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# **Polychlorinated Biphenyls in Precipitation and Stormwater within the Upper Rio Grande Watershed**

Prepared by the Environmental Programs Directorate

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## **EXECUTIVE SUMMARY**

This report presents baseline, base-flow, and storm-flow concentrations of polychlorinated biphenyls (PCBs) in certain surface waters located in the upper Rio Grande watershed and in areas in and around Los Alamos National Laboratory (LANL) as part of a cooperative investigation by the U.S. Department of Energy (DOE), the New Mexico Environment Department–DOE Oversight Bureau, and LANL.

The objectives of this study were to establish (1) baseline levels of PCB concentrations in precipitation and snowpack near Los Alamos, New Mexico, and from alpine peaks overlooking the northern Rio Grande watershed up to the state border with Colorado; (2) baseline levels of PCB concentrations in stormwater in northern New Mexico streams and arroyos that are tributaries to the Rio Grande and Rio Chama; (3) the range of PCB concentrations found in the Rio Grande during base-flow (dry weather flow) and storm-flow conditions; (4) baseline levels of PCBs in stormwater from undeveloped watersheds of the Pajarito Plateau and the northeast flank of the Jemez Mountains near Los Alamos; (5) the concentrations of PCBs in urban runoff from the Los Alamos townsite adjacent to LANL; and (6) how these findings may be used to target significant sources of PCBs.

PCB concentrations were measured using a high-precision analytical method (U.S. Environmental Protection Agency Method 1668A) that is capable of measuring concentrations as low as a few parts per quadrillion. The results were statistically reviewed to identify any anomalous contamination present at the sites. The concentrations were then compared with the New Mexico Water Quality Control Commission water-quality criteria (WQC) to gauge the magnitude of baseline PCB concentrations in surface waters. The WQC for total PCBs in water are 0.64 ng/L (0.64 ppt) for the protection of human health and 14 ng/L for the protection of wildlife habitat. The WQC for acute and chronic protection of aquatic life are 14 ng/L and 2 µg/L, respectively. With the exception of the chronic life criterion, which only applies under stable conditions, these criteria apply to all surface waters, whether base flow, storm flow, or storm runoff. Under base-flow conditions, results show the water column contained nearly universally low PCB concentrations in the Rio Grande, Rio Chama, and groundwater-fed tributaries. In contrast, surface waters during storm runoff generally contained PCB concentrations above 5 ng/L and substantially above the New Mexico WQC for protection of human health. Such concentrations were measured even in the most remote parts of the watershed and can be attributed to the increased concentrations of suspended soils and sediments carried by surface waters during storm runoff. Heightened PCB concentrations above 100 ng/L were measured in Los Alamos County urban runoff, presumably from the increase in diffuse sources in urban environments commonly reported in the scientific literature.

These findings will assist in identifying PCBs in surface waters originating from local industrial and urban sources versus global atmospheric deposition, thereby providing a context for future monitoring results used to determine environmental remedy priorities.



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## 1.0 INTRODUCTION

This report summarizes the findings of a multi-year cooperative investigation conducted by the U.S. Department of Energy (DOE), the New Mexico Environment Department– (NMED-) DOE Oversight Bureau (hereafter, the Oversight Bureau), and Los Alamos National Laboratory (LANL) to characterize PCBs in certain surface waters located in the upper Rio Grande watershed and in areas in and around LANL. The principal objectives of the study were to determine (1) baseline levels of polychlorinated biphenyl (PCB) concentrations in precipitation and snowpack in northern New Mexico; (2) baseline levels of PCB concentrations in stormwater in northern New Mexico streams and arroyos that are tributaries to the Rio Grande and Rio Chama; (3) the range of PCB concentrations found in the Rio Grande during base-flow and storm-flow conditions; (4) baseline levels of PCBs in stormwater from undeveloped watersheds of the Pajarito Plateau and the northeast flank of the Jemez Mountains near Los Alamos, New Mexico (hereafter referred to as the Pajarito Plateau); (5) the concentrations of PCBs in urban runoff from the Los Alamos townsite neighboring LANL; and (6) and how these findings may be used to target significant sources of PCBs. This information is intended to help guide corrective actions implemented under Clean Water Act programs at LANL including National Pollutant Discharge Elimination System (NPDES) permit(s) and prospective total maximum daily loads (TMDLs).

According to the U.S. Environmental Protection Agency (EPA), environmental cycling of past releases of PCBs is a major source of PCB contamination worldwide (<http://www.epa.gov/ogwdw/pdfs/factsheets/soc/tech/pcbs.pdf>, <http://www.epa.gov/osw/hazard/tsd/pcbs/pubs/about.htm>). This cycling consists of volatilization of PCBs from land and water, atmospheric dispersion, wet or dry deposition, followed by revolatilization. Evidence for this dispersion is reported in a large body of work documenting widespread distribution of PCBs in environmental media around the world even in the absence of point sources of PCBs (Peel 1975, 209555; Risebrough et al. 1976, 209557; Lunde et al. 1977, 213420; Atlas and Giam 1981, 213335; Tanabe et al. 1983, 209558; Hargrave et al. 1988, 209553; Gregor and Gummer 1989, 209552; Brun et al. 1991, 213404).

Recent studies by the NMED–Surface Water Quality Bureau (SWQB), the Oversight Bureau, and LANL have characterized PCBs in stormwater or storm flow from drainages to the Rio Grande, the Rio Grande itself, LANL, and tributaries draining the Pajarito Plateau in areas not associated with LANL (NMED 2010, 213452).

Results from these efforts indicate PCBs concentrations in stormwater samples collected from remote locations are similar to the New Mexico Water Quality Control Commission (NMWQCC) water-quality criteria (WQC), 20 New Mexico Administrative Code (NMAC) 6.4, for total PCBs in surface waters and are at or above New Mexico WQC at locations affected by industrial and urban activities. The WQC for total PCBs are 0.64 ng/L for the protection of human health and 14 ng/L for the protection of wildlife habitat. The WQC for acute and chronic protection of aquatic life are 14 ng/L and 2 µg/L, respectively. With the exception of the chronic life criterion, which only applies under stable conditions, these criteria apply to all surface waters, whether base flow, storm flow, or storm runoff (NMED 2011, 218281).

The recently issued EPA National Pollutant Discharge Elimination System (NPDES) Individual Permit (IP) for LANL requires monitoring for PCBs in stormwater (EPA 2010, 213450). The action level for total PCBs in the IP is 0.64 ng/L, a concentration based directly on the New Mexico WQC for human health. While this action level is not an effluent limit, the IP requires implementation of corrective action when an average of stormwater sample results exceeds this value for a particular location.

The IP requires analysis of total PCBs by EPA Method 1668 Revision A, a high-resolution gas chromatography/high-resolution mass spectrometry analytical method not promulgated by EPA. This

method is capable of detecting PCBs at low part per quadrillion levels (EPA 2003, 209599). The IP requires minimum quantitation levels ranging from 0.025 ng/L to 0.050 ng/L (25 to 50 ppt) for each of the 209 PCBs congeners that are then summed for a total PCB result. Compared with less sensitive analytical methods prescribed in NPDES permits in the past, the analysis of PCB congeners by EPA Method 1668A is much more sensitive.

Baseline concentrations of PCBs in stormwater have not been rigorously evaluated in the upper Rio Grande watershed. This investigation was designed to characterize PCB concentrations in stormwater and receiving waters throughout the region to establish the concentrations that can be attributed to a common regional/global baseline source as opposed to LANL and local non-LANL sources.

Baseline elemental concentrations of inorganic chemicals and radionuclides have been determined for LANL based on sediment investigations. However, these investigations focused on prehistoric channels and floodplains, not on exposed landscape surfaces containing global atmospheric deposition of PCBs (McDonald et al. 2003, 076084).

Understanding baseline concentrations of PCBs is critical to identifying and controlling LANL contribution of PCBs to stormwater and establishing measures of the success of corrective actions resulting from implementation of the IP. At the same time, a regional understanding of baseline PCB concentrations in northern New Mexico is of interest to NMED to develop TMDLs and other water-quality planning needs.

This investigation is a cooperative effort by the following organizations:

- DOE Los Alamos Area Office (LASO)
- LANL
- the NMED DOE-Oversight Bureau

Geographically, this investigation includes the Los Alamos townsite, LANL watersheds, remote watersheds on the Pajarito Plateau, and the Rio Grande upstream and downstream of LANL.

## **1.1 Site Description**

LANL is located in Los Alamos County in north-central New Mexico, approximately 60 mi north-northeast of Albuquerque and 25 mi northwest of Santa Fe (Figure 1). The lands surrounding LANL are held by the Santa Fe National Forest, the U.S. Bureau of Land Management, Bandelier National Monument, the U.S. General Services Administration, and Los Alamos County. The Pueblo de San Ildefonso borders LANL to the east.

LANL lies in the upper Rio Grande watershed denoted by U.S. Geological Survey (USGS) hydrologic unit codes 13020101 and 13010005 (<http://water.usgs.gov/wsc/reg/13.html>). The upper Rio Grande is a large watershed (approximately 7500 mi<sup>2</sup>) that generally flows from north to south. The New Mexico portion of the watershed is within seven counties: Rio Arriba, Taos, Santa Fe, Los Alamos, Sandoval, Mora, and San Miguel. For the purposes of this study, the upper Rio Grande watershed includes the geographic area and tributaries draining into the Rio Grande from the New Mexico–Colorado border to Cochiti Reservoir. Cochiti Reservoir is approximately 31 river miles upstream of Albuquerque, New Mexico. A variety of land uses exist within the watershed, including range lands, agriculture, light industry, and urban development.

Geologic materials transported by stormwater in the upper Rio Grande watershed consist of a complex distribution of weathered Precambrian metamorphic rocks, Paleozoic sedimentary rocks, and Tertiary volcanics with sediment, including the Santa Fe Formation, which is widely distributed in the Rio Grande Rift basin (Chronic 1987, 213488). LANL is located on the eastern flanks of the Jemez Mountains on fingerlike mesas capped mostly by the Bandelier Tuff.

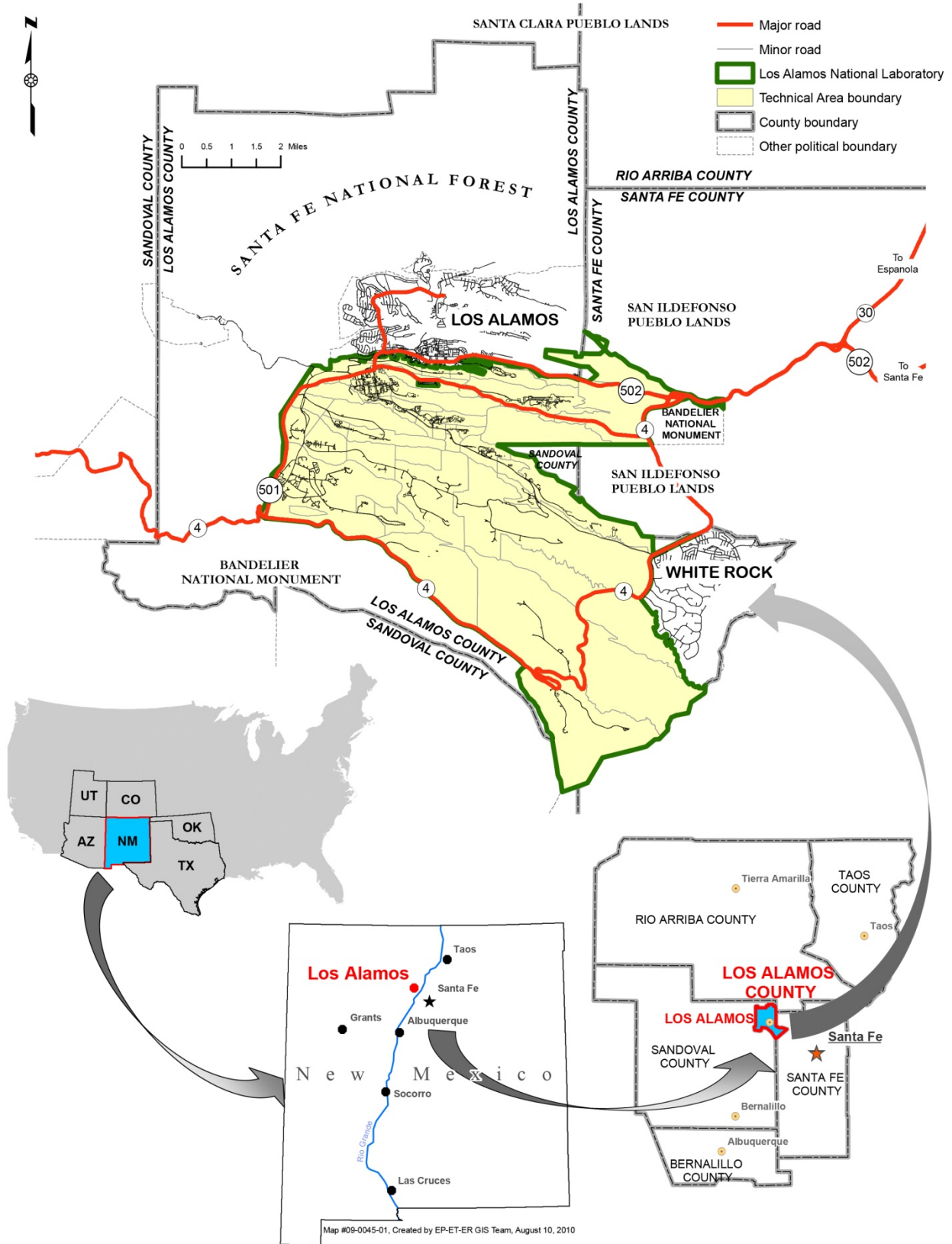


Figure 1 Regional view of study area

## 1.2 Previous NMED and LANL PCB Investigations

Annual watershed monitoring, site-specific stormwater monitoring, and TMDL baseline studies conducted by LANL and NMED have identified elevated levels of PCBs in stormwater in tributaries draining the Pajarito Plateau (NMED 2010, 213452; NMED 2012, 215121). The results indicate the presence of PCBs in stormwater runoff from some LANL solid waste management units (SWMUs) and areas of concern (AOCs) on mesa tops, in some samples from Pajarito Plateau canyons, and in a number of instances from the Rio Grande and several of its tributaries. An unpublished cooperative PCB study conducted by DOE, LANL, NMED, Los Alamos County, and San Ildefonso Pueblo in 2002–2003 identified additional sources of PCBs in stormwater from other portions of the upper Rio Grande watershed.

## 2.0 BACKGROUND

### 2.1 History of PCBs

PCBs are mixtures of synthetic organic chemicals with the same basic chemical structure and physical properties that range from oily liquids to waxy solids. No known natural sources of PCBs exist. Because of their nonflammability, chemical stability, high boiling point, and electrical insulating properties, PCBs were historically used in hundreds of industrial and commercial applications. These applications included electrical, heat-transfer, and hydraulic equipment; plasticizers in paints, plastics, calking, and rubber products; pigments, dyes, and carbonless copy paper; and many other uses. More than 1.5 billion pounds of PCBs were manufactured in the U.S. until domestic manufacture of commercial mixtures, known as Aroclors, ceased in 1977. Approximately 450 million pounds of PCBs have been released to the environment (ATSDR 2000, 213440).

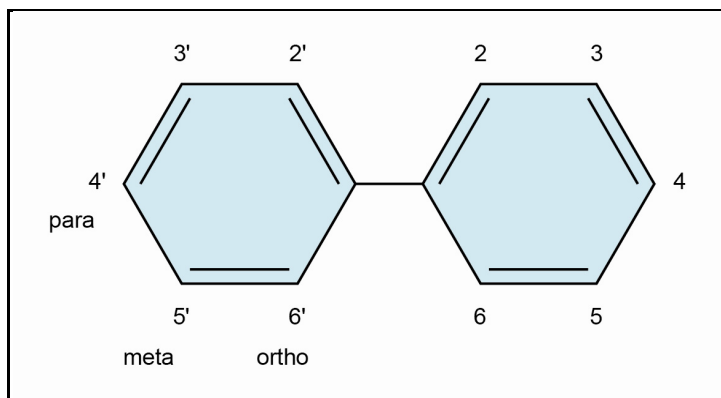
Concern over the toxicity and persistence of PCBs in the environment led Congress to enact Section 6(e) of the Toxic Substances Control Act (TSCA), 15 United States Code 2605(e), in 1976. This legislation included, among other requirements, prohibitions on the manufacture, processing, and commercial distribution of PCBs. TSCA legislated true “cradle to grave” (i.e., from manufacture to disposal) management of PCBs in the U.S. (Additional information is available at <http://www.epa.gov/epawaste/hazard/tsd/pcbs/index.htm>.)

Despite the commercial ban of PCBs and the cradle-to-grave management of these products, sources of PCBs have continued to be detected across the world not only from (1) global dispersion of PCBs released before the ban; (2) diffuse releases from continued volatilization from commercial products manufactured before the ban but still in use such as caulks, sealants, adhesives, and plasticizers as well as leaks from items such as transformers and capacitors; and (3) point-source releases from spills and improper disposal (ATSDR 2000, 209548; Du and Rodenburg 2007, 209551; Jartun and Pettersen 2010, 213416).

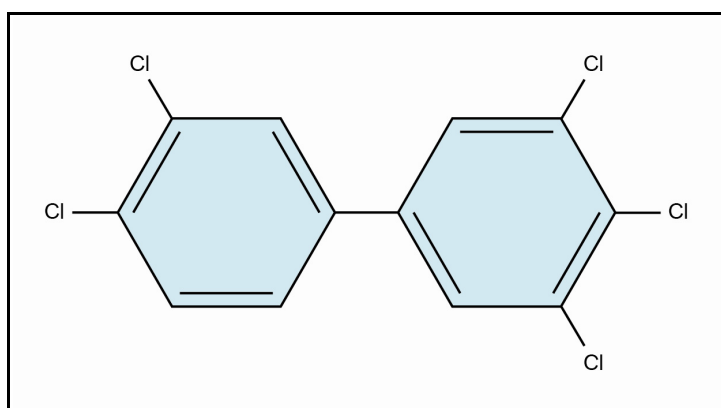
### 2.2 The PCB Molecule

A PCB molecule consists of two 6 carbon rings with a chemical bond joining a carbon from each ring. Either chlorine or hydrogen atoms can be attached to any of the other 10 carbon atoms at the numbered locations shown in Figure 2.

