hinder the transport of contaminants to the aquifer.

Similar behavior concerning fast, long-range flow both horizontally and vertically in the unsaturated zone may occur at other locations with the necessary site characteristics. The INEEL tracer detections were at depths of 30 m and more, suggesting emphasis on arid and semiarid areas where the unsaturated zone is deep. It is important that the unsaturated zone be highly stratified, which is common, but usually not to the obvious extreme of the Snake River Plain. The unsaturated zone must have preferential flow paths such as fractures or coarse granular material, also common at many sites. Long-range horizontal continuity of individual preferential paths and impeding layers has importance that is hard to assess; such continuity could exist at the INEEL, though if essential, the number of such paths must be strikingly large to permit the multiple BC-level tracer detections (Fig. 1). Ponded water is needed to provide a large volume of inflow to the unsaturated zone, and episodic occurrence is important so that conditions are normally unsaturated. Features that might play this role, for example, ephemeral streams and ponds, playas, and artificial recharge ponds, are fairly common on plains and valleys, though less so in mountains.

Where all the relevant features are present in some degree, this sort of rapid, long-range flow might be expected. Alluvial valleys (e.g., Mojave desert, basins of basin and range topography) have many of these characteristics, though commonly with an unsaturated zone that contains only granular material. Horizontal flow is most likely where some of the granular materials are coarse, or underlain by fractured rock. Several sites of major contaminant transport concerns are of interest. At the Hanford Site in Washington, much of the unsaturated zone has depth in the 60- to 90-m range. It has less pronounced layer contrasts than the INEEL site and no significant fractured rock in the unsaturated zone, though there are strong textural contrasts of silt to gravel size, and caliche. These differences may not be very significant for transport rates. The Nevada Test Site has an extremely deep unsaturated zone in many places, and more diversity in layers than the Hanford site. Subsurface behavior there might easily be comparable to that found at INEEL, though ponded water would be more unusual. Yucca Mountain likewise has an extremely deep unsaturated zone and clearly lacks a major source of ponded infiltration. Its stratigraphy is analogous in many ways to the Snake River Plain. For example, the layer referred to as "paintbrush tuff" is less fractured than its surrounding layers and so has been hypothesized to play a role similar to that hypothesized for the INEEL interbeds in interrupting preferential flow and inhibiting downward solute transport. In both cases, these hypotheses may be invalid; evidence for such effects in paintbrush tuff is lacking (Flint et al., 2001), while our study shows that preferential flow can

move downward through or past INEEL interbeds. Our experiment suggests that even if the impeding layer can allow substantial downward movement, it does not prevent long-range horizontal flow.

At smaller scales, similar fast-flow behavior may occur in unsaturated zones a few meters thick, as commonly exist in humid as well as arid climates. Small-scale stratification and preferential paths commonly exist, so it is entirely possible to have analogous phenomena over the shorter distances. Nimmo (2002) found that field data from a wide variety of field sites do show similar behavior and have transport speeds similar to those in this study.

CONCLUSIONS

A naphthalene sulfonate tracer detectable at concentrations down to about 0.2 $\mu g\ L^{-1}$ has proven to be stable and conservative in the subsurface to the degree necessary for large-scale saturated- and unsaturated-zone investigations. With introduction, sampling, and analysis techniques as applied in this study, it can trace water movement over a spatial scale of at least 1.3 km and a time scale of at least 1 yr.

Besides testing the chosen combination of tracer and techniques, this study was to assess long-range subsurface flow paths that might result from episodic ponded infiltration. The geologic nature, hydraulic properties, spatial distribution, source localities, and other characteristics of these flow paths remain of great interest and are poorly known. Results of the present experiment suggest several improvements for field experiments to explore these characteristics and processes further. The observed long distances and high speeds of travel suggest an extensive network of sampling wells, and a schedule that has even the most distant of these sampled early in the experiment. Multiple tracers, for example other naphthalene sulfonates (Fig. 6), are desirable for different portions of the surface water. With three tracers one could distinguish water from individual spreading areas A and B, and the Big Lost River. This would answer questions such as whether tracer in USGS 92 came from spreading area A or B. Repeat sampling of the tracer-containing surface water would give a better estimate of the initial concentration, for evaluation of attenuation and dilution. Besides offering a better understanding of subsurface preferential flow paths and their effect on solute transport, an improved study of this sort would allow the testing of important hypotheses concerning the permeability, continuity, and dip of interbeds, the role of rubble and fractures, and the partitioning of vertical and horizontal flow in the unsaturated zone.

This experiment shows that with a large input of water, the overall structure of the unsaturated zone of the Snake River Plain can generate rapid transport both vertically and horizontally. At least under ponded infiltration, fine-textured interbeds and layers of particularly dense basalt do not prevent the rapid, high-volume, vertical flow that is expected through fractured basalt. Some impediments to vertical flow, however, are effective in causing substantial perching and horizontal diversion. The observed rapid horizontal flow can persist over distances >1 km, entirely within the unsaturated zone, 100 m and more above the aquifer. Possible conduits for this horizontal flow include basalt fractures, tension cracks, lava tubes, or rubble zones positioned above low-permeability layers of basalt or interbeds. These observed behaviors are likely to enhance the vertical and horizontal spreading of contaminants in the subsurface, though by exposing the contaminants to a greater volume of sedimentary materials they may also have effects that tend to reduce aquifer contamination. Because the rapid vertical and horizontal transport in the unsaturated zone seems to be caused by natural features responding to a common sort of ponded infiltration, these results suggest that similar phenomena may occur at a variety of sites.

APPENDIX

Quality Assurance

Samples were collected and analyzed according to the guidelines of the Quality-Assurance Program at the USGS INEEL Project Office, which includes: (i) analytical methods used by the laboratories, (ii) quality-control samples, (iii) review of analytical results, (iv) audits of field performance, (v) corrective actions to resolve problems with field and laboratory methods, and (vi) reporting of data. A chain-of-custody record tracked samples from collection to delivery.

Wells equipped with dedicated submersible pumps require decontamination of detachable sampling equipment. At the wellhead, a stainless-steel discharge pipe is equipped with a sample port and a gate valve to control the flow rate. The sampling equipment, discharge pipe, and fittings were rinsed with deionized water before and after installation at the wellhead. Subsequent flushing with purged water in amounts of about 2 to 30 m^3 further reduced the possibility of cross-contamination with water from previously sampled wells. Additionally, before each sampling, at least three well-bore volumes of water were pumped from the well to remove any stagnant water. This purged water was disposed of to the ground. This is not expected to influence the subsurface movement of tracer because the amount of water was small (on the order of 10^3 m^3) and was distributed over a substantial area of vegetated land under high-evapotranspiration conditions. For wells in which a bailer was used to collect a water sample, careful decontamination procedures were followed to prevent cross-contamination between well bores by rinsing with deionized water and wiping with lab tissues. Bailed samples were poured directly from the bailer into sample bottles after three consecutive rinses of the bailer with sample water. After sampling, the bailer was rinsed thoroughly with several liters of deionized water and placed in a clean plastic bag to prevent possible contamination during transport.

The quality-assurance program includes archival retention of replicate samples for evaluation of erroneous results, occasional submission for analysis of blind replicates (duplicate samples with different sample identification numbers), blank samples (deionized water labeled as a regular sample), equipment blanks (rinsate collected during decontamination procedures), and spiked samples (of known concentration). In general, about 15 to 20% of the samples that were analyzed for tracer concentration were dedicated to quality assurance.

This study included determinations of the analytical preci-

Table 2. Results of analytical precision estimates using high performance liquid chromatography to measure concentrations of 1,5-naphthalene disulfonate. $\bar{x}$ is measured mean concentration, s is standard deviation, $s/\bar{x}$ is relative error expressed as a percentage and n is the number of replicate determinations.

Nominal concentration†	0.1	0.2	0.3	0.4	0.5	1.0	5.0	10.0	50.0	100.0
$\bar{x}$	0.15	0.24	0.35	0.46	0.57	1.20	5.32	10.74	52.45	106.1
s	0.07	0.06	0.08	0.08	0.06	0.14	0.13	0.13	0.45	0.79
$s/\bar{x}$	47	25	23	17	10	12	2.4	1.2	0.8	0.7
n	8	8	8	8	8	8	8	8	8	8

† Concentrations are in micrograms per liter.

sion or uncertainty associated with the measurement of 1,5-naphthalene disulfonate concentrations using the high performance liquid chromatograph with reverse-phase column separation. The column was a reverse phase 50 by 4.6 mm Keystone BetaBasic-18 with 3-μm particle size (Thermo Hypersil-Keystone, Bellefonte, PA).[1] The mobile phase consisted of a solution of 3.17 m*M* Na_2HPO_4, 6.21 m*M* KH_2PO_4, and 5.0 m*M* TBAP in 30:70% methanol/water. Test standards, consisting of nominal solution concentrations ranging from 0.1 to 100.0 μg L^{-1}, were prepared from the industrial grade tracer that was used in the field experiment.

Table 2 and Fig. 8 present the measured results for determination of the analytical precision or uncertainty. The absolute error of a measurement, taken as the standard deviation ($\bar{s}$) of eight replicate measurements of the same laboratory-grade standard, is affected primarily by the gain or sensitivity setting of the instruments. Between 0.1 and 0.5 μg L^{-1} it is essentially constant at about 0.07 μg L^{-1}. Between 1 and 10 μg L^{-1} it also is essentially constant, at about 0.13 μg L^{-1}. At higher ranges, higher gain settings result in higher absolute errors, as shown for nominal tracer concentrations of 50 and 100 μg L^{-1}. To indicate relative error, absolute error estimates are normalized ($\bar{s}/\bar{x}$) with respect to the measured means. Figure 8 shows that in the range of 0.1 to 100 μg L^{-1}, the log of the relative error is nearly linear with respect to the log of measured concentrations, and decreases as the concentration increases. At 0.15 μg L^{-1}, the lowest measured concentration, the relative error is 47% of the measured mean.

USGS-92 had the lowest of all nonzero measured concentrations in the study, and required assessment of whether the measurements were repeatable and not the result of vagaries of analytical uncertainty. Table 3 gives detailed sampling and analysis data for USGS-92, including sample splits and replicates. Five splits of an archived duplicate sample taken 122 d after introduction produced a mean value that was consistent with the value derived from a single measurement of the original sample. The repeatability, expressed as standard deviation, of the five splits (± 0.07 μg L^{-1}) is within the analytical uncertainty for measured mean concentrations near 0.4 μg L^{-1} (± 0.08 μg L^{-1}). Twenty replicate determinations of the originally analyzed sample from 122 d after introduction were run and the results (± 0.05 μg L^{-1}) indicate that the measurement uncertainty can be attributed to analytical error. Similar conclusions can be drawn for multiple independent samples taken on 13 Jan. and 16 Feb. 2000 as shown in Table 3. These results indicate that tracer detections at USGS-92 are repeatable and that most of the uncertainty in the measured concentrations can be attributed to limitations in analytical precision.

For aquifer samples from USGS-120, it needs to be established whether the positive detections are true indications of transport within the aquifer and not the result of unsaturated-zone water moving vertically downward along the annular space between the borehole casing and the surrounding wall-rock. The initial detection of tracer 9 d after introduction was followed by four sampling sessions that showed no evidence of tracer over the period of 11 to 22 d after introduction. Detections in UZ98-2, 20 m from USGS-120 and completed above the BC interbed, show that tracer was present in the unsaturated zone at this location. To test the possibility that tracer may have been carried down the side of the borehole instead of flowing through the aquifer, a 1.3 L s^{-1} pump-discharge test was conducted 84 d after introduction of tracer, with 15 independent samples taken during the 45-min duration of the test. If the tracer is from the aquifer, its concentration should be relatively constant with time, indicative of widespread dispersion before the test. If derived from annular leakage, its concentration should be highly variable, indicative of local dispersion near the borehole. Results of this test (Table 4) showed the variability of the mean (± 0.34 μg L^{-1}) to be greater than twice the analytical uncertainty (± 0.13 μg L^{-1}) for tracer concentrations between 1 and 5 μg L^{-1}. Although the multiple-sample analysis of variability was high, it was not sufficient to establish that annular leakage was occurring. A second test, lasting 24 h, was run starting 141 d after introduction. The pump discharge rate during this test was also 1.3 L s^{-1}. Nineteen independent samples were taken at various times during this test. Results indicate that the measurement uncertainty (± 0.15 μg L^{-1}) was within the analytical uncertainty (± 0.13 μg L^{-1}) for the measured concentration and was consistent with expectations for a homogeneous population. Thus, we conclude that the detection of tracer in the aquifer did not result from the transport of unsaturated-zone water in the annular space around the borehole casing, and therefore indicates a migration of tracer to the aquifer through naturally existing paths.

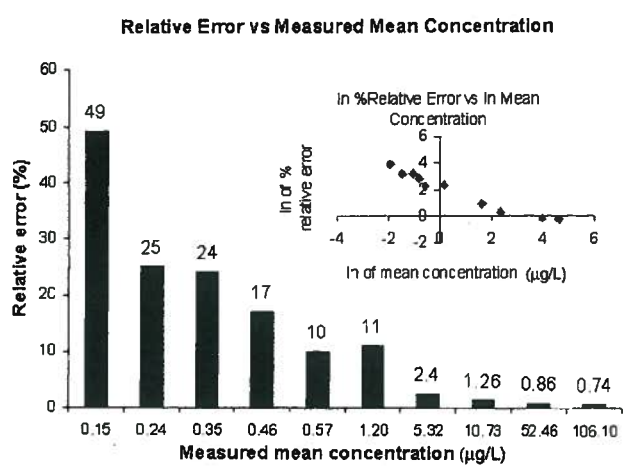


Fig. 8. Relative errors determined in measurements of analytical precision.

[1] Product names are given only to identify the equipment used, and do not imply endorsement by the USGS.

Table 3. Sampling data for USGS-92: concentrations of 1,5-nephthalene disulfonate in micrograms per liter. Day 0 is 21 June 1999, x is concentration from a single measurement; n is the number of independent samples, splits, or replicate determinations; and other symbols are as defined for Table 2.

Date	Day	x	$\bar{x}$	$\bar{s}$	n	$\bar{s}/\bar{x}$	Remarks
18 Apr. 1997	−794	0.0					Pretest archive sample
30 Mar. 1999	−83	0.0					Pretest archive sample
20 Sept. 1999	91	0.69					
21 Oct. 1999	122	0.40	0.39	0.07	5	18	5 splits of archived sample from 21 Oct. 1999
			0.40	0.05	20	12.5	20 replicate determinations of original sample on 21 Oct. 1999
15 Nov. 1999	147	0.21	0.21	0.02	5	9.5	5 replicate determinations
20 Dec. 1999	182	0.37					
13 Jan. 1999	206	0.42					3 independent samples
		0.33					
		0.30					
16 Feb. 2000	240	0.21					2 independent samples
		0.21					
17 Apr. 2000	301	0.0					

Table 4. Selected sampling data for USGS 120. Symbols are as defined for Table 3.

Date	Day	$\bar{x}$	$\bar{s}$	n	$\bar{s}/\bar{x}$	Remarks
13 Sept. 1999	84	3.29	0.34	15	10.3	45-min discharge test. 15 independent samples
		3.26	0.07	20	2.1	20 replicate determinations of Sample 13 from 13 Sept. 1999
9–10 Nov. 1999	141	3.18	0.15	19	4.7	24-h discharge test. 19 independent samples

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The application of the polyaromatic sulfonates as tracers in geothermal reservoirs

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Abstract

Five polyaromatic sulfonate compounds, 1,3,6,8-pyrene tetrasulfonate, 1,5-naphthalene disulfonate, 1,3,6-naphthalene trisulfonate, 2-naphthalene sulfonate, and 2,7-naphthalene disulfonate, were tested for use as geothermal tracers. They were subjected to a simulated hydrothermal environment in batch autoclave reactors in order to determine their thermal decay kinetics. The decay kinetics study indicated that all of the compounds are suitable for use in reservoirs having temperatures up to 310 °C, whereas some are suitable for use in reservoirs as hot as 350 °C. Methods were developed for the chemical analysis of the polyaromatic sulfonates and their detection limits were shown to be approximately 200 parts per trillion by conventional high-performance liquid chromatography. The tracers were successfully tested in a series of field studies at Dixie Valley, Nevada; Steamboat Springs, Nevada; Ohaaki, New Zealand; and Awibengkok, Indonesia. © 2001 CNR. Published by Elsevier Science Ltd. All rights reserved.

Keywords: Tracers; Geothermal reservoirs; Polyaromatic sulfonates; Naphthalene sulfonates; Liquid chromatography; Dixie Valley; Ohaaki; Awibengkok

1. Introduction

Injection of produced fluids is essential to prudent geothermal reservoir-management strategies, both as a means of disposing of an environmental pollutant as well as a method of maintaining reservoir pressures. The location of the injection wells within the three-dimensional network of fractures that forms the reservoir is crucial

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to the successful exploitation of the field. Proper well location leads to increased power production due to enhanced pressures, less reservoir scaling from boiling around the production wells, and reduced thermal breakthrough. Introduction of tracers into the injection-production loops is the fastest and most effective method of obtaining data that reveal the flow patterns of injected fluids.

