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Published online August 16, 2005

Barium and High Explosives in a Semiarid Alluvial System, Cañon de Valle, New Mexico

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ABSTRACT

Concentrations and distributions of Ba, a component of the high explosive baritol, and RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine), a high explosive, were evaluated from 1996 to 2002 within a semiarid alluvial system in Cañon de Valle, New Mexico. A high explosive machining facility discharged effluent containing these chemicals to the canyon from 1951 to 1996. The connectivity between alluvial groundwater, surface water, and sediment was specifically addressed to understand the distributions and dynamics of Ba and RDX in the alluvial system. Surface water, groundwater, and sediment were characterized by conducting hydrologic measurements, geomorphic mapping, and collecting samples. Barium and RDX in sediment preferentially reside in fine-grained deposits that represent the suspended load redeposited on floodplains following channel scour. However, RDX and Ba show markedly different behaviors in surface water and alluvial groundwater because of contrasting geochemical characteristics and transport mechanisms. Barium precipitates in sediments as barite and witherite and readily sorbs to sediment minerals. Therefore, sediment transport is an important control on its distribution in the canyon. In contrast, RDX appears to occur predominantly in the dissolved phase, behaves conservatively, and is most significant in groundwater. There is a strong correlation between RDX concentrations in water and the saturated thickness of the alluvial aquifer. During prolonged wet periods, the alluvial aquifer enlarges, causing more RDX to be mobilized within the alluvial system. Subsurface processes in the alluvial aquifer are therefore most important in controlling present RDX transport, whereas surface processes associated with floods are most important in controlling Ba transport.

High explosives are contaminants of interest at many active and inactive installations that support weapons production. High explosive production sites are widespread across the United States and the world and represent potential sources of widespread high explosive contamination to the environment. High explosives contamination is also associated with firing sites, but at these sites contamination is often difficult to precisely locate and heterogeneously distributed. Many previous environmental studies of high explosives focused on remediation technologies, including biodegradation (Sheremata and Hawari, 2000; Beller, 2002; Rainwater et al., 2002; Pudge et al., 2003; Ringelberg et al., 2003; Zhang and Hughes, 2003; Beller et al., 2004), phytoremediation (Sikora et al., 1997; Best et al., 1999; Bhadra et al., 2001), constructed wetlands (Best et al., 1999), zero-valent iron (Comfort et al., 2003), and monitored natural attenuation (Pennington et al., 2001).

Identifying the key surface and subsurface transport processes of high explosive contamination is critical to modeling transport and predicting contaminant concentrations in environmental media (Pennington and Brannon, 2002). However, we are unaware of any studies that have focused on high explosives and Ba contamination in alluvial and vadose zone canyon settings. In addition, studies that have examined contaminants in alluvial canyon settings do not typically consider all of the hydrogeomorphic components (e.g., surface water, groundwater, unsaturated bedrock, and canyon bottom soils and sediments). Previous studies of contaminated mining sites have partially focused on hydrologic connections between groundwater and surface water, as well as the role of contaminant exchange between the two (e.g., Fuller and Harvey, 2000; Winde and van der Walt, 2004). However, these do not explicitly include interactions between the unsaturated zone, canyon bottom sediments, and the surface water and groundwater systems. A geomorphic approach has proven effective in identifying the sources and distribution of contaminants in river valleys (Rowan et al., 1995; Hudson-Edwards et al., 2001; Marcus et al., 2001; Miller et al., 2003) and semiarid canyons (Katzman et al., 1999; Reneau et al., 1998, 2004; Ryti et al., 2005). Thus, a combination of hydrologic and geomorphic sampling and analysis was thought to be a more complete way of assessing high explosive contaminant extent, distribution, and transport. The objective of this study was to use a combined geomorphic and hydrologic approach to determine the extent and distribution of high explosive–related compounds in a semiarid alluvial canyon environment to support potential remedial actions. The connectivity between groundwater, surface water, and sediment was specifically addressed to understand the distributions and dynamics of Ba, a component of the high explosive baritol, and RDX in the alluvial system. Using this approach, relationships between contaminants in sediment, surface water, and groundwater were revealed. This knowledge can also be applied to improve the implementation of remedial actions in similar contaminated systems.

BACKGROUND

Los Alamos National Laboratory (LANL) was established in the early 1940s with the primary goal of producing

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Published in Vadose Zone Journal 4:744–759 (2005).
Special Section: Los Alamos National Laboratory
doi:10.2136/vzj2004.0174
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Abbreviations: AW, alluvial well; bgs, below ground surface; FOC, fraction of organic C; LANL, Los Alamos National Laboratory; SEM, scanning electron microscopy; SP, stream profile; TA, Technical Area; XRF, X-ray fluorescence.

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nuclear weapons. One legacy of these activities is environmental contamination. This study focused on a semiarid canyon within Technical Area (TA)-16 of LANL contaminated with high explosives (Fig. 1). TA-16 was established during World War II for the development of explosive formulations, production and machining of explosive charges, and the assembly and testing of explosive components for the U.S. nuclear weapons program. Most of the high explosive machining activities were completed in the TA-16-260 facility. Machine turnings and high explosive wastewater were routed as waste to 13 outdoor sumps associated with the building. Historically, discharge from the sumps was routed to an outfall located on the southern edge of a narrow canyon (Cañon de Valle). The outfall was used since 1951 and was deactivated in November 1996. Discharge measurements from the early 1990s show that releases were several million liters per year (LANL, 2003a). Once discharges were stopped, surface flow in the outfall area and channel into Cañon de Valle was limited to overland flow, primarily in response to spring snowmelt and to runoff events associated with the summer rainy season. Within Cañon de Valle just downstream from the outfall, there is an approximately 1000-m-long reach of perennial surface flow. The mean annual flow is approximately 0.5 L s^{-1}, the average depth of the active channel is 0.25 m, and the average width is approximately 0.5 m (Fig. 2) (LANL, 2003a). The photograph in Fig. 2 was taken in June 2000 following a 16-mm precipitation event. Flattened grasses and debris on the floodplain indicate overbank flooding occurred during this event.

The outfall is the primary source of contamination to the Cañon de Valle alluvial system, although characterization data indicate a secondary upstream source from an old landfill that contains high explosives (LANL, 2003a). The outfall, the drainage channel below the outfall, and the canyon bottom, as well as surface water, alluvial groundwater, and deep perched groundwater

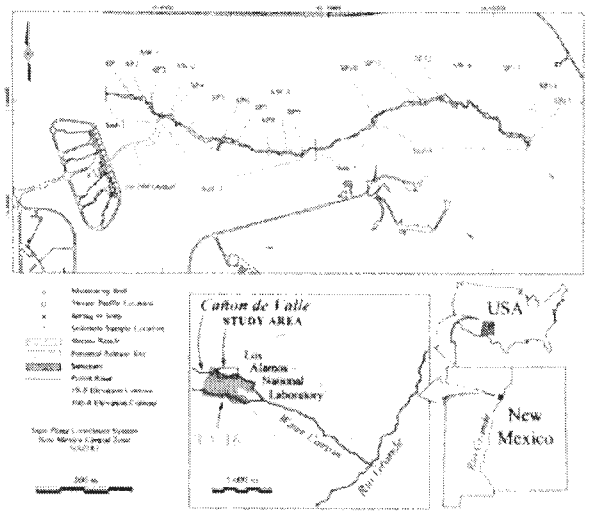

Fig. 1. Location of the study area within LANL, New Mexico, and the locations of the TA-16-260 outfall, stream monitoring stations, alluvial wells, and springs in Cañon de Valle.

are contaminated with high explosive wastes, including RDX, HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine), TNT (2,4,6-trinitrotoluene), and Ba (LANL, 2002, 2003a). The Ba contamination results from a high explosive, baritol, which is a mixture of $Ba(NO_3)_2$ and TNT. This paper focuses on Ba and RDX, which typically have the highest contaminant concentrations in the canyon.

Geochemical Properties of Barium and RDX

An important part of understanding the hydrogeological and contaminant transport mechanisms involves evaluating the chemical and physical properties of the contaminants and their behavior in the environment. Specific properties include the degree of saturation, the potential for ion exchange (Ba) or sorption (e.g., RDX on natural organic carbon or Ba on clays, iron oxides, or manganese oxides), and the potential for natural bioremediation (LANL, 2003a, 2003b).

RDX

The USEPA health advisory limit for RDX in drinking water is 2.0 μg L^{-1} (USEPA, 2000). This limit is quite low, highlighting the importance of understanding how environmental conditions will affect the stability and transport of RDX. The high specific gravity of RDX indicates that most of the RDX particulates from high explosive machining were likely deposited near the TA-16-260 outfall and former settling pond, rather than carried into Cañon de Valle. This is consistent with contaminant concentration data that show localized zones with high explosive concentrations in the outfall area of a few weight percent (LANL, 1999, 2003a). Such high concentrations have not been observed in Cañon de Valle (LANL, 2003a). The solubility of RDX is relatively high (between 42 and 60 mg L^{-1} at 25°C) (Layton et al., 1987; Card and Autenrieth, 1998), and surface water and alluvial groundwater concentrations in the canyon are typically two or more orders of magnitude lower than the solubility limit, suggesting that most of the transport into and especially within the canyon is in the dissolved phase.