There are 209 possible arrangements of atoms on the two-ring PCB base. These are called congeners. Each congener is named based on the location of chlorines in the molecule. For example, 3,3',4,4',5-pentachlorobiphenyl is illustrated in Figure 3.



**Figure 2** Structure of a PCB molecule



**Figure 3** Structure of 3,3',4,4',5-pentachlorobiphenyl

PCB congeners are also referred to by sequential numbers based on the number of chlorines and the location of the chlorines within the molecule. For example, 3, 3',4, 4', 5-pentachlorobiphenyl is also known as PCB 126.

The number and position of chlorine atoms determine the molecule's physical and chemical properties. For instance, some of the most toxic PCBs congeners have at least four chlorines in the 3,3',4,4',5,5' (meta and para) positions but none or only one in the 2,2',6,6' (ortho) positions (Figure 2) (Henry and DeVito 2003, 213487). The World Health Organization calls these molecules dioxin-like PCB congeners ([http://www.who.int/foodsafety/chem/tef\\_update/en/index.html](http://www.who.int/foodsafety/chem/tef_update/en/index.html)).

Congeners with the same number of chlorines are called homologs. Table 1 lists the PCB homologs, their common abbreviations, the different congeners that fall into each homolog category, and the alternate nomenclature for those congeners by sequential number.

An additional name encountered for commercially produced mixtures of PCBs sold in the U.S. is Aroclor, named for the number of carbons in their rings and their chlorine content. For instance, Aroclor-1254 is primarily comprised of mixtures with a 12-carbon backbone (biphenyls) and an average chlorine content of 54%.

**Table 1**  
**List of PCB Homologs**

PCB Homolog	Abbreviation	Number of Chlorines	Number of Congeners	IUPAC* Congener Numbers
Biphenyl		0	1	
Monochlorobiphenyl	mono-CB	1	3	1–3
Dichlorobiphenyl	di-CB	2	12	4–15
Trichlorobiphenyl	tri-CB	3	24	16–39
Tetrachlorobiphenyl	tetra-CB	4	42	40–81
Pentachlorobiphenyl	penta-CB	5	46	82–127
Hexachlorobiphenyl	hexa-CB	6	42	128–169
Heptachlorobiphenyl	hepta-CB	7	24	170–193
Octachlorobiphenyl	octa-CB	8	12	194–205
Nonachlorobiphenyl	nona-CB	9	3	206–208
Decachlorobiphenyl	deca-CB	10	1	209

\*IUPAC = International Union of Pure and Applied Chemistry.

### 2.3 PCBs in the Environment

PCBs are ubiquitous around the world as a result of environmental cycling of past releases of PCBs (<http://www.epa.gov/ogwdw/pdfs/factsheets/soc/tech/pcbs.pdf>; <http://www.epa.gov/osw/hazard/tsd/pcbs/pubs/about.htm>). PCBs can volatilize, be dispersed as aerosols, or be adsorbed to windblown dust from land and water, which are dispersed in the atmosphere and then deposited. These PCBs may then be re-volatilized and the cycle begins again (Risebrough et al. 1976, 209557; Lunde et al. 1977, 213420; Atlas and Giam 1981, 213335; Tanabe et al. 1983, 209558; Hargrave et al. 1988, 209553; Gregor and Gummer 1989, 209552; Brun et al. 1991, 213404; Breivik et al. 2002, 209549; Breivik et al. 2002, 209550).

PCBs adsorb to organic materials, sediment, and soil and are transported by several mechanisms in the environment. Adsorption tends to increase with the chlorine content of the PCBs and the organic content of the substrate (<http://www.epa.gov/ogwdw/pdfs/factsheets/soc/tech/pcbs.pdf>). Although PCBs have relatively low solubility in water, they adsorb readily to sediment and other fine-grained material and are transported as suspended solids or bedload in stormwater. Congeners with low chlorine content tend to be more volatile and also more soluble in water (Dunnivant and Elzerman 1988, 213455). Vaporization rates and water solubility of individual congeners vary over several orders of magnitude (Dunnivant and Elzerman 1988, 213455). Generally, PCBs are not detected in groundwater at elevated concentrations because of the low solubility and the lack of abundant colloids in aquifers (Baker et al. 1986, 213402; Wilson et al. 1996, 213434).

Biodegradation transforms the chemical composition of PCB mixtures in the environment. Anaerobic bacteria in sediment selectively remove chlorines from the meta- and para- positions (see Figure 2), appearing to reduce the toxicity and bioaccumulation potential of fractionated residues (Lake et al. 1992, 213418; Abramowicz 1995, 213333; Chen et al. 2001, 213339; Fava et al. 2003, 213342; EPA 2008, 213448). Dechlorination is not synonymous with detoxification because congeners having carcinogenic activity can be formed through dechlorination (EPA 1996, 213444). Aerobic bacteria remove chlorines from PCBs with low chlorine content (1–4 chlorines) and break open the carbon rings through oxidation (Abramowicz 1995, 213333). PCBs with higher chlorine content are extremely resistant to oxidation and

hydrolysis; however, photolysis can slowly break down congeners with high chlorine content (Pomerantz et al. 1978, 213456). Overall, dechlorination processes are slow, resulting in atmospheric half-lives of PCBs of 10 to 20 yr or more (Sinkkonen and Paasivirta 2000, 213430).

Bioaccumulation through the food chain tends to concentrate congeners of higher chlorine content, producing residues that are considerably different from the original composition (Schwartz et al. 1987, 213428; Oliver and Niimi 1988, 213426). In general, because some toxic congeners are preferentially retained, bioaccumulated PCBs appear to be more toxic than commercial PCBs (<http://www.epa.gov/iris/subst/0294.htm>).

Figure 4 shows the transport and exposure pathways for PCBs in the environment most relevant to LANL, the Pajarito Plateau, and the upper Rio Grande watershed. Some site monitoring areas within LANL boundaries may be sources of PCBs to sediment in downstream canyons. The sediment is eventually transported by storm flows to the Rio Grande. In addition, rainfall has baseline PCB concentrations, runoff has baseline PCB concentrations, and upstream and downstream sources of PCBs to the Rio Grande exist that are unrelated to LANL.

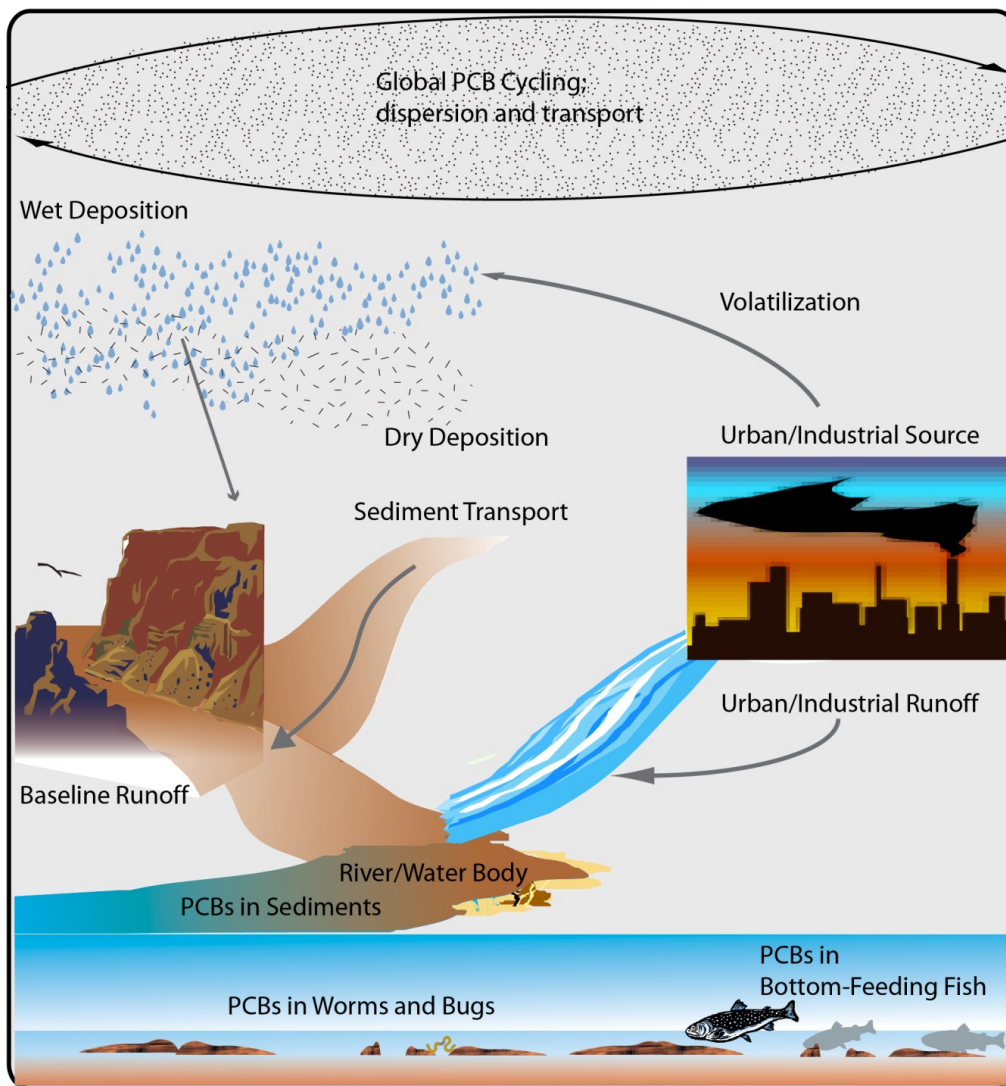


Figure 4 PCB transport and exposure pathways

### 3.0 METHODS

The sampling network (Figures 5 and 6) was designed to characterize precipitation, stormwater runoff, and storm flow in receiving waters (LANL 2009, 106090; LANL 2009, 106092). The sampling locations encompassed the following at five different types of locations.

1. Precipitation locations subdivided into the following types:
  - a. Rain gauge stations on the Pajarito Plateau
  - b. Snowpack sampling locations from peaks in the Jemez and Sangre de Cristo mountain ranges draining into the Rio Grande watershed
2. Locations within northern New Mexico intended to characterize runoff distant from LANL and urban Los Alamos County sources, subdivided into two subsets:
  - a. Ephemeral and intermittent streams and arroyos within the Rio Grande or Rio Chama watershed, hereafter referred to as ephemeral tributaries
  - b. Perennial streams within the Rio Grande or Rio Chama watershed, hereafter referred to as perennial tributaries
3. Northern New Mexico locations on the Pajarito Plateau in closer proximity to LANL and urban Los Alamos County sources intended to characterize runoff unaffected by LANL and urban Los Alamos County sources, subdivided into two subsets:
  - a. Ephemeral, intermittent, and perennial tributaries to the Rio Grande to the west and upstream of LANL and urban Los Alamos County referred to as Western Boundary stations
  - b. Ephemeral tributaries to the Rio Grande north of LANL and urban Los Alamos County referred to as Reference sites.
4. The upper Rio Grande and its largest tributary in northern New Mexico, the Rio Chama intended to characterize the base-flow levels of PCBs and variations of those levels during storm-flow conditions
5. Urban Los Alamos County locations that generate runoff from non-LANL properties or operations (urban runoff)

The locations were chosen based on historical data analysis that identified potentially contaminated locations for exclusion from the study (LANL 2009, 106090). Locations were also selected based on their spatial relationship to drainages from LANL and developed areas within Los Alamos County.

Precipitation and snowpack samples were collected by the Oversight Bureau. Western Boundary, Reference, and urban Los Alamos County samples were collected by LANL and the Oversight Bureau. Although not formal collaborators in this study, NMED-SWQB provided valuable PCB data from earlier sampling efforts of base-flow and stormwater runoff within the study area.

Samples were analyzed for PCBs and in some instances for suspended sediment concentration (SSC), particle size, total organic carbon (TOC), and target analyte list metals. Limited metal data are presented in this report. A more detailed analysis of metal data collected during this study will be presented in a separate report.



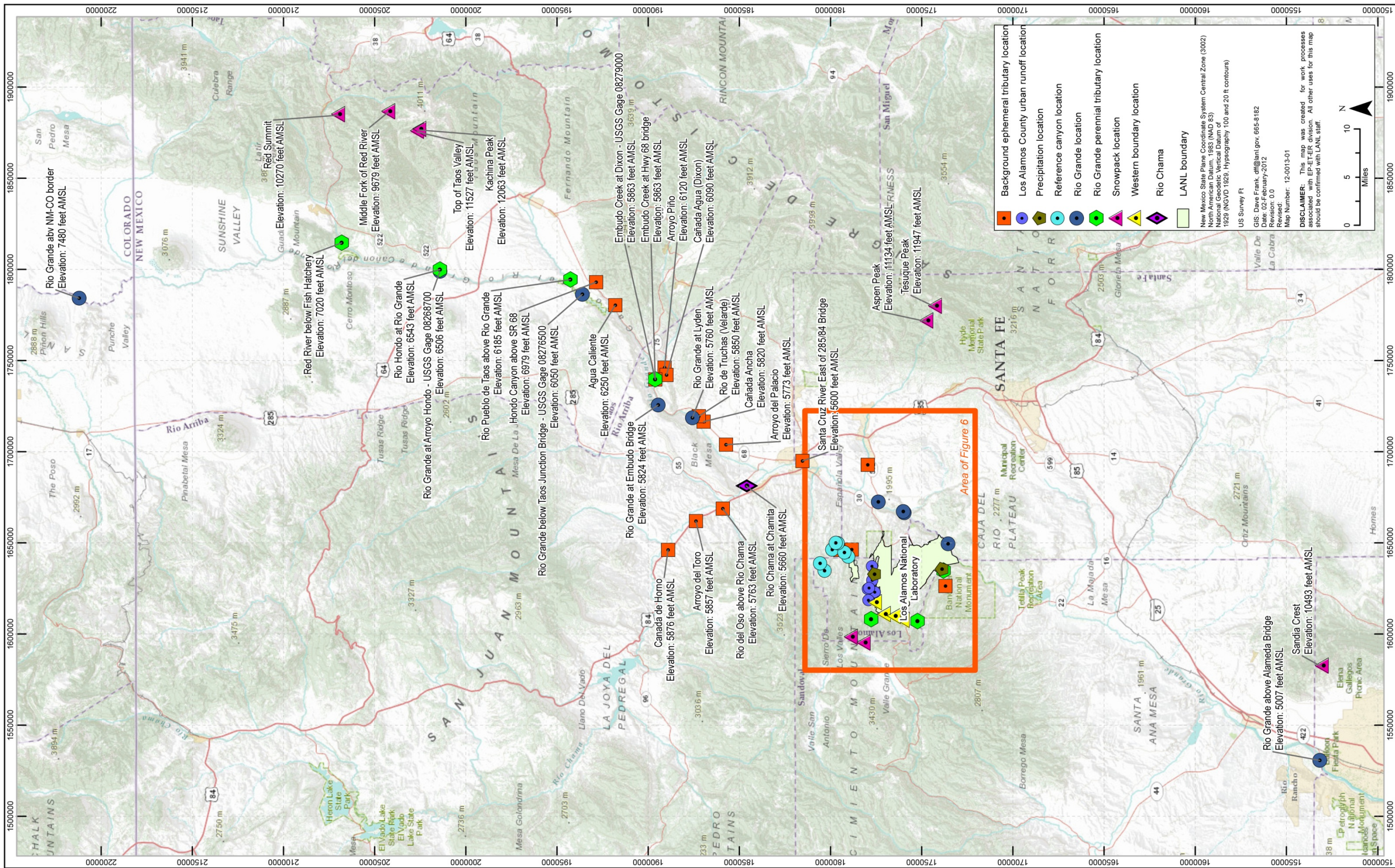


Figure 5 Sampling locations

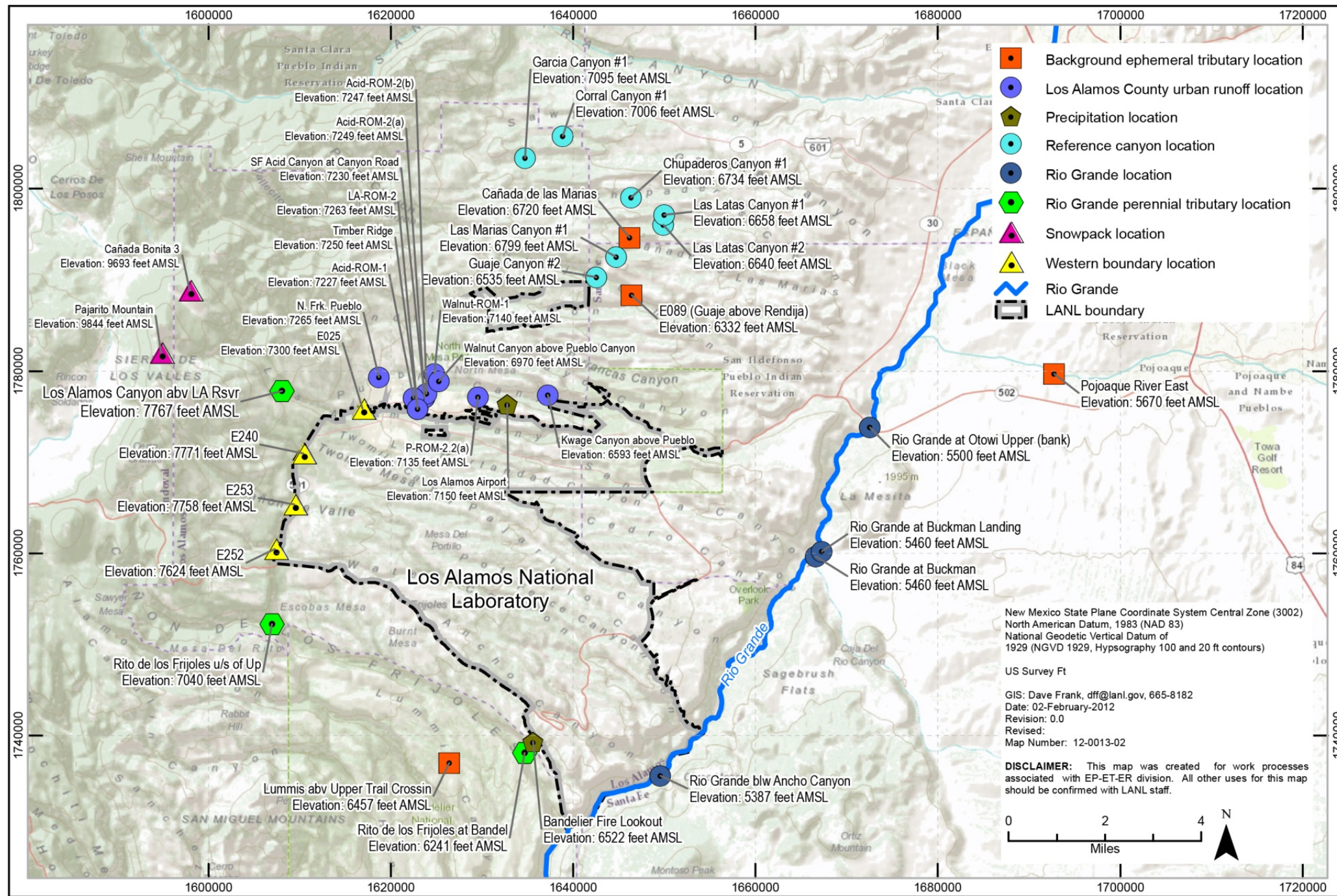


Figure 6 Map of sampling locations around LANL

### **3.1 Sampling Methodology**

Snowpack samples were collected by digging a pit and collecting an integrated sample from the top to the bottom of the snowpack (but not the ground surface interface). Precipitation samples were composites of a variable number of days and rain or snowfall events. The number of days from deployment to sample retrieval ranged from 2 to 105 d, with an average of 30 d. Samples were collected using automated ADS/NTN Atmospheric Precipitation Samplers from N-CON Systems Co., Inc. When a sensor detects precipitation, a protective lid automatically moves off the bucket to allow rain or snowfall to be collected. When precipitation ends, the lid moves back over the bucket to prevent deposition of windblown dust and evaporation of the sample. Dry deposition was not characterized in this study.