The xanthene dye fluorescein has been used extensively to trace fluid flow patterns in geothermal reservoirs (Adams et al., 1989; Adams and Davis, 1991; Rose et al., 1995, 1998, 1999). With the exception of rhodamine WT, which has been used only in low-temperature geothermal fields (Gudmundsson et al., 1983; Rose and Adams, 1994), no other visible-fluorescent compounds have been shown to possess sufficient thermal stability to qualify for use as geothermal tracers. Because of the need for simultaneously identifying individual injector/producer flow paths in reservoirs containing multiple injection wells, however, many tracers are needed by the geothermal industry.

The UV-fluorescent polyaromatic sulfonates are excellent candidates for geothermal tracing applications because they are environmentally benign, very detectable by fluorescence spectroscopy, affordable if purchased in bulk quantities, and very thermally stable. In this paper, we report the results of laboratory decay kinetics studies that show that these compounds are suitable for use in reservoirs exceeding 310 °C. We then describe a series of tracer tests wherein the polyaromatic sulfonates were used to determine the injection/production flow patterns in geothermal reservoirs at Steamboat Springs, Nevada; Dixie Valley, Nevada; Ohaaki, New Zealand; and Awibengkok, Indonesia.

2. Concept evolution

Adams et al. (1992) evaluated 39 carboxylic and benzene sulfonic acids for use as hydrothermal tracers. The thermal stability of these compounds was attributed, in part, to their refractory aromatic ring. Since aromatic compounds are strong absorbers of ultraviolet light, they could be readily analyzed by high performance liquid chromatography (HPLC) using uv-absorbance detection. The carboxylic and sulfonic acid groups impart a strong electronegative charge to these compounds, rendering them both water-soluble and resistant to adsorption on negatively charged reservoir rock. Whereas the carboxylic acids possess reasonably good thermal stability (rendering them suitable for use in reservoirs as hot as 275 °C), the benzene sulfonic acids are even more stable. Four aromatic sulfonic acids showed no measurable decay upon exposure to simulated hydrothermal conditions for 2 weeks at 300 °C (Adams et al., 1992).

Smart and Laidlaw (1977) conducted a seminal study of eight fluorescent compounds for application as groundwater tracers. Two of these compounds, amino G and pyranine, were amino- and hydroxyl-substituted polyaromatic sulfonates, respectively, and, due to their structural relationship to benzene sulfonate, were considered to be good candidates for use as geothermal tracers (see Fig. 1). From coal liquefaction and gasification studies, the polyaromatic hydrocarbons (e.g.

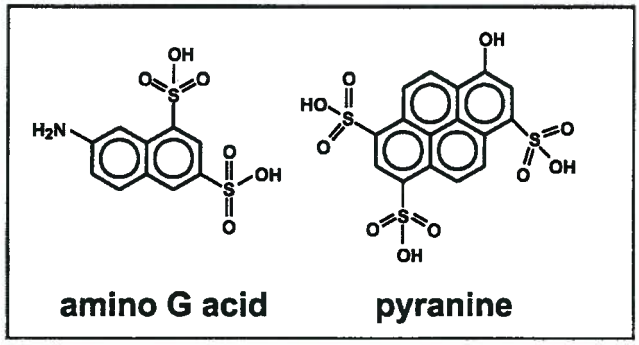


Fig. 1. The chemical structures of two substituted polyaromatic sulfonates, amino G and pyranine.

naphthalene, anthracene, and pyrene) were known to be very thermally stable, due, in large measure, to pi-bonding within the condensed aromatic rings. Given the refractory nature of the polyaromatic hydrocarbon backbone in conjunction with the apparent strength of the aryl-sulfonate bond, the substituted polyaromatic sulfonates were considered to possess sufficient thermal stability for use as geothermal tracers.

In addition to possessing good thermal stability, the substituted polyaromatic sulfonates were known to be detectable at concentrations in the low parts per trillion (ppt) by conventional fluorescence-spectroscopy techniques. Since the detection limit of aromatic acids is in the low parts-per-billion (ppb) range, the substituted polyaromatic sulfonates are more detectable than the aromatic acids by a factor of approximately 1000.

Adams and coworkers studied the thermal stability of amino G (7-amino-1,3-naphthalene disulfonic acid) under simulated geothermal conditions at temperatures of 210 and 230 °C and found this tracer candidate to be moderately stable and suitable for use in geothermal reservoirs as hot as 250 °C (unpublished results). Rose and coworkers further studied amino G acid and an isomer, sulfotobias acid (2-amino-1,5-naphthalene disulfonic acid), under simulated geothermal conditions between 215 and 245 °C (unpublished results). They confirmed the results of Adams and coworkers that showed that amino G acid was moderately thermally stable and that these two amino-substituted naphthalene sulfonates could be used in reservoirs as hot as 250 °C. They also determined that each of these amino-substituted naphthalene sulfonates reacted to form stable, highly fluorescent compounds of indeterminate structure that showed no thermal decay upon exposure to simulated geothermal conditions at 245 °C (unpublished results). It appears that the naphthalene backbone of these molecules is not destroyed under these reaction conditions, since the products remain highly fluorescent. Given the refractory nature of both the condensed aromatic ring structure and the aryl-sulfonate bond, it is suspected that the labile amino group is responsible for the reactivity of amino G and sulfotobias acid.

Rose and coworkers studied the thermal stability of pyranine by exposing it to simulated geothermal conditions at 215 °C for 1 week (unpublished results). They observed that, like amino G, pyranine reacts to form a stable and strongly fluorescent compound of unknown identity. Pyranine has excitation and emission band maxima at 455 and 510 nm, respectively. The thermal degradation product has

excitation and emission band maxima at 416 and 448 nm, respectively, with an extinction coefficient comparable in strength to that of pyranine. As with amino G, it is probable that neither the condensed aromatic ring structure nor the aryl-sulfonate bonds were altered, but that the labile hydroxyl group was involved in pyranine's reactivity. The acidic hydroxyl group also complicates the analysis of pyranine, since pyranine fluorescence is a strong function of pH over the pH range of interest for hydrothermal waters.

The substituted naphthalene sulfonate, amino G, was successfully tested in the Dixie Valley geothermal reservoir (Rose et al., 1998). With a measured detection limit of approximately 200 ppt using HPLC and UV-fluorescence detection (excitation and emission band maxima at 245 and 445 nm, respectively), amino G concentrations were observed to be well above the detection limit after approximately 250 days in a reservoir with fluid temperatures approaching 250 °C.

The amino- and hydroxyl-substituted polyaromatic sulfonates showed good thermal stability and excellent detectability. The limitations of the substituted polyaromatic sulfonates as tracers, however, appeared to be related to the presence of either the hydroxy or amino groups. Therefore, it was expected that the unsubstituted polyaromatic sulfonates would possess the desirable qualities of the substituted polyaromatic sulfonates, without the problems arising from the presence of amino or hydroxy groups.

3. Experimental methods

Five polyaromatic sulfonates, 1,3,6,8-pyrene tetrasulfonate, 1,5-naphthalene disulfonate, 1,3,6-naphthalene trisulfonate, 2-naphthalene sulfonate, and 2,7-naphthalene disulfonate were selected for study based upon commercial availability. The structures of these compounds are shown in Fig. 2. The excitation and emission band maxima for each compound indicate that they all fluoresce in the ultraviolet.

When a compound fluoresces, it absorbs radiant light energy at a given wavelength(s) and re-emits that energy at a (usually) longer wavelength. A fluorescence spectrum (see Fig. 3) for one of the polyaromatic sulfonates, 1,5-naphthalene disulfonate, was measured using a Perkin Elmer LS30 spectrofluorometer. The excitation band has two major peaks with maxima at 218 and 285 nm, respectively, and an emission band with a maximum at 334 nm.

The polyaromatic sulfonates were analyzed using HPLC with fluorescence detection (Waters Corporation, Milford, MA). In order to take advantage of the high-resolution capability of a reverse-phase C-18 column (Keystone BetaBasic-18, 30×4.6 mm, 3-μm particles), paired-ion chromatography (PIC) was employed. The mobile phase consisted of a pH-7.5, phosphate-buffered (3.17 mM $Na_2HPO_4 \cdot 7H_2O$, 6.21 mM anhydrous KH_2PO_4), 5 mM solution of tetrabutyl ammonium phosphate (TBAP) in 25% methanol. The flow rate was 1.5 ml/min, ramping to 2.0 ml/min after 1 min. This HPLC method allowed for the chromatographic separation of analytes both from each other and from reservoir interferences. The detection limit for the polyaromatic sulfonates using this approach was approximately 200 ppt.

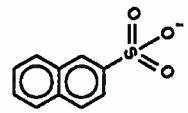
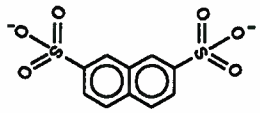
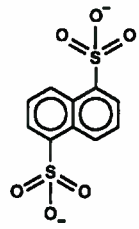
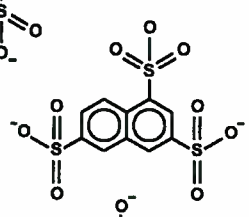
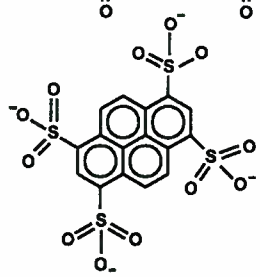
Compound	Structure	Excitation / Emission (nm)
2-naphthalene sulfonate		220 / 336
2,7-naphthalene disulfonate		226 / 339
1,5-naphthalene disulfonate		218 / 334
1,3,6-naphthalene trisulfonate		228 / 342
1,3,6,8-pyrene tetrasulfonate		346 / 386

Fig. 2. Chemical names, structures, and excitation and emission band maxima for the five polyaromatic sulfonates studied in the laboratory and in the field.

The decay kinetics of the five polyaromatic-sulfonate tracer candidates was studied using autoclave batch reactors under controlled conditions designed to simulate a geothermal environment. The compounds were dissolved in buffered aqueous solutions at target concentrations of 25 ppm by weight and adjusted to a room-temperature pH of 6.5. The buffer consisted of 0.747 g/l of KH_2PO_4 and 0.403 g/l of Na_2HPO_4.

Eighteen-milliliter aliquots of the buffered tracer solution were transferred to 30 ml quartz ampules and purged with argon to remove air. The ampules were carefully sealed using an oxymethane flame, while being purged with argon. For each experiment, four ampule-solutions were prepared: three samples and one control.

The sealed vials were transferred to a water-filled, one-liter autoclave (Autoclave Engineers, Philadelphia, PA), which was heated to the target temperature. The time required for the autoclave to attain operational temperature was between 1.5 and 2

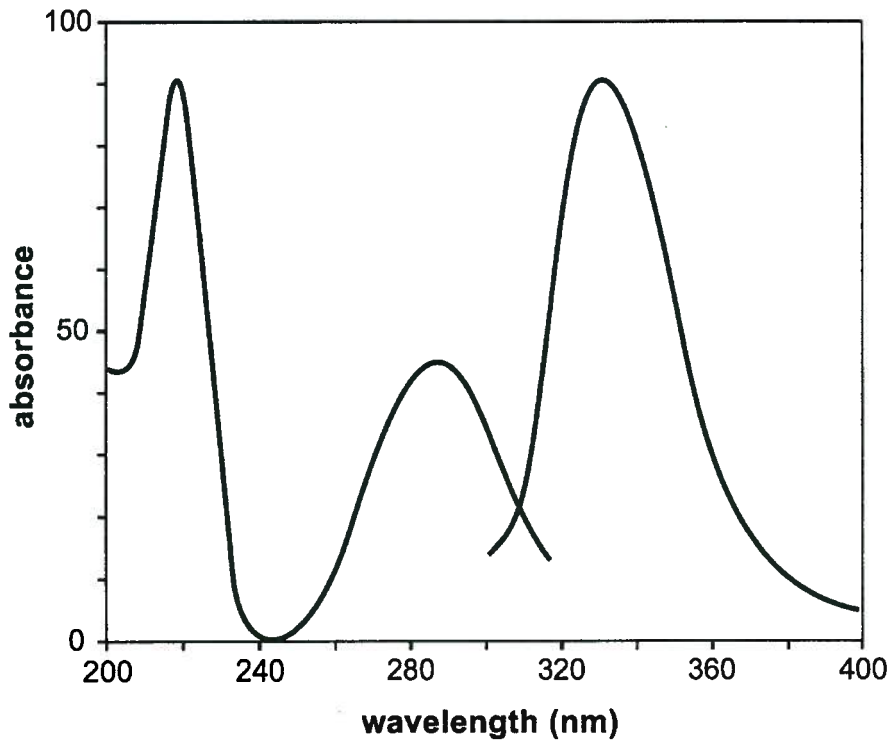


Fig. 3. A fluorescence spectrum for the candidate tracer 1,5-naphthalene disulfonate, consisting of two excitation peaks and one emission peak.

h, whereas the cool-down time was about 4 h. In all cases, the interior of the reactor was maintained within 1 °C of the target temperature for one week. The pressure inside the autoclave was the pressure of steam under saturated conditions at the target temperature. The control ampules were stored at 2 °C for the duration of the autoclave experiments.

The thermal decay data for 1,5-naphthalene disulfonate, 1,3,6-naphthalene trisulfonate and 1,3,6,8-pyrene tetrasulfonate are summarized in Table 1. 1,5-naphthalene disulfonate and 1,3,6-naphthalene trisulfonate showed modest decay (~20%) upon exposure to simulated geothermal conditions for one week at 330 °C, whereas 1,3,6,8-pyrene tetrasulfonate was almost thoroughly decomposed under similar conditions. No decay was observed for either 2-naphthalene sulfonate or 2,7-naphthalene disulfonate at 330 °C, indicating that these two compounds are the most thermally stable of the five tested.

4. Decay kinetics of the polyaromatic sulfonates

The thermal decay kinetics of the polyaromatic sulfonates was modeled by the first-order differential equation:

$$-\mathrm{d}C_n/\mathrm{d}t = k_n \cdot C_n \quad (1)$$

Table 1
Thermal decay data for three of the polyaromatic sulfonates studied[a]

Reactant	Reaction temp. (°C)	Initial conc. (mg/l)	Average final conc. (mg/l)	Standard deviation (mg/l)
1,5-Naphthalene disulfonate	310	25.00	24.05	0.24
	320	25.00	21.62	0.40
	330	25.00	19.80	–
1,3,6-Naphthalene trisulfonate	310	25.00	23.62	–
	320	25.00	21.81	0.20
	330	25.00	19.56	0.89
1,3,6,8-Pyrene tetrasulfonate	300	24.56	18.675	–
	325	25.00	4.363	0.14
	330	25.00	2.668	0.21

[a] No data are shown for either 2-naphthalene sulfonate or 2,7-naphthalene disulfonate, since no decay was measured for either compound upon exposure to simulated geothermal conditions for 1 week at 330 °C.

where C_n is the concentration of the polyaromatic sulfonate and k_n is the first-order decay rate constant. Solution of this equation results in the following relationship between C_n and t:

$$\ln\left(\frac{C_n}{C_n^0}\right) = -k_n \cdot t \tag{2}$$

where C_n^0 is the initial concentration of polyaromatic sulfonate. The temperature dependence of k_n can be described by the Arrhenius relationship:

$$k_n = Ae^{(-E_a/RT)} \tag{3}$$

where A is the pre-exponential factor, E_a is the energy of activation, R is the gas constant and T is absolute temperature. A linearization of the Arrhenius expression results in the following:

$$\ln k_n = \ln A - \frac{E_a}{RT} \tag{4}$$

Fig. 4(a) shows Arrhenius plots of ln k_n vs. inverse temperature between 300 and 330 °C for the three compounds 1,5-naphthalene disulfonate, 1,3,6-naphthalene trisulfonate, and 1,3,6,8-pyrene tetrasulfonate. The linear relationship between ln k_n and inverse temperature indicates that the Arrhenius equation provides a good means of expressing the temperature dependence of the decay rate constant.