Dissolved high explosives in groundwater will partition between a soluble and a sorbed phase. The dissolution rate of high explosives is dependent on surface area, temperature, and mixing rate. In a bench-top study, the diffusivity of RDX in water was determined to be 2.2×10^{-6} cm^2 s^{-1} (Lynch et al., 2002). Once in solution, RDX will interact with particles in the canyon alluvium. Particles derived from the local rhyolitic tuff bedrock, dacitic volcanic rocks from upstream, and erosion of local soils (in part derived from eolian input), are present within the alluvium. RDX has been found to have a low sorption capacity for sediments (Singh et al., 1998; Sheremata et al., 2001), but a higher sorption capacity for organic C (Layton et al., 1987). Thus, the amount of RDX adsorption will largely be controlled by the amount of organic C in the soils and sediments (Layton et al., 1987). Although the fraction of organic C (FOC) in the Cañon de Valle alluvium was not measured, FOC data

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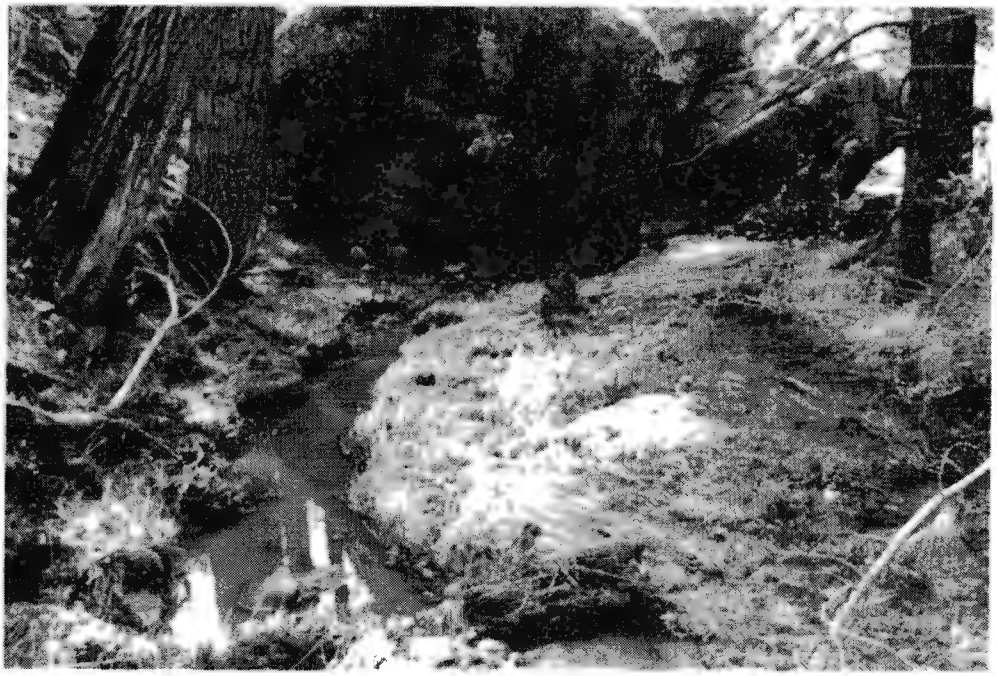

Fig. 2. Cañon de Valle main channel looking downstream. Channel is approximately 0.5 m wide. Photograph was taken in June 2000 following a 16-mm rainstorm.

have been obtained in a hydrologically and ecologically similar canyon 2 km north of Cañon de Valle (Reneau et al., 1998). In this canyon, FOC ranges from 0.1 to 5% Finer fractions, like fine sand and silt, that are representative of floodplain deposits tend to be in the higher end of the FOC concentration range (e.g., 2–5%), but FOC in the medium sand and larger fractions representative of channel deposits tend to be in the lower end of that range (e.g., 0.1–2%). Thus, it is likely there is some RDX adsorption in the canyon, although this is expected to be minor relative to the amount of dissolved RDX.

The potential for biodegradation is another chemical property important in the long-term environmental fate of high explosives (Pudge et al., 2003; Ringelberg et al., 2003; Zhang and Hughes, 2003). The biodegradation of RDX in the environment occurs both aerobically and anaerobically (Rosenblatt et al., 1991). Anaerobic degradation rates are typically greater than aerobic rates (Layton et al., 1987; Sheremata and Hawari, 2000). In either pathway, nutrient concentrations are also important. In subsurface regions at Los Alamos, including the mesa vadose zone, canyon alluvium, and alluvial groundwater, the rate of natural biodegradation of RDX is likely to be low, given the infrequency of appropriate anaerobic conditions and low organic C and nutrient concentrations. Favorable anaerobic conditions in canyon alluvium are limited in space and time (LANL, 2003a; Newman et al., 2002), and the adjacent tuff vadose zone is largely oxidizing. The variability of reducing conditions in semiarid alluvial aquifer systems such as this one is largely controlled by oxygenation during recharge and subsequent depletion of dissolved oxygen as a result of biological activity between recharge events, and by spatial variations in organic C content (Groffman and Crossey, 1999). RDX breakdown products have only been detected occasionally and at concentrations slightly above detection limits (LANL, 2003a).

RDX can also degrade through photolysis; however, the rate of degradation is very slow (Hawari et al., 2002). RDX can also degrade through an inorganic hydrolysis reaction (Layton et al., 1987). Groundwater and surface water in Cañon de Valle typically have pH values that are high enough that hydrolysis may be important in the long term.

Despite the possible breakdown pathways of RDX, it is generally viewed to be much more recalcitrant than some of the other types of high explosives (e.g., TNT). It is difficult to break down and can be quite mobile in low organic C environments. To illustrate the mobile behavior of RDX in the Cañon de Valle area, sampling of a perched aquifer approximately 230 m below ground surface (bgs) at TA-16 detected RDX at concentrations between 12 and 84 $\mu g\ L^{-1}$ (LANL, 1999).

Barium

The EPA drinking water standard for Ba is 1000 $\mu g\ L^{-1}$ (EPA, 2000). In contrast to RDX, which does not dissociate in water, barium nitrate ($Ba[NO_3]_2$) readily dissociates into the barium cation and nitrate anion. However, because of low solubility, Ba has the potential to form solid-phase minerals, including barite ($BaSO_4$) and witherite ($BaCO_3$). If these minerals form, they have the potential to limit the extent of Ba mobility and may also act as an important control on sediment vs. water Ba distributions (Hickmott et al., 1997).

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Barium has an affinity for adsorption on clays, oxides, and hydrous oxides, with literature values for equilibrium sorption coefficients in soil ranging up to 2800 mL g^{-1} (Li and Chan, 1979). Clay content in the fine-grained floodplain sediment in Cañon de Valle averages about 11%. The fine-grained sediment deposits in Cañon de Valle contain the highest contaminant inventories, indicating that the clay content of the fine-particle size fraction may be important in affecting the distribution of Ba (LANL, 2003a). Barium sorption on clay and oxide minerals occurs by ion exchange and chemisorption, with sorption on clays primarily through ion exchange. Furthermore, Ba sorption on clay is thought to be irreversible under natural conditions. Consequently, ion exchange of Ba on natural clay can serve as a means of immobilizing Ba or retarding its movement in the environment. Differences between the chemical behaviors of Ba and RDX provide a rationale for distributions of metals and organic chemicals in the Cañon de Valle alluvial system.

METHODS

Barium and RDX concentrations in soil, sediment, and water were evaluated from 1996 to 2002 within the Cañon de Valle alluvial system. Surface water, alluvial groundwater, active channel sediments, and floodplain sediments were characterized along a 2- to 4-km-long reach of canyon downstream from the TA-16-260 facility. Surface water and alluvial groundwater were characterized by conducting stream discharge profiles, installing shallow alluvial wells, and collecting samples for analysis. Active channel sediments and floodplain sediments were characterized by mapping depositional units, determining sediment thickness and volume, and collecting samples for analysis. Chemical data were analyzed by media type, and connections between different media were evaluated. Details of these sampling and measurement activities are provided below.

Surface Water Discharge Measurements

In Cañon de Valle there are 15 gauging stations (identified as Stream Profile [SP] 2 through SP16) established along a 1.8-km stretch of canyon (Fig. 1). Surface water discharge was calculated using stage measurements from a portable Parshall flume or were measured directly by collecting water in a calibrated-volume container and measuring the container fill rate with a stopwatch. In addition to the stream profile locations, two springs, Burning Ground spring and SWSC spring, were also monitored. The mean annual spring discharge is 0.25 L s^{-1} for Burning Ground spring and 0.03 L s^{-1} for SWSC spring. At each gauging station, field parameters (discharge, pH, conductivity, and temperature) were measured quarterly or in response to specific flow events.