Water samples were collected using three methods: automated samplers, passive samplers, and manual grab samples. When and where possible, manual grab samples were preferred because the sample collection time, presence of flow, and visual indicators could be recorded. The vast majority of stream channels within the study area were remote ephemeral drainages that flowed only in response to rainfall events. Consequently, unattended sampling approaches were required to collect samples, given the vagaries of weather forecasting and remote locations across the landscape. Two types of passive samplers and two types of automated samplers were used to collect unattended samples.

Automated samplers included Teledyne ISCO, Inc. (model 3700, 6712, or GLS), and suitcase automated samplers (Global Water WS-700 or WS-750). Automated samplers were set to begin collecting samples immediately after water reached a prescribed water level or “stage” indicated by the respective sensors to collect a single grab sample within the first 30 min of runoff (EPA 1992, 213443). Teflon sample suction lines were used to collect water samples and were located above the stream bottom to minimize the collection of bedload sediment and to provide consistency in suspended sediment measurements. ISCO samplers contained 12 or 24 1-L bottles. Glass bottles were used for PCB analyses, and high-density polyethylene bottles were used for SSC, particle-size, TOC, and metals analyses. These bottles filled sequentially and continuously until all bottles were filled or insufficient water levels were reached.

Global Water samples were equipped with two 1-gal. glass bottles that collected simultaneously from two separate inlet tubes until the bottles were full or insufficient water levels were reached. Water collected from Global Water samplers was decanted from the bottles into 1-L glass or high-density polyethylene bottles depending on the analysis, with the exception of particle size analysis samples, which were sent for analysis in either a 1-gal. glass container or decanted into a 1-L polyethylene bottle. Samplers deployed in the Rio Grande and Rio Chama were programmed to collect storm flow immediately following a quick rise in river stage.

Passive single-stage samplers were employed to collect water samples in watercourses or slopes that generate minimal flow, or flow over short time durations, or in locations that are difficult to access for auto samplers. Passive samplers employed were either D-Tec, Inc., Environmental Liquid Samplers, or NALGENE Stormwater Sampler. Each of these devices has one 1-gal. sample container that has a float apparatus designed to close the sample inlet when the bottle is filled. However, neither unit provides a time stamp indicating when the bottle was filled. These devices were set with intakes at an estimated water level above the channel bottom to prevent or minimize bedload sediment collection. In low-gradient shallow channels, the devices were buried in the channel bottom so sufficient head was available to fill the sample bottle. In channels where deeper flows were anticipated, the units were mounted above the channel bottom as long as the expected head was sufficient to fill the container.

When buried, the height of the sampler inlet port above the surface of the stream bottom typically ranged from 2 to 4 in., depending upon the stream order of the watercourse to be sampled. For first- and second-order streams, the inlet was set closer to the bottom. For higher-order streams, the inlet ports were mounted farther off the bottom to allow for collection at the higher flows expected in larger streams. In any of these cases, the samplers were potentially subject to interference from bedload if bedload depths approached or exceeded the sampler inlet. At the contract analytical laboratory, samples collected with passive samplers were split into appropriate aliquots using a Dekaport or churn splitter in a clean, controlled, indoor environment to prevent sample contamination. The splitters were cleaned between each sample.

While a range of surface water sampling methodologies were used in the study, the mix mimics actual equipment and techniques used in PCB monitoring programs of local municipalities and industries. The data collected by the different samplers were grouped together to capture a spectrum of baseline PCB concentrations, and make the results more widely applicable to these entities.

### **3.2 Analytical Methods**

Analytical results presented in this section were determined using the following methods:

- PCBs—EPA 1668A
- SSC—EPA160.2 or American Society for Testing and Materials (ASTM) D3977-97
- Laser particle-size analysis—ASTM C1070-01
- TOC—EPA SW-846-9060
- Target analyte list metals—EPA 200.7, EPA 200.8, and EPA 245.2

### **3.3 Quality Assurance/Quality Control**

#### **3.3.1 Field Quality Control**

To test for residual PCB contamination from previous sample collection, selected auto samplers were activated to collect PCB-free water purchased from a commercial chemical supply. Rinsate blanks were also collected from precipitation samplers and the sample splitter used for samples collected with passive samplers. Although sufficient sample volumes were often difficult to collect, several duplicate samples were analyzed when sufficient volume was present. Quality control (QC) samples were sent to the corresponding contract laboratory for analysis; the results are presented in Appendix B.

Eleven sampler equipment rinsate blanks were collected in the field by rinsing with high-performance liquid chromatography (HPLC) water. Six of the 11 blanks were collected from automated samplers using each automated sampler's program that included two rinse cycles to purge sample tubing before HPLC water was pumped through the equipment for sample collection. Five blanks were collected from passive samplers by pouring HPLC water over and through the sampling equipment. Total PCB concentrations of the sampler blanks ranged from not detected to 0.649 ng/L, which is slightly above the New Mexico WQC for protection of human health. It is possible this wide range resulted from the use of different numbers of purge cycles programmed to rinse the sample tubing between aliquots, different amounts of residual sediment and corresponding PCB load, immediate environmental

influences in the field or during sample splitting, or potential contamination in the different sources of HPLC water. In this study, none of the HPLC water was analyzed for PCB contamination, but low levels of PCB contamination in HPLC trip blanks opened and decanted in the field have been reported in unpublished LANL studies. These studies also found trip blanks opened in facilities typically had more contamination than blanks treated in the field

Four equipment rinsate blanks of equipment used by the analytical laboratory to split samples were analyzed. These blanks were collected after a field sample was split and the splitter was cleaned. Concentrations of these blanks ranged from 0.0198 ng/L to 0.386 ng/L.

Two equipment rinsate blanks were collected for precipitation samplers. These blanks were prepared by rinsing the sampler with 225 mL of methanol, followed by 225 mL of dichloromethane. The blank collected at the Bandelier National Monument Fire Lookout (hereafter referred to as Bandelier) precipitation sampling location contained 0.017 ng of total PCB contamination, while 1.77 ng was detected at the Los Alamos County Airport precipitation sampling location. Because these results were reported as ng/sample, not ng/L, they cannot be compared with New Mexico WQC concentrations. The contamination characterized in these samples indicates possible plating out of PCBs on the container sides. However, these values cannot be used to identify the degree of contamination in field samples because of differences of PCB solubility in organic solvents versus water. A solvent rinse was added to the equipment decontamination procedure to ensure no carryover occurred from one sample to subsequent samples.

Five stormwater duplicate samples were collected: two from passive samplers and three from automatic samplers. The relative percent difference (RPD) of the total PCB results from the passively collected samples were both less than  $\pm 20\%$  and within the range recommended in the validation procedures discussed in section 3.3.2. The total PCB RPD of one of the three duplicate samples collected with automatic samplers was 12%, within the recommended RPD. The other two duplicates were outside the suggested range listed in the validation procedures described in section 3.3.2. The variability in the samples collected by automated samplers can be attributed to issues with sample preparation before they were shipped to the analytical laboratory. Unlike the samples collected with the passive samplers that were split using a Dekaport or churn splitter, the samples collected with automated samplers were collected using Global Water samplers in two 1-gal. bottles. Each duplicate sample was prepared by shaking the 1-gal. bottle and decanting an aliquot into a 1-L bottle. In addition, each duplicate sample was prepared from a different 1-gal. bottle than the original sample several days after the original sample was prepared, resulting in some sediment settling that may not have been resuspended adequately when the 1-gal. containers were shaken.

Four field duplicate precipitation samples and one triplicate sample were collected. The RPDs of these samples were above the range recommended in the validation procedures of  $\pm 30\%$  in section 3.3.2.

### **3.3.2 Analytical Laboratory QC**

All LANL analytical laboratory results underwent validation by an independent DOE contractor, Analytical Quality Associates, Inc. (AQA), in Albuquerque, New Mexico, following the guidelines in the DOE National Nuclear Security Administration Model Data Validation Procedure (DOE 2006, 213441) and U.S. EPA Contract Laboratory Program National Functional Guidelines for Data Review

(EPA 2004, 213445; EPA 2004, 213446; EPA 2008, 213449). NMED data were assessed using analytical laboratory–applied qualifiers. LANL and NMED data are available as part of the Intellus database (<http://intellusnm.com>).

Method blank correction was performed on all data to account for the presence of pervasive, low-level (ambient) PCB contamination found in analytical laboratories at the extremely low detection limits achieved with EPA Method 1668A (EPA 2003, 209599). For a variety of reasons, all analytical laboratories occasionally have elevated batch-specific contamination that biases sample results. This bias is typically addressed by analyzing a method blank and, if an analyte is detected, by qualifying any sample result associated with the method blank that is less than 5 times the method blank concentration as not detected. This is known as the 5-times rule. However, in the case of PCBs, often a relatively constant, detectable, ambient concentration is present in the laboratory even when no batch-specific contamination is present. The use of the 5-times rule under these conditions probably leads to the qualification of samples as not detected when small quantities of PCBs are present in concentrations between the ambient blank concentration and 5 times that value. This situation is addressed by the use of method blank subtraction.

To accomplish method blank subtraction the running average plus two standard deviations of the method blank population is used to represent the ambient laboratory blank contamination (called the method blank correction value [MBCV]). The MBCV is subtracted from each sample result to give a result that more accurately represents the analyte concentration in the sample without the ambient laboratory contamination. This result is called the method blank corrected result (MBCR). The basis for using the running average plus 2 standard deviations (SD) to calculate the MBCV is discussed in EPA Method 1668A (EPA 2003, 209599).

The Oversight Bureau calculated each MBCV in-house either by using the first 10 method blanks of the year or all the method blanks run in the previous calendar year to calculate the MBCV for the current year's samples. NMED personnel then determined method blank corrected results (MBCRs) by subtracting each result from its MBCV.

The analytical laboratory calculated the MBCRs for LANL results. The MBCV was calculated from the 10 most recent method blanks run by the analytical laboratory, not including the batch-specific method blank run with the samples. Alternatively, a contemporary method blank population that was updated no less than monthly was used. This contemporary method blank population was required to include 10 or more method blanks, not including the batch-specific method blank run with the samples. Method blanks used in these calculations were reported down to the method detection limit.

Once MBRVs were determined for a sample and its batch-specific method blank, the 5-times rule was applied (in most cases) to account for conditions when significantly higher PCB contamination was present in the analytical laboratory. Samples collected by the NMED SWQB were method blank corrected but the 5-times rule was not. All other results were method blank corrected and qualified using the 5-times rule.

### 3.4 Statistical Methods

Statistical analysis of data sets consists of the following three steps:

1. Prepare data for analysis
2. Evaluate data heterogeneity:
  - a. Determine representativeness of PCB congener data in terms of meteorological and hydrological conditions present at times of sampling
  - b. Determine if previously collected PCB congener data can be combined with newer data to establish one set of PCB results applicable to a given study area
3. Calculate baseline levels of PCBs in storm runoff

#### 3.4.1 Prepare Data for Analysis

All statistical analyses were performed on blank-corrected PCB data. Total PCB concentrations are reported with no substitution made for undetected congeners, and these undetected concentrations were considered to be zero in the analyses. Estimated concentrations, “J” qualified, were used in the calculations. Data were analyzed using Statistica 8.0 (StatSoft, Tulsa, Oklahoma) and ProUCL 4.1 (<http://www.epa.gov/nerlesd1/databases/datahome.htm>). Statistical analyses were considered significant at  $p < 0.05$ .

#### 3.4.2 Evaluate Data Heterogeneity

Both graphical and quantitative lines of evidence were used to help determine if baseline data represented a single population or should be viewed as distinct subpopulations. Box plots were used as the main graphical data display to evaluate any differences between drainages and between LANL and NMED data sets. Statistical tests and summary statistics were used as quantitative lines of evidence to support the visual impression provided by the box plots.

Box plots were used to graphically display the median, interquartile range, and quartile skew for selected data. The median is the 50<sup>th</sup> percentile value, which indicates 50% of the data are less than or equal to that reported value. The center line in the box plot represents the median. The interquartile range represents the middle 50% of the data, which is bounded by the 75<sup>th</sup> percentile value and the 25<sup>th</sup> percentile value. The enclosed portion of the box represents the interquartile range. The quartile skew is easily seen by comparing the portion of the box above and below the median line. When plotted on a linear scale, if the upper portion of the interquartile box is larger than the lower portion, then the data are skewed to the high concentrations. The lines extending from the top and bottom of the box plot are drawn to the 10<sup>th</sup> and 90<sup>th</sup> percentile values of the data.

When plotted on the same scale, box plots of different data sets can be compared visually and differences and similarities among stations can be identified. The data for a given station also were compared statistically with other individual stations using the Wilcoxon-Mann-Whitney (WMW) test, which is equivalent to the Wilcoxon Rank Sum test. This nonparametric technique uses the ranks of the data and calculates the probability that two independent statistical samples came from the same population. The null hypothesis tested is the data from two stations have the same distribution. The alternative hypothesis tested is that data from one of the stations has larger (or smaller) values than the other. The chance of making an error by rejecting the null hypothesis when the null hypothesis is true is measured

by probability. If the probability level is 0.05, there is a 5% chance of error when rejecting the null hypothesis. In tests to determine statistically significant differences in PCB concentrations, a probability level of 0.05 was used.

### 3.4.3 Calculation of Runoff Baseline Values

To determine runoff baseline values, the data sets were first inspected for potential outlying values that were exceptionally high or low relative to the rest of the data. Next, the data were evaluated to determine if they derive from a single statistical population, which involved fitting the data to standard statistical distribution (e.g., normal, lognormal, or gamma) and determining the best fitting distribution (Appendix E). All the Reference and Western Boundary station locations were upstream of and distant from LANL liquid discharges; thus, the potential of contamination to be present in the baseline samples was minimized by site selection. It was important to ensure the baseline data sets represented "single" populations free of contamination or outliers. Both graphical and quantitative lines of evidence were used to help determine if these baseline data represented a single population or should be viewed as distinct populations. Probability plots were used as the main graphical displays to identify multiple or mixture samples that might have been present in a data set (see probability plot descriptions at <http://www.itl.nist.gov/div898/handbook/eda/section3/eda33.htm>). Dixon outlier tests and summary statistics were used as quantitative lines of evidence supporting the visual impression of the probability plots.

The probability plots show each analytical result ordered from lowest to highest. The x-axis is the standard normal quantile scale. The units of the standard normal quantile are in standard deviations, where 1 represents one sigma or standard deviation. The y-axis of the probability plot is the concentration of the analyte. The purpose of these plots is twofold. First, they provide a succinct way to present all the data for each analyte. Second, they provide a way to assess the statistical distribution of each analyte. If the data for an analyte follow a straight line when plotted on a standard normal scale, these data are considered to originate from a normal statistical distribution. One can assess the fit to other statistical distributions by transforming the y-axis to another scale. For example, chemical data are frequently derived from a lognormal distribution, and transforming the y-axis into a logarithmic scale assesses the fit to a lognormal distribution. Data that fit the normal distribution are symmetrically centered about the mean. Most environmental data, however, naturally contain the occasional high value, and the upper half of the distribution is stretched, or skewed, in the direction of the high values. Both the lognormal and gamma distributions describe skewed data sets and often best match environmental results. Probability plots help determine the high values are not caused by contamination beyond natural levels, by determining if the data fit along a straight line after transformation.

The distribution of PCB concentrations also was tested to determine if they approximated the normal probability function (or normally distributed after a logarithmic or gamma transformation) with the Lillifors and Kolmogorov-Smirnov methods. Upper tolerance limits (UTLs) were calculated in ProUCL for the best-fit distribution to calculate the upper limit concentrations for PCBs under baseline conditions. The appropriate statistical distribution for each analyte was selected based on reviewing probability plots and the distribution fit test results. Concentrations of PCBs in surface water may vary dramatically because of the concentrations found in suspended sediment and the amount of suspended sediment entrained in each sample. Thus, outlier PCB water concentrations can be explained by the amount of sediment in the samples. This possibility was accounted for by assessing the PCB concentrations in the sample sediment fraction as well. Total PCB concentrations in suspended sediment were calculated by dividing the total PCB in water by the corresponding SSC and multiplying by a unit conversion factor. If an anomalous



water concentration was verified to also have an enriched PCB concentration in suspended sediment, the result was removed from the baseline data set.