The straight lines in Fig. 4(a) were determined by linear least-squares fits to the data. The values for the pre-exponential factor, A, and the energy of activation, E_a, obtained from a regressional analysis of each of the three compounds, are listed in Table 2. From these data, the rate constant for the thermal decay of each compound

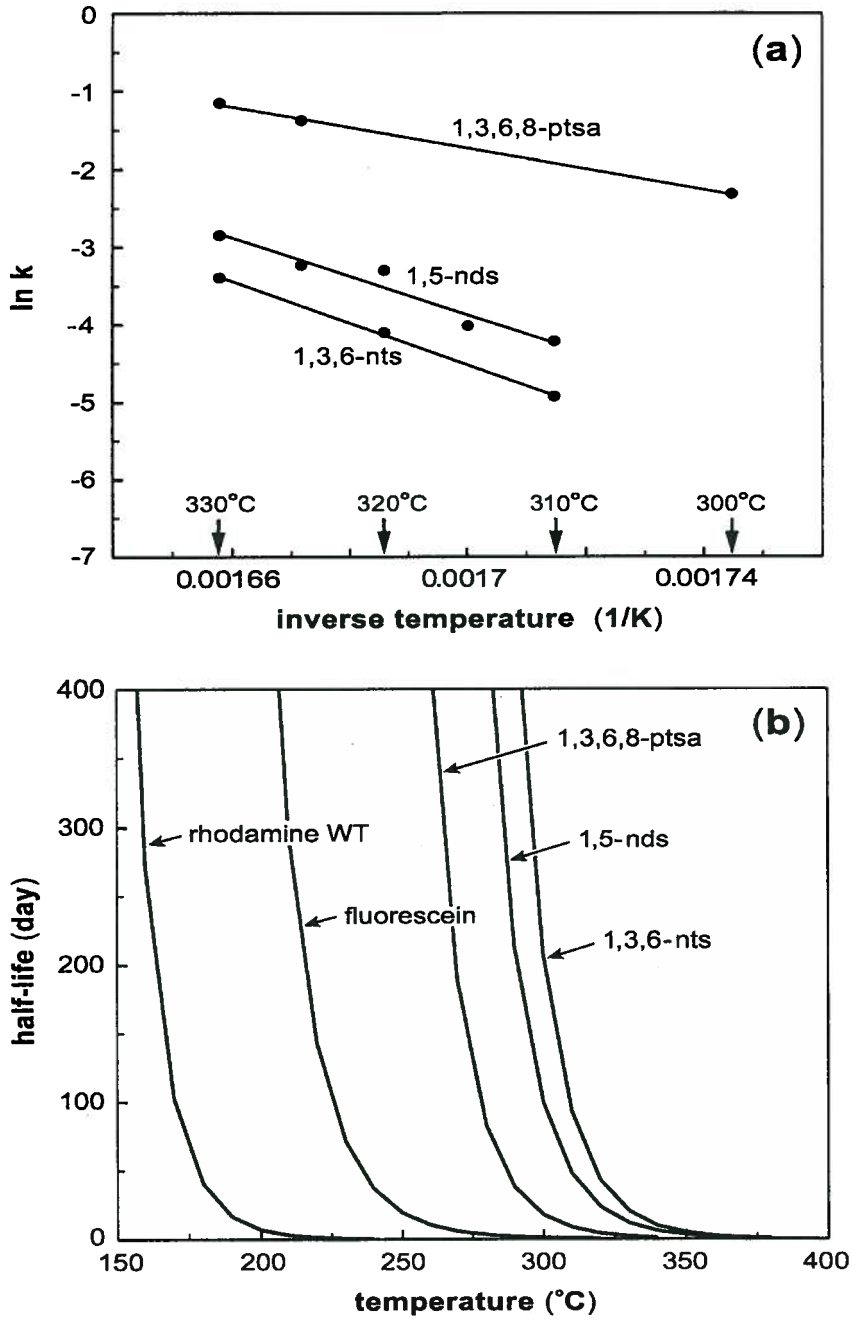


Fig. 4. (a) Arrhenius plots of ln k_n vs. inverse temperature between 300 and 330 °C for the three compounds 1,5-naphthalene disulfonate, 1,3,6-naphthalene trisulfonate, and 1,3,6,8-pyrene tetrasulfonate. (b) Plots of half-life vs. temperature based upon the Arrhenius decay data shown in (a). Also included is a speculative plot of half-life vs. temperature representing the compounds 2,7-naphthalene disulfonate and 2-naphthalene sulfonate. These latter two compounds were so thermally stable that no decay was measured upon exposure to geothermal conditions for 1 week at 330 °C. Also shown are plots for the lower-temperature geothermal tracers fluorescein and rhodamine WT.

Table 2
Arrhenius constants for three of the polyaromatic sulfonates studied in the laboratory under conditions that simulate a geothermal environment

Compound	Pre-exponential factor, A (day^{-1})	Energy of activation, E_a (J/mol)	Temperature range (°C)	R^2
1,5-Naphthalene disulfonate	3.49E16	205,000	310–330	0.944
1,3,6-Naphthalene trisulfonate	7.12E17	223,000	310–330	0.998
1,3,6,8-Pyrene tetrasulfonate	1.73E17	205,000	300–330	0.998

can be determined at any temperature within the indicated range. Using these data, the half-lives of these three polyaromatic sulfonates are plotted as functions of temperature in Fig. 4b. For comparison, the half-lives of two xanthene dyes that have been used as geothermal tracers, fluorescein and rhodamine WT, are also plotted. No plots are shown for the two compounds 2-naphthalene sulfonate and 2,7-naphthalene disulfonate, since no decay was observed for either compound after exposure to geothermal conditions for 1 week at 330 °C.

5. Tracer testing at Dixie Valley using the polyaromatic sulfonates

The polyaromatic sulfonate candidate tracers were extensively tested in a series of field studies between 1997 and 2000 at the Dixie Valley geothermal field (Rose et al., 1998, 2000, 2001) located in west-central Nevada (Fig. 5). This reservoir is a classical example of a hydrothermal system located along a narrow fault zone. Dixie Valley is an asymmetric basin and range graben that is bounded on the west by the Stillwater range and on the east by the Clan Alpine mountains. The geothermal field is located on the west side of the valley. Benoit (1999) has reviewed the conceptual, structural and numerical models of the Dixie Valley hydrothermal system.

Since the early 1980s, the prevailing structural model for interpreting flow patterns within the Dixie Valley geothermal field was based upon a single range-front fault dipping 52–54° to the SE with a roughly planar geometry to depths of at least 3 km (Benoit, 1995). It assumed that production was controlled primarily by fracture permeability associated with this range-front fault and its related secondary fractures.

A recent reinterpretation based primarily upon Bouguer gravity data and reflection seismic profiles suggests a more complex geometry with a steeper-dipping range front fault that accommodates most of the topographic displacement and a series of steep-dipping piedmont faults that splay off the range front fault and account for most of the displacement at depth (Blackwell et al., 1999). According to this model, the known reservoir is primarily associated with the piedmont faults.

The production wells produce up to 125 kg/s mostly from three to six individual fractures located between depths of 2500 and 3100 m (Barton et al., 1998). Until recently, injection was into three different geologic environments: an areally restricted Miocene basalt aquifer at a depth of approximately 2225 m, a fault zone at a depth of about 1860 m, and the main fault zone between depths of 2700 and 2950 m (Benoit, 1992). In 1999, injection was initiated into well 27-32, which penetrated a

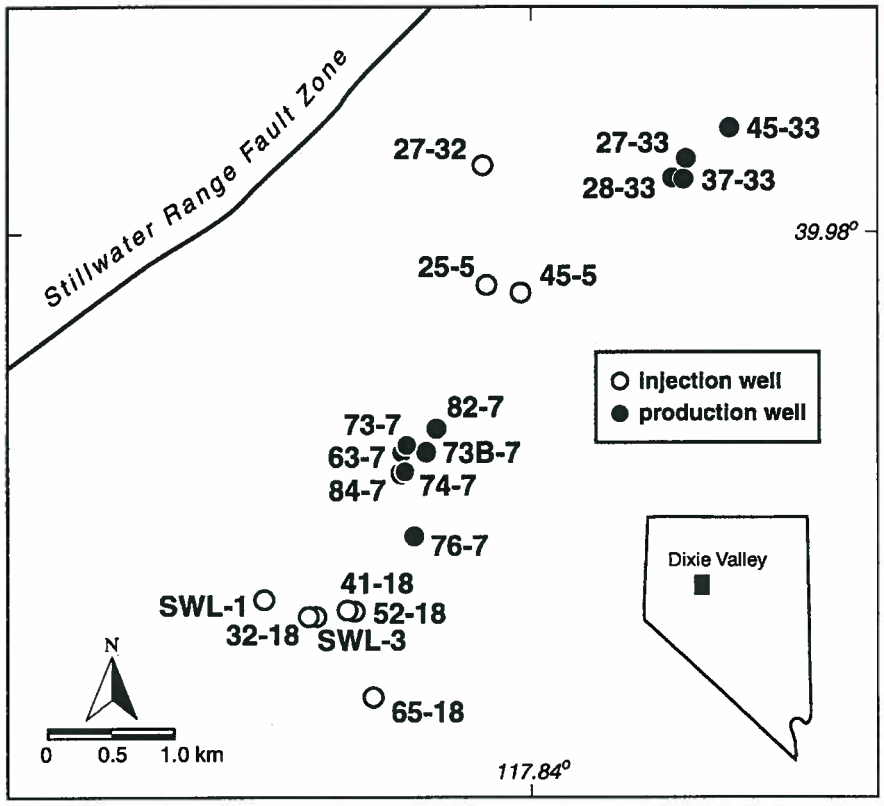


Fig. 5. Map of the Dixie Valley geothermal reservoir, showing the injection and production wellhead locations.

shallow fault zone at approximately 180 m. The reservoir is hosted primarily by metamorphosed Mesozoic sedimentary and mafic igneous rocks (Waibel, 1987).

5.1. 1,3,6,8-Pyrene tetrasulfonate

On 3 September 1997, 1818 kg of a 10 wt.% aqueous solution of 1,3,6,8-pyrene tetrasulfonate (Hilton Davis, Cincinnati) was injected into well 45-5 over a period of about 20 min. The injectate flow rate was approximately 300 kg/s. Nine production wells were sampled twice weekly throughout the subsequent year.

Shown in Fig. 6 are plots of the return curves of 1,3,6,8-pyrene tetrasulfonate that was injected into well 45-5. The tracer first arrived in about 90 days, with the strongest return to well 73-7. The next strongest returns were to wells 73B-7 and 63-7, followed by 82A-7. No 1,3,6,8-pyrene tetrasulfonate was observed in any of the section-33 wells.

5.2. 1,5-Naphthalene disulfonate and 1,3,6-naphthalene trisulfonate

On 14 July 1998, 100 kg of 1,5-naphthalene disulfonate (Konishi Chemical, Japan) was dissolved in approximately 400 l of flashed reservoir water and injected over a

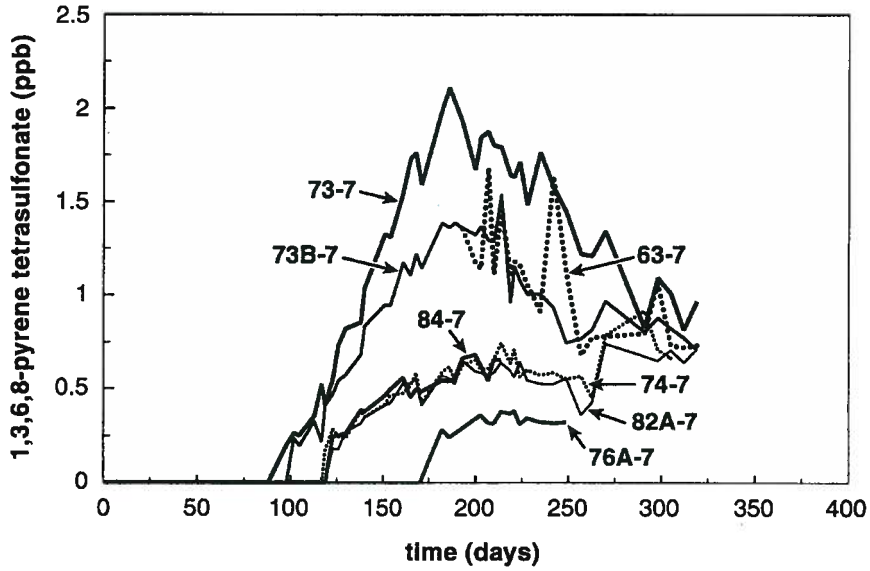


Fig. 6. 1,3,6,8-Pyrene tetrasulfonate returns observed from the testing of injector 45-5 at Dixie Valley.

period of about 15 min into well 41-18 (see Fig. 5). This injector accepts fluids at a rate of approximately 40 kg/s. Similarly, 100 kg of 1,3,6-naphthalene trisulfonate (Konishi Chemical, Japan) was mixed with approximately 300 l of flashed reservoir water and injected over a period of 20 min into injector 65–18 (see Fig. 5), which accepts fluids at a rate of approximately 65 kg/s. All of the producing wells in the field were subsequently monitored for the two tracers over the subsequent 2.5 years.

The return curves for 1,5-naphthalene disulfonate are plotted in Fig. 7. These return curves reflect tracer production in the six wells in Section 7 (see Fig. 5) only, as no tracer was observed in any of the production wells monitored further to the northeast in Section 33. The first arrivals of tracer were between 40 and 54 days for all of the wells except 82A-7, which did not produce tracer until 79 days after injection.

The return curves from the tagging of injector 65-18 with 1,3,6-naphthalene trisulfonate are shown in Fig. 8. Like the test that was associated with injector 41-18, tracer was produced in Section 7 only. First arrivals for three of the wells were between 75 and 79 days, although a long sampling hiatus between days 79 and 97 may have obscured the first arrival of tracer to 74-7. Tracer did not arrive in well 73B-7 until day 103, but the slowest arrival of tracer, again, was to 82A-7, which did not show return until 145 days into the test.

There are striking similarities between the return-curve plots for the two injectors tagged with 1,5-naphthalene disulfonate and 1,3,6-naphthalene trisulfonate. In both tests, the strongest returns were to producers 63-7, 74-7 and 76A-7. Also, in each test, tracer was measured in well 82A-7 much later than it was measured in any of the other section 7 wells. These similarities suggest a similar path for injectate flowing between the two tagged injectors (41-18 and 65-18) and the Section-7 producers.

In spite of these similarities, a significant difference exists between the return curves for the two tests. The peak concentrations of 1,5-naphthalene disulfonate tracer injected in well 41-18 are approximately 11 ppb, whereas the peak con-

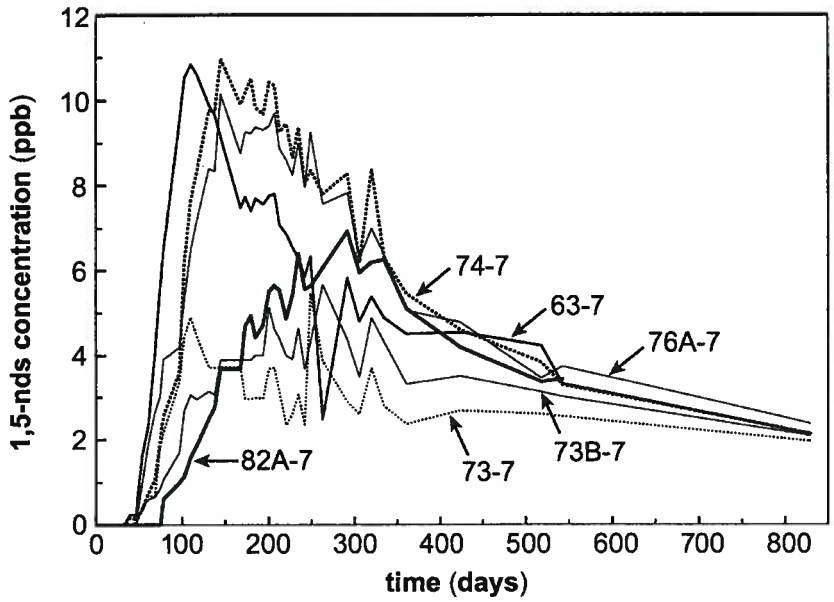


Fig. 7. 1,5-Naphthalene disulfonate returns observed from the testing of injector 41-18 at Dixie Valley.

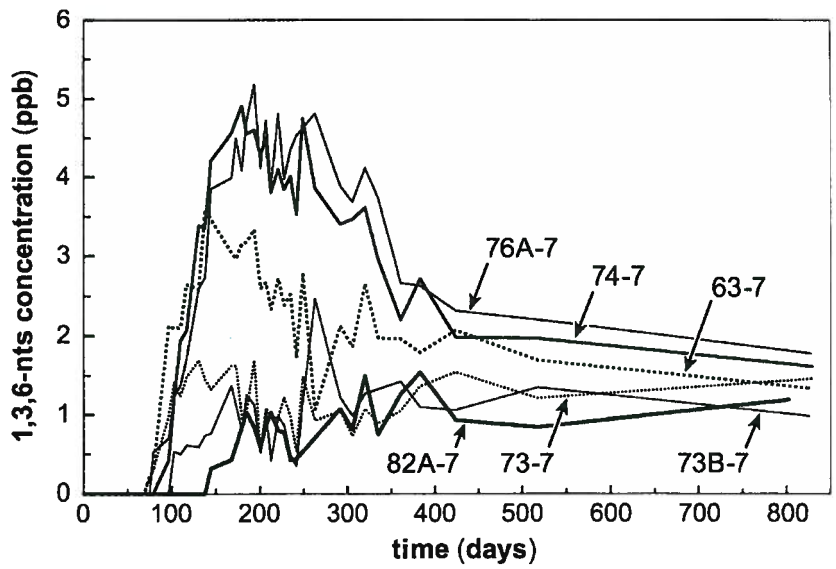


Fig. 8. 1,3,6-Naphthalene trisulfonate returns observed from the testing of injector 65-18 at Dixie Valley.

centrations of 1,3,6-naphthalene trisulfonate are approximately 5 ppb. Since equal quantities of tracer were injected in each injection well and since 65-18 is further away from the Section 7 producers than is 41-18, it is reasonable to assume that the tracer injected in 65-18 was diluted with a greater volume of reservoir water before being produced. The differences in concentration cannot be explained by thermal degradation of tracer, since the reservoirs fluids, whose temperatures measure less than 250 °C, are too cool to cause any measurable decay of 1,3,6-naphthalene trisulfonate over such a short duration.