Alluvial Well Measurements

Four shallow alluvial wells (AW) were drilled in the fall of 1997 and are designated AW-1 through AW-4 (Fig. 1). AW-1 is located 60 m upstream of the TA-16-260 outfall and downstream of the secondary contaminant source from the old landfill. AW-2 is located immediately downstream of the confluence of the TA-16-260 outfall and Cañon de Valle. AW-3 is located 460 m downstream of the outfall and downstream of SWSC and Burning Ground springs. AW-4 is located approximately 1100 m downstream from the outfall. The average hydraulic gradient is approximately 0.038 m m^{-1} between the four monitoring wells (LANL, 2003b). All wells were drilled to a total depth of approximately 3 m bgs and screened across the sediment–tuff interface. The wells are 5- or 10-cm diameter polyvinyl chloride and screened in the bottom 1.5-m interval. The canyon bottom alluvium is composed predominately of coarse sands and gravels with some secondary fine sands and silts. In June 1999, each well (with the exception of AW-2) was equipped with a battery-powered data logger to continuously record water level, conductivity, and temperature.

Analytical Methods for Water Samples

The samples were collected following EPA protocols and were analyzed at off-site laboratories for alkalinity, anions and perchlorate, metals, nitrate and nitrite, nitrogen isotopes, low-level tritium, hydrogen isotopes, oxygen isotopes, volatile organic compounds, total uranium, high explosives, and high explosive breakdown products, such as amino-2,6-dinitrotoluene[4-]; amino-4,6-dinitrotoluene[2-]; hexahydro-1-nitroso-3,5-dintro-1,3,5-triazine (MNX); hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine (DNX); and hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine (TNX). Once a year samples were collected and analyzed for semivolatile organic compounds. All samples were unfiltered with the exception of samples for metals analysis, which included both a filtered and an unfiltered sample. Only Ba and RDX results are discussed in this paper.

Sediment Investigations

Sediment investigations focused on characterizing the concentrations, distribution, and inventory of Ba and RDX in sediment deposits on floodplains and on abandoned channels, and in identifying spatial and temporal variations in these analytes in coarser-grained sediment in the active channel. Forty active channel samples were collected in 1996 along 3.5 km of channel before discharges from the TA-16-260 outfall were discontinued, and nine of these locations were resampled in 2002. Geomorphic units in the bottom of Cañon de Valle were mapped and sampled in 1999 to characterize the occurrence and distribution of contaminants across the width of the canyon bottom, particularly in fine-grained sediment deposits outside the active channel. Soil pits were dug in each geomorphic unit to determine the texture and thickness of sediment deposits that postdate initial releases from the TA-16-260 outfall. One or more layers from each soil pit were screened for Ba using X-ray fluorescence (XRF) analyses, and a subset of these layers were screened for RDX using field immunoassay kits. A subset of the screened layers were then submitted for off-site laboratory analysis, with their number and locations determined using statistical methods to ensure accurate estimates of contaminant inventory. Representative sediment samples were collected and analyzed from each geomorphic unit. Approximately 1.3 km of Cañon de Valle was mapped downstream from the TA-16-260 outfall, supplemented by additional investigation upstream, and field screening was completed on a total of 59 samples at 23 locations. Thirty of these samples were analyzed for high explosives, metals, and particle-size distribution. Data on contaminant concentration were combined with data on the area, density, and average thickness of sediment in different geomorphic units to estimate contaminant inventory in a series of reaches and evaluate the spatial distribution of contaminants.

In addition to the geomorphic characterization described above, 17 sediment and soil samples were also analyzed using scanning electron microscopy (SEM) and XRF. Polished thin sections were cut from grain mounts and C coated for analysis.

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The objective of the SEM analyses was to look for evidence of Ba precipitation in the canyon sediments.

RESULTS

During the study period from 1998 to 2002, the average annual precipitation was 373 mm, approximately 100 mm below a long-term average of 470 mm for the site (Bowen, 1990).

Alluvial Groundwater

Time-series plots of RDX and Ba concentration data from alluvial groundwater samples collected in Cañon de Valle from 1998 to 2002 are shown in Fig. 3A and 3B. Several key points are apparent from these plots:

- RDX trends are generally stable to slightly decreasing with time, with occasional periods of higher concentration. However, AW-2 is an exception, and the highest concentrations of RDX were measured in samples from AW-2 just down gradient of the TA-16-260 outfall.
- RDX concentrations in samples from AW-4 (located the greatest distance downstream from the outfall) are consistently higher than AW-1 and AW-3, indicating that that there is no down canyon trend of decreasing concentration.
- Barium concentration trends through time are generally stable, with AW-3 showing a slight decreasing trend. Periods of higher concentration are most likely associated with the redistribution and mobilization of Ba in the system.
- The highest Ba concentration (center of mass) was observed in AW-3, downstream of Burning Ground spring and approximately at the midpoint of the study area. The Ba concentrations of spring water are typically below 500 μg L^{-1}, which is lower than all of the alluvial well values. The lowest concentration of Ba is observed in AW-1, upstream of the outfall, followed by AW-4.

RDX and Ba concentrations in AW-4 as a function of saturated thickness between 1998 and 2002 are shown in Fig. 4A and 4B. For Ba there does not appear to be a correlation between the saturated thickness and concentration, but for RDX a strong positive correlation is evident (R^2 = 0.93). This contrast indicates different behaviors for Ba and RDX in the alluvial system, with mobility of RDX increasing with rises in the alluvial water table. The natural conditions do not favor RDX degradation and RDX appears to be quite mobile in response to seasonal moisture inputs. The vadose zone serves as a continued source of RDX. Flushing of the vadose zone may mobilize RDX by releasing stored inventory. The flushing of the vadose zone does not directly affect the concentration of Ba in the alluvial system. The high concentrations and presence of Ba minerals in the sediment buffer changes in Ba concentrations in water.

Surface Water

Results for Ba and RDX concentrations for a high-flow and a low-flow event are shown in Fig. 5A, 5B, 6A, and 6B. These two events were selected because they were representative of the trends observed during other stream profile sampling events. These figures show alluvial groundwater, spring, and surface water contaminant concentrations, and surface discharge as a function of distance from the TA-16-260 outfall. Three of the four years during the study period had below average annual precipitation; only 2 of 13 stream profiles were conducted under high flow conditions. The following generalizations can be made regarding surface water concentrations and how they differ from alluvial groundwater concentrations (Fig. 5 and 6):

- RDX concentrations in groundwater were higher (up to 759 μg L^{-1}) during the high flow event than during the low flow event.
- RDX concentrations in surface water were higher (up to 150 μg L^{-1}) during the high flow event, and, unlike low flow event data, did not show decreasing concentrations downstream.
- During low flow, RDX concentrations were relatively low, with the highest concentrations occurring in surface water near the TA-16-260 outfall. Below Burning Ground spring the concentrations were <25 μg L^{-1}.
- The RDX data show higher RDX concentrations in surface water during spring snowmelt conditions.
- Barium concentrations are consistently lower in surface water than in alluvial groundwater. Concentrations in surface water are relatively insensitive to high vs. low flow conditions.
- Based on the Ba concentrations, surface water and alluvial groundwater do not appear to mix extensively until near AW-4.
- Surface discharge measurements suggest that during low flow conditions, the stream loses surface water downstream of Burning Ground spring. However, during high flow conditions there is an apparent gaining reach beginning approximately 1065 m down gradient.

Average Cañon de Valle RDX and Barium Trends in Water

To summarize the trends in water data during the study period, the study area was divided into reaches, and average concentrations were calculated for each reach. The reaches are as follows, (A) upstream of TA-16-260 outfall, (B) outfall to Burning Ground spring, (C) Burning Ground spring confluence to SP9, and (D) SP10 through SP16. The springs, alluvial wells, and surface water monitoring stations for each reach are listed in Table 1.

To further investigate contaminant trends and the potential relationships between alluvial groundwater and surface water, average Ba and RDX concentrations for each reach were calculated and plotted as a function of distance from the TA-16-260 outfall (Fig. 7A and 7B).