Suspended PCB concentrations were calculated using the following formula:

$$\text{Suspended PCB } \left( \frac{\text{ng}}{\text{g}} \right) = \frac{\text{Total PCBs in water } \left( \frac{\text{ng}}{\text{L}} \right)}{\text{Suspended sediment concentration } \left( \frac{\text{mg}}{\text{L}} \right)} \times \text{Conversion Factor} \quad \text{Equation 1}$$

Correlation analysis was used to test the hypothesis that a relation exists among PCB concentrations, TOC concentrations, and suspended sediment or metal concentrations. The Spearman nonparametric rank correlation test was used to quantify these associations. The correlation coefficient measures the strength of association between two variables and can vary between  $-1$  and  $1$ . The closer the coefficient is to  $-1$  or  $1$ , the stronger the correlation. The coefficient describes the degree that two variables increase or decrease together. The Spearman test is useful for this type of reconnaissance because it does not require that the variables change in a linear fashion. In some cases, when the data are sufficient, the associated probability can indicate a significant correlation, even if the correlation coefficient is not large. In these cases, a weak but true correlation between the variables exists, although other effects may influence the results (Anderholm et al. 1995, 213422). For this study, the sample sizes are relatively small, and the correlation coefficient can be excessively influenced by a single data pair. Consequently, an attempt was made to examine not only the coefficients themselves but also to examine the general relationships among PCBs, TOC, and SSC. A correlation with an associated probability of  $0.05$  or less was considered significant.

General similarities in PCB compositions in samples were evaluated using homolog results. If a more rigorous quantitative comparison between sampling sites was needed, the congener results were used. Congener profiles across study areas were evaluated by correlation analyses. Congener profiles, or concentration patterns, were compared across an area on a sample-by-sample basis by calculating the coefficient of determination ( $R^2$ ) and associated probability value for detected congeners.  $R^2$  is a measure of the strength of association between each sample and the probability value is a measure of the significance (odds of the association resulting from random chance).  $R^2$  is the square of the Pearson product moment correlation coefficient,  $r$ , which ranges from  $0$  to  $1$  and is the fraction of the variance in the two variables that is shared. For example, if  $R^2$  was  $0.63$ , then  $63\%$  of the variance in Sample A can be explained by variation in Sample B and vice versa. The greater the proportion of explained variation, the closer are the sample values, hence the stronger the linear relationship. Samples with a  $R^2$  greater than  $0.64$  ( $r = 0.8$ ) and a probability of  $0.05$  or less were assumed to be strongly associated.

Trend analysis was used to evaluate temporal variation in the sample data. Trends through time are more often evident when a smoothing routine is used on plots of concentration versus time. Consequently, the locally weighted scatter plot smoothing (LOWESS) method (Cleveland 1979, 213341) was used to highlight trends or patterns in PCB data through time.

## 4.0 RESULTS

### 4.1 Precipitation and Snowpack

Precipitation delivers a diffuse source of PCBs to the landscape throughout northern New Mexico. As with radioactive fallout, PCBs are found globally in the atmosphere and periodically are rained out to the ground. A starting point in evaluating baseline PCB concentrations in northern New Mexico surface waters is quantifying PCB levels in precipitation.

A total of 34 precipitation events were sampled at two stations near Los Alamos. Sampling stations were located near the fire-lookout tower above the visitor's center of the Bandelier National Monument and at the Los Alamos County Airport. In addition, 12 snowpack samples were collected from nine peaks located along mountain ranges bordering the Rio Grande corridor between Albuquerque and Taos, near the Colorado–New Mexico border (Figure 7).

#### 4.1.1 Variation of Baseline PCB Concentrations in Precipitation and Snowpack

The concentrations of total PCBs in precipitation and snowpack samples are illustrated in Figure 8 in box plot form and are summarized in Table 2. The precipitation total PCB concentrations ranged from 0.0 ng/L to 0.60 ng/L (Bandelier median: 0.12 ng/L; Los Alamos County Airport median: 0.14 ng/L). Concentrations in snowpack samples ranged from 0.003 ng/L to 0.65 ng/L (median: 0.14 ng/L). One PCB precipitation sample result (4.04 ng/L) was removed from the Bandelier data set because it was an extreme outlier based on the Dixon test ( $p < 0.01$ ) when compared with other Bandelier precipitation results and with a paired result obtained at the Los Alamos County Airport for the same event. Detected PCB concentrations in precipitation and snowpack samples that were slightly skewed appear to be derived either from a normal or gamma distribution (see probability plots in Appendix C).

The results for the precipitation samples were nearly identical to those for the snowpack samples. Los Alamos–area precipitation PCB concentrations were statistically indistinguishable from those measured in snowpack samples collected from high elevation locations throughout northern New Mexico (WMW test,  $p = 0.24$ ). Similarly, total PCB concentrations in Bandelier precipitation samples were indistinguishable from those measured at the Los Alamos County Airport (WMW test,  $p = 0.493$ ). All but 1 of the 34 precipitation and snowpack samples were below the New Mexico human health WQC of 0.64 ng/L, and all were below the wildlife habitat WQC of 14 ng/L.

The results show the distribution of total PCB concentrations in precipitation and snowpack samples is relatively uniform throughout northern New Mexico. The consistency in results across the region indicates that local sources of atmospheric PCBs have limited regional impacts. The two largest PCB concentrations measured in snowpack were collected at Sandia Crest and probably demonstrate higher urban contributions from Albuquerque (population approximately 500,000). For the other snowpack sites, however, Figure 9 shows no clear relation between PCB concentrations and population sizes. For example, snowpack samples collected in the mountains above and predominantly upwind of Taos (population approximately 5700) contained larger average PCB concentrations than those collected above and upwind of Santa Fe (population approximately 75,000). Similarly, Figure 10 shows no correlation ( $R^2 = 0.003$ ) between total PCB concentrations and sample elevation.

Limited data from the upper Rio Grande and tributaries indicate PCB concentrations in snowmelt runoff may be considerably less than in the snowpack itself. One hypothesis to explain this finding is that infiltration and through-flow within the forest litter and upper soil layers effectively remove particulate bound PCBs before they reach watercourses. However, such an attenuation mechanism probably would not operate when overland flow dominates over infiltration, such as when large snowpack undergoes rapid melting. Rapid melting is known to occur in the Jemez Mountains (e.g., see snow depth measurements at Quemazon SNOTEL site, U.S. Department of Agriculture, <http://www.wcc.nrcs.usda.gov/nwcc/site?sitenum=708&state=nm>). Under rapid melting conditions, PCBs in the snowpack would probably be carried quickly by overland flow into watershed channels.

Baseline PCB concentrations in precipitation near Los Alamos were relatively low compared with other locations in studies around the globe (Tables 3 and 4). The concentration of total PCBs in precipitation from remote global locations ranged from a low of 0.02 ng/L to a high of 6.9 ng/L.

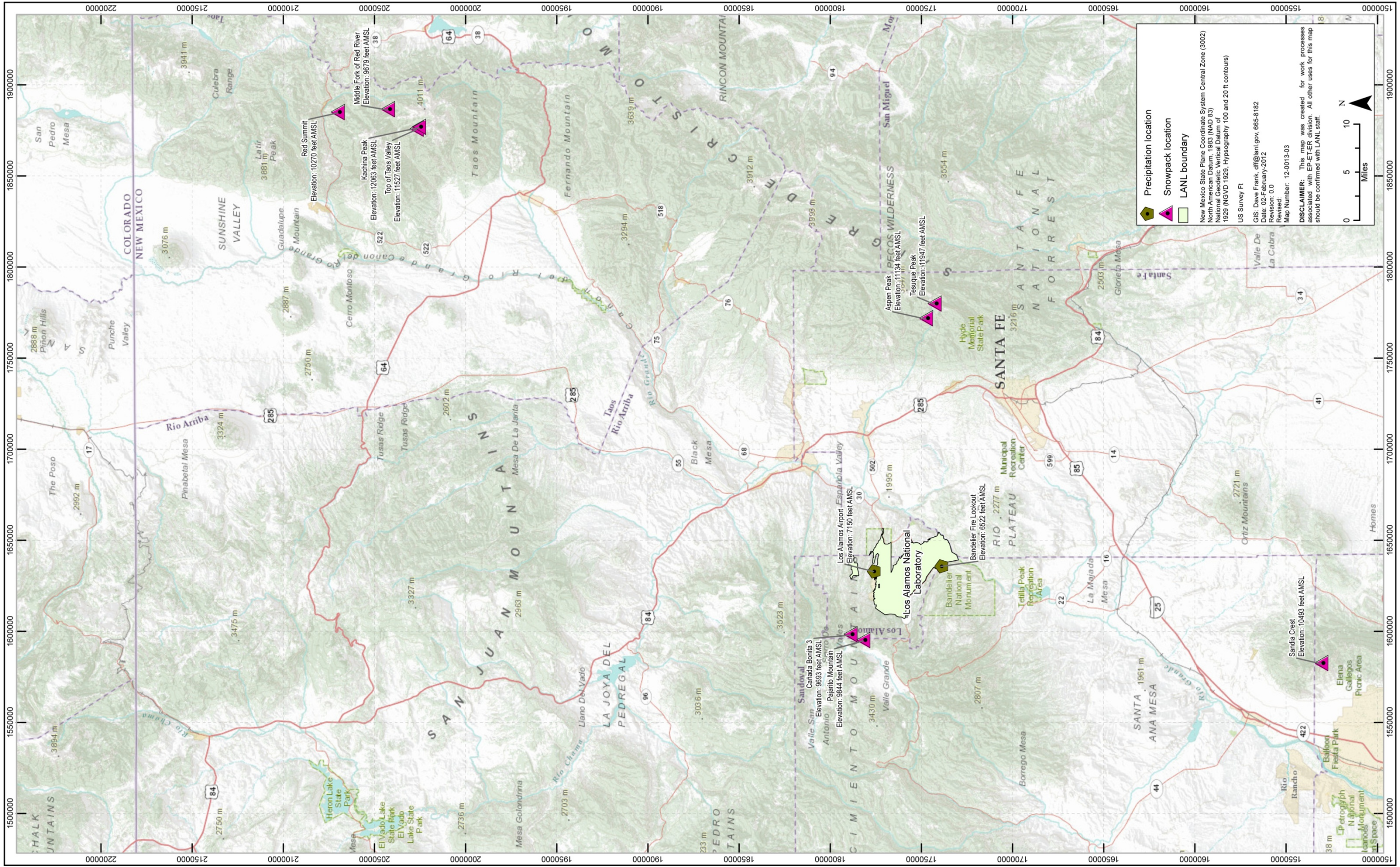
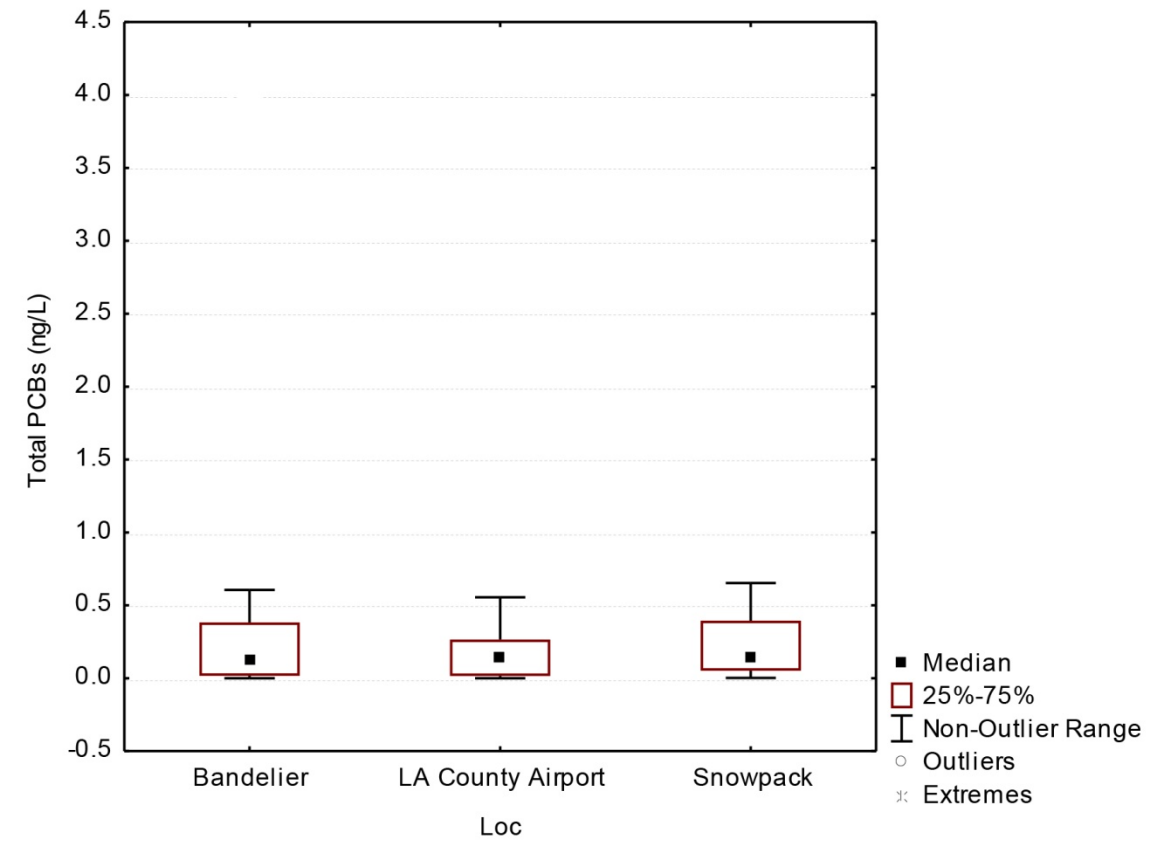


Figure 7 Locations of precipitation and snowpack stations



**Figure 8** Box plot of total PCB concentrations in precipitation and snowpack samples collected in northern New Mexico

**Table 2**  
Total PCB Concentrations in Precipitation and Snowpack Samples, Northern New Mexico 2009–2010

Location	Mean	N	SD	Min	Max	Median
Bandelier	0.184	17	0.194	0.000	0.607	0.117
LA County Airport	0.167	16	0.160	0.000	0.556	0.143
Snowpack	0.221	12	0.217	0.003	0.653	0.144

Note: Units are in ng/L.

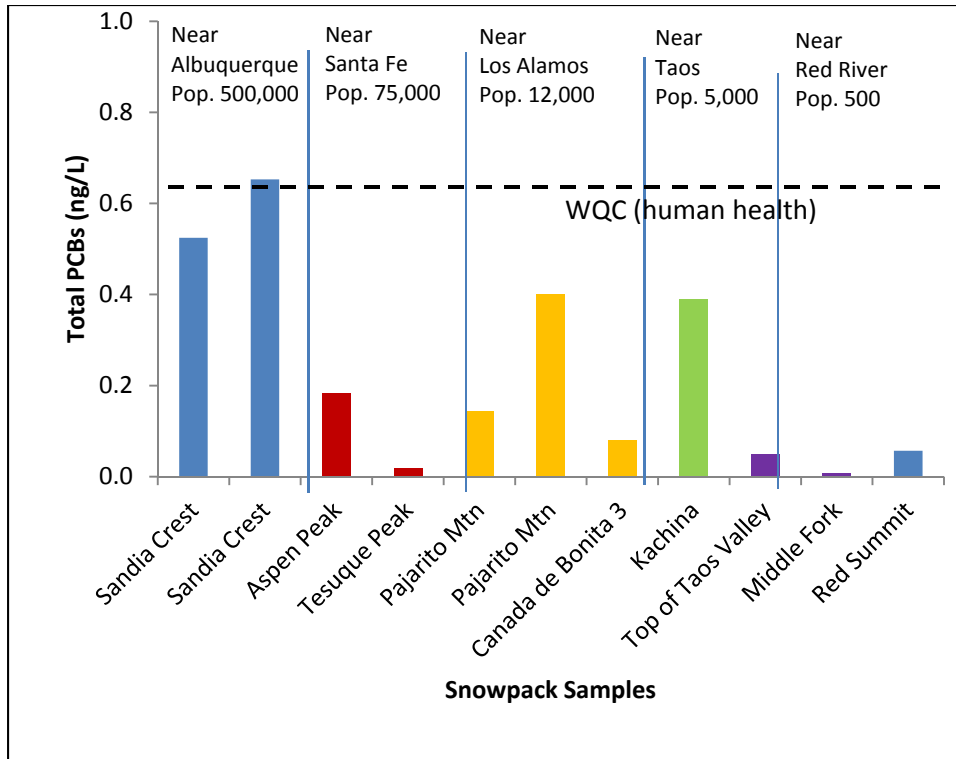


Figure 9 Total PCB concentrations in snowpack samples and population size of closest municipality

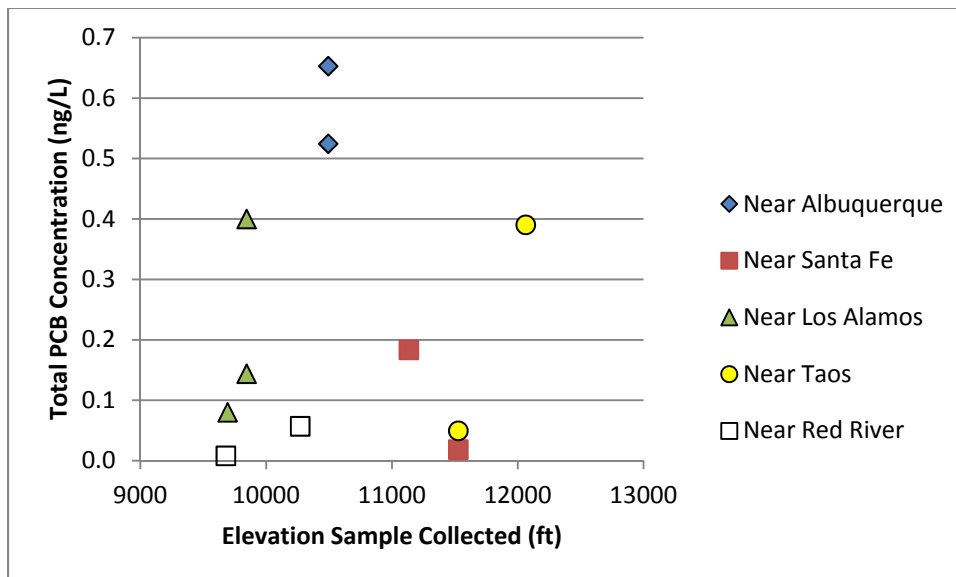


Figure 10 Total PCB concentrations in snowpack samples compared to elevation for study locations

**Table 3**  
**Worldwide PCB Concentrations in Snow**

Location	Site Characterization	PCB Concentration (ng/L) Average or Range	Reference
Antarctic	Rural/Remote	0.16–1	Tanabe et al. 1983, 209558
Prince Edward Island	Rural/Remote	4.6	Brun et al. 1991, 213404
New Brunswick	Rural/Remote	4	Brun et al. 1991, 213404
Nova Scotia	Rural/Remote	1.9	Brun et al. 1991, 213404
Ice Island (Arctic)	Rural/Remote	0.17–0.54	Hargrave et al. 1988, 209553
Canadian Arctic	Rural/Remote	0.02–1.76	Gregor and Gummer 1989, 209552