5.3. 2-Naphthalene sulfonate and 2,7-naphthalene disulfonate

On 17 November 1999, 198 kg of 2,7-naphthalene disulfonate (Yick-Vic Chemicals, Hong Kong) was slurried with approximately 400 l of flashed reservoir water and injected over a period of about 4 min into well 27-32 (Fig. 5). Water was continuously injected into the well at a rate of approximately 73 kg/s. Similarly, on 18 November 1999, 199 kg of 2-naphthalene sulfonate (Yick-Vic Chemicals, Hong Kong) was dissolved into approximately 400 l of flashed reservoir water and injected over a period of 2 min into injector 25-5 (Fig. 5), which was flowing at a rate of approximately 310 kg/s. All of the producing wells in the field were subsequently monitored for the two naphthalene sulfonates over the subsequent year.

The return curves for the 2,7-naphthalene disulfonate that was injected into well 27-32 are plotted in Fig. 9. These return curves show tracer production in three producers in Section 33 only (Fig. 5), as no tracer was observed in any of the production wells monitored further to the southeast in Section 7. This represents the first observation of tracer production ever to Section 33. The tracer first arrived at two producers (28-33 and 37-33) approximately 135 days after tracer injection. This is the longest measured duration before first arrival of tracer in any tracer tests conducted at Dixie Valley.

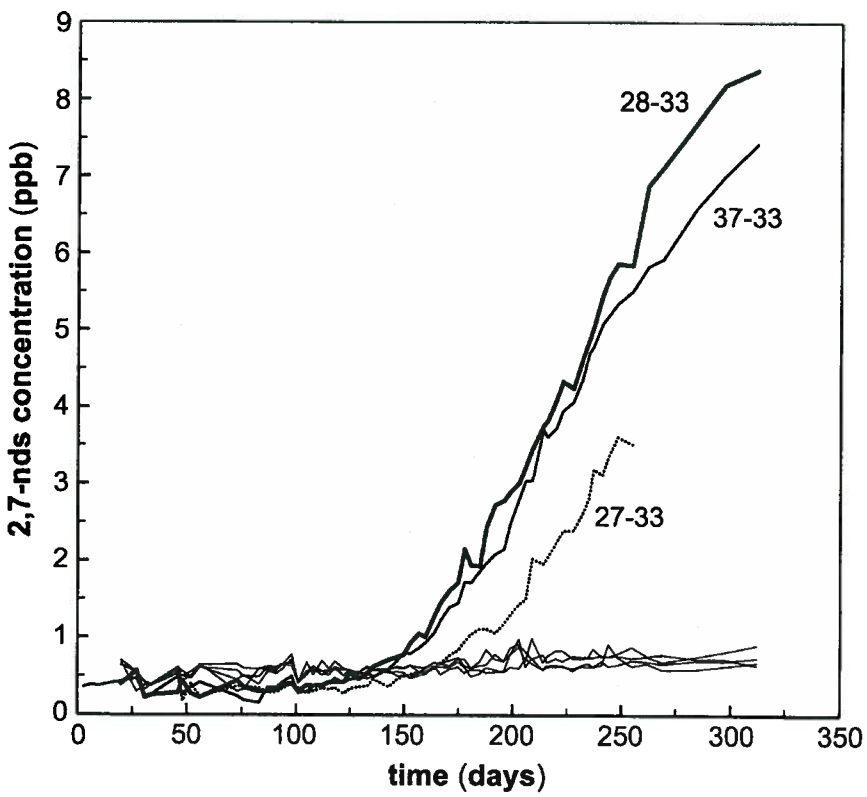


Fig. 9. 2,7-Naphthalene disulfonate returns observed from the testing of injector 27-32 at Dixie Valley.

The return curves for the 2-naphthalene sulfonate that was injected into well 25-5 are plotted in Fig. 10. These return curves show tracer production in all of the operating producers in Section 7 except well 76A-7 (Fig. 5). No tracer was observed in any of the production wells monitored further to the northeast in Section 33. The tracer first arrived to two producers, 63-7 and 73B-7, approximately 100 days after tracer injection.

A plot of the return curves of 2,7-naphthalene disulfonate show a significant background concentration of approximately 0.5 ppb in all of the wells monitored during the test (Fig. 9). The identity of this background contaminant is not known, although it is possible that it is 2,7-naphthalene disulfonate, which was created as either an isomerization product or partial decomposition product of other naphthalene sulfonates injected in previous tracer tests. There is also a significant background concentration between approximately 2 ppb and 3.8 ppb of an apparent contaminant that is chromatographically indistinguishable from 2-naphthalene sulfonate (Fig. 10). Again, the identity of this compound is not known. And, again, it is possible that it is either 2-naphthalene sulfonate or a similar compound that co-elutes with 2-naphthalene sulfonate.

Neither 2,7-naphthalene disulfonate nor 2-naphthalene sulfonate had ever been used as tracers at Dixie Valley prior to the two tests described here. The existence of strong background contaminant concentrations that are chromatographically indistinguishable from these two compounds is therefore somewhat troubling. Since nearly all of the water produced at the Dixie Valley reservoir is reinjected and since

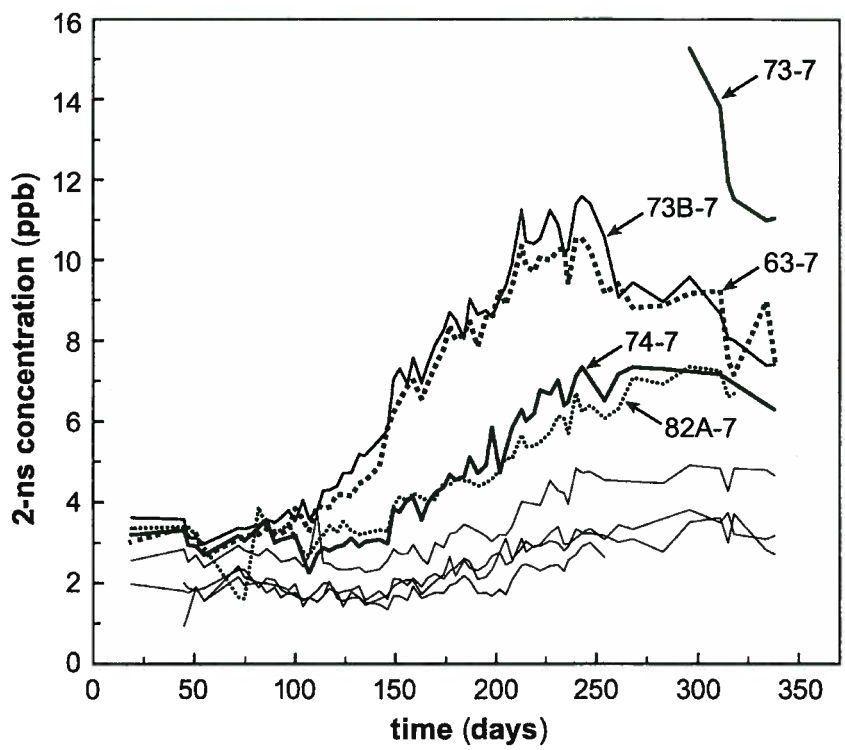


Fig. 10. 2-Naphthalene sulfonate returns observed from the testing of injector 25-5 at Dixie Valley.

the production wells within the reservoir are underpressured relative to the surrounding aquifers, thermally stable tracers such as the naphthalene sulfonates remain in the reservoir until they decay. The result is that tracers tend to remain in solution in the reservoir for a long time. In addition to the four naphthalene sulfonate tracers tested in the Dixie Valley reservoir and reported here (1,5-naphthalene disulfonate, 1,3,6-naphthalene trisulfonate, 2-naphthalene sulfonate, and 2,7-naphthalene disulfonate), an amino-substituted naphthalene disulfonate (amino G) and a dimerized naphthalene sulfonate (Crisotan R5) were also recently tested (Rose et al., 1998). Therefore, the background concentrations may be attributed to a combination of isomerization and/or partial decomposition of a number of naphthalene sulfonates and an amino-substituted naphthalene disulfonate tested at the Dixie Valley reservoir over the past several years. These examples illustrate the result of using conservative tracers in reservoirs where all of the produced fluids are reinjected and where there is very little natural fluid leakage into surrounding aquifers.

6. Tracer testing at Steamboat Springs using 1,5-naphthalene disulfonate

The Far West Capital (FWC) Steamboat Springs geothermal field is located approximately 14 km south of Reno, Nevada. Fig. 11 shows the location of production, injection and exploratory slim holes drilled on the FWC Steamboat Springs geothermal operations area. Average geothermal fluid production temperature is approximately 160 °C. The combined production flow rate to the SB 1/1A and SB 2/3 power plants is approximately 1370 kg/s. The combined electrical power output from these two plants is approximately 31 MW.

Fractured granodiorite underlies the volcanic sequence and comprises the geothermal reservoir system at Steamboat Springs (Rose et al., 1999). The permeability of the fractured granodiorite is very high. The total thickness of the granodiorite is unknown. The deepest hole drilled in the area (GTH 87-29) encountered granodiorite to a depth of 1220 m.

The tracer test at Steamboat Springs was designed to compare the performance of the candidate tracer 1,5-naphthalene disulfonate with the well-characterized geothermal tracer, fluorescein. On 24 July 1998, 91 kg of uranine (sodium salt of fluorescein) was mixed with 100 kg of the disodium salt of 1,5-naphthalene disulfonic acid in a tank with approximately 3.8 m^3 of water (Rose et al., 1999). Upon dissolution of the tracers, the solution was injected over a period of approximately 45 min into slim hole GTH 87-29. Brine was then injected continuously into GTH 87-29 at a rate of 9 kg/s.

The 1,5-naphthalene disulfonate return curves for selected wells are shown in Fig. 12. The strongest return is to well HA-4, which is located only 10 m from the tagged slim hole GTH 87-29. The distance separating the completion intervals of the two wells is much greater, since producer HA-4 has a total depth of only 220 m, whereas the slim hole injection well is completed in a deeper region of the reservoir below a depth of about 670 m.

Fig. 13 shows the normalized fluorescein and 1,5-naphthalene disulfonate return curves for production well HA-4. Each return curve has been normalized for the

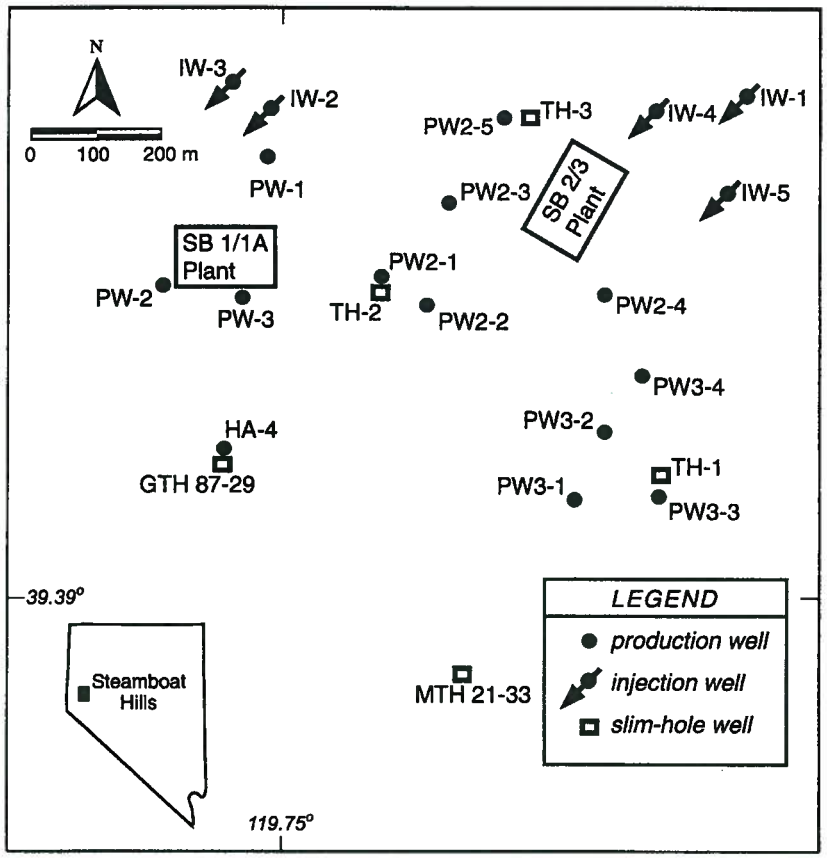


Fig. 11. Location map of production, injection and exploratory slim holes drilled in the Far West Capital Steamboat Springs geothermal operations area.

quantity of tracer injected, and the fluorescein plot has been corrected for the initial background concentration of approximately 200 ppt. It is evident from this figure that the normalized return-curve concentrations are nearly identical. In a tracer test at Dixie Valley, Nevada, Adams and coworkers (1989) showed that fluorescein did not adsorb on reservoir rock when its normalized return curve was compared to that of the tracer benzoic acid, which was assumed to behave conservatively. Since 1,5-naphthalene disulfonate was shown to have a normalized return curve that was essentially identical to that of fluorescein (Fig. 13), it is unlikely that either 1,5-naphthalene disulfonate or fluorescein adsorbed on the reservoir rock at Steamboat Springs.

7. Tracer testing at Ohaaki, New Zealand using 1,5-naphthalene disulfonate

The Ohaaki geothermal field is located 30 km northeast of Lake Taupo on either side of the Waikato river (Fig. 14). The geology at Ohaaki represents about 750,000 years of accumulation of rhyolitic and sedimentary rocks in a subsiding basin at the eastern margin of the Taupo Volcanic zone (Clotworthy et al., 1995). The basement

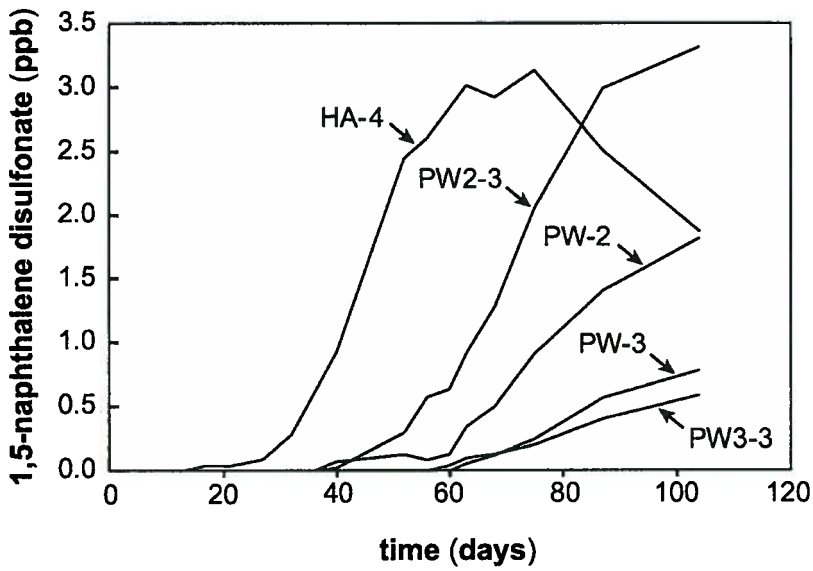


Fig. 12. 1,5-Naphthalene disulfonate returns observed from the testing of injector GTH 87-29 at Steamboat Springs.