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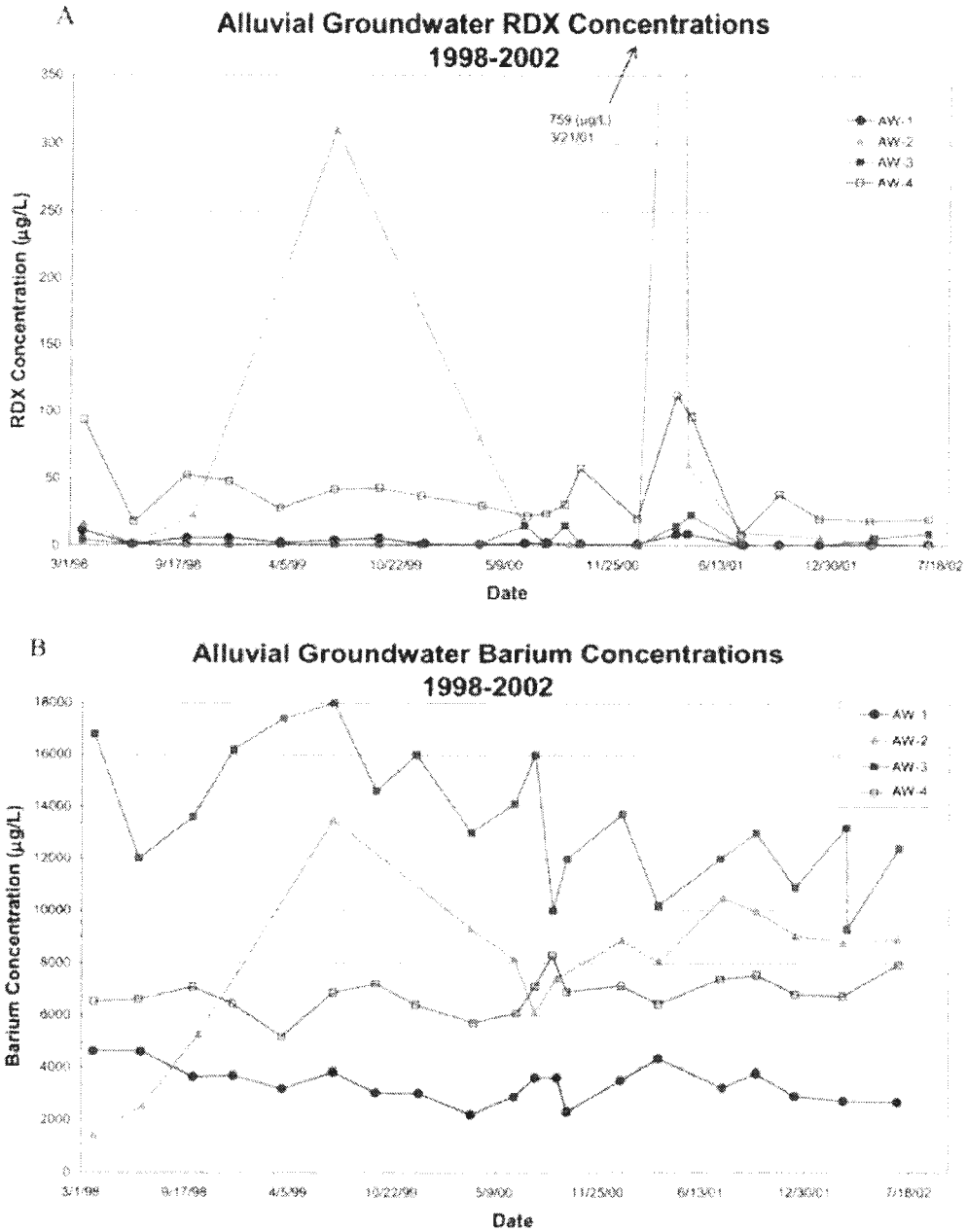

Fig. 3. (A) RDX and (B) Ba concentration results for the four alluvial groundwater wells from 1998 to 2002.

The following generalizations can be made based on these graphs:

1. Average RDX concentration in alluvial groundwater is lower than in surface water. This is in contrast to Ba, which is higher in the alluvial groundwater.
2. Average RDX concentration in both the surface and alluvial groundwater follow the same trends down canyon, peaking near the TA-16-260 outfall, decreasing down canyon and then slightly increasing at the final reach.
3. Average Ba concentrations in alluvial groundwater increase down canyon to approximately 0.5 km from the outfall, then decrease to the final reach. The Ba center of mass is near AW-3.
4. Average Ba concentration in surface water follows an opposite trend, decreasing down canyon, then slightly increasing in the final reach.

Sediments

Average Ba and RDX concentrations in the active channel sediments and fine-grained floodplain sedi-

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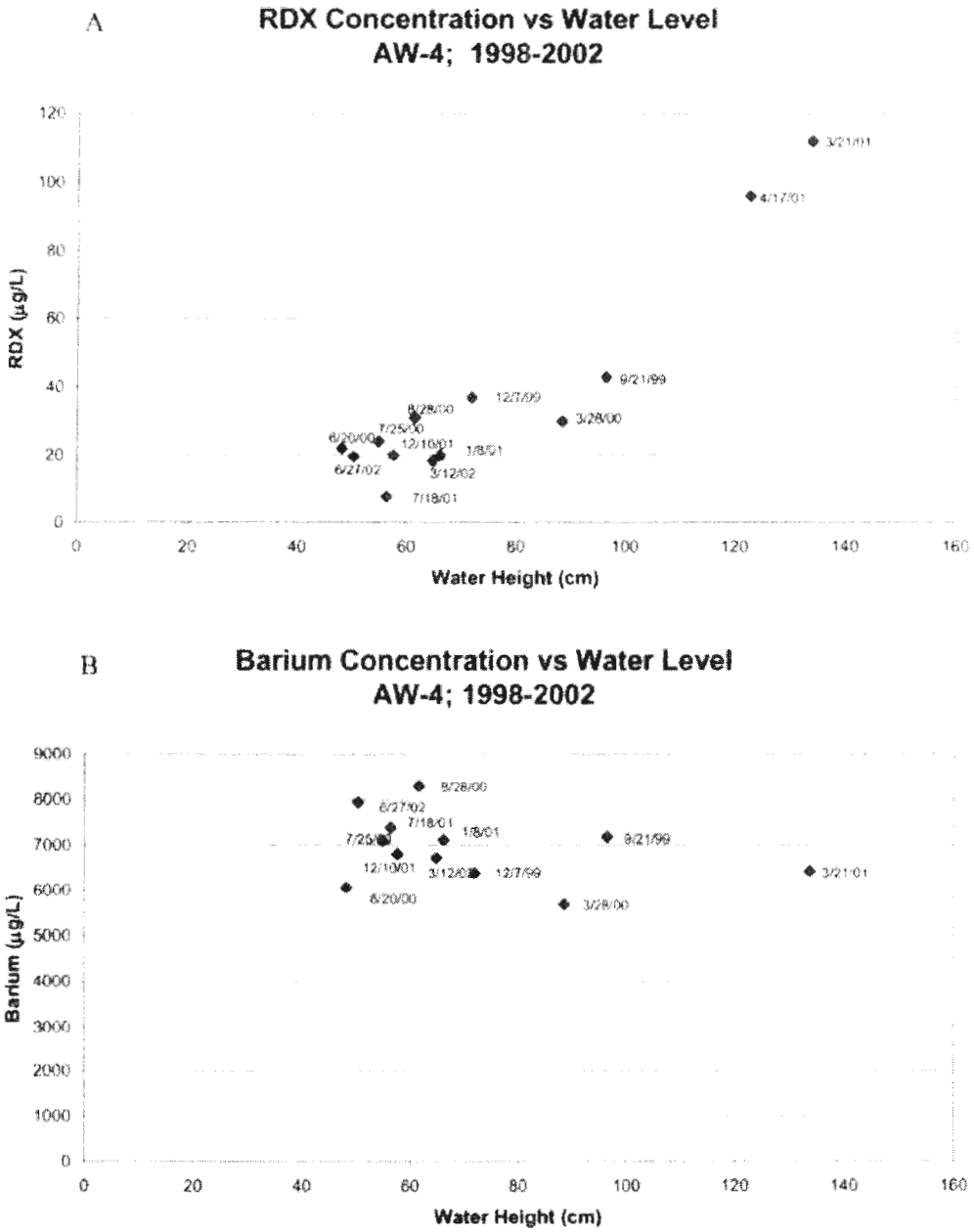

Fig. 4. (A) RDX and (B) Ba concentrations as a function of water height in alluvial well, AW-4, 1998 to 2002.

ments as a function of the distance from the outfall are presented in Fig. 8A and 8B. Higher concentrations of both Ba and RDX are found in fine-grained sediments than in the active channel, consistent with sorption onto fine particles and preferential redeposition onto floodplains during floods. Comparison of Ba and RDX in the active channel sediments in 1996 and 2002 shows a dramatic decrease in their concentration near the TA-16-260 outfall following the cessation of discharges in 1996.

Analyses of sediment samples from Cañon de Valle reaches were used to estimate average Ba and RDX concentrations in each geomorphic unit in these reaches. These estimates were combined with data on the area, density, and average thickness of sediment in different geomorphic units to estimate contaminant inventory in each reach. The sediment reaches roughly correspond to the water reaches. The partial noncorrespondence is because of different emphases during the course of the project. The characteristics of the sediment reaches are listed in Table 2.