**Table 4**  
**Worldwide PCB Concentrations in Rain**

Location	Site Characterization	PCB Concentration (ng/L) Mean or Range	Reference
Lake Michigan, IL	Background of Chicago	5.8	Offenberg and Baker 1997, 213425
Green Bay, WI (3 sites)	Coastal	2.2	Franz and Eisenreich 1993, 213408
Tuckerton, NJ	Coastal (light residential)	0.35	Van Ry et al. 2002, 213431
Finokalia, Greece	Coastal, remote	1.8	Mandalakis and Stephanou 2004, 213421
Pinelands, NJ	Forest	0.38	Van Ry et al. 2002, 213431
Baltic Sea (916 sites)	Marine background	2.3	Agrell et al. 2002, 213334
South Sweden (9 sites)	Regional background	2.4	Backe et al. 2002, 213338
Cedar Creek, MN	Rural	2.3–2.8	Franz et al. 1991, 213409
Enewetok Atoll	Rural/Remote	<0.6	Atlas and Giam 1981, 213335
College Station, TX	Rural/Remote	2.3	Atlas and Giam 1988, 213336
Ellerslie, Prince Edward Island	Rural/Remote	250	Brun et al. 1991, 213404
Kejimikujik, Nova Scotia	Rural/Remote	61	Brun et al. 1991, 213404
Ferté sous Jouarre, France	Rural/Remote	23–520	Chevreuil et al. 1996, 213340
Chesapeake Bay, MA	Rural/Remote	0.1–37	(Leister and Baker 1994, 213419)

Table 4 (continued)

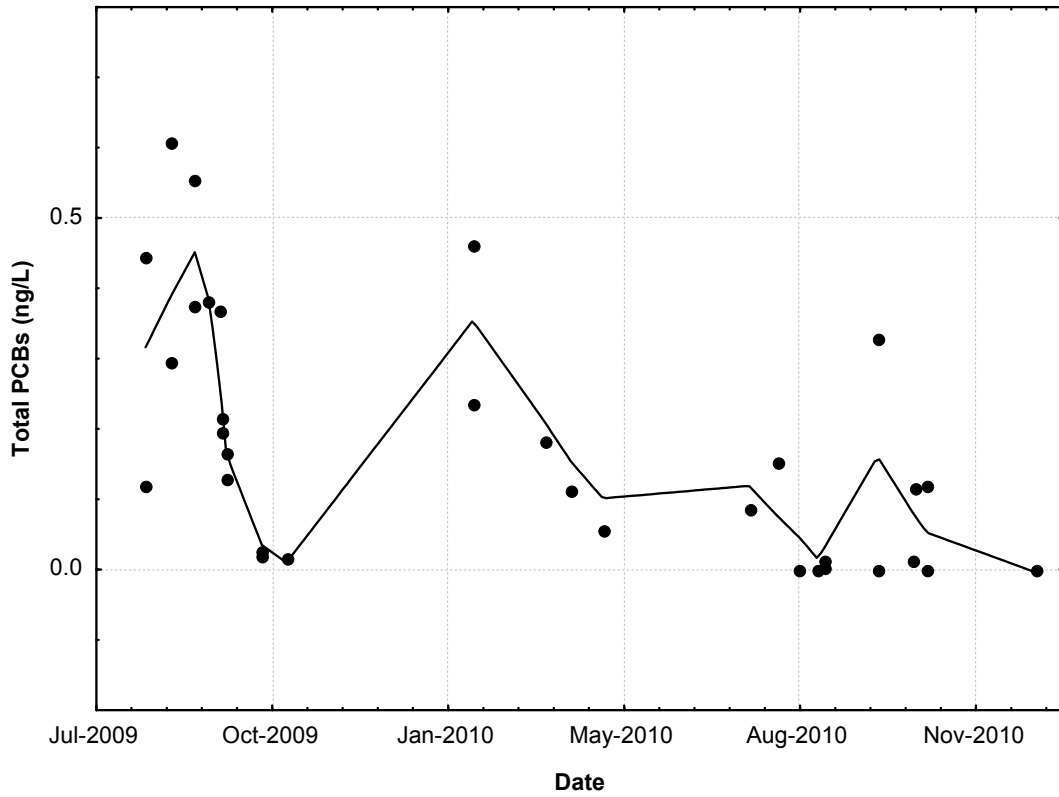
Location	Site Characterization	PCB Concentration (ng/L) Average or Range	Reference
Norway	Rural/Remote	<2.2–7.6	Lunde et al. 1977, 213420
Southern France	Rural/Remote	1.0–92.6	Villeneuve and Cattini 1986, 213432
United Kingdom	Rural/Remote	1.8–74	Wells and Johnstone 1978, 213433
Heraklion, Greece	Semiurban	2.3	Mandalakis and Stephanou 2004, 213421
New Brunswick, NJ	Suburban	1.3	Van Ry et al. 2002, 213431
Paris, France	Urban	86–340	Chevreuil et al. 1996, 213340
Kiel, Germany	Urban	1.5	Duinker and Bouchertall 1989, 213405
Madison, WI	Urban	3.5	Murray and Andren 1992, 213424
Chicago, IL	Urban	29.3	Offenberg and Baker 1997, 213425
Lausanne and Geneva, Switzerland	Urban	35	Rossi et al. 2004, 213427

While concentrations vary greatly depending on sampling technique and analysis, in general, higher concentrations have been observed near industrial and urban centers. Table 3 presents some worldwide PCB concentrations measured in snowpack, while Table 4 presents reported PCB concentrations in rainwater worldwide.

Variability in the Los Alamos precipitation PCB values appears to be mostly from variability caused by natural washout from the atmosphere. Figure 11 combines data from both the Bandelier and Los Alamos County Airport precipitation stations and shows the fluctuation of PCB concentrations over time. The graph indicates PCB concentrations appear to fluctuate with patterns. Figure 12 indicates concentrations are highest near the start of a series of precipitation events and then progressively decline to low concentrations. Other studies show that PCB washout is affected by many factors, including the period of dry weather between two rain events, the intensity of rain, the duration of the rain event, and the total amount of rain (Rossi et al. 2004, 213427).

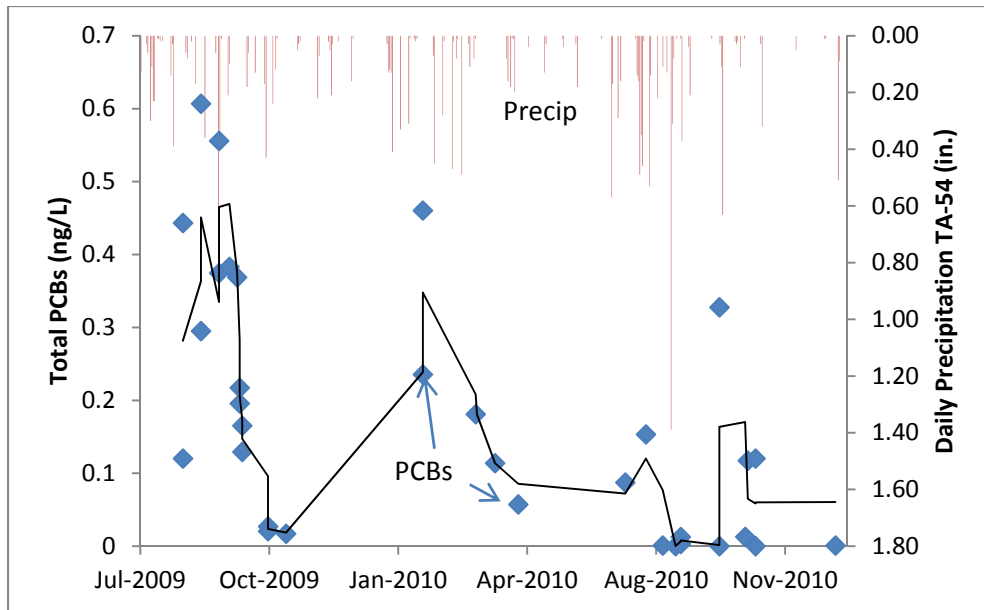
#### 4.1.2 Fingerprint of PCBs in Precipitation

The distribution of the PCB congeners and homologs is a useful tool for qualitatively evaluating their source or origin. To establish a fingerprint or signature pattern for PCBs in precipitation, the amount of each homolog is divided by the sum of all homologs (total PCB concentration).



Note: Best fit line is locally weighted regression (LOWESS).

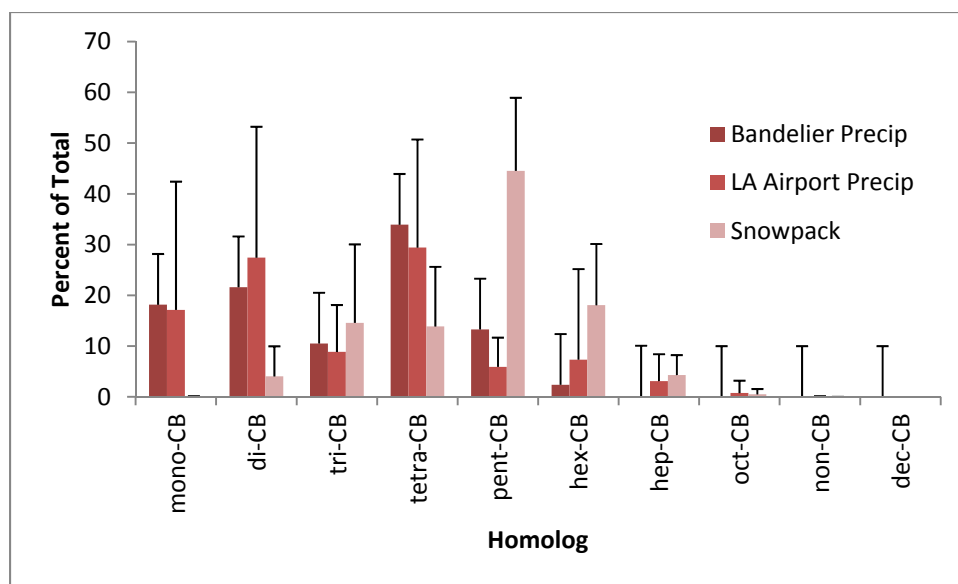
**Figure 11 Variations over time in total PCB concentrations in precipitation, Los Alamos, New Mexico**



**Figure 12 Relation of Total PCBs in rainfall to daily precipitation measured at LANL Technical Area 54 (TA-54) meteorological station**



Snowpack and precipitation homologs had different average signatures, as Figure 13 shows. Data from both stations show bimodal distributions, reflecting a mixture of two distinct groups of homologs. One group has abundant light and volatile mono-CBs and di-CBs homologs, and the second group is dominated by tetra-CBs. By contrast, the snowpack samples are mostly centered on penta-CBs. Penta-CBs and hexa-CBs increase and mono-CBs and di-CBs decrease in the snowpack when compared with the precipitation distributions. This pattern may result from the increased dust loading of snowpack and/or the volatilization of lower chlorinated PCB congeners from the snowpack over the winter. Precipitation samples are collected only when the sampler is activated by precipitation and the collection bucket is covered between each event to prevent dust deposition between samplings and to minimize the influence of dust on the sample.



Note: Vertical error bars show data spread equal to 1 SD.

**Figure 13 Average PCB homolog distributions in precipitation and snowpack samples**

Although the homolog patterns for the two precipitation stations are quite similar on average, large differences occurred in the homolog signatures from storm to storm. In particular, the abundance of the light mono- and di-CBs was greatest in the summer months and was reduced during the winter months when contributions from the tetra- and penta-CBs were greater. The four winter precipitation samples more closely resembled snowpack samples.

## 4.2 Regional Soil

Wet and dry atmospheric deposition provides a continual, but diffuse, source of PCBs to the landscape. Some fraction of these deposited PCBs will be transported directly by stormwater runoff or snowmelt into watercourses. Yet other PCB fractions will volatilize and return to the atmosphere. Meanwhile, a fraction of the PCBs binds to surface soils and is present long-term, forming a reservoir. The surface soil compartment can contain a relatively large mass of atmospheric PCBs because intact soil can collect and integrate decades' worth of PCB deposition. Through erosion, surface soil may eventually be entrained by runoff events and enter watercourses. Consequently, PCBs can enter surface water in significant amounts when surface soil is mobilized. The following discussion describes previously published baseline

levels data of PCBs in regional soil and evaluates potential water-quality impacts if the soil enters surface water.

In a previous study, soil was sampled along the Rio Chama and Rio Grande drainages to discern whether baseline atmospheric sources of PCBs for these water bodies of water next to LANL may exist (Gonzales and Fresquez 2003, 213451). Five of the nine samples were collected from relatively undisturbed mesa-top sites next to the Rio Grande along an approximately 250-mi reach, starting from the Rio Grande Reservoir in Colorado to near Cochiti Reservoir in Santa Fe County, New Mexico. Four of the nine samples were collected from relatively undisturbed mesa-top sites next to the Rio Chama along an approximately 100-mi reach, from the head of the Rio Chama in Colorado to the San Juan Pueblo in Rio Arriba County, New Mexico. All soil samples were distant from municipal or industrial sources and away from localized surface sources such as runoff.

#### 4.2.1 Variation in Baseline PCB Concentrations in Regional Soil

Mean total PCBs for the nine bulk soil samples was 0.046 ng/g-dry weight (dw), with a standard deviation of 0.077 ng/g-dw, and maximum of 0.28 ng/g-dw.

The concentrations compare favorably with analyses of 15 Rio Grande sediment samples collected upriver of Los Alamos Canyon near Otowi Bridge (LANL 2009, 108621; LANL 2010, 111232; LANL 2011, 207316). PCB concentrations in the sediment averaged 0.080 ng/g, with a maximum of 0.347 ng/g. As sampled, the bulk soil may include a mixture of clay, silt, sand, and organic matter. Once runoff begins, the smaller particles, such as clay and organic matter, are more easily eroded and are preferentially carried by the surface water, while the coarser, heavier sand is commonly left in place. This particle-size separation results in higher PCB concentrations associated with particulates in surface water compared with the bulk soil concentrations. This partitioning affects the concentration of PCBs in surface water because PCBs tend to become concentrated in finer-grained sediment or organic matter (Ghosh et al. 2003, 213410; LANL 2009, 108621; Huang et al. 2011, 213414).

The baseline soil concentrations were used to model PCB concentrations in surface water that might result if native soil became suspended in the water column. More specifically, scoping calculations were performed to forecast the SSCs needed to bring PCB water column concentrations equal to the New Mexico human health WQC of 0.64 ng/L. The estimate was made using the following equation:

$$SSC\left(\frac{mg}{L}\right) = \frac{WQC\left(\frac{ng}{L}\right) - PCB\ Precip\left(\frac{ng}{L}\right)}{PCB\ Soil\left(\frac{ng}{g}\right) \times EF} \times 1000 \quad \text{Equation 2}$$

where SSC = suspended sediment concentration

WQC = water-quality criterion (human health) = 0.64 ng/L

PCB<sub>precip</sub> = regional precipitation PCB baseline concentration

PCB<sub>soil</sub> = PCB concentration in baseline bulk soil

EF = enrichment factor, to adjust for enriched suspended PCB concentrations once the finer textured portion of bulk soil become eroded and carried by surface water.

Table 5 summarizes the scoping calculations. Reasonable ranges of values were input into the calculations to project the range of SSCs needed to reach the WQC. Average PCB concentrations in precipitation and soil varied by factors of 1 and 2, and the enrichment factors varied by 1, 2, 5, and 10. The results indicate it is feasible the WQC could be approached *under baseline conditions* with SSCs of a few grams per liter, or 1000 to 2000 mg/L. Such SSCs are commonly measured in natural ephemeral

channel runoff in northern New Mexico. In the Rio Grande, however, such SSCs have been measured infrequently, 20% or fewer of the samples, based on analysis of data compiled from the USGS Water Information System database.

**Table 5**  
**Modeled SSCs Needed for Surface Water PCB**  
**Concentrations to Reach New Mexico Human Health WQC of 0.64 ng/L**

WQC (ng/L)	Precipitation Baseline (ng/L)	Bulk Soil PCB (ng/g)	EF <sup>a</sup>	SSC Needed to Equal WQC (mg/L)	Frequency SSC Equaled or Exceeded in USGS Water Samples Collected in Rio Grande at Otowi Bridge (1960–2009) <sup>b</sup>
0.64	0.2	0.05	1	8800	6%
0.64	0.2	0.05	2	4400	11%
0.64	0.4	0.05	2	2400	19%
0.64	0.2	0.05	5	1760	23%
0.64	0.4	0.1	5	480	52%
0.64	0.4	0.1	10	240	69%

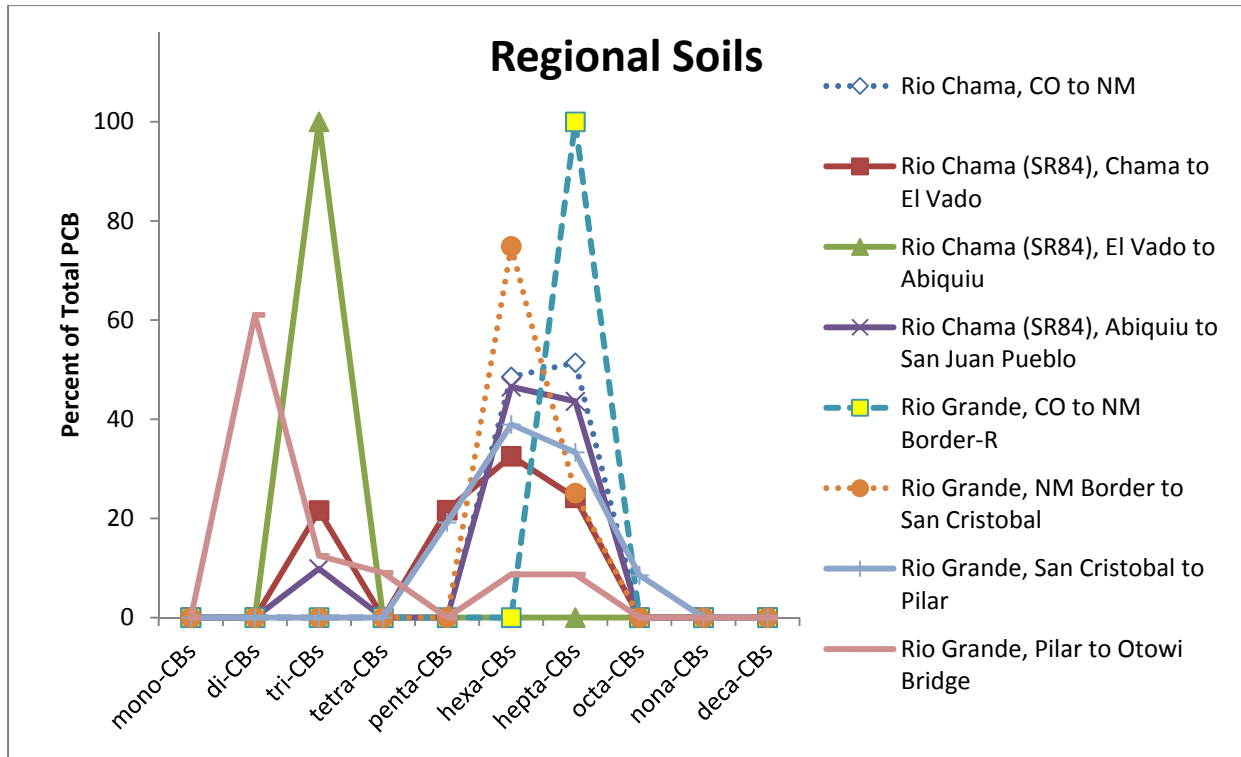
<sup>a</sup> EF = Enrichment factor.