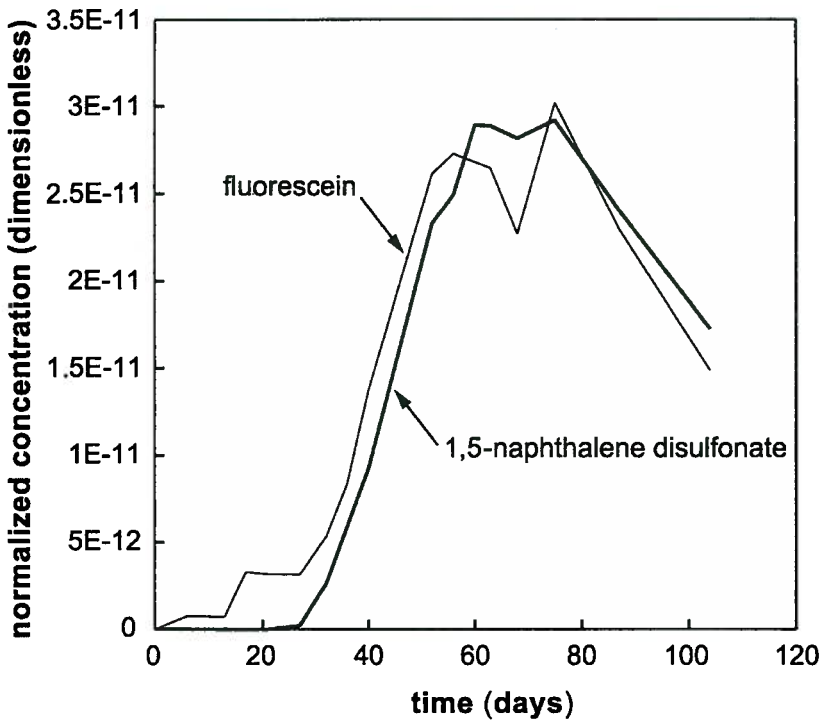


Fig. 13. Normalized fluorescein and 1,5-naphthalene disulfonate returns from injection well GTH 87-29 to production well HA-4.

comprises mainly greywacke sandstones of the Mesozoic Torlesse Terrane to the depths currently explored, or about 2.5 km. Above the basement, the Waikora Formation greywacke conglomerates are interbedded with undifferentiated Ohakuri

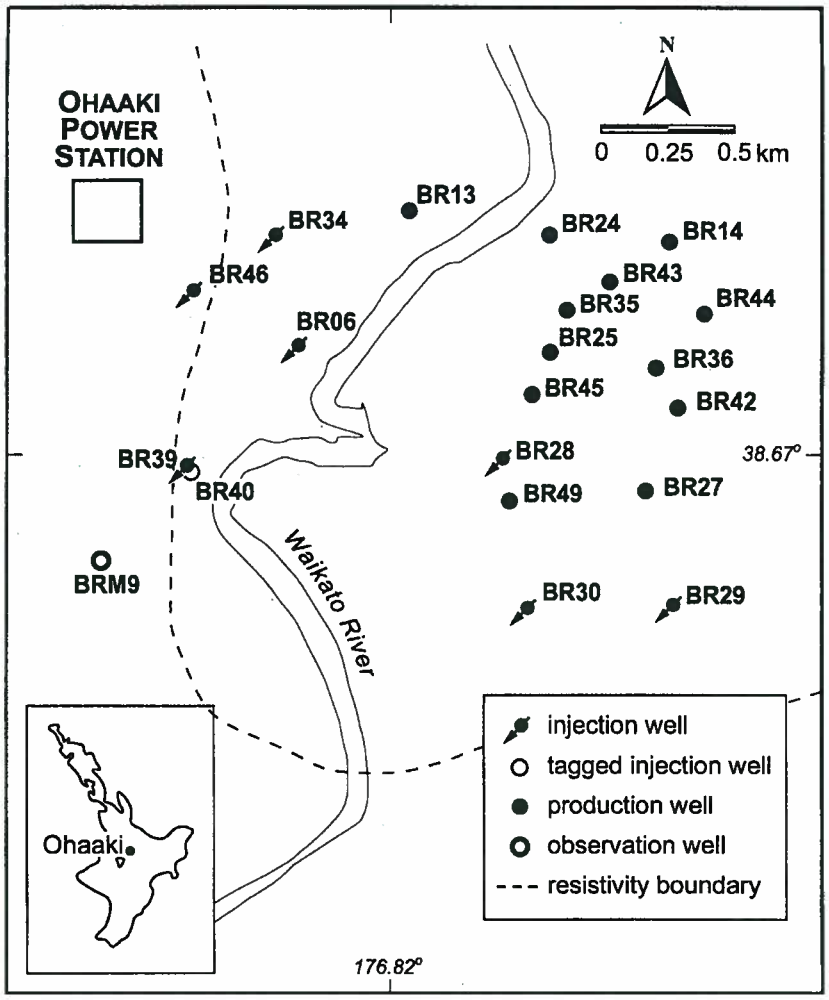


Fig. 14. Map of the southwest portion of the Ohaaki, New Zealand, geothermal field showing the injection and production wellhead locations.

Group volcanics, forming a wedge of rocks of poorly known production potential. The 330,000-year-old Rangitaiki ignimbrite forms a thick, field-wide marker horizon above which are 800–1000 m of variable deposits which include lacustrine sediments (lower siltstone, Huka Falls Formation), lava domes (east Broadlands rhyolite, Broadlands dacite, Broadlands rhyolite, Ohaaki rhyolite), and bedded volcanics (Rautawiri breccia, Waiora formation) (Clotworthy et al., 1995).

The thick, ubiquitous, pumiceous tuffs of the Rautawiri breccia and the more restricted Waiora Formation are generally permeable and productive. The Broadlands rhyolite has good fracture permeability, and occurs only near the western margin of the field where it is used for reinjection. The Ohaaki rhyolite is present in the western and central parts of the field. It has fracture permeability where it is thickest, west of the Waikato River. Prior to field development, it acted as a mixing aquifer for cooler shallow waters and hot geothermal fluids originating from depth. Unlike the two large rhyolite domes (Ohaaki and Broadlands rhyolites), the similar-

sized Broadlands dacite dome in the southeastern part of the field has low permeability. The inner rhyolite overlying the west-bank production wells is poorly connected to the outer Ohaaki rhyolite to the south (Clotworthy et al., 1995).

On 25 May 1999, 150 kg of 1,5-naphthalene disulfonate (Pfaltz and Bauer, USA) was injected into well BR-40 at the Ohaaki geothermal reservoir (see Fig. 14). Various production and monitoring wells were sampled and analyzed for tracer over several subsequent months (Rose et al., 2000).

Shown in Fig. 15 are the returns of the 1,5-naphthalene disulfonate tracer within and adjacent to the Ohaaki reservoir. The strongest returns were to the observation well BRM-9, which is in close proximity to BR-40 and just outside of the resistivity boundary for the field. Modest returns were also observed to wells BR-25, BR-36, BR-44, and BR-45 within the field, with first arrivals approximately 140 days into the test. These two producers are among the closest to the tagged injector. It is evident, however, that the tracer returns to the wells within the field are much weaker than the returns to the observation well, which is just outside of the field, indicating that most of the injectate into BR40 flows away from the field.

8. Tracer testing at Awibengkok, Indonesia using 1,5-naphthalene disulfonate and 1,3,6-naphthalene trisulfonate

The Awibengkok geothermal field is located in West Java, Indonesia, approximately 60 km south of Jakarta. The resource is liquid-dominated, containing relatively benign

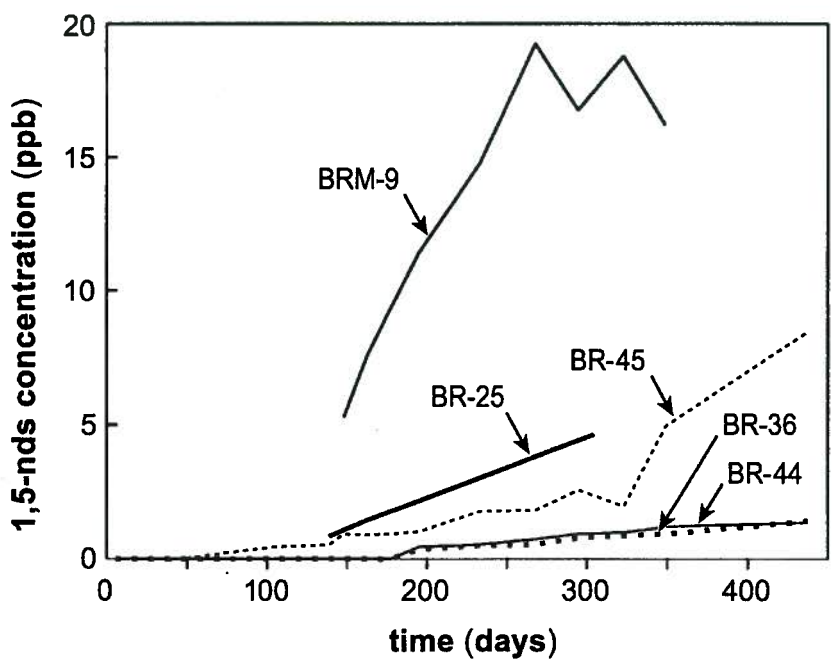


Fig. 15. 1,5-Naphthalene disulfonate tracer returns observed from the testing of injector BR-40 at Ohaaki.

fluid with reservoir temperatures ranging from 221 to 312 °C. It is a highly fractured reservoir set in andesitic rocks. Within the reservoir, the matrix rocks are propylitically altered.

The first tracer tests at Awibengkok were conducted in 1994 using fluorescein. These tests successfully identified good hydraulic connections between closely spaced injection and production wells (Murray et al., 1995). Because of the better thermal stability offered by the naphthalene sulfonates, these compounds were chosen for use in hotter parts of the reservoir and where the hydraulic connections between injection wells and production wells appear to be weak or the flow paths relatively long.

In the eastern part of the field where the naphthalene sulfonates tracers were injected (Fig. 16), there are 19 production wells on three locations (AWI-1, AWI-13 and AWI-16). The total mass production rate of these 19 wells averages approximately 1400 kg/s. There are seven injection wells in the area grouped on two locations (AWI-14 and AWI-15) that accept approximately 1390 kg/s of separated brine, which is about 50% of the total brine injected at Awibengkok.

On 6 November 1998, 150 kg of 1,5-naphthalene disulfonate and 150 kg of fluorescein were dissolved in approximately 2400 l of fresh water and injected over a period of about 6 min into AWI 15-2, which was accepting about 110 kg/s of brine (Rose et al., 2000). This resulted in a final concentration of 3600 ppm for each tracer. On 8

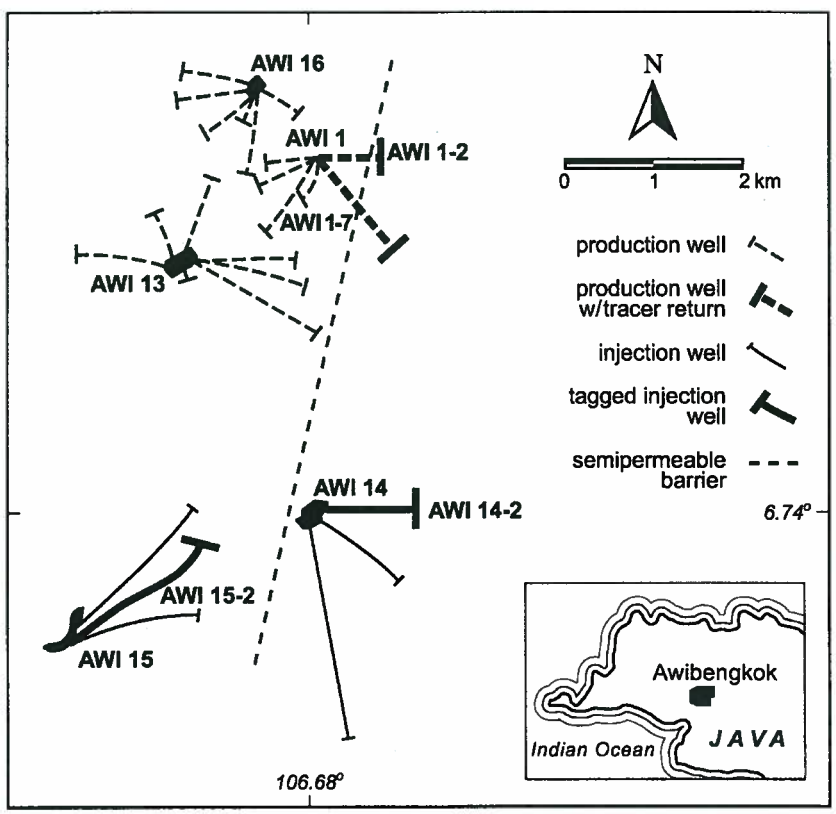


Fig. 16. Map of the eastern portion of the Awibengkok, Indonesia, geothermal field showing the injection and production wellhead locations.

November 1998, 150 kg of 1,3,6-naphthalene trisulfonate was dissolved in approximately 1500 l of fresh water and injected over a period of about 5 min into AWI 14-2, which was accepting about 90 kg/s of brine. This resulted in a final tracer concentration of 5200 ppm. All production wells in the field were subsequently monitored for the three tracers for approximately 8 months.

Neither 1,5-naphthalene disulfonate nor fluorescein was detected in any of the production wells. 1,3,6-naphthalene trisulfonate was observed in two production wells, AWI 1-2 and AWI 1-7 (Fig. 17). That returns of the 1,3,6-naphthalene trisulfonate injected at AWI 14-2 were observed in only two producers supports the existence of a semi-permeable barrier separating AWI 14-2, AWI 1-2 and AWI 1-7 from the rest of the field (Fig. 16). This barrier was first proposed to explain pressure interference tests conducted prior to commercial operations (Murray et al., 1995). The tracer tests reported here, however, offer the most conclusive evidence to date of the existence of this barrier. That no returns of 1,5-naphthalene disulfonate or fluorescein injected at AWI 15-2 were detected in any of the producing wells may be explained by the fact that the fluid injected into this well exits the wellbore below a thick rhyodacite unit that extends over the entire field, while most eastern production wells

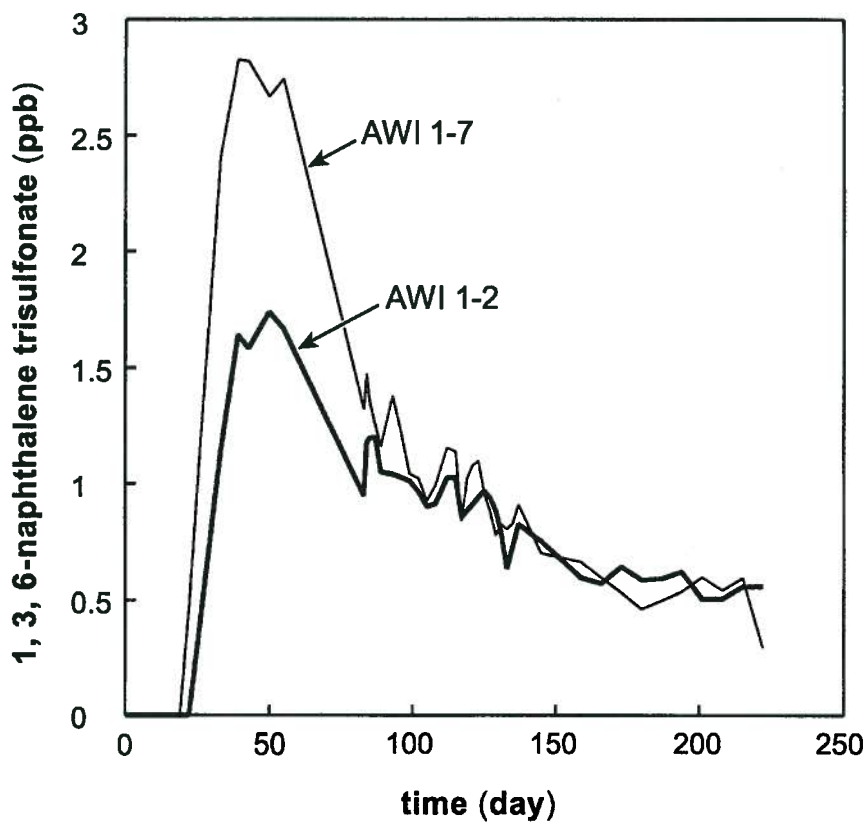


Fig. 17. 1,3,6-Naphthalene trisulfonate tracer returns observed from the testing of injector AWI 14-2 at Awibengkok.

have entries above this unit. Clay-rich tuffs associated with the rhyodacite unit may act as semi-permeable barriers impeding vertical flow in the reservoir.

9. Conclusions

The polyaromatic sulfonates were successfully tested in laboratory and field studies and shown to be robust geothermal tracers. In addition to being environmentally benign and very affordable, these fluorescent compounds have detection limits of approximately 200 ppt using conventional HPLC analysis. Decay kinetics studies indicate that the five polyaromatic sulfonates tested (1,3,6,8-pyrene tetrasulfonate, 1,5-naphthalene disulfonate, 1,3,6-naphthalene trisulfonate, 2-naphthalene sulfonate, and 2,7-naphthalene disulfonate) possess excellent thermal stability and are suitable for use in high-temperature, liquid-dominated geothermal reservoirs. An Arrhenius model was used to determine the temperature dependence of the decay rate constants on temperature. Using this model, we showed that 1,3,6,8-pyrene tetrasuflonate can be used in reservoirs as hot as 310 °C, 1,5-naphthalene disulfonate and 1,3,6-naphthalene trisulfonate in reservoirs as hot as 340 °C, and 2-naphthalene sulfonate and 2,7-naphthalene sulfonate in reservoirs having fluid temperatures of 350 °C or hotter.

In a series of tracer tests at the Dixie Valley geothermal reservoir, all five polyaromatic sulfonate tracers were successfully tested. The tests revealed that Section-18 and Section-5 injectate flows to the Section-7 production wells. Injection into the newly drilled 27-32 injector flows to the Section-33 producers.

In a tracer test at Steamboat Springs, Nevada, 1,5-naphthalene disulfonate was tested in combination with fluorescein. Normalized return curves of the two tracers showed that 1,5-naphthalene disulfonate does not adsorb relative to fluorescein at a reservoir-fluid temperature of 160 °C, indicating that the naphthalene sulfonates are suitable for use in low-temperature geothermal reservoirs.

A tracer test at the Ohaaki geothermal reservoir using 1,5-naphthalene disulfonate revealed that most of the water injected via well BR-40 flows away from the reservoir. A small fraction of the injectate returns to some of the production wells in the southwest portion of the field.

In a field test at the Awibengkok geothermal reservoir, both naphthalene sulfonate tracers were used. The lack of tracer response from well AWI 15-2, which was tagged with 1,5-naphthalene disulfonate, indicates that this well is not immediately connected with any production wells. Tracer returns show, however, that well AWI 14-2, which was tagged with 1,3,6-naphthalene trisulfonate, is connected to two producers in the eastern portion of the reservoir.

The polyaromatic sulfonates that we tested for this study are all sufficiently stable to be used in liquid-dominated geothermal reservoirs with temperatures exceeding 310 °C. Two of them (2-naphthalene sulfonate and 2,7-naphthalene sulfonate) are sufficiently stable for use in reservoirs whose temperatures exceed 350 °C. Whereas none of the reservoir waters in which the polyaromatic sulfonates were tested possess such high temperatures, the field tests nevertheless showed that these com-

pounds can serve as conservative tracers to simultaneously tag injection wells in a variety of geothermal settings.