An estimate of the total inventory of Ba in near-surface sediment deposits in Cañon de Valle was made by using available data and extrapolating to nonsampled

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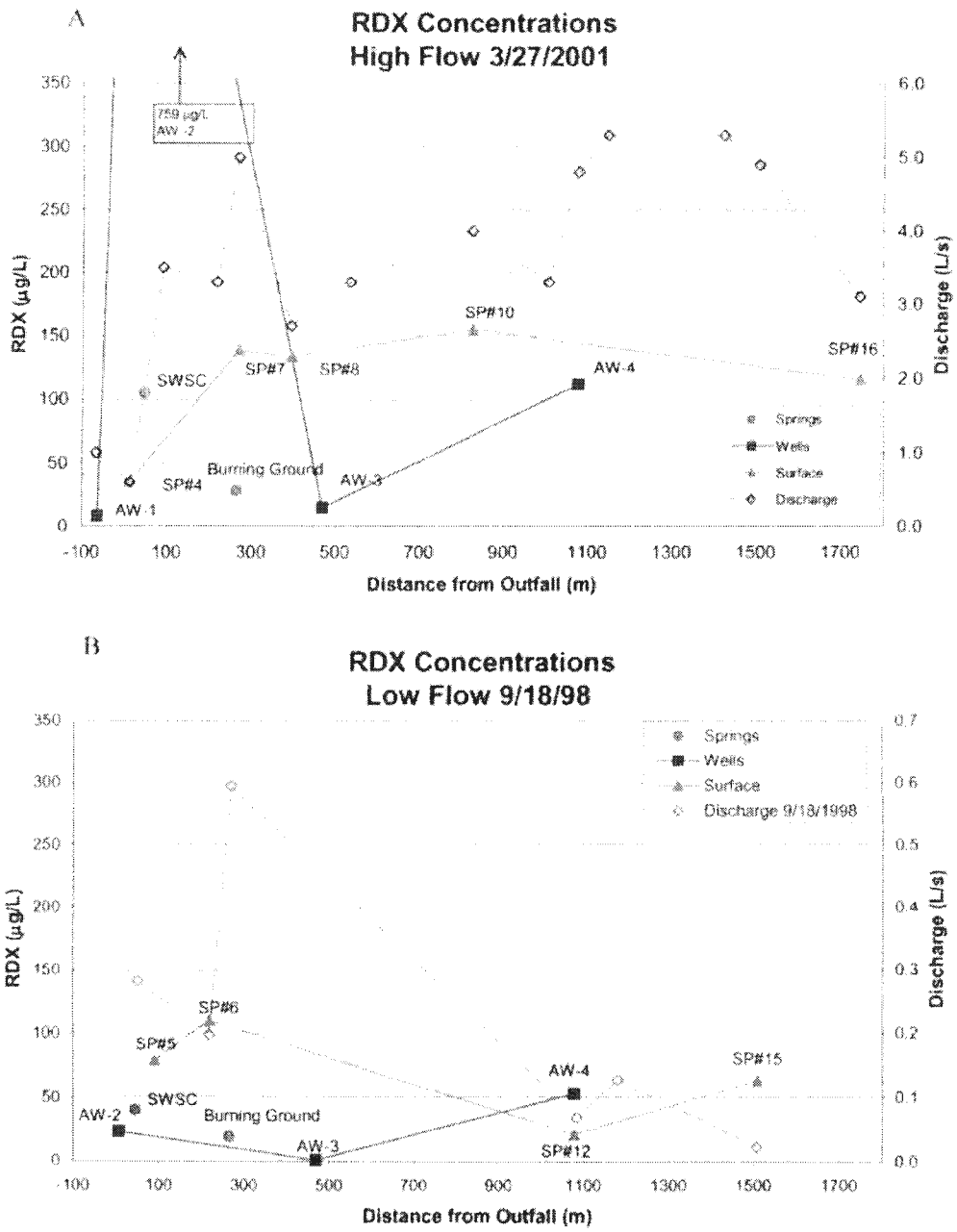

Fig. 5. Concentrations of RDX in surface water, alluvial groundwater, and spring water during high flow (A, 27 Mar. 2001) and low flow (B, 18 Sept. 1998) conditions.

reaches. A total of about 21 000 kg of Ba is estimated to have been in sediment in the study reaches in 1999. About 62% is estimated to have been stored in fine-grained sediment deposits outside the active channel, about 10% in the active channel, and the remainder in coarse-grained deposits in abandoned channel units. Upstream of the TA-16-260 outfall, the Ba concentration in fine-grained sediments was elevated, but was three to four times lower than downstream of the outfall. Downstream of the TA-16-260 outfall, the highest Ba inventory was in fine-grained sediments. The lowest inventory was in coarse-grained active channel sediments (Fig. 9A and 9B).

Detailed SEM and XRF analysis of sediments collected in Cañon de Valle showed the presence of solid phase Ba. Barium occurred primarily as witherite (barium carbonate), typically with pronounced dissolution features (Fig. 10A and 10B), or as barite (barium sulfate), which tends to form secondary precipitation rims on individual sediment grains (Fig. 10C and 10D).

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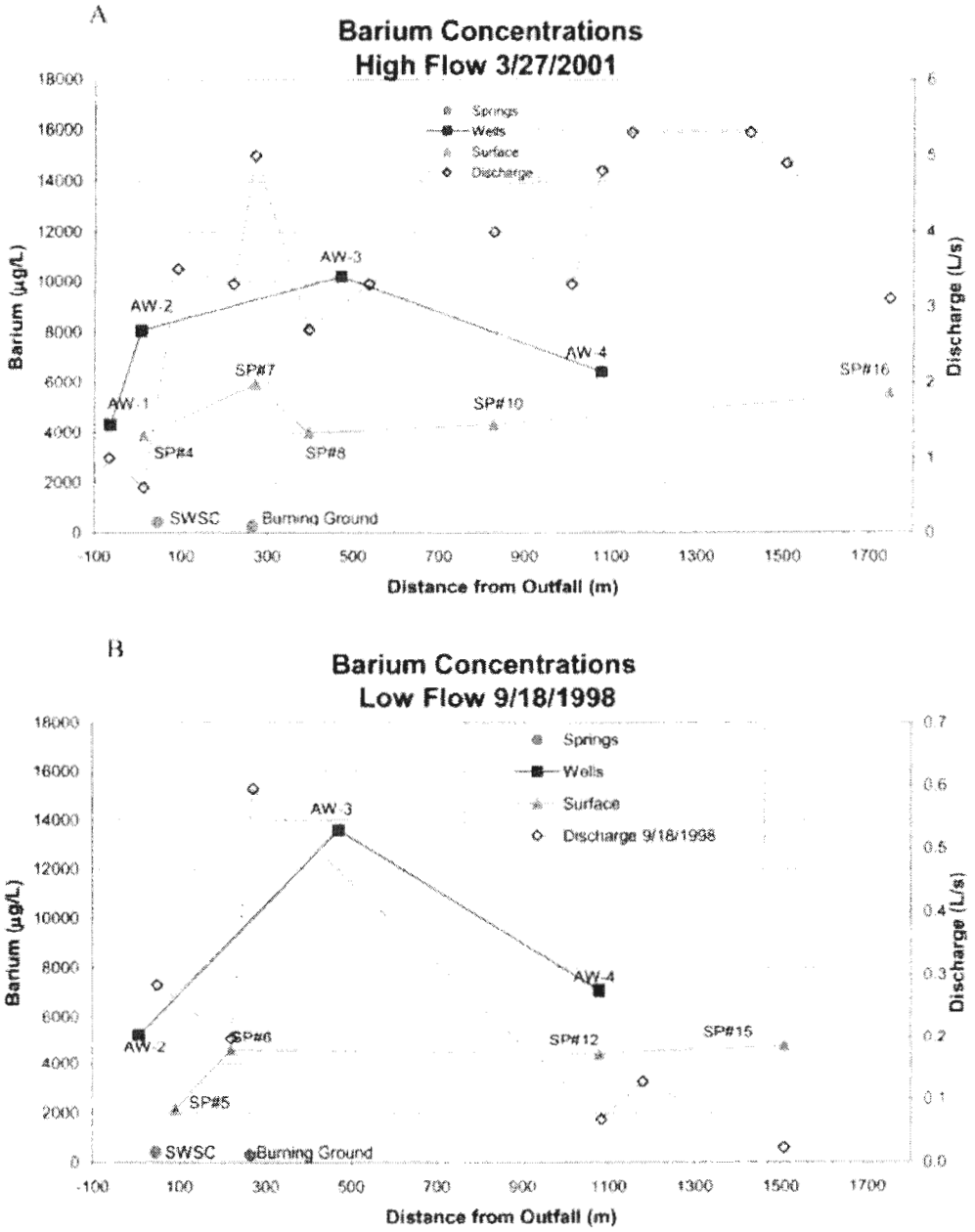

Fig. 6. Concentrations of Ba in surface water, alluvial groundwater, and spring water during high flow (A, 27 Mar. 2001) and low flow (B, 18 Sept. 1998) conditions.

Table 1. Alluvial water reaches.

Reach	Length	Alluvial well distance from LA-16-260 outfall	Alluvial well	Surface water stations	Springs	Notes
	m	m				
A	210	−60	AW-1	SP1, 2, 3		upstream of outfall
B	520	10	AW-2	SP4, 5, 6	SWSC	at outfall confluence
C	220	470	AW-3	SP7, 8, 9	Burning Ground	downstream of Burning Ground spring confluence (only perennial reach)
D	600	1080	AW-4	SP10, 11, 12, 13, 14, 15, and 16		surface water flow in this reach is intermittent.