<sup>b</sup> SSC raw data retrieved from USGS Water Information System database.

The scoping calculations assume that soil PCB concentrations fall within the range measured by Gonzales and Fresquez (2003, 213451) and reflect what concentrations that might occur in drainages with relatively stable landscapes. However, in drainages with substantial erosion or incision, the baseline soil PCB concentrations could be significantly lower. In these conditions, the intact surface soil—those exposed to atmospheric deposition for long periods—will be mixed with older sediment that have not been regularly exposed to deposition-derived PCBs, and as a result the overall soil PCB concentrations decreased.

#### 4.2.2 Fingerprint of PCBs in Regional Baseline Soil

Distributions of homologs in the baseline soil were described as being distinctly bimodal with peaks at the tri- and hexa-CB homologs (Gonzales and Fresquez 2003, 213451). However, further examination shows that the bimodal distribution was limited to the lower-elevation sampling stations (Figure 14). The samples collected from higher elevations in the drainage basins near the Colorado border do not contain appreciable amounts of the low-chlorinated homologs and were dominated by the high-chlorinated hexa- and hepta-CB homologs. Gonzales and Fresquez (2003, 213451) proposed that the most likely source for the low-chlorinated PCBs was atmospheric macroscale wind-pattern deposition, while the high-chlorinated PCBs were attributed to more local wind-blown sources of PCB-entrained dust. Alternatively, several other studies indicate the presence of low-chlorinated homologs may result from anerobic biodegradation of older, deeper PCB-containing soil (Lake et al. 1992, 213418; Abramowicz 1995, 213333; Chen et al. 2001, 213339; Fava et al. 2003, 213342; EPA 2008, 213448), resulting in a shift to lower chlorinated PCBs at depth in the soil/sediment profile.



Note: Highest elevation stations are noted by dashed lines; solid lines signify lower elevation stations.

**Figure 14 PCB homolog distributions in nine baseline soil samples from Rio Grande and Rio Chama drainages**

### 4.3 Northern New Mexico Ephemeral Tributaries

The Rio Grande and Rio Chama drainage basins have numerous small tributaries in northern New Mexico. Most of these are ephemeral tributaries where the frequency of flow is largely determined by proximity to the mountains. To gain a broad understanding of the quality of flows contributed by these tributaries, 13 primarily ephemeral drainages within both basins were assessed for PCB concentrations (Figure 15). A few small villages are located along the drainages, but overall the landscape is undeveloped.

Along the Rio Chama, storm runoff was collected within approximately 1 mi of the river from three tributaries: Cañada de Horno, Arroyo del Toro, and Rio del Oso. These are primarily ephemeral drainages that drain the northeast side of the Jemez Mountains, northwest of Española, and southeast of Abiquiu. Along the Rio Grande, storm runoff was collected from 10 tributaries along an approximately 60-mi-long segment, primarily above the towns of Española, Dixon, and Taos. These channels drain the eastern edge of the Rio Grande valley, bounded by the Sangre de Cristo Mountains.

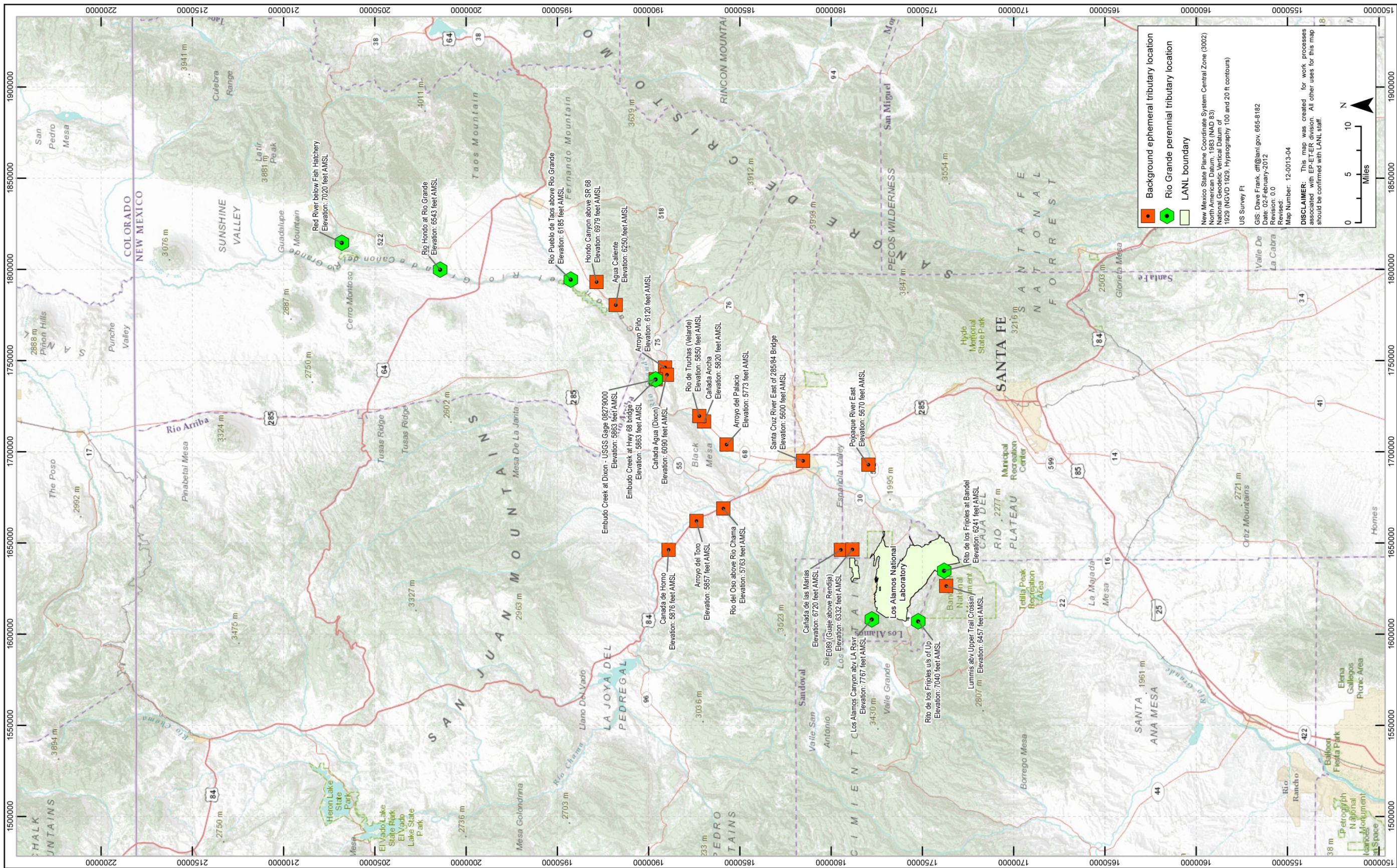
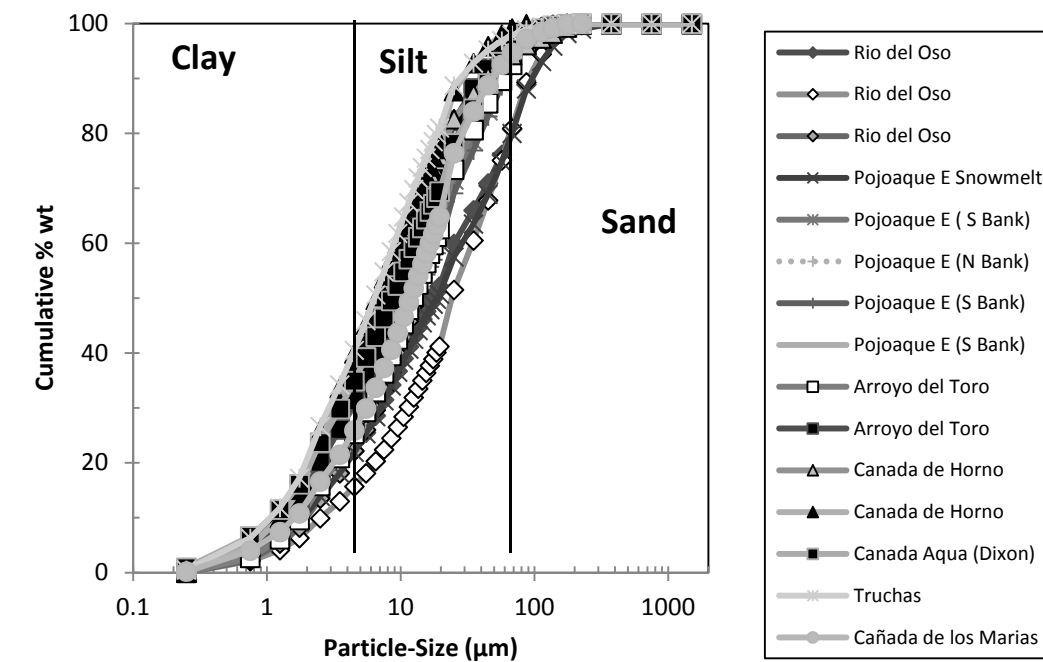


Figure 15 Northern New Mexico stream sampling locations

Sampling stations along the Rio Chama were situated within tilted Tertiary sandstone and siltstone deposits of the Santa Fe Group. The deposits consist of several old river floodplain deposits that were laid before the Rio Grande became a through-flowing river. They are laden with volcanic ash from eruptions in volcanic centers to the north and west. Much of the badland topography in the vicinity is from clay derived from the volcanic ash (Chronic 1987, 213488). The Rio Grande stations also drain some Santa Fe Group deposits but are more influenced by the resistant lava flows of the Taos volcanic field and surface rocks of the Sangre de Cristo Mountains consisting of Pennsylvanian sedimentary rocks and Precambrian granite and gneiss.

Sediment was largely dominated by the silt-size fraction (3.9  $\mu\text{m}$  to 62.5  $\mu\text{m}$ ), with silt contents ranging from 67% to 86% by weight. The least abundant size fraction was sand, with a median content of 7.5%, although its abundance varied with each runoff event. The overall high abundance of silt+clay of nearly 90% is significant because these particles have a high surface area per mass and potentially have chemically reactive surfaces that enhance adsorption of contaminants.

Cumulative frequency plots of the particle-size data indicate the texture of suspended sediment in the northern ephemeral tributaries is relatively uniform across the samples (Figure 16). The Rio del Oso samples showed an overall higher abundance of sand than did samples from the other locations but were still dominated by silt+clay fractions.



**Figure 16** Cumulative frequency plots for particle-size distribution for 15 suspended sediment samples in runoff from northern New Mexico tributaries

The lack of sand in the samples primarily indicates the water velocity and turbulence were not sufficient to cause the transport of coarser sediment, although stream discharge measurements are not available for these samples.

**4.3.1 Variation in PCB Concentrations in Northern New Mexico Tributaries**

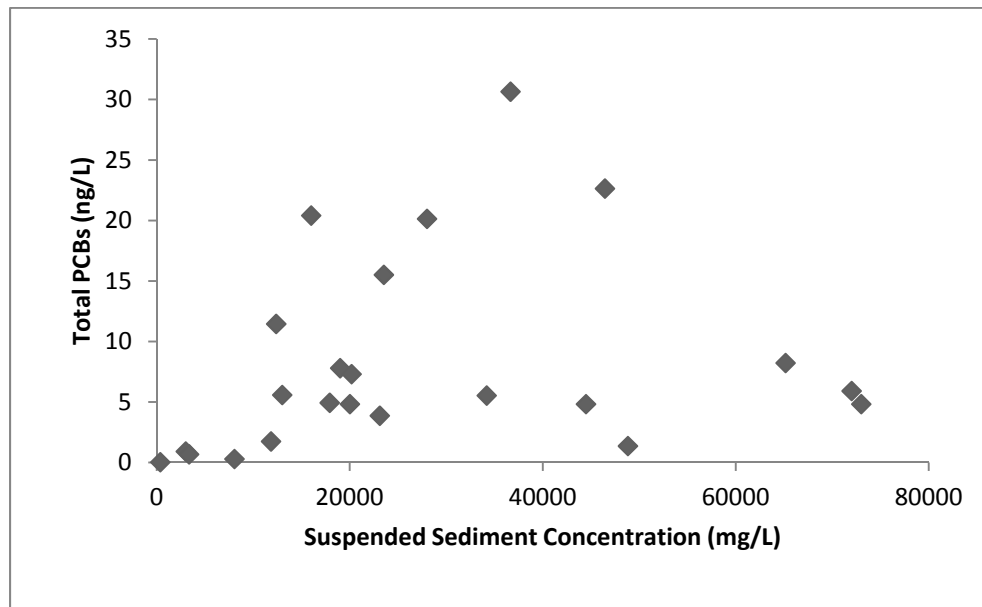
Total PCB concentrations in northern New Mexico tributaries were highly variable, ranging over 4 orders of magnitude. All but 2 of the 29 results (93%) exceeded the New Mexico human health WQC of 0.64 ng/L, and 6 of 29 results (21%) were above the wildlife habitat WQC of 14 ng/L. Table 6 summarizes the PCB concentrations in tributary runoff.

**Table 6**  
**Summary Statistics of PCB Concentrations in Northern New Mexico Tributary Runoff**

	N	Min	Max	Mean	SD	Median	Distribution	UTL*
Total PCB (ng/L)	29	0.28	29.5	7.5	8.2	4.9	Gamma	24.86
<b>Calculated Suspended PCB Concentration (ng/g)</b>	23	0.03	1.276	0.353	0.329	0.241	Gamma	1.135

\*95% Wilson-Hilferty (W-H) approximate gamma UTL with 90% coverage.

PCB concentrations were affected by the concentration of suspended sediment in the samples. In the northern New Mexico tributary samples, PCB concentrations tended to increase with SSC in some samples but plateaued above approximately 20,000 mg/L in others for reasons that cannot yet be explained (Figure 17).

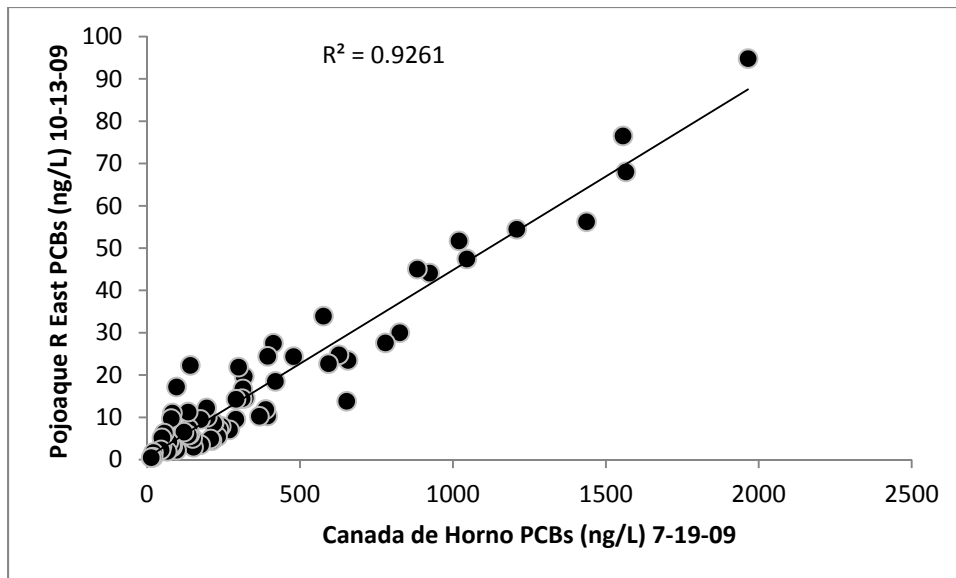


**Figure 17** Plot of total PCBs versus SSC in northern New Mexico tributaries

### 4.3.2 Fingerprint of PCBs in Northern New Mexico Tributary Runoff

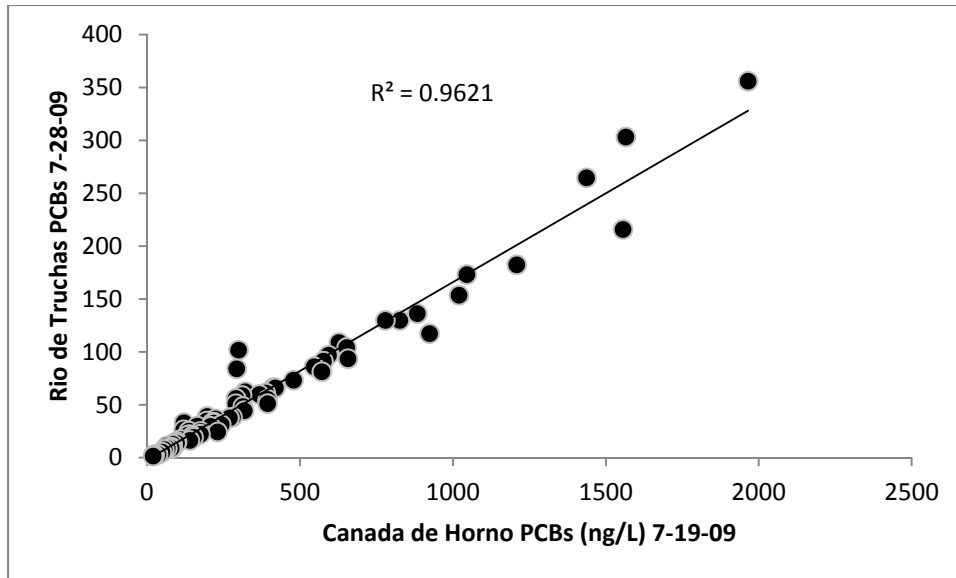
To evaluate the similarity in PCB congener profiles across the northern New Mexico tributaries, correlation analyses were performed. In the analyses, concentrations of PCBs detected in one sample were matched to the same congener concentrations detected in the comparison sample (section D-1 of Appendix D presents additional details), resulting in tens of concentration pairs to correlate within each intersample comparison. Of the 27 profiles (plus 2 duplicates) compared with correlation analyses, all but 2 were strongly associated. The median  $R^2$  value of the 380 intersample comparisons was 0.8. The consistency in congener profiles across the tributaries indicates most of the variation can be attributed to a common source and possibly to a regionally extensive PCB signature. In addition to geographic consistency, the congener profiles were consistent over time, as profiles obtained in 2008 were consistent with those collected 3 yr later at the same location.