Acknowledgements

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ENCLOSURE 4

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TOXICITY AND ECOTOXICITY OF SULFONIC ACIDS: STRUCTURE-ACTIVITY RELATIONSHIP

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ABSTRACT

Currently available data on toxicological and ecotoxicological endpoints for sulfonic acids have been compiled by the BUA. This compilation reveals a common toxicological profile for the sulfonic acids when all the properties of these substances are taken into consideration. In contrast, the sulfonic acids show a much less uniform pattern with respect to their ecotoxicological properties.

INTRODUCTION

The task of the Advisory Committee on Existing Chemicals of Environmental Relevance (BUA) of the Gesellschaft Deutscher Chemiker (GDCh) in systematically evaluating existing chemicals is complicated by the fact that the toxicological and ecotoxicological database is often incomplete (1, 2,). In order to fill in the data gaps, a great number of tests should be performed, which would require many experimental animals, much time and money. BUA is thus examining whether conclusions can be drawn as to the toxicological and ecotoxicological potential of structurally related chemicals by considering structure-activity relationships, thus avoiding unnecessary testing according to the law of animal protection and increasing our general knowledge about toxic effects being relative to certain functional chemical structures. The data for the group of sulfonic acid compounds which are shown below were compiled by BUA for this purpose.

Within the framework of the chemical group analysis, the sulfonic acid compounds were subdivided into the following subgroups: benzene sulfonic acids, stilbene sulfonic acids, diphenyl sulfonic acids, naphthalene sulfonic acids, alkane sulfonic acids, and other sulfonic acid compounds which could not be assigned to a particular category.

A total of 33 substances were evaluated and their toxicological and ecotoxicological properties compared. The data presented below were obtained from the basic data sets (3, 4, 5) and further from unpublished data from the chemical industry. Some of the chemicals listed are being evaluated by the Advisory Committee of the BG Chemie (6).

Further investigations are recommended if the data on a certain endpoint are insufficient or contradictory. The experimental studies recommended below are to be performed by the chemical industry at its own expense.

RESULTS and DISCUSSION

1. Toxicology

The currently available data as to the toxicological properties of sulfonic acid compounds are presented in Table 1. The analysis of this data as detailed below shows that these compounds, regardless of their structure and the route or duration of their application, have a low systemic toxicity and are neither mutagenic nor carcinogenic. This fact is possibly related to the pharmacokinetics of the sulfonic acids in the organism. The findings on irritation and skin sensitization do not indicate any common effect for the group.

a) Metabolism

The hydrophilic properties of the sulfonic acids result in the rapid excretion of these substances from the organism. Some sulfonic acid compounds have been shown to undergo no metabolism whatsoever in the organism. e.g. 2-amino-1-naphthalenesulfonic acid (81-16-3) was detected in urine solely as the unmodified form of the originally applied compound.

b) Acute Toxicity

The acute toxicity of the sulfonic acid compounds is low, regardless of the particular structure involved. The LD_{50} values (determined for oral administration to rats) are at least 1000 mg/kg body weight and are mostly in excess of 5000 mg/kg body weight.

c) Skin and Mucous Membrane Tolerance

The varying results of skin irritation tests do not indicate a uniform profile for this chemical group. The local irritation effect of the acid group seems to be influenced by the other substituents.

d) Sensitization

Although a skin sensitizing effect was shown with two benzene sulfonic acids in animal experiments, it was not observed with other benzene sulfonic acids, with alkane sulfonic acids, with naphthalene sulfonic acids or with other sulfonic acid compounds. This leads to the assumption that the varying results possibly depend on the properties of substituents within the molecules. In the light of the frequently insufficient documentation of the studies, however, it is also possible that positive results were due to contaminations. Positive results may also represent misinterpretations of the effects of irritating and corrosive substances.

Test Recommendation:

The varying results of skin sensitization tests on benzene sulfonic acids should be clarified. Since the differing results are possibly dependent on substituent characteristics, the sensitizing activity should be tested with two other substances of this subgroup: 3-amino-benzenesulfonic acid, monosodium salt (1126-34-7), and 3-nitro-benzenesulfonic acid, sodium salt (127-68-4), are recommended. Accordingly, a supplementary study pertaining to the subgroup stilbene sulfonic acids should be conducted with 2,2'-(1,2-ethenediyl)bis(5-amino)-benzenesulfonic acid, disodium salt (7336-20-1).

e) Subacute, Subchronic and Chronic Toxicity

Only a few studies are available on this topic: they indicate practically no hazard. In view of the typical rapid excretion of the sulfonic acid compounds, these are presumed to be without systemic effect, regardless of structure. This assumption must be tested in further studies.

Test Recommendation:

The benzene sulfonic acid representatives 4-amino-benzenesulfonic acid (121-57-3) and 3-nitro-benzenesulfonic acid, sodium salt (127-68-4) should be tested. Subacute studies should be conducted with 4-amino-5-hydroxy-2,7-naphthalenedisulfonic acid, monosodium salt (5460-09-3) and naphthalenesulfonic acid (68153-01-5) as representatives of the subgroup of naphthalene sulfonic acids.

f) Genetic Toxicity

Sulfonic acid compounds were not mutagenic in *Salmonella typhimurium* (Ames test). Positive results with two naphthalene sulfonic acids, possibly due to contaminations, were reported in studies which could not be validated; however, new studies with these compounds according to international guidelines revealed negative results. The few studies which were carried out for cytogenetic effects *in vitro* and *in vivo* were negative. Consequently, the current data indicate that the sulfonic acids do not exert any genotoxic effects.

Test Recommendation:

To provide a representative sampling of the group, another test for genetic toxicity should be perfomed for the following sulfonic acid compounds for which there is a high exposure level. A micronucleus test should be

performed with 4-amino-benzenesulfonic acid (121-57-3) and 3-nitro-benzenesulfonic acid, sodium salt (127-68-4).

g) Carcinogenicity

Carcinogenicity studies have been carried out with one chemical of each of the following subgroups: stilbene, naphthalene, and alkane sulfonic acids. These compounds do not show any carcinogenic potential. Similar results have been recently reported concerning the genotoxic and carcinogenic potential of aromatic aminosulfonic acids (7).

h) Reproductive Toxicity

The results of the teratogenicity studies (on one benzene sulfonic acid and three alkane sulfonic acids) were negative. Since the known studies on acute and long-term systemic toxicity demonstrate effects independent of the type of substituents, comparable results are expected for teratogenicity as well. This hypothesis should be validated exemplarily by testing several chemicals from different subgroups.

Test Recommendation:

Teratogenicity studies should be carried out with the following substances to provide the missing data: 4-amino-benzenesulfonic acid (121-57-3), as an example of the benzene sulfonic acids, and branched and linear butyl derivatives of naphthalenesulfonic acids, sodium salts (91078-64-7), in view of the structural uniqueness of these compounds. Possibly also (1-methylethyl)-benzenesulfonic acid, sodium salt (28348-53-0), used in the consumer sector, and C10-13-sec-alkyl derivatives of benzenesulfonic acid, sodium salts (68411-30-3) should be investigated.

2. Ecotoxicology

The currently available data on the ecotoxicological properties of sulfonic acid compounds are presented in Table 2.

a) Biodegradability

Both (1-methylethyl)-benzenesulfonic acid, sodium salt (28348-53-0) and C10-13-sec-alkyl derivatives of benzenesulfonic acid, sodium salts (68411-30-3) are readily biodegradable. With the exception of 3-(ethylamino)-4-methyl-benzenesulfonic acid (98-40-8) (degradation rate < 20%), the extent of degradation of the other benzene sulfonic acids is greater than 70% in the Zahn-Wellens or coupled-unit test.

2,2'-(1,2-ethenediyl)bis(5-nitro)-benzenesulfonic acid, dipotassium salt (78447-91-3) showed no degradation in the OECD screening test. 2,2'-(1,2-ethenediyl)bis(5-amino)-benzenesulfonic acid (81-11-8) and 2,2'-(1,2-ethenediyl)bis(5-amino)-benzenesulfonic acid, disodium salt (7336-20-1) proved to be not inherently degradable, exhibiting a degradation rate < 10% in the Zahn-Wellens test.

The degree of degradation of both (1,1'-biphenyl)-4-sulfonic acid, sodium salt (2217-82-5) and (1,1'-biphenyl)-4,4'-disulfonic acid (5314-37-4) is less than 20% (OECD screening test). These compounds must therefore be categorized as not readily degradable.

No degradation was observed for six of the eight naphthalene sulfonic acids listed; for 4-amino-5-hydroxy-2,7-naphthalenedisulfonic acid, monosodium salt (5460-09-3), the extent of degradation was less than 10%. Accordingly, the substances must be classified as "not readily biodegradable". In the Zahn-Wellens test, 6-amino-4-hydroxy-2-naphthalenesulfonic acid (90-51-7) and 4-amino-5-hydroxy-2,7-naphthalenedisulfonic acid, monosodium salt (5460-09-3) proved to be not inherently degradable. The degradation rate of naphthalenesulfonic acids (68153-01-5) was > 60% in the OECD confirmatory test.

Based on their degradation rates, four of the five alkane sulfonic acids listed should be classified as "not readily biodegradable". Only C14-16-alkene sulfonic acids, sodium salts (68439-57-6) was examined with the Zahn-Wellens test; it proved to be inherently degradable.

In the group of "others," three out of six compounds (1-amino-4-bromo-9,10-dihydro-9,10-dioxo-2-anthracenesulfonic acid, monosodium salt [6258-06-6]; 2-methyl-2-propene-1-sulfonic acid, sodium salt [1561-92-8]; and naphthalenesulfonic acids [reaction products with sulfonylbisphenol and formaldehyde], ammonium salts [94094-87-8]) showed a degradation extent < 60%; they are therefore classified as "not readily biodegradable". The other compounds are rated as "readily biodegradable" according to their degradation > 70%.

Test Recommendation:

A Zahn-Wellens test should be carried out for branched and linear butyl derivatives of naphthalenesulfonic acids, sodium salts (91078-64-7).

b) Accumulation

The $LogP_{ow}$ for all benzene, stilbene, diphenyl, naphthalene and other sulfonic acids tested was determined to be equal to or less than 2.2; therefore, no significant bioaccumulation is expected. The $LogP_{ow}$ is > 6 for two of the alkane sulfonic acids, C10-21-alkane sulfonic acids, phenylesters (91082-17-6) and C16-34-alkane, chloro, sulfonyl chlorides (91082-32-5). In these cases accumulation is expected.

c) Toxicity to Fish

The data on fish toxicity were determined for the following species: *Leuciscus idus, Brachydanio rerio, Salmo gaidneri, Pimephales promelas, Lepomis macrochirus, Poecilia reticulata.*

The LC_{50} is greater or equal to 100 mg/l for seven of the benzene sulfonic acids. For both C10-13-sec-alkyl derivatives of benzenesulfonic acid, sodium salts (68411-30-3) and C10-13-sec-alkyl derivatives of benzenesulfonic acid (85536-14-7) the 48-hour LC_{50} is 5 mg/l.

The value of acute toxicity to fish is $\geq$ 100 mg/l for all of the stilbene sulfonic acids.

The LC_0 for (1,1'-biphenyl)-4-sulfonic acid, sodium salt (2217-82-5) is greater than 5 mg/l. No data are available for the other diphenyl sulfonic acid.

The value of acute toxicity to fish is greater than 100 mg/l for seven of the naphthalene sulfonic acids. There is an acute fish toxicity value less than 100 mg/l only for branched and linear butyl derivatives of naphthalenesulfonic acids, sodium salts (91078-64-7).

The effect concentrations are below 10 mg/l for C14-16-alkane hydroxy and C14-16-alkene sulfonic acids, sodium salts (68439-57-6) and alkane sulfonic acids, sodium salts (68608-15-1). The compounds C10-21-alkane sulfonic acids, phenylesters (91082-17-6) and C16-34-alkane, chloro, sulfonyl chlorides (91082-32-5) show effect concentrations above 100 mg/l. There are no data for C10-21-alkane sulfonyl chlorides (91082-29-0).

The value of acute toxicity to fish is > 100 mg/l for most of the aromatic sulfonic acids. In comparison, LC_0 values of 5 and < 10 mg/l were determined for alkane, chloro sulfonic acid, sodium salts (68910-45-2) and naphthalenesulfonic acids (reaction products with sulfonylbisphenol and formaldehyde) ammonium salts (94094-87-8).

d) Toxicity to Daphnia

The acute effect concentrations (EC_{50}) for daphnia are above 100 mg/l for five of the benzene sulfonic acids. The sodium salt of (1-methylethyl)-benzenesulfonic acid (28348-53-0) has a 21-day NOEC > 30 mg/l. Twenty-four hour EC_{50} values are below 10 mg/l for C10-13-sec-alkyl derivatives of benzenesulfonic acid, sodium salts (68411-30-3) and C10-13-sec-alkyl derivatives of benzenesulfonic acid (85536-14-7).

For the stilbene sulfonic acids, diphenyl sulfonic acids and naphthalene sulfonic acids, an acute effect concentration is available for only one chemical each: 2,2'-(1,2-ethene-diyl)bis(5-amino)-benzenesulfonic acid, disodium salt (7336-20-1): 24-hour EC_0 = 100 mg/l; (1,1'-biphenyl)-4,4'-disulfonic acid (5314-37-4): 24-hour EC_0 > 1000 mg/l; naphthalenesulfonic acids (68153-01-5): the 48-hour EC_{50} is 34 mg/l and the 24-hour EC_{50} is 85 mg/l.

For two of the alkane sulfonic acids, an EC_{50} of 53.1 mg/l was determined for the sodium salts (68608-15-1), and a value of above 100 mg/l for the C10-21-alkane sulfonyl chlorides (91082-29-0).

96-hr EC_{50} values of 10-100 mg/l were determined for hydroxy-methanesulfonic acid, monosodium salt (870-72-4). (Further data are not available.)

Test Recommendations:

Due to the poor biodegradability and varying values for fish toxicity of the sulfonic acids, 3-(ethylamino)-4-methyl-benzenesulfonic acid (98-40-8) should be tested for chronic toxicity to daphnia .

The compound (1,1'-biphenyl)-4-sulfonic acid, sodium salt (2217-82-5) should be tested for its acute toxicity to daphnia, thus supplying the missing data for diphenyl sulfonic acids on toxicity to daphnia.

The acute toxicity to daphnia should also be determined for naphthalenesulfonic acids (reaction products with sulfonylbisphenol and formaldehyde), ammonium salts (94094-87-8).

e) Toxicity to Algae

Values for acute toxicity to algae are only available for four sulfonic acids from three subgroups. For 3-amino-benzenesulfonic acid, monosodium salt (1126-34-7) and 3-(diethylamino)-benzenesulfonic acid, sodium salt (5123-63-7) the corresponding EC_{20} values are above 100 mg/l.

For naphthalenesulfonic acids (68153-01-5) the 96-hr effect concentrations are 54.3 and 73.3 mg/l.

For hydroxy-methanesulfonic acid, monosodium salt (870-72-4) the 7-day EC_0 is < 100 mg/l.

Test Recommendations:

Toxicity to algae should be tested exemplarily for the subgroup of stilbene sulfonic acids with 2,2'-(1,2-ethenediyl)bis(5-amino)-benzenesulfonic acid, disodium salt (7336-20-1); the data for this substance will then be complete, and an evaluation can follow.

The missing data for diphenyl sulfonic acids on toxicity to algae should be supplied for (1,1'-biphenyl)-4-sulfonic acid, sodium salt (2217-82-5).

The toxicity to algae should be determined for alkane sulfonic acids, sodium salts (68608-15-1) as a representative of the subgroup of the alkane sulfonic acids.

The toxicity to algae should also be determined for naphthalenesulfonic acids (reaction products with sulfonylbisphenol and formaldehyde), ammonium salts (94094-87-8).

f) Toxicity to Bacteria

The acute toxicity to bacteria, based on different methods of testing, resulted in the determination of effect concentrations > 100 mg/l for six benzene sulfonic acids. In that they exhibit effect concentrations between 10 and 100 mg/l, (1-methylethyl)-benzenesulfonic acid, sodium salt (28348-53-0), C10-13-sec-alkyl derivatives of benzenesulfonic acid, sodium salt (68411-30-3), and C10-13-sec-alkyl derivatives of benzenesulfonic acid (85536-14-7) can inhibit the activity of unadapted biological waste water treatment plants during times of extreme peak loads.

The acute toxicity concentrations to bacteria are over 100 mg/l for all stilbene sulfonic acids and their salts, based on different EC values and test procedures, while for the diphenyl sulfonic acids they are in the range of EC values > 1000 mg/l. For four of the alkane sulfonic acids, EC values > 100 mg/l are cited; there are no data for C16-34-alkane, chloro, sulfonyl chlorides (91082-32-5).

For the naphthalene and for five of the aromatic sulfonic acids, the acute toxicity concentrations to bacteria are > 100 mg/l, based on different test procedures. There is a possibility that the activity of unadapted biological waste water treatment plants may be inhibited during times of extreme peak loads only for 2-methyl-2-propene-1-sulfonic acid, sodium salt (1561-92-8), exhibiting an acute toxicity to bacteria of 29.7 mg/l.