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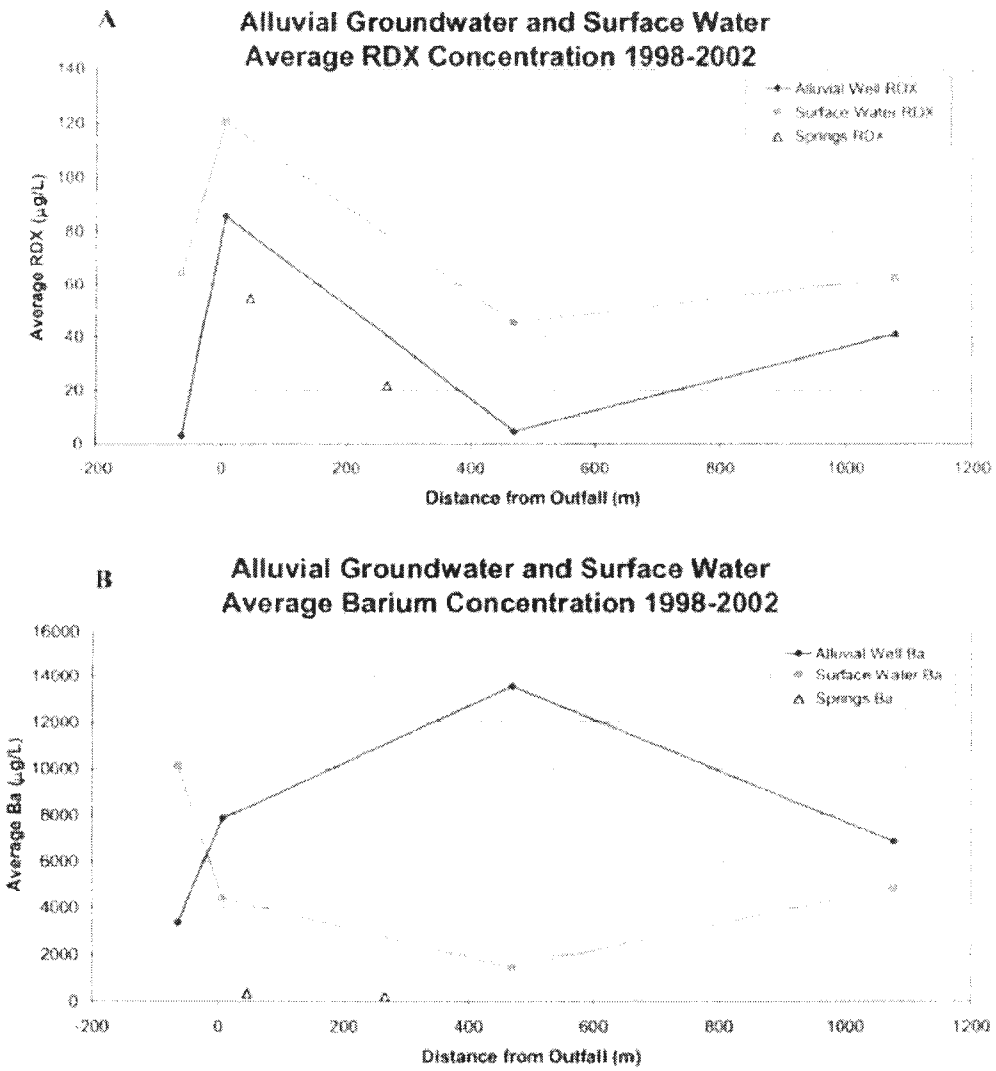

Fig. 7. Alluvial groundwater and surface water average (A) RDX and (B) Ba concentrations for the study reaches from 1998 to 2002.

RDX in near-surface sediments follows a similar trend as Ba, with the highest inventory in the fine-grained sediments peaking in the midcanyon reach (Fig. 10A). Compared with Ba, relatively little RDX is present in near-surface Cañon de Valle sediments. Approximately 5 kg of RDX was estimated to reside in the canyon sediment in 1999, and most of the RDX occurs in fine-grained sediment.

DISCUSSION

Archival records and process knowledge, supported by analytical data collected in this study, indicate that the TA-16-260 outfall is the primary source of Ba and RDX in the watershed, supplemented by additional upstream contaminant releases from the old landfill. In the alluvial groundwater, the highest Ba concentrations are in the midcanyon reach. The alluvial groundwater has longer contact times with the sediment and correspondingly has higher Ba concentrations than the surface water. The surface water is markedly different with the lowest Ba concentrations at the midcanyon reach. The alluvial groundwater and the surface water do not appear to thoroughly mix until the lower reach near AW-4. A temperature anomaly has also been observed in this reach, with an input of warmer water observed in the cooler months and an input of cooler water observed in the warmer months. Temperature has proven to be a good diagnostic of groundwater input in other studies of groundwater–surface water exchange (Constantz et al., 2001; Oxtobee and Navakowski, 2002). Additionally, during high flow periods the stream appears to gain in this reach.

Barium precipitates out of the surface water and alluvial groundwater as barite or witherite, and this is likely more pronounced during frequent dry periods. Barite should be relatively insoluble once it is formed, but witherite is relatively soluble and may redissolve during

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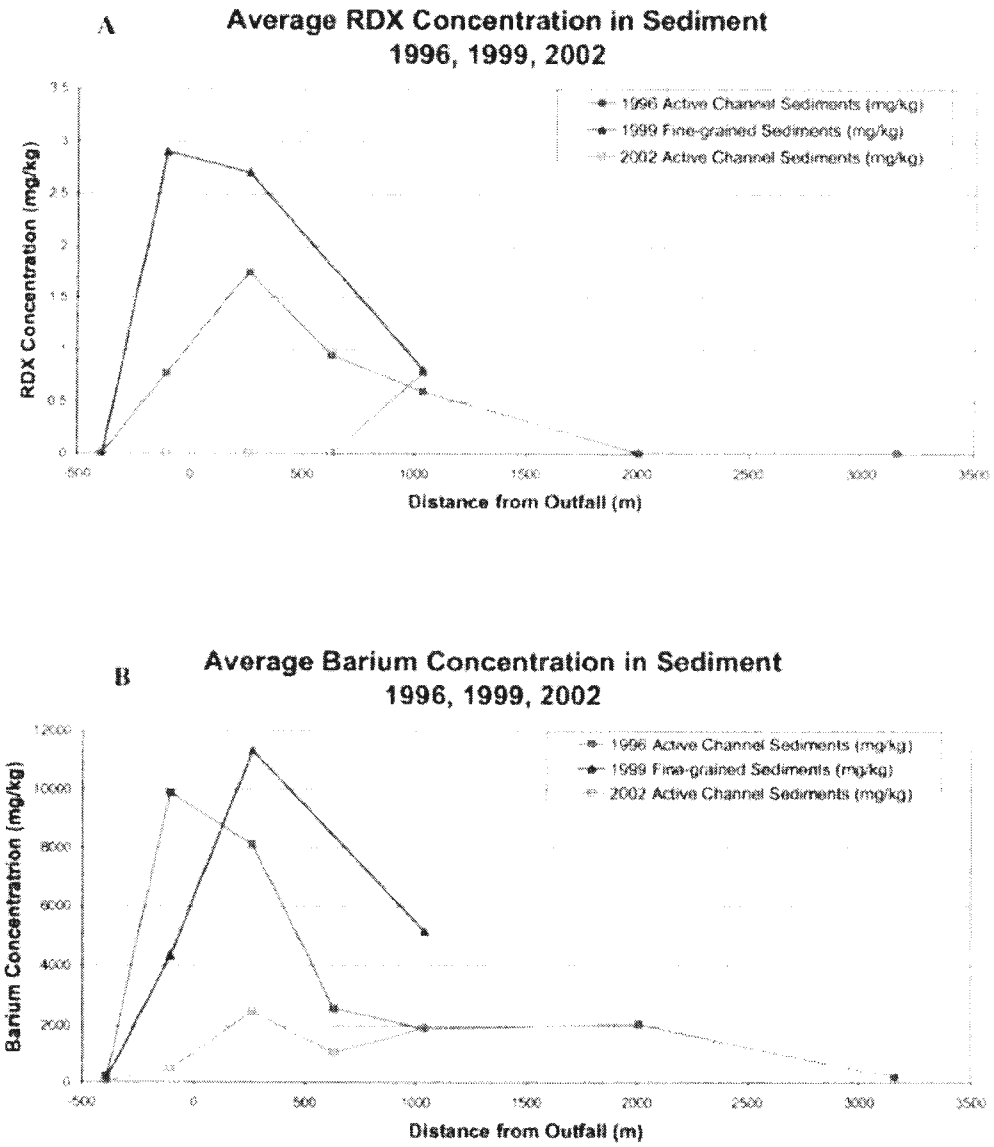

Fig. 8. Concentrations of (A) RDX and (B) Ba in sediment. Samples were collected in 1996, 1999, and 2002.

wet periods or during pH changes, causing temporal variability in alluvial groundwater Ba concentrations. The pockmarked witherites shown in Fig. 10A are consistent with this interpretation. The presence of Ba minerals in the sediments along with sorbed Ba partially buffers fluctuations of Ba concentration in surface water, but more dramatically buffers fluctuations of Ba concentration in the alluvial groundwater. Surface water Ba concentrations were higher upstream of the outfall. This correlates with higher Ba inventories found in the active channel sediments upstream of the outfall, and are probably associated with the old landfill. The distri-

Table 2. Sediment reaches.