To illustrate the geographic consistency, profiles in samples collected along Rio Chama tributaries usually matched well with those collected below the Sangre de Cristo range at Velarde and with those collected in the Rio Grande valley near Pojoaque. A graphical comparison of three PCB congener profiles is presented in Figures 18 and 19. The scatter plots compare the congener profile for a stormwater runoff sample from Cañada de Horno in the Rio Chama Valley (collected in 2009) with profiles from the Rio Pojoaque East (collected in 2011) and the Rio de Truchas (collected in 2009). Total PCB concentrations in the three samples were 29.5 ng/L, 1.20 ng/L, and 4.68 ng/L, respectively. Although the total PCB concentrations varied widely, the congener profiles were substantially alike. With  $R^2$  values greater than 0.90 and probabilities less than 0.05, the congener profiles were strongly associated.



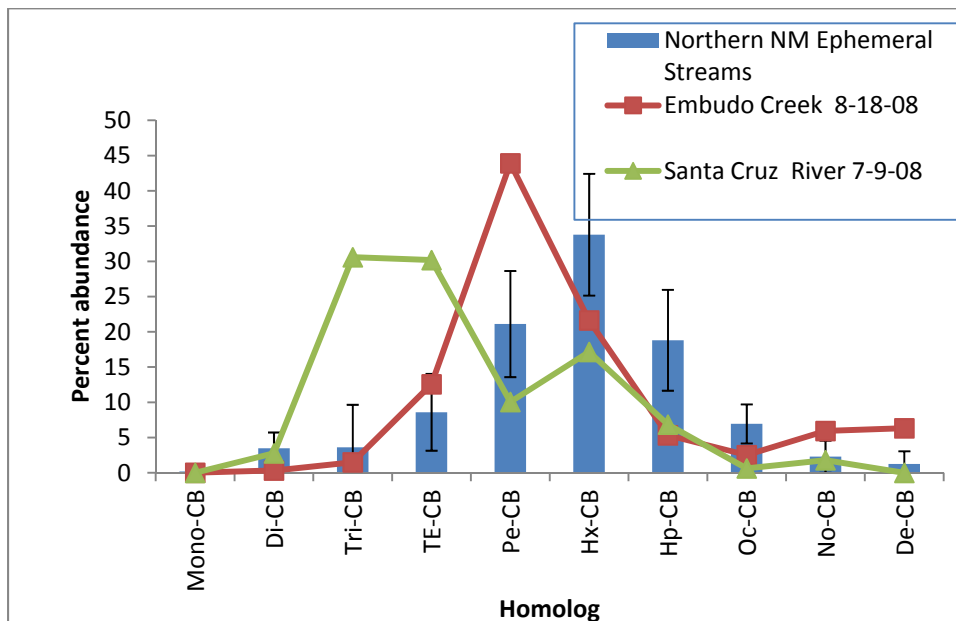
**Figure 18** Relation between PCB congener concentrations detected in stormwater runoff samples collected from Cañada de Horno and from Rio Pojoaque East





**Figure 19** Relation between PCB congener concentrations detected in stormwater runoff samples collected from Cañada de Horno and from Rio de Truchas

Two unexplained deviations from this pattern of strongly associated congener profiles occur: (1) fair to moderate correlation in profiles was found in a sample from Embudo and (2) poor correlation was found in one of two samples collected near Santa Cruz. Each of those samples contained greater proportions of the lighter homologs than the other tributary samples (Figure 20).



Note: Columns show average (+/- 1 sd) of 27 samples from with strongly associated PCB profiles. Lines show two samples with PCB profiles different than the rest.

**Figure 20** PCB homolog distribution in stormwater samples from northern New Mexico tributaries

Figure 20 shows the average homolog distribution for the tributary samples. The distribution is symmetrically centered on the hexa-CB homolog in nearly every sample. The bimodal distribution noted in precipitation and regional soil samples is evident in only one sample (Santa Cruz River) and not in a later repeat sample from the same location. Of the PCBs in the samples, 60% is contained in the moderate chlorinated penta-, hexa-, and hepta-CB homologs; the low-chlorinated CB homologs comprised less than 10% of the total PCB concentration.

#### **4.4 The Rio Grande and Rio Chama**

The Rio Grande is the largest river in New Mexico, and the Rio Chama is its largest tributary within the state. Historically, stream flow in these rivers was influenced by spring snowmelt (April through June) and summer monsoon thunderstorms (July and August). This natural stream-flow pattern has been altered and regulated by reservoirs on the main stem and tributaries that store the water for later use, primarily for irrigation. In addition to the precipitation and reservoir-controlled fluctuations, base flow is maintained by regional groundwater discharge from the Rio Grande basin. Consequently, significant variability in PCB concentrations is expected in the Rio Grande and Rio Chama, given the variety of source waters and suspended sediment fluctuations commonly observed in these rivers.

Congener-specific PCB analyses of the Rio Grande and Rio Chama waters began in 2002 with an unpublished joint NMED-LANL regional reconnaissance investigation. NMED collected additional data in 2006–2007. Subsequent sampling was conducted in 2009–2010 to measure PCB concentrations in the rivers during runoff conditions. LANL also collected paired samples from the Rio Grande at Otowi Bridge and at Buckman nominally on a bimonthly basis from 2008–2010. Sampling locations are displayed in Figure 21. This investigation primarily assessed the data collected since 2006. PCB samples NMED collected were labeled according to the flow regime present at the time of sampling. NMED used the terms “Ambient” and “Storm” while LANL used the terms “base flow” and “runoff.” Both naming systems categorize samples collected during relatively stable base-flow conditions and those collected during storm-induced runoff events. For this analysis, it is assumed “ambient” and “base flow” are synonymous. With a few exceptions, the SSC in the “base flow” samples were low, usually below 100 mg/L. All the stormwater samples were collected by NMED for this study, while the ambient results were compiled from other LANL and NMED sampling efforts.

Figure 22 shows the stream flow history for the Rio Grande at Otowi Bridge gage (USGS #08313000) during the years from 2006 to 2010. Superimposed on the hydrograph are notations when “Ambient” and “Storm” PCB samples were collected. Most samples were collected during the summer and autumn months when thunderstorm runoff events can cause flows to quickly rise well above base-flow levels. Fewer samples were collected during snowmelt-fed spring runoff, but two samples were taken near the peak flow for the season to help capture the range of flow-related water-quality changes. Either an ambient or storm sample was collected during 9 of 10 deciles of flow for the years 2006–2010 in every month, except for March and April. (The deciles divide the sorted daily discharge measurements into equal parts, so each part represents 1/10 of all the measurements.) Overall, the samples were collected in a variety of seasons and flow conditions and provide a reasonably representative picture of total PCB concentrations for the Otowi and Buckman sites.

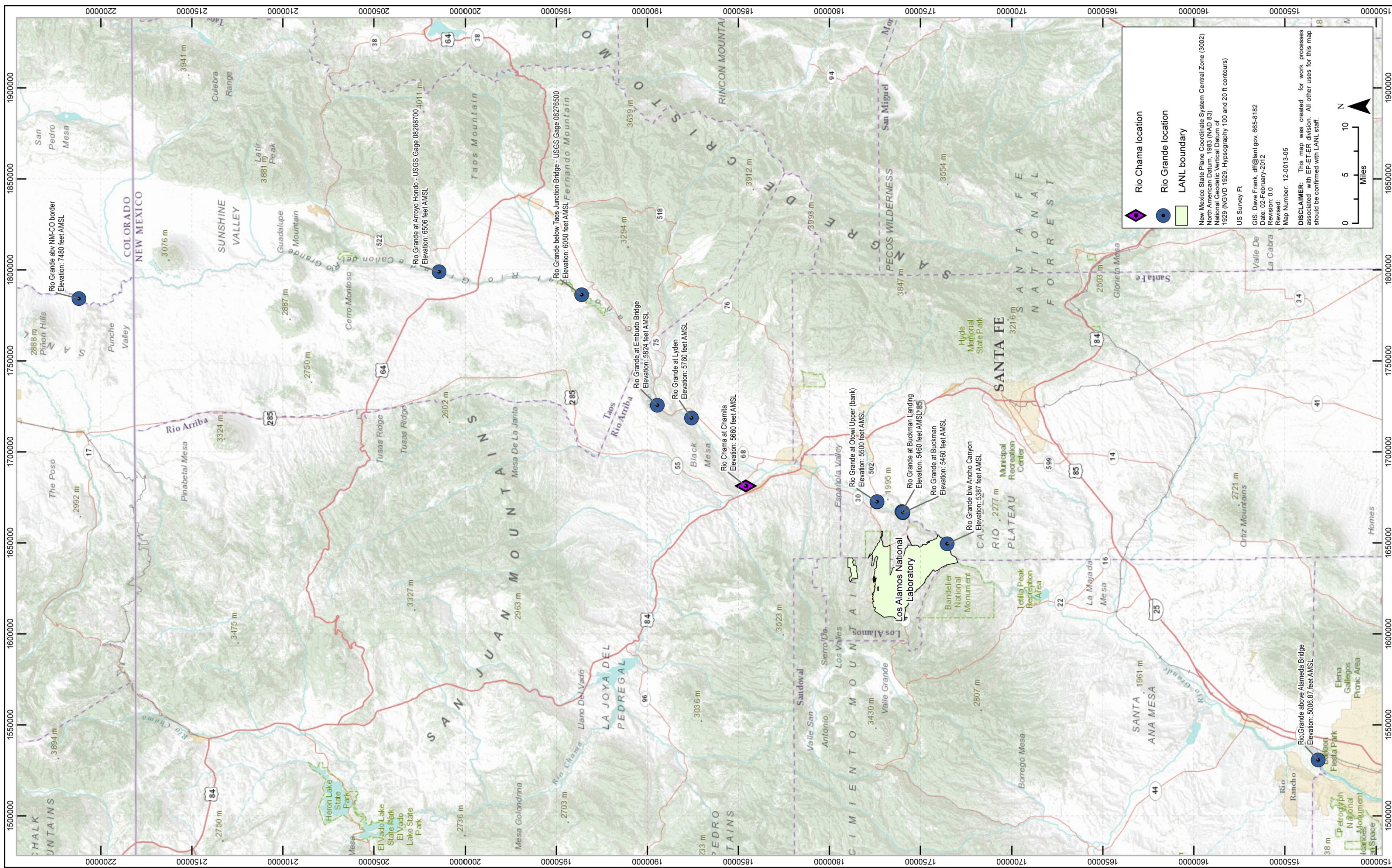


Figure 21 Rio Grande and Rio Chama sampling locations

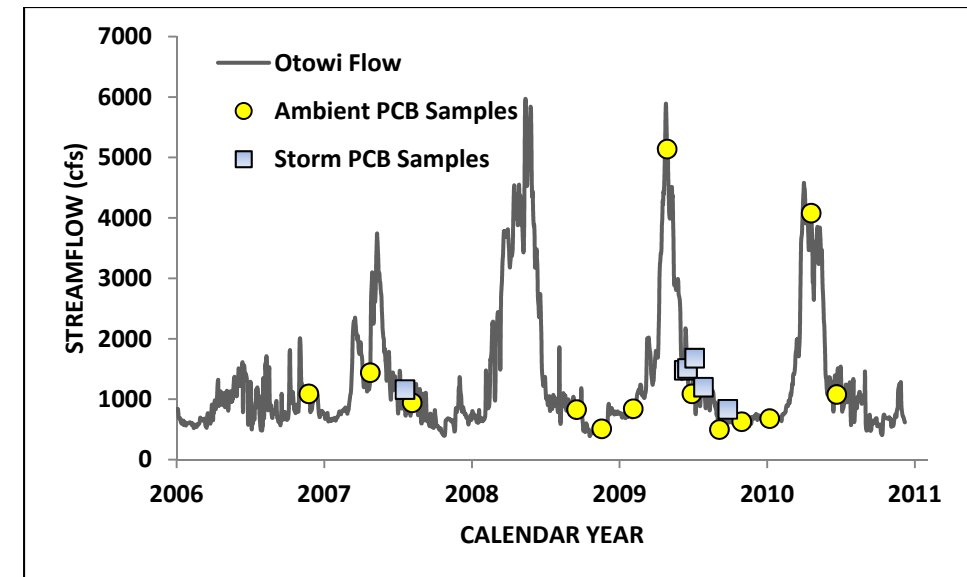


Figure 22 PCB sampling dates and stream flow for the Rio Grande at Otowi Bridge station

#### 4.4.1 Variation in PCB Concentrations in the Rio Grande and Rio Chama

Table 7 summarizes the total PCB concentrations and SSCs measured in samples collected from the northern Rio Grande and the Rio Chama. The overall median total PCB concentration for 68 samples collected above Cochiti Reservoir was 0.05 ng/L, which is substantially below the New Mexico human health WQC of 0.64 ng/L. Only 2 of 35 (6%) “Ambient” samples had total PCB concentrations above the human health WQC, and none were higher than the wildlife habitat WQC of 14 ng/L. For the “Storm” samples, 13 of 33 (39%) were above the human health WQC, and 3 of 33 (9%) were above the wildlife habitat WQC.

The greatest density of sampling was conducted at the Rio Grande at Otowi Bridge and Rio Grande at Buckman stations, located above and below LANL drainages, respectively. No significant difference in median total PCB concentrations between the Otowi and Buckman stations were evident for the “Ambient” samples (WMW Test,  $p = 0.991$ ), for the “Storm” samples ( $p = 0.47$ ), or for all samples combined ( $p = 0.615$ ).

Suspended PCB concentrations (calculated) were included in Table 7 for storm samples with two or more results. Median concentrations ranged from 0.005 ng/g to 0.13 ng/g, bracketing the regional soil baseline median value of 0.02 ng/g. As with the water PCB concentrations, no significant difference in the median suspended PCB concentrations was evident at the Otowi and Buckman stations (WMW test,  $p = 0.428$ ). The higher suspended PCB concentrations shown in Figure 22 at the Otowi and Buckman stations may reflect the occasional contribution of additional PCBs beyond global atmospheric deposition levels. The net effect on the Rio Grande, however, was not sufficient to bring about substantial changes in trends along the river.

**Table 7**  
**Summary of Total PCB Concentrations and**  
**SSC Measured in Rio Grande and Rio Chama, 2006–2010**

Station Name	Sample Type	Total PCBs (ng/L)			SSC (mg/L)			Suspended PCBs (Calculated) (ng/g)	
		N	Median	Max	N	Median	Max	N	Median
Rio Chama near Chamita	Ambient	4	0.05	0.14	2	1027	1390	—*	—
	Storm	3	0.10	0.11	2	993	1040	2	0.05
	Combined	7	0.06	0.14	4	993	1390	—	—
Rio Grande above NM-CO border	Ambient	1	0.10	0.10	1	4	4	—	—
Rio Grande at Lyden	Storm	3	0.01	7.09	2	1611	2816	2	0.005
Rio Grande below Rio Hondo	Ambient	1	0.76	0.76	1	12.2	12.2	—	—
Rio Grande below Taos Junction Bridge	Ambient	4	0.04	0.09	2	75.5	100	—	—
Rio Grande at Otowi Bridge	Ambient	14	0.02	1.36	12	63	2160	—	—
	Storm	10	0.24	50.0	7	1911	78870	7	0.13
	Combined	24	0.06	50.0	19	158	78870	—	—
Rio Grande at Buckman	Ambient	10	0.00	0.00	10	81.1	122	—	—
	Storm	17	0.55	51.4	11	1393	42100	11	0.06
	Combined	23	0.02	24.1	21	533.7	42100	—	—
Rio Grande below Ancho Canyon	Ambient	1	0.03	0.03	1	104	104	—	—

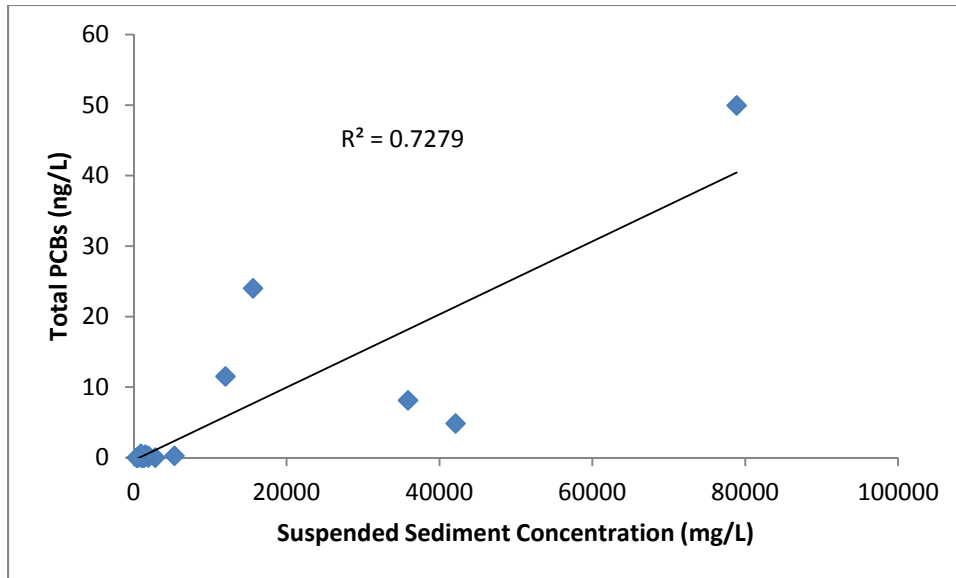
\* — = Ambient suspended PCB concentrations not calculated because ambient samples typically did not contain appreciable amounts of suspended sediment.