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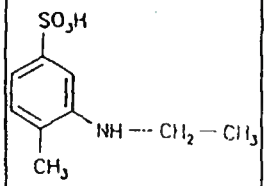
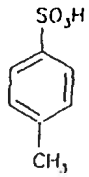
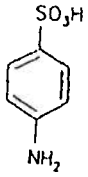
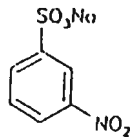
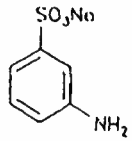
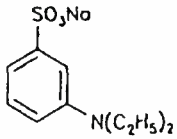
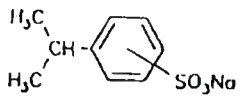
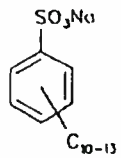
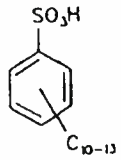
TABLE 1: TOXICITY DATA OF SULFONIC ACIDS

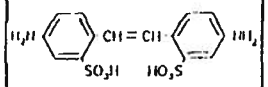
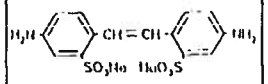
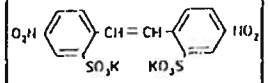
CAS No. CAS Name Company	Structural Formula	TOXICITY					Other Comments
		Acute Toxicity	Irritation (I) Sensitization (S)	Repeated Dose Toxicity	Genotoxicity (G) Carcinogenicity (C)	Reproductive Toxicity	Test Recom-mendations
BENZENE SULFONIC ACIDS							
98-40-8 3-(ethylamino)-4-methyl-benzenesulfonic acid *BASF AG*		Rat LD50: > 5000 mg/ kg b. w.	I: nonirritating to eye nonirritating to skin S: no data	no data	G: Ames test neg. C: no data	no data	
104-15-4 4-methyl-benzenesulfonic acid Hoechst AG		Rat LD50: 1410 mg/ kg b. w.	I: strongly irritating, eye corrosive to skin S: neg.	no toxico-logical effect, rat p.o., 28 d	G: Ames test neg. cytogenicity neg.		no data
121-57-3 4-amino-benzenesulfonic acid Bayer AG		Rat LD50: 12300 mg/ kg b. w.	I: moderately irritating, eye slightly irritating, skin S: pos.	no data	G: Ames test neg. C: no data	no data	toxicological evaluation BG Chemie No. 252 MNT/subacute toxicity/terato-genicity being tested

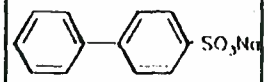
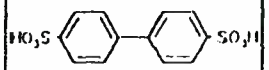
2211

CAS No. CAS Name Company	Structural Formula	TOXICITY					Other Comments
		Acute Toxicity	Irritation (I) Sensitization (S)	Repeated Dose Toxicity	Genotoxicity (G) Carcinogenicity (C)	Reproductive Toxicity	Test Recom-mendations
127-68-4 3-nitro-benzene-sulfonic acid, sodium salt BASF AG		Rat LD50: > 5000 mg/ kg b. w.	I: nonirritating to eye nonirritating to skin S: no data	no data	G: Ames test neg. C: no data	no data	sensitization/ subacute toxicity/ MNT
1126-34-7 3-amino-benzenesulfonic acid, mono-sodium salt BASF AG		Rat LD50: 5200 mg/ kg b. w.	I: strongly irritating, eye skin--no data S: no data	no data	G: Ames test neg. C: no data	no data	sensitization
5123-63-7 3-(diethylamino)-benzenesulfonic acid, sodium salt BASF AG		Rat LD50: > 5000 mg/ kg b. w.	I: corrosive to eye corrosive to skin S: no data	no data	G: Ames test neg. C: no data	no data	

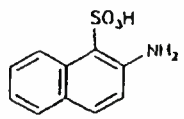
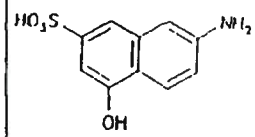
CAS No. CAS Name Company	Structural Formula	TOXICITY					Other Comments Test Recom-mendations
		Acute Toxicity	Irritation (I) Sensitization (S)	Repeated Dose Toxicity	Genotoxicity (G) Carcinogenicity (C)	Reproductive Toxicity	
28348-53-0 (1-methylethyl)-benzenesulfonic acid, sodium salt Hüls AG		Rat LD50: > 7000 mg/ kg b. w.	I: nonirritating to eye nonirritating to skin S: neg.	NOEL rat, 400mg/ kg b. w.	G: Ames test neg. MNT: neg. C: no data	no data	
68411-30-3 C10-13-sec-alkyl derivs. benzene-sulfonic acid, sodium salts Hüls AG		Rat LD50: 1250-1600 mg/ kg b. w.	I: nonirritating to eye nonirritating to skin S: neg.	NOEL rat, ape 30-338 mg/ kg b. w.	G: Ames test neg. MNT: neg. C: transforma-tion neg.	only in mice in matern. toxic doses embryotoxic and teratog., rat & rabbit: neg. multigener. study neg.	together with 85536-14-7
85536-14-7 C10-13-sec-alkyl derivs. benzene-sulfonic acid Hüls AG		Rat LD50: 1350 mg/ kg b. w.	I: corrosive to eye corrosive to skin S: clearly skin sensitizing	no data	G: Ames test neg. MNT: neg. C: no data	no data	together with 68411-30-3

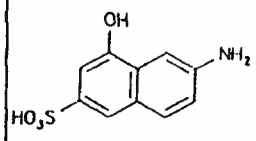
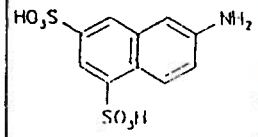
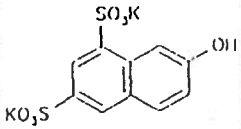
2213

CAS No. CAS Name Company	Structural Formula	TOXICITY					Other Comments
		Acute Toxicity	Irritation (I) Sensitization (S)	Repeated Dose Toxicity	Genotoxicity (G) Carcinogenicity (C)	Reproductive Toxicity	Test Recom-mendations
STILBENE SULFONIC ACIDS							
81-11-8 2,2'-(1,2-ethene-diyl)bis(5-amino)-benzenesulfonic acid Bayer AG		Guinea pig LD50: 47000 mg/kg b. w.	I: no data for eye or skin S: no data	no data	G: Ames test neg. P. mut.: neg. CHO: SCE/ Chr. neg.; mouse lym. planned C: no data	no data	
7336-20-1 2,2'-(1,2-ethene-diyl)bis(5-amino)-benzenesulfonic acid, *disodium* salt Bayer AG		Rat LD50: > 5000 mg/kg b. w.	I: slightly irritating, eye nonirritating to skin S: *no data*	no signifi-cant findings	G: Ames test neg. CHO: SCE/ Chr. neg. C: *no incr.* incidence of tumors	no data	sensitization
78447-91-3 2,2'-(1,2-ethene-diyl)bis(5-nitro)-benzenesulfonic acid, *dipotas-sium* salt Bayer AG		Rat LD50: > 2000 mg/kg b. w.	I: nonirritating to eye nonirritating to skin S: no data	no data	G: Ames test neg. P. mut.: E. coli ques-tionable neg. C: no data	no data	

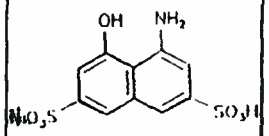
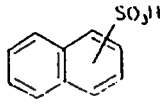
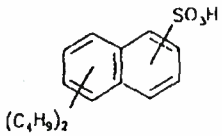
CAS No. CAS Name Company	Structural Formula	TOXICITY					Other Comments
		Acute Toxicity	Irritation (I) Sensitization (S)	Repeated Dose Toxicity	Genotoxicity (G) Carcinogenicity (C)	Reproductive Toxicity	Test Recom-mendations
DIPHENYL SULFONIC ACIDS							
2217-82-5 (1,1'-biphenyl)-4-sulfonic acid, sodium salt Bayer AG		Rat LD50: > 2000 mg/ kg b. w.	I: slightly irritating, eye nonirritating to skin S: no data	no data	G: Ames test neg. C: no data	no data	
5314-37-4 (1,1'-biphenyl)-4,4'-disulfonic acid Bayer AG		male rat LD50: >2000 mg/ kg b. w. fem. rat LD50: 1000-2000 mg/ kg b. w.	I: corrosive to eye corrosive to skin S: no data	no data	G: Ames test neg. C: no data	no data	production discontinued

2215

CAS No. CAS Name Company	Structural Formula	TOXICITY					Other Comments
		Acute Toxicity	Irritation (I) Sensitization (S)	Repeated Dose Toxicity	Genotoxicity (G) Carcinogenicity (C)	Reproductive Toxicity	Test Recom-mendations
NAPHTHALENE SULFONIC ACIDS							
81-16-3 2-amino-1-naphthalene-sulfonic acid Bayer AG		Rat LD50: > 5000 mg/kg b. w.	I: nonirritating to eye nonirritating to skin S: no data	no significant findings	G: Ames test neg. or weakly pos. MNT: neg. UDS: neg. C: no incr. incidence of tumors	no data	
87-02-5 7-amino-4-hydroxy-2-naphthalene-sulfonic acid Bayer AG		Rat LD50: > 5000 mg/kg b. w.	I: nonirritating to eye nonirritating to skin S: no data	no data	G: Ames test pos., in repeat study, neg. C: no data	no data	toxicological evaluation BG Chemie No. 226

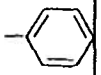
CAS No. CAS Name Company	Structural Formula	TOXICITY					Other Comments
		Acute Toxicity	Irritation (I) Sensitization (S)	Repeated Dose Toxicity	Genotoxicity (G) Carcinogenicity (C)	Reproductive Toxicity	Test Recom-mendations
90-51-7 6-amino-4-hydroxy-2-naphthalene-sulfonic acid Bayer AG		Rat LD50: > 5000 mg/ kg b. w.	I: nonirritating to eye nonirritating to skin S: no data	no data	G: Ames test pos., in repeat study, neg. C: no data	no data	toxicological evaluation BG Chemie No. 227
118-33-2 6-amino-1,3-naphthalene-disulfonic acid Bayer AG		Rat LD50: 2000 mg/ kg b. w.	I: corrosive to eye strongly irritating/ corrosive to skin S: no data	no data	G: Ames test neg. C: no data	no data	
842-18-2 7-hydroxy-1,3-naphthalene-disulfonic acid, dipotassium salt Bayer AG		Rat LD50: > 5000 mg/ kg b. w.	I: irritating to eye nonirritating to skin S: no data	no data	G: Ames test neg. C: no data	no data	

2217

CAS No. CAS Name Company	Structural Formula	TOXICITY					Other Comments
		Acute Toxicity	Irritation (I) Sensitization (S)	Repeated Dose Toxicity	Genotoxicity (G) Carcinogenicity (C)	Reproductive Toxicity	Test Recom-mendations
5460-09-3 4-amino-5-hydroxy-2,7-naphthalene-disulfonic acid, monosodium salt Bayer AG		Rat LD50: > 5000 mg/ kg b. w.	I: nonirritating to eye nonirritating to skin S: neg.	no data	G: Ames test neg. C: no data	no data	subacute toxicity
68153-01-5 naphthalene-sulfonic acids BASF AG		Rat LD50: 1400 mg/ kg b. w.	I: irritating to eye corrosive to skin S: no data	no data	G: Ames test neg. C: no data	no data	subacute toxicity
91078-64-7 branched and linear butyl derivs. naphtha-lenesulfonic acids, sodium salts Bayer AG		Rat LD50: 1790 mg/ kg b. w.	I: irritating to eye nonirritating to skin S: neg.	no serious damage	G: Ames test neg. C: no data	no data	teratogenicity

CAS No. CAS Name Company	Structural Formula	TOXICITY					Other Comments
		Acute Toxicity	Irritation (I) Sensitization (S)	Repeated Dose Toxicity	Genotoxicity (G) Carcinogenicity (C)	Reproductive Toxicity	Test Recom-mendations
ALKANE SULFONIC ACIDS							
68439-57-6 C14-16-alkane hydroxy and C14-16-alkene sulfonic acids, sodium salts Hoechst AG	$R-CH=CH-CH_2-SO_3Na$ $R = C_{n-23}H_{23-27}$ $R-\underset{\underset{OH}{\vert}}{CH}-CH_2-CH_2-SO_3Na$	Rat LD50: > 2000 mg/ kg b. w.	I: nonirritating to eye irritating to skin S: neg.	no data	G: Ames test neg. cytogenicity neg. C: no indic. of carcinogenic potential, rat p.o./dermal	rat: no effect mouse and rabbit: embryotoxic, fetotoxic, teratogenic effects	
68608-15-1 alkane sulfonic acids, sodium salts Bayer AG	alkane (SO_3Na) average chain length C_{13} - C_{15}	Rat LD50: 2000-2400 mg/ kg b. w.	I: corrosive to eye corrosive to skin S: neg.	no serious damage	G: Ames test neg. C: no data	no serious damage	

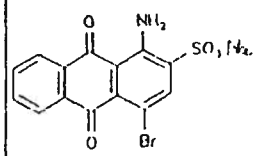
2219

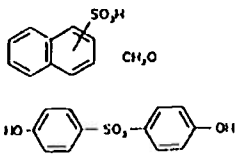
CAS No. CAS Name Company	Structural Formula	TOXICITY					Other Comments
		Acute Toxicity	Irritation (I) Sensitization (S)	Repeated Dose Toxicity	Genotoxicity (G) Carcinogenicity (C)	Reproductive Toxicity	Test Recom-mendations
91082-17-6 C10-21-alkane sulfonic acids, phenylesters Bayer AG	$H_{n+1}C_n - SO_2 - O -$ 	Rat LD50: > 15000 mg/ kg b. w.	I: nonirritating to eye nonirritating to skin S: no data	no damage to organs	G: Ames test neg. C: no data	no impair-ment of reproductive capability	
91082-29-0 C10-21-alkane sulfonyl chlorides Bayer AG	alkane (SO_2Cl) average C number 15	Rat LD50: > 15000 mg/ kg b. w.	I: slight redness, eye slightly irritating to skin S: no data	no data	G: Ames test neg. C: no data	no data	
91082-32-5 C16-34-alkane, chloro, sulfonyl chlorides Hoechst AG	alkane $(SO_2Cl)_n$	Rat LD50: > 2000 mg/ kg b. w.	I: nonirritating to eye nonirritating to skin S: no data	no data	G: no data C: no data	no data	

CAS No. CAS Name Company	Structural Formula	TOXICITY					Other Comments
		Acute Toxicity	Irritation (I) Sensitization (S)	Repeated Dose Toxicity	Genotoxicity (G) Carcinogenicity (C)	Reproductive Toxicity	Test Recom-mendations
OTHERS							
870-72-4 hydroxy-methanesulfonic acid, mono-sodium salt Bayer AG	$HO - CH_2 - SO_3Na$	Rat LD50: > 5000 mg/kg b. w. > 3200 mg/kg b. w.	I: nonirritating to eye nonirritating to skin S: neg.	subacute/inh.: incr. glucoprot. secretion, trachea; incr. lung wt.; no deaths oral: no serious damage NOEL : 200 mg/kg (rat)	G: Ames test neg. C: no data	no data	
1561-92-8 2-methyl-2-propene-1-sulfonic acid, sodium salt Hüls AG	$CH_2 = C(CH_3) - CH_2 - SO_3Na$	Rat LD50: > 5000 mg/kg b. w.	I: nonirritating to eye nonirritating to skin S: neg.	no data	G: Ames test neg. HPRT: neg MNT: neg C: no data	no data	

2221

2222

CAS No. CAS Name Company	Structural Formula	TOXICITY					Other Comments
		Acute Toxicity	Irritation (I) Sensitization (S)	Repeated Dose Toxicity	Genotoxicity (G) Carcinogenicity (C)	Reproductive Toxicity	Test Recom-mendations
3039-83-6 ethenesulfonic acid, sodium salt Hoechst AG	$CH_2=CH-SO_3Na$	Rat LD50: > 15000 mg/ kg b. w.	I: nonirritating to eye nonirritating to skin S: neg.	no data	G: Ames test neg. C: no data	no data	toxicological evaluation BG Chemie No. 247
6258-06-6 1-amino-4-bromo-9,10-dihydro-9,10-dioxo-2-anthracene-sulfonic acid, monosod. salt Bayer AG		Rat LD50: > 5000 mg/ kg b. w.	I: slightly irritating, eye nonirritating to skin S: no data	no severe effects NOEL: 40-200 mg/ kg b. w. (rat, oral)	G: Ames test (+S9) pos. (-S9) neg. MNT/UDS: neg. C: no data	no data	production discontinued
68910-45-2 alkane, chloro sulfonic acid, sodium salts Bayer AG	$(Cl)_x$--alkane(SO_3Na) average C number 21	Rat LD50: > 5000 mg/ kg b. w.	I: nonirritating to eye nonirritating to skin S: no data	no data	G: Ames test neg. C: no data	no data	production discontinued