Reach	Length	Midpoint distance from TA-16-260 outfall	Alluvial well	Surface water stations	Springs	Notes
	m					
1	210	105	AW-1	SP1, 2, 3		corresponds to water reach A
2	520	260	AW-2, AW-3	SP4, 5, 6, 7, 8, 9	SWSC, BG	corresponds to water reach B and C
3	220	630	None	None		no sediment analyses; inventory based on data from adjacent reaches
4	600	1040	AW-4	SP10, 11, 12, 13, 14, and 15		corresponds to water reach D

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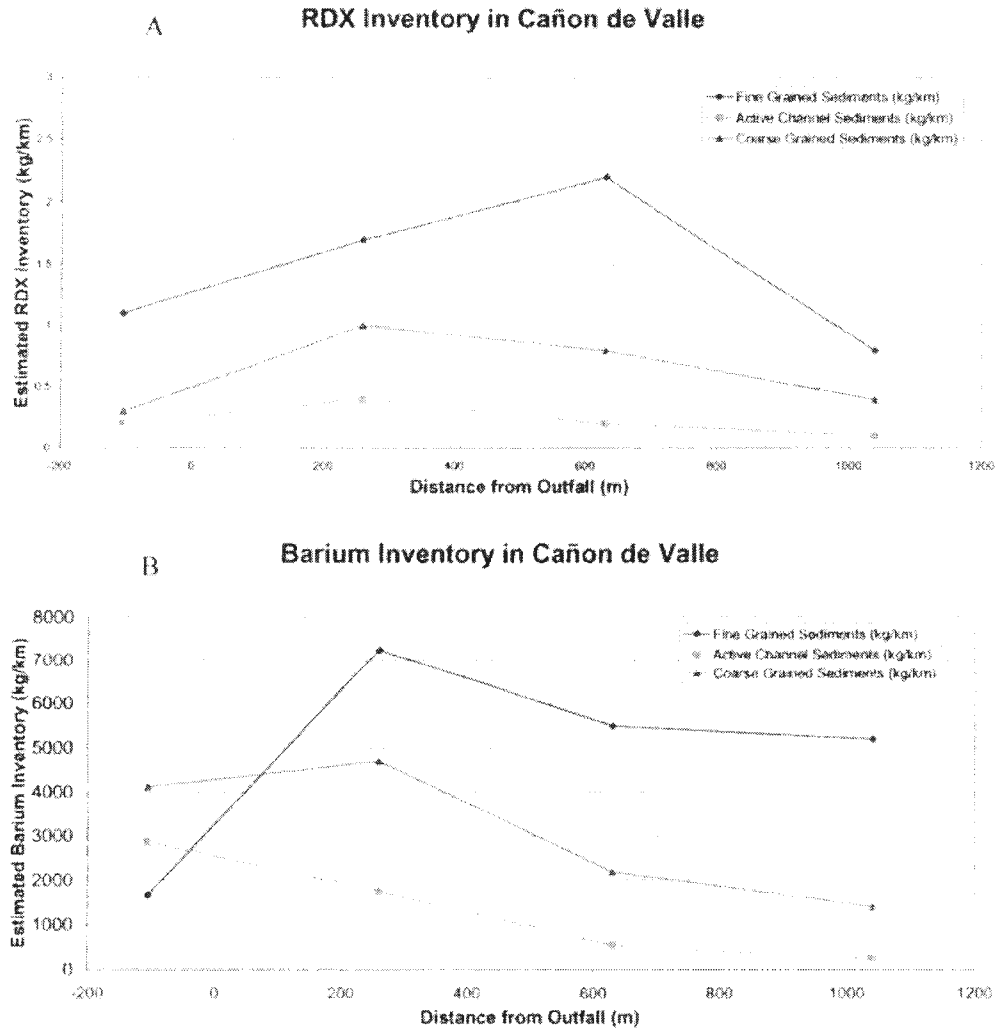

Fig. 9. Average inventories in canyon sediments of (A) RDX and (B) Ba, normalized by reach length to units of kilograms per kilometer.

bution of Ba in the study area sediments shows evidence of Ba being mobilized in the channel by scour during floods, followed by the redeposition of the suspended load of overbank floodwaters on floodplains.

RDX in Cañon de Valle showed elevated concentration spikes near the outfall following wet periods. RDX resides in part in the vadose zone associated with original infiltration of effluent and is mobilized during wet periods when the water table rises and groundwater flow rates increase. Because there is no apparent difference between RDX trends in the surface and alluvial groundwater, RDX is likely conservative in this alluvial system, which is consistent with its geochemical characteristics and explains why there is a high concentration down canyon at AW-4. The alluvial groundwater has lower RDX concentrations than the surface water; one possible explanation for this trend is that the organic material within the hyporheic zone could bind RDX as it infiltrates to the alluvial groundwater. Organic matter has been observed to accumulate in the hyporheic zone (Jones et al., 1995), and the hyporheic zone has also been the location of surface water and groundwater exchange, with the direction of flow often changing daily (Winde and van der Walt, 2004). The lateral hyporheic area has been observed to vary by as much as 50% during the course of a year in a semiarid environment (Wroblicky et al., 1998). This zone is very dynamic (Biksey and Gross, 2001) and can also be a contaminant sink (Fuller and Harvey, 2000; Winde and van der Walt, 2004).

Subsurface samples of tuff collected from boreholes at the TA-16-260 outfall contained concentrations of RDX of up to 1200 mg kg^{-1} (LANL, 1999). High concentrations of RDX could reside in volcanic surge beds and fractures within the tuff as well as the tuff matrix (LANL, 2003a). During dry periods the RDX is not mobilized, and with the low organic C in tuff and generally oxidizing conditions, there is little opportunity for biologically driven degradation. It is anticipated that residual high explosive contamination in the vadose zone will continue to serve as a source for contamination

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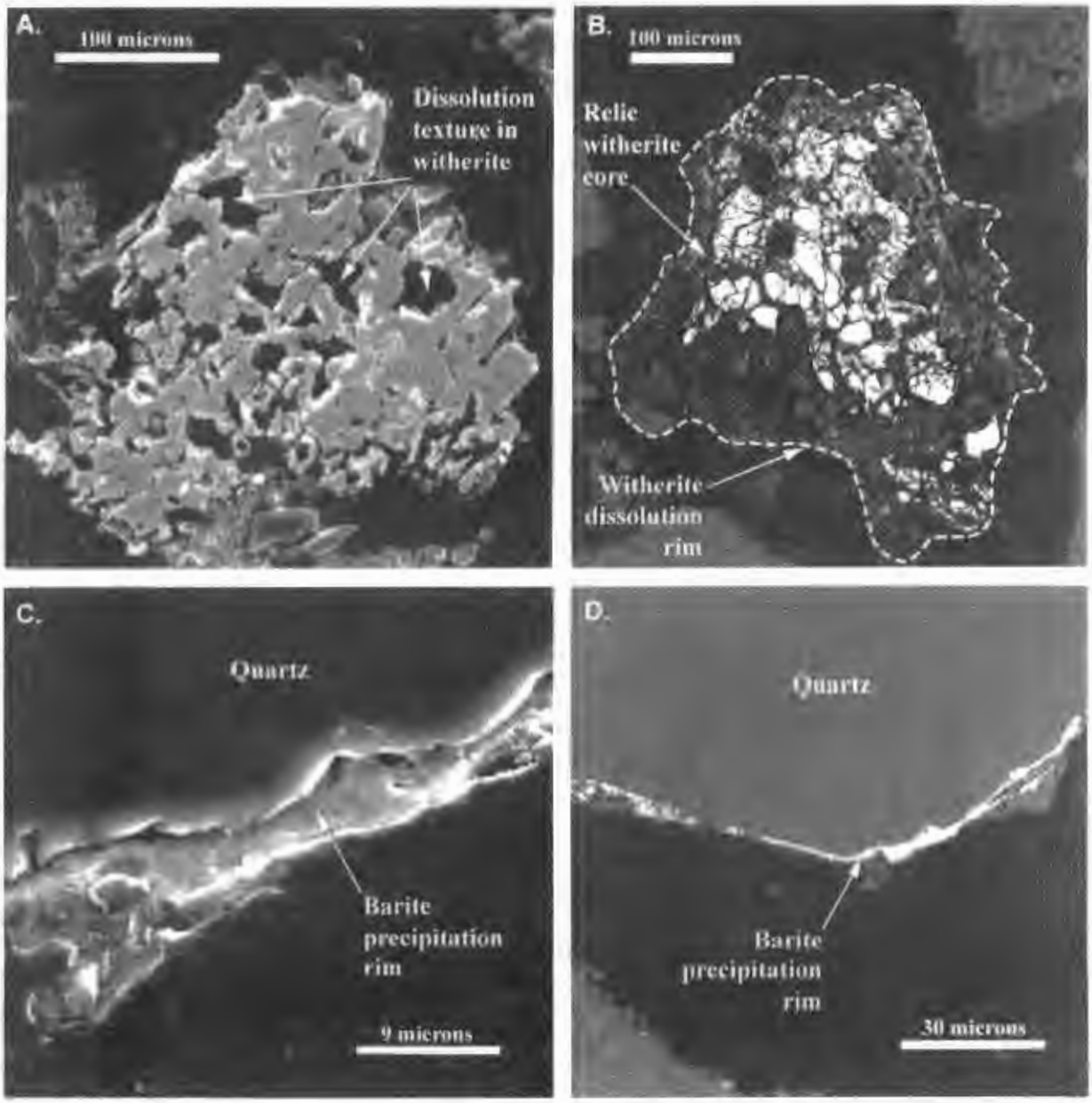

Fig. 10. Scanning electron micrographs: (A) back-scattered electron image of witherite showing dissolution textures; (B) secondary electron image showing a dissolution rim surrounding the relic core of a witherite grain; (C) close-up secondary electron image of a barite precipitation rim on quartz grain; and (D) back-scattered electron image of barite precipitation rim.

in the alluvial system, particularly during spring snowmelt and other prolonged periods of saturation.

The fluctuating pattern observed for both RDX and Ba time-series concentration data supports a model that involves the redistribution of vadose zone and alluvial system contaminants as a result of rainfall or snowmelt runoff events. These contaminants are dispersed in subsurface alluvium, in near-surface deposits in the active channel, below adjacent abandoned channels, on floodplains, and in the tuff along the margins of the canyon. The interactions between these components and their affects on RDX and Ba transport are summarized in two conceptual models of the canyon that represent wet and dry hydrologic regimes (Fig. 11A and 11B). The largest inventory of contaminants in the near-surface environment is in fine-grained sediment deposits on floodplains, where they are relatively stable. Remobilization of these contaminants occurs largely by lateral bank erosion, constituting a relatively minor and discontinuous supply of contaminants to the channel. In contrast, the contaminant inventory in the subsurface is susceptible to mobilization by alluvial groundwater, particularly

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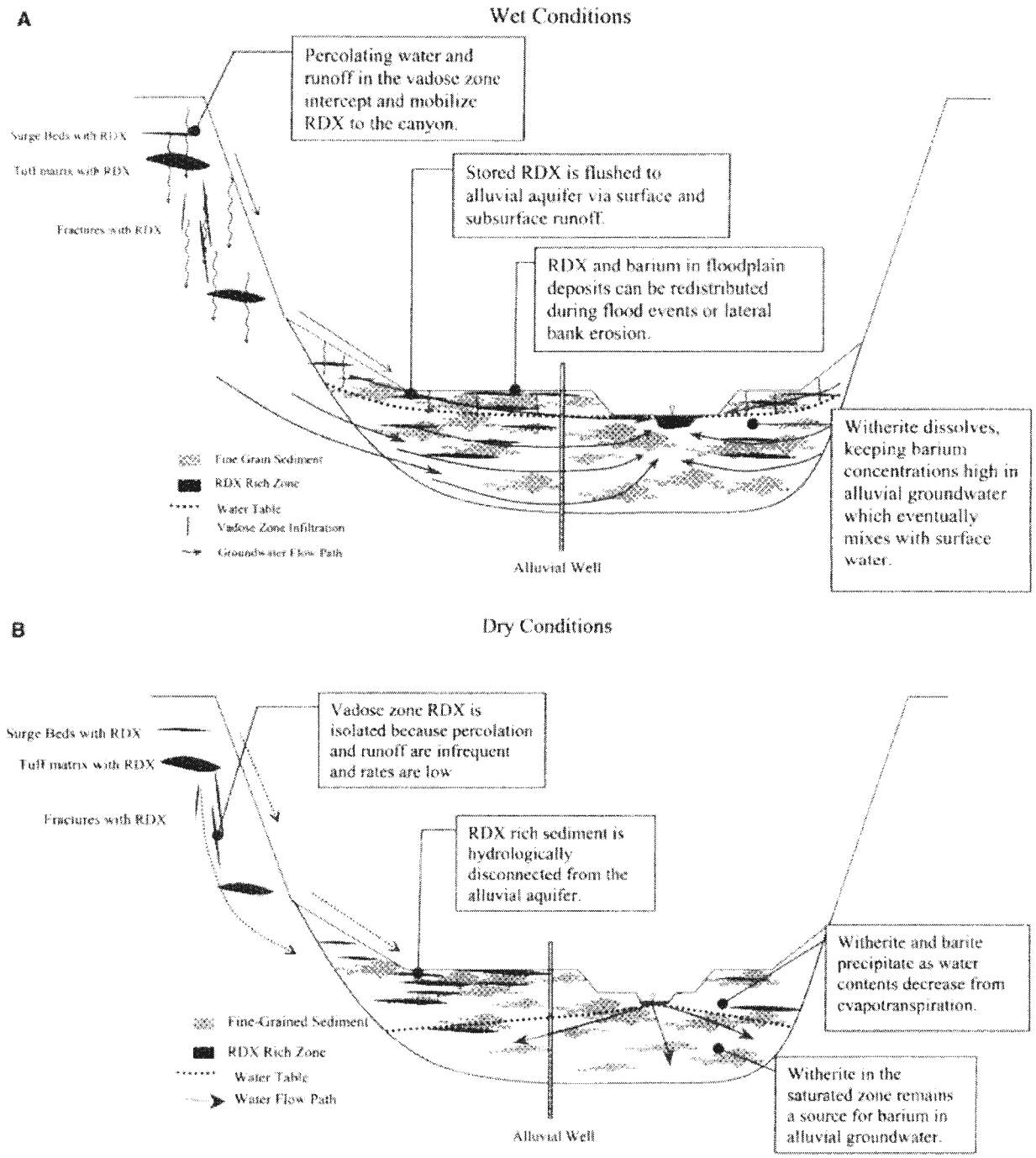

Fig. 11. (A) During wet conditions, such as spring snowmelt or prolonged precipitation events, residual RDX is flushed through the vadose zone and alluvial system. RDX is stored in fine-grained sediments in the canyon bottom and in the tuff matrix, surge beds, and fractures. More flow paths are active during wet periods, and some of these flow paths may bypass the alluvial groundwater and enter the stream channel directly. Barite will remain insoluble while witherite can dissolve following influx of fresh water. (B) Under dry conditions RDX is isolated in unsaturated fine-grained sediments and the vadose zone. As the alluvium dries, witherite and barite precipitate.

during times of high water tables, directly remobilizing and/or dissolving solid-phase Ba minerals and supplying them to the channel. Interflow (subsurface runoff) can also be an important process for mobilizing contaminants. It can be a major component of spring runoff in this environment, with interflow accounting for as much as 20% of snowpack snow water equivalent, and sometimes greatly exceeds surface runoff on an annual basis

(Wilcox et al., 1997). Macropore flow along root channels is a primary control on interflow generation in these environments, having a large affect on flow dynamics and water chemistry (Newman et al., 1998, 2004). For example, there appears to be an important water content threshold that when crossed, creates large increases in dissolved species concentrations in interflow (Newman et al., 1998). Such water content thresholds may also be important controls on contaminant mobility in the Cañon de Valle vadose zone.

These various flow mechanisms can impact the dynamics of RDX transport through the hillslope to the alluvial aquifer. RDX in particular is mobilized from the vadose zone during periods of high flow and high water tables. In laboratory column studies, RDX was shown to be highly mobile under saturated conditions (Ringelberg et al., 2003). Barium exists at relatively high concentrations in both water and sediment and seems to precipitate and dissolve throughout the canyon.

CONCLUSIONS

Barium and the high explosive RDX display complex spatial and temporal variations in surface and near surface media in the study area. Although released from the same location over roughly the same time period, the differing geochemical characteristics of these contaminants cause marked differences in their mobility and distribution, both at the surface and in the vadose zone. Barium is primarily associated with sediment particles and redistributed by floods, whereas RDX is most significant as a dissolved component in alluvial groundwater. Remobilization of RDX in the alluvial system also potentially provides a continuing source for transport to deeper groundwater zones. In this environment, remediation alternatives for RDX should specifically address high flow and high water table conditions because this is when the highest concentrations and corresponding highest mass flow rates occur. By focusing on the interrelationships of sediment, surface water, and groundwater, an improved understanding of contaminant fate and transport is achieved, in turn leading to an improved basis for designing and implementing remedial actions to reduce the impacts of contaminants on the environment.

ACKNOWLEDGMENTS

Funding for this work was provided by the U.S. Department of Energy through the Los Alamos National Laboratory Remediation Services project. Contributions to data interpretation, analyses, and field work by John M. Pietz, Devon E. Jercinovic, Peter L.M. Gram, Jeff M. Heikoop, Donna Sharp, Elmer D. Alcon, Dewight Bazzell, Kristi Beguin, Katherine Campbell, Katherine A. Herrell, David S. Lawler, Randy Johnson, Andi Kron, Seth McMillan, Jonathan Myers, Bradley H. Reid, Louie Romero, Jacinto Garduño, and Joe Allen Bird are greatly appreciated.

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