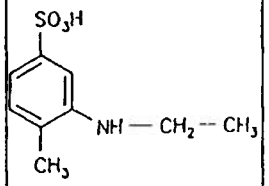
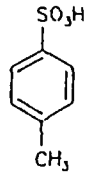
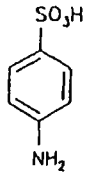
CAS No. CAS Name Company	Structural Formula	TOXICITY					Other Comments
		Acute Toxicity	Irritation (I) Sensitization (S)	Repeated Dose Toxicity	Genotoxicity (G) Carcinogenicity (C)	Reproductive Toxicity	Test Recom-mendations
94094-87-8 naphthalene sulfonic acids, reaction prod. w. formaldehyde + sulfonylbis-phenol, ammon. salts Bayer AG		Rat LD50: > 5000 mg/ kg b.w.	I: nonirritating to eye nonirritating to skin S: no data	no data	G: Ames test neg. C: no data	no data	production discontinued

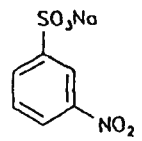
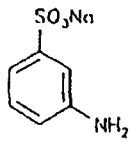
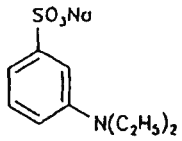
ABBREVIATIONS:

b. w.: body weight
CHO: Chinese hamster ovary cells
Chr.: chromosome
fem.: female
HPRT: hypoxanthine phosphoribosyl transferase
incr.: increased
indic.: indication
inh.: inhalation
lym.: lymphona
MNT: micronucleus test
multigener.: multigeneration
neg.: negative
P. mut.: point mutation
pos.: positive
SCE: sister chromatid exchange
teratog.: teratogenicity
UDS: unscheduled DNA synthesis

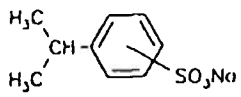
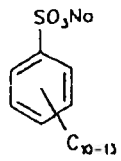
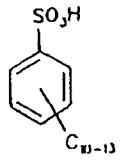
2223

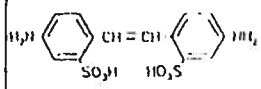
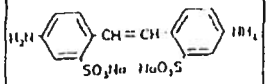
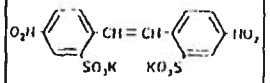
TABLE 2: ECOTOXICITY DATA OF SULFONIC ACIDS

CAS No. CAS Name Company	Structural Formula	ECOTOXICITY (Data in mg/l)				Degrada-bility	Accu-mula-tion	Other Comments Test Recom-mendations
		Toxicity to Bacteria	Toxicity to Algae	Toxicity to Daphnia	Toxicity to Fish			
BENZENE SULFONIC ACIDS								
98-40-8 3-(ethylamino)-4-methyl-benzenesulfonic acid BASF AG		EC50 17 h 190	no data	EC50 24 h 170 EC50 48 h 154	LC0 96 h > 1000 LC0 96 h 215 LC50 96 h >220 <460	< 20 % ISO < 20 % Zahn-Wellens test	log Pow -1.71	chronic daphnia toxicity
104-15-4 4-methyl-benzenesulfonic acid Hoechst AG		EC0 > 2500 (fermenta-tion tube)	no data	EC0 24 h > 2500	LC0 96 h > 500	100 % Zahn-Wellens test 30-79 % activated sludge	log Pow 0.934	
121-57-3 4-amino-benzenesulfonic acid Bayer AG		EC0 24 h 10000	no data	EC50 24 h 109.13	LC0 48 h 1000 LC50 96 h 100.4	> 90 % (mod. OECD screen; Sturm test) 55 % closed bottle test	not expect.	

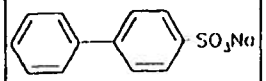
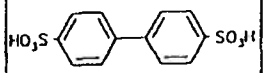
CAS No. CAS Name Company	Structural Formula	ECOTOXICITY (Data in mg/l)				Degrada-bility	Accu-mula-tion	Other Comments Test Recom-mendations
		Toxicity to Bacteria	Toxicity to Algae	Toxicity to Daphnia	Toxicity to Fish			
127-68-4 3-nitro-benzene-sulfonic acid, sodium salt BASF AG		EC50 17 h > 10000	no data	EC50 24 h 8665	LC50 48 h LC50 96 h > 500 LC50 24 h 1350	> 70 % Zahn-Wellens test	log Pow -2.61	
1126-34-7 3-amino-benzenesulfonic acid, mono-sodium salt BASF AG		EC50 17 h 7000	EC20 72 h 140 EC20 96 h 470 EC50 72/96 h > 500 EC90 72/96 h > 500	EC50 24 h 48 h > 500	LC50 96 h > 10000	> 70 % Zahn-Wellens test	log Pow -3.4	
5123-63-7 3-(diethylamino)-benzenesulfonic acid, sodium salt BASF AG		EC50 17 h 3800	EC20 72 h 130 EC50 72 h > 500 EC90 72 h > 500	EC50 24 h 48 h > 500	LC0 96 h 2200 LC100 96 h 4600	> 70% Zahn-Wellens test	low Pow -1.6	

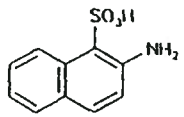
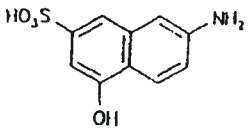
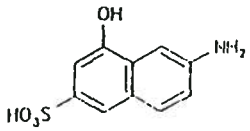
2225

CAS No. CAS Name Company	Structural Formula	ECOTOXICITY (Data in mg/l)				Degrada-bility	Accu-mula-tion	Other Comments Test Recom-mendations
		Toxicity to Bacteria	Toxicity to Algae	Toxicity to Daphnia	Toxicity to Fish			
28348-53-0 (1-methylethyl)-benzenesulfonic acid, sodium salt Hüls AG		EC10 48 h 40	no data	NOEC 21 days > 30	LC0 48 h > 1000	82.5 - 91.5 % coupled unit 94 % OECD screen 100 % Zahn-Wellens test	not expect.	
68411-30-3 C10-13-sec-alkyl derivs. benzene-sulfonic acid, sodium salts Hüls AG		EC10 18 h 50	no data	EC50 24 h 8.8 NOEC 21 days 0.3	LC50 48 h 5	76.6 - 84.2 % coupled unit 86 % OECD screen	not expect.	
85536-14-7 C10-13-sec-alkyl derivs. benzene-sulfonic acid Hüls AG		EC10 18 h 50	no data	EC50 24 h 5.9	LC50 48 h 5	41 % OECD screen 77 % coupled unit	no data	

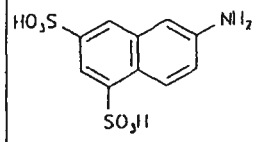
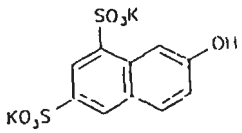
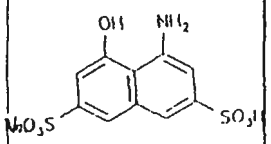
CAS No. CAS Name Company	Structural Formula	ECOTOXICITY (Data in mg/l)				Degrada-bility	Accu-mula-tion	Other Comments Test Recom-mendations
		Toxicity to Bacteria	Toxicity to Algae	Toxicity to Daphnia	Toxicity to Fish			
STILBENE SULFONIC ACIDS								
81-11-8 2,2'-(1,2-ethene-diyl)bis(5-amino)-benzenesulfonic acid Bayer AG		EC0 24 h 1000	no data	no data	LC0 48 h 200	no degrad. 5 % Zahn-Wellens test	not expect. log Pow -1.7	
7336-20-1 2,2'-(1,2-ethene-diyl)bis(5-amino)-benzenesulfonic acid, disodium salt Bayer AG		EC0 24 h 1000	no data	EC0 24 h 100	LC0 72 h > 1000	no degrad. closed bottle test Zahn-Wellens test	not expect. log Pow -1.7	toxicity to algae
78447-91-3 2,2'-(1,2-ethene-diyl)bis(5-nitro)-benzenesulfonic acid, dipotas-sium salt Bayer AG		EC50 3 h > 10000	no data	no data	LC50 96 h > 10000	no degrad. OECD screen	log Pow 0.2	

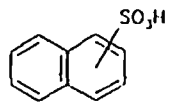
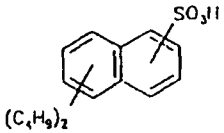
2227

CAS No. CAS Name Company	Structural Formula	ECOTOXICITY (Data in mg/l)				Degrada-bility	Accu-mula-tion	Other Comments Test Recom-mendations
		Toxicity to Bacteria	Toxicity to Algae	Toxicity to Daphnia	Toxicity to Fish			
DIPHENYL SULFONIC ACIDS								
2217-82-5 (1,1'-biphenyl)-4-sulfonic acid, sodium salt Bayer AG		EC0 3 h 5164 EC50 3 h 9131	no data	no data	LC0 24 h ≥ 5	12 % OECD screen	log Pow 2.2	toxicity to daphnia toxicity to algae degradation
5314-37-4 (1,1'-biphenyl)-4,4'-disulfonic acid, Bayer AG		EC50 3 h > 10000	no data	EC0 24 h > 1000	no data	18 % OECD screen 28 days	log Pow 0.3	production discontinued

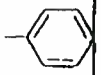
CAS No. CAS Name Company	Structural Formula	ECOTOXICITY (Data in mg/l)				Degrada-bility	Accu-mula-tion	Other Comments Test Recom-mendations
		Toxicity to Bacteria	Toxicity to Algae	Toxicity to Daphnia	Toxicity to Fish			
NAPHTHALENE SULFONIC ACIDS								
81-16-3 2-amino-1-naphthalene-sulfonic acid Bayer AG		EC50 > 10000	no data	no data	LC0 96 h 5000 LC100 96 h 7071	no degrad. OECD screen	not expect.	
87-02-5 7-amino-4-hydroxy-2-naphthalene-sulfonic acid Bayer AG		EC0 24 h 1000	no data	no data	LC0 96 h 1000	no degrad. closed bottle test	not expect.	
90-51-7 6-amino-4-hydroxy -2-naphthalene-sulfonic acid Bayer AG		EC0 24 h 500	no data	no data	LC0 48 h 1000	no degrad. closed bottle test; 9 % Zahn-Wellens test, 28 days	not expect.	

2229

CAS No. CAS Name Company	Structural Formula	ECOTOXICITY (Data in mg/l)				Degrada-bility	Accu-mula-tion	Other Comments Test Recom-mendations
		Toxicity to Bacteria	Toxicity to Algae	Toxicity to Daphnia	Toxicity to Fish			
118-33-2 6-amino-1,3-naphthalene-disulfonic acid Bayer AG		EC0 24 h 1000	no data	no data	LC0 96 h 1000	no degrad. BOD 30	log Pow -1.6	
842-18-2 7-hydroxy-1,3-naphthalene-disulfonic acid, dipotassium salt Bayer AG		EC0 24 h 10000	no data	no data	LC0 72 h ≥ 1000	no degrad. closed bottle test	not expect.	
5460-09-3 4-amino-5-hydroxy-2,7-naphthalene-disulfonic acid, monosodium salt Bayer AG		EC0 24 h 1000	no data	no data	LC0 96 h > 1000	< 10 % closed bottle test; 8 % Zahn-Wellens test	not expect. log Pow -2.3	

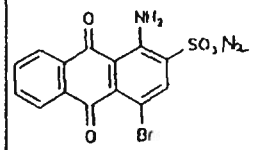
CAS No. CAS Name Company	Structural Formula	ECOTOXICITY (Data in mg/l)				Degrada-bility	Accu-mula-tion	Other Comments Test Recom-mendations
		Toxicity to Bacteria	Toxicity to Algae	Toxicity to Daphnia	Toxicity to Fish			
68153-01-5 naphthalene-sulfonic acids BASF AG		EC50 17 h 91 EC50 133	EC10 96 h 73.3 EC50 96 h 54.3	EC50 24 h 85 EC50 48 h 34	LC50 96 h 100-500	> 60 % mod. OECD conf.	log Pow -0.94	
91078-64-7 branched and linear butyl derivs. naphtha-lenesulfonic acids, sod. salts Bayer AG		EC0 24 h 500	no data	no data	LC0 48 h 20 LC100 48 h 100	no degrad. closed bottle test	not expect.	Zahn-Wellens test

CAS No. CAS Name Company	Structural Formula	ECOTOXICITY (Data in mg/l)				Degrada-bility	Accu-mula-tion	Other Comments Test Recom-mendations
		Toxicity to Bacteria	Toxicity to Algae	Toxicity to Daphnia	Toxicity to Fish			
ALKANE SULFONIC ACIDS								
68439-57-6 C14-16-alkane hydroxy and C14-16-alkene sulfonic acids, sodium salts Hoechst AG	$R-CH=CH-CH_2-SO_3Na$ $R = C_{11-23}H_{23-27}$ $R-CH(OH)-CH_2-CH_2-SO_3Na$	ferment. tube 24 h > 2500 EC50 3 h 230 act. sludge EC50 24 h 1250 4000 > 5000	no data	no data	LC50 96 h 4.2 LC50 48 h 96 h 1 - 10	90 % 70 % 83 % Zahn-Wellens test	not expect.	
68608-15-1 alkane sulfonic acids, sodium salts Bayer AG	alkane (SO_3Na) average chain length C_{13} - C_{15}	EC50 3 h 278	no data	EC0 24 h 8.8 EC50 24 h 53.1	LC0 96 h 5	> 90 % OECD conf. test > 60 % BOD 28	not expect.	long-term study on fish u. e.

CAS No. CAS Name Company	Structural Formula	ECOTOXICITY (Data in mg/l)				Degrada-bility	Accu-mula-tion	Other Comments Test Recom-mendations
		Toxicity to Bacteria	Toxicity to Algae	Toxicity to Daphnia	Toxicity to Fish			
91082-17-6 C10-21-alkane sulfonic acids, phenylesters Bayer AG	$H_{n+1}C_n - SO_2 - O -$ 	EC50 > 10000	no data	no data	LC0 96 h 100	> 70 % closed bottle test	log Pow > 6	hydrolysis u. e.
91082-29-0 C10-21-alkane sulfonyl chlorides Bayer AG	alkane (SO_2Cl) average C number 15	EC50 3 h > 10000	no data	EC0 24 h 88 EC100 24 h 354	no data	> 90 % closed bottle test	not expect.	
91082-32-5 C16-34-alkane, chloro, sulfonyl chlorides, Hoechst AG	alkane $(SO_2Cl)_n$	sat. soln. without results (fermenta-tion tube)	no data	no data	LC50 96 h > 500	68 % respirometer test	log Pow > 6.5	toxicity to algae toxicity to daphnia

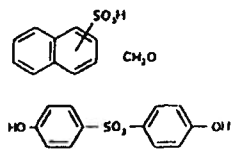
2233

CAS No. CAS Name Company	Structural Formula	ECOTOXICITY (Data in mg/l)				Degrada-bility	Accu-mula-tion	Other Comments Test Recom-mendations
		Toxicity to Bacteria	Toxicity to Algae	Toxicity to Daphnia	Toxicity to Fish			
OTHERS								
870-72-4 hydroxy-methanesulfonic acid, monosod. salt Bayer AG	$HO - CH_2 - SO_3Na$	EC0 30 min 500	EC0 7 days < 100	EC50 96 h 10-100	LC0 96 h > 100	80 % closed bottle test	log Pow -1.6	
1561-92-8 2-methyl-2-propene-1-sulfonic acid, sodium salt Hüls AG	$CH_2=C(CH_3)-CH_2-SO_3Na$	EC10 18 h 29.7	no data	no data	LC0 48 h > 1000	2 % coupled unit, 19 % OECD screen	not expect.	

CAS No. CAS Name Company	Structural Formula	ECOTOXICITY (Data in mg/l)				Degrada-bility	Accu-mula-tion	Other Comments Test Recom-mendations
		Toxicity to Bacteria	Toxicity to Algae	Toxicity to Daphnia	Toxicity to Fish			
3039-83-6 ethenesulfonic acid, sodium salt Hoechst AG	$CH_2 = CH - SO_3Na$	EC0 24 h 5000	no data	no data	LC0 24 h > 500	> 90 % respirometer test	log Pow -1.04	
6258-06-6 1-amino-4-bromo-9,10-dihydro-9,10-dioxo-2-anthracene-sulfonic acid, monosod. salt Bayer AG		EC0 10000	no data	no data	LC0 48 h 200	30-40 % closed bottle test 69 % Zahn-Wellens test	not expect.	production discontinued
68910-45-2 alkane, chloro sulfonic acid, sodium salts Bayer AG	$(Cl)_x$--alkane(SO_3Na) average C number 21	EC0 24 h 1000	no data	no data	LC0 48 h 5	> 60 % closed bottle test > 70 % OECD conf. test	not expect.	production discontinued

2235

2236

CAS No. CAS Name Company	Structural Formula	ECOTOXICITY (Data in mg/l)				Degrada-bility	Accu-mula-tion	Other Comments Test Recom-mendations
		Toxicity to Bacteria	Toxicity to Algae	Toxicity to Daphnia	Toxicity to Fish			
94094-87-8 naphthalene sulfonic acids (reaction prod. w. formaldehyde + sulfonylbis-phenol), ammon. salts Bayer AG		EC50 3 h > 100	no data	no data	LC0 48 h > 10	10 % closed bottle test	not expect.	toxicity to fish, toxicity to daphnia Zahn-Wellens

ABBREVIATIONS:

act.: activated
BOD: biological oxygen demand
conf.: confirmatory
degrad.: degradation
expect.: expected
ferment.: fermentation
mod.: modified
sat. soln.: saturated solution
u.e.: under evaluation