Total PCB concentrations were strongly correlated (Pearson  $R^2 = 0.73$ ;  $p < 0.00001$ ) to SSCs in the storm samples, as shown in Figure 23. No apparent correlation was evident in the base-flow samples, however, probably because the overall SSC is low and PCBs are detected at a lower frequency in that group of ambient samples.

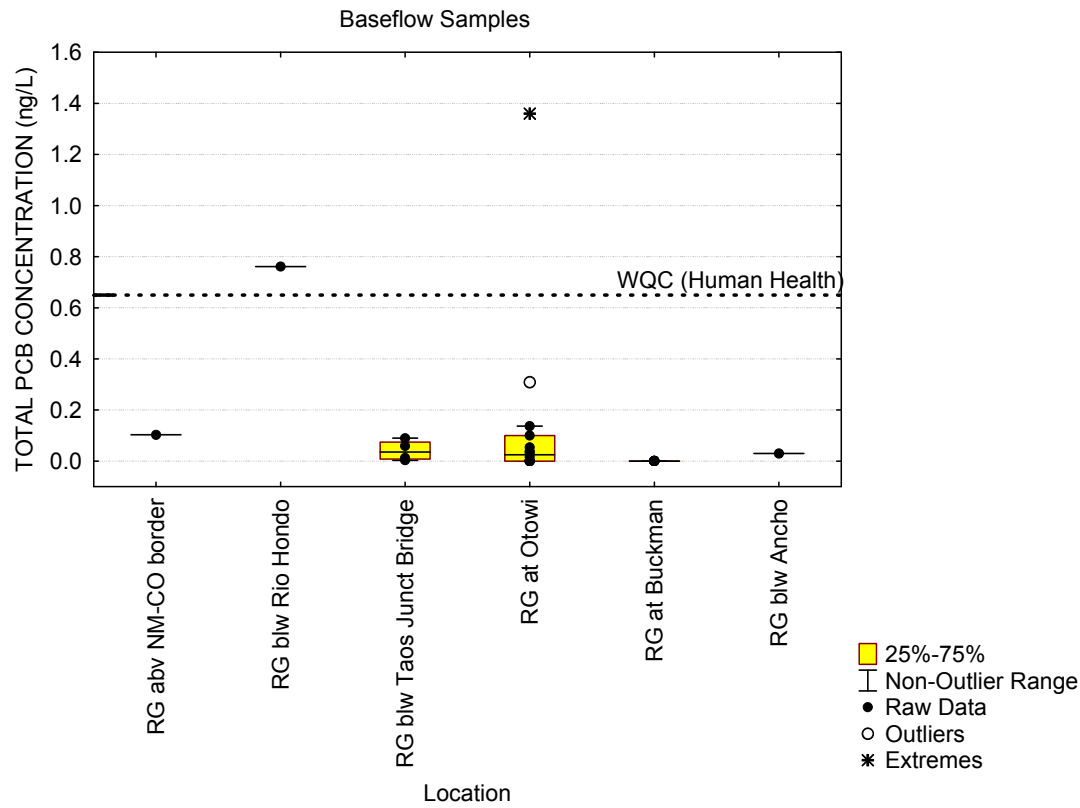
The Rio Grande PCB sampling stations were located along an approximately 100-mi segment that extends into Colorado. The sample results within the upper part of the segment were too few to allow for a formal analysis of longitudinal concentration trends. However, a visual comparison of concentrations is presented in Figures 24 to 26. For each Rio Grande station, the raw results and station median are plotted for both water samples and calculated suspended PCB concentrations in the samples. No significant longitudinal pattern trends are apparent, and median concentrations are relatively consistent upstream to downstream.

#### 4.4.2 Fingerprint of PCBs in Northern Rio Grande and Rio Chama

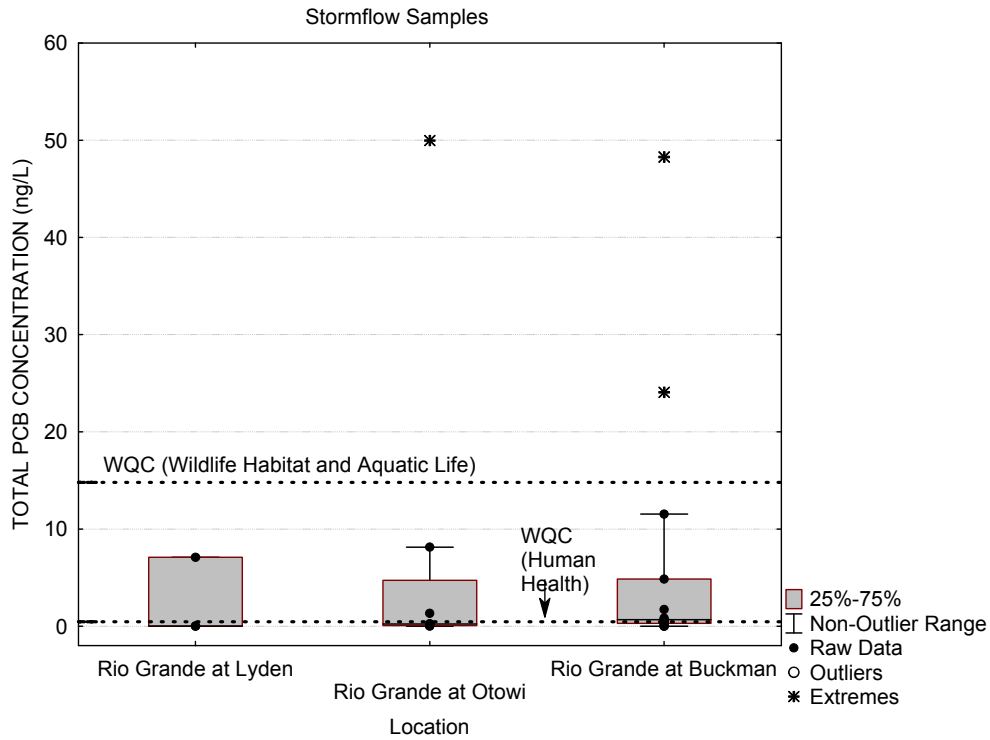
The upper Rio Grande and Rio Chama drainage systems encompass large geographic areas, with landscapes varying from desert grasslands to verdant alpine ecosystems. The PCB fingerprints in the rivers potentially may vary widely within such diverse settings. Not only do the PCB fingerprints of precipitation vary, so do those of native soil. Coupled with these factors are the various sources of surface water that feed the rivers. During the late spring, flows in these rivers are dominated by melting snow near the New Mexico–Colorado border. Thunderstorm runoff may be locally plentiful during the summer and early autumn, while flows in intervening periods are heavily influenced by discharge of regional groundwater via springs and seeps.



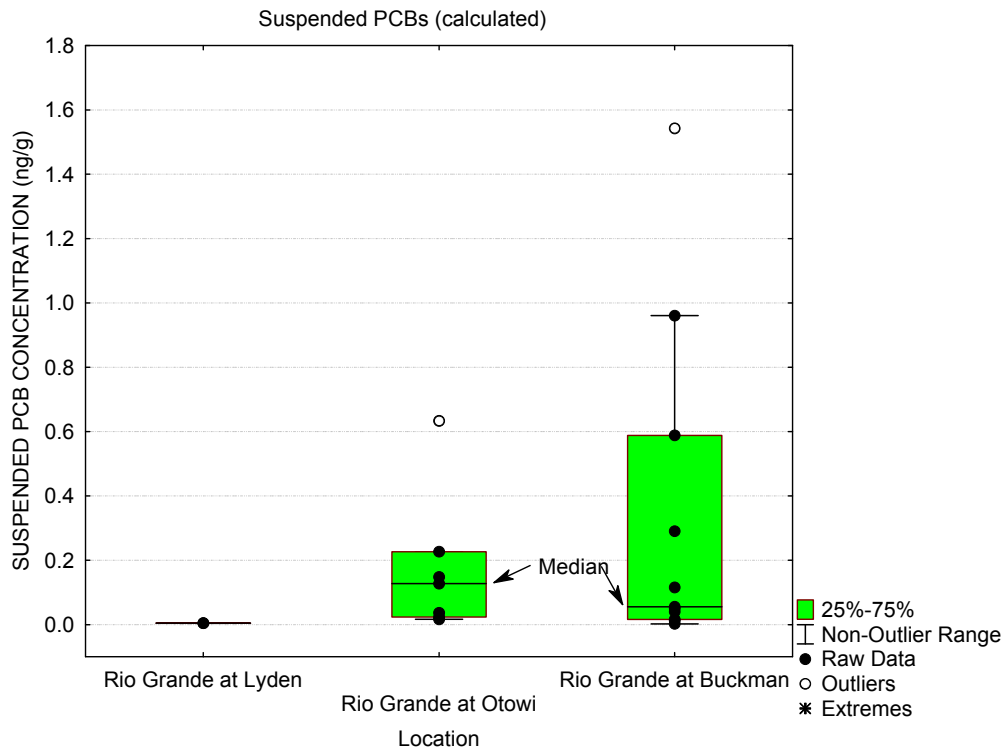
**Figure 23** Relation between SSC and total PCBs concentrations in stormwater runoff samples collected in the northern Rio Grande and Rio Chama, 2007–2010



**Figure 24** Box plot of total PCB concentrations in base-flow samples along the Rio Grande, 2006–2010



**Figure 25** Box plot of total PCB concentrations in storm runoff samples from the Rio Grande, 2006–2010



**Figure 26** Box plot of calculated suspended PCB concentrations in storm-flow samples from the Rio Grande, 2007–2010

This study indicates no single fingerprint or pattern describes surface waters in the Rio Grande or Rio Chama. The fingerprint varies significantly within the seasons—possibly within the same day—and with location. Although other studies have shown that the fingerprint is helpful in identifying sources of PCBs, the available data indicate it would be difficult to do the same in the Rio Grande drainage basin without a substantial effort. The scales are too great to describe a typical PCB profile with a small number of samples collected at random through the year. A snapshot of PCB profiles along the Rio Grande may be achieved when multiple samples are collected through the drainage system within a relatively short time.

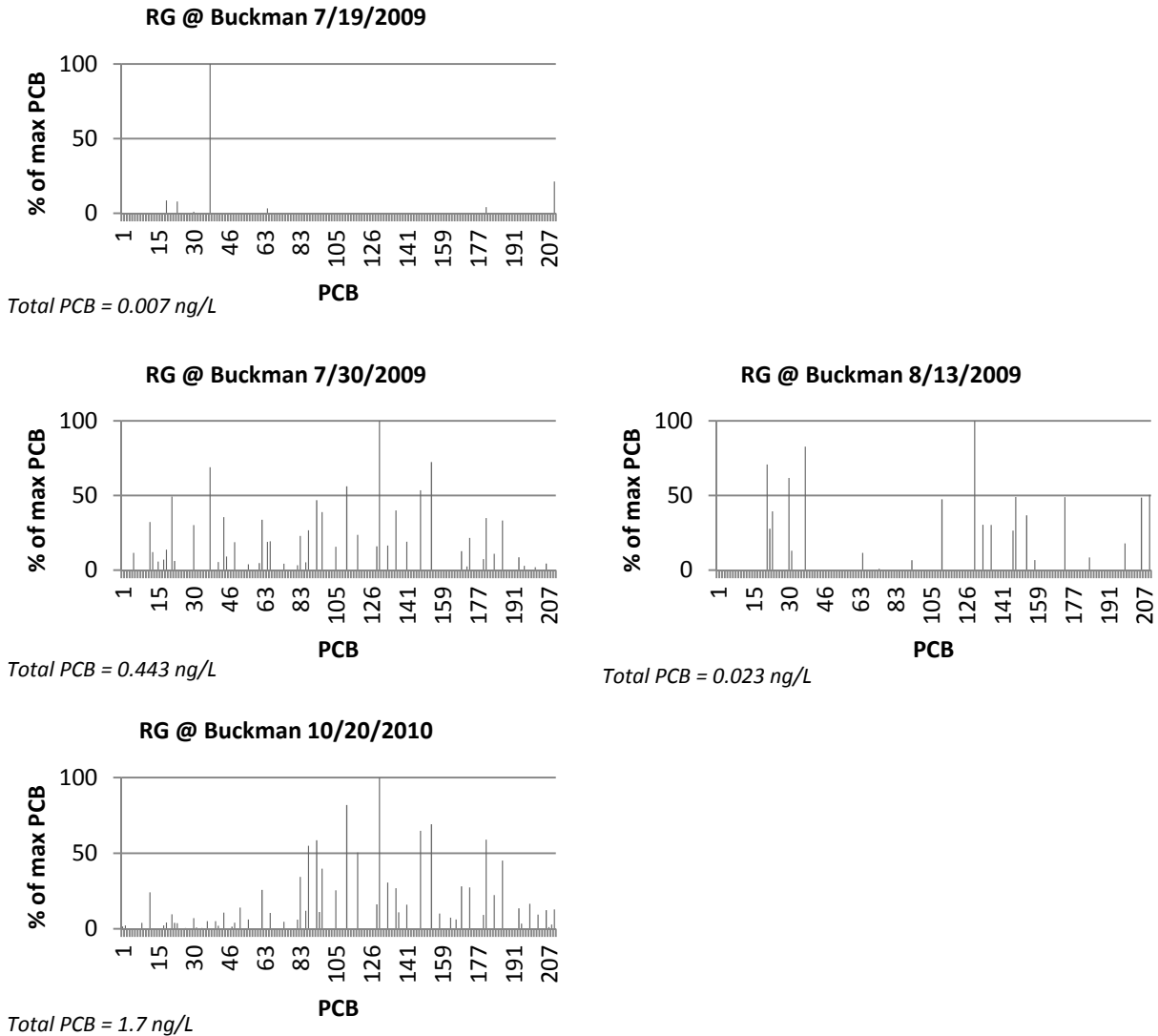
To illustrate this inherent variability, the normalized congener profiles (the percent contribution of each congener to the sum of all congeners) for Buckman storm runoff samples are presented in Figure 27. Over the 3-mo span shown in the figure, the congener profiles range from an abundance of low-chlorinated PCBs (7/19/2009), to a bimodal distribution (7/30/2009 and 8/13/2009), to one dominated by moderate and high-chlorinated PCBs (10/20/2010). Similar variability in congener and homolog profiles was seen at other stations in the rivers, for both ambient and storm samples.

Correlation analyses support this indication that congener profiles vary considerably along the Rio Grande and Rio Chama, both in space and time. Only 27% of the 340 intersample comparisons was strongly associated (section D-2 of Appendix D). Although occasional strong associations between the Otowi and Buckman Rio Grande stations were evident, those largely occurred when the two stations were sampled within a day or two of each other—in other words, when paired samples were collected during the same runoff event. The overall median  $R^2$  value for all Otowi versus Buckman comparisons was 0.4, a relatively weak association.

#### **4.5 Pajarito Plateau Storm Runoff**

The Pajarito Plateau is an approximately 10-mi-wide transition area between the steep, high-altitude slopes of the Jemez Mountains and the Rio Grande. LANL is located in an approximately 40 mi<sup>2</sup> portion of the Plateau drained by a large number of canyons and streams. Surface water is carried downstream toward the Rio Grande through relatively small channels situated in the bottom of canyons that have cut into the Plateau surface (erodible Bandelier Tuff). A few canyons contain relatively short segments of “perennial” streams that flow year around because of spring sources, snowmelt, and rainfall, largely from watersheds extending into the mountains. However, most of the canyons originating on the Plateau have ephemeral streams with flow limited to short duration periods in response to intense thunderstorm rainfall events. Because of the intensity of these events and the partial vegetative cover, the storm runoff can carry substantial amounts of sediment. Any landscape-associated contaminants, such as PCBs, are also expected in sediment entrained in the runoff.





**Figure 27 PCB congener profiles in storm runoff samples from Rio Grande (RG) at Buckman station**

The quality of stormwater runoff from most facilities of LANL is rigorously monitored through several programs. However, without knowledge of baseline concentrations, it is difficult to distinguish certain contaminant levels resulting from current or historical LANL operations from those related to the landscape itself. Previous investigations established baseline elemental concentrations for inorganic chemicals and radionuclides in sediment by focusing on prehistoric channels and floodplains (McDonald et al. 2003, 076084). However, quantitative descriptions of baseline concentrations for PCBs in surface waters have not been conducted. Because baseline PCB concentrations include those derived from global atmospheric deposition, sampling for baseline levels must be focused on exposed landscape surfaces, rather than buried strata.

This study was initiated in 2009 to measure baseline levels of PCBs in surface waters of the Pajarito Plateau unaffected by LANL. Sampling locations were selected to avoid any known contamination and to provide reasonable estimates of baseline concentrations, including a wide variety of bedrock source

areas and sediment texture. Surface-water samples were collected from two primary groups of locations: tributaries that enter the LANL's western boundary, and tributaries in a remote area north of the community of Los Alamos (Figure 24).

The four Western Boundary stations were located in tributaries flowing from the eastern edge of the Jemez Mountains, where the topography flattens with the Pajarito Plateau. Western Boundary stations were located in the tributaries known as upper Water Canyon (E252), upper Cañon de Valle (E253), upper Pajarito Canyon (E240), and upper Los Alamos Canyon (E025), as shown in Figure 24. Surface water monitored at the Western Boundary stations is generated from the slopes of the mountains. Upper Water Canyon is designated as a perennial stream (20 NMAC 6.4.126), while the other three streams are designated as ephemeral or intermittent (20 NMAC 6.4.128). Although the mountain front was substantially burned in 2000 by the Cerro Grande wildfire, groundcover was well reestablished with grasses and brushes. The northernmost tributary sampling stations, collectively referred to as the Reference sites, were situated in the middle portion of the Pajarito Plateau, several miles away from the mountain front. Reference sites were located in middle Guaje Canyon, upper Cañada de Las Marias, upper Cañada de Las Latas, upper Chupaderos Canyon, upper Garcia Canyon, and upper Corral Canyon (Figure 28). Surface water monitored at the Reference sites is mostly generated as stormwater from local storms affecting the northern portion of the Pajarito Plateau. No liquid industrial discharges were released above any of the sampling stations, and most of the contributing watersheds were within the Santa Fe National Forest or on San Ildefonso Pueblo lands with little to no development.

A total of 34 runoff events were sampled during 2009 and 2010 at the Pajarito Plateau baseline sites: 20 at the Reference stations and 14 at the Western Boundary stations. Figures 29 and 30 compare the dates when samples were collected with the corresponding daily total rainfall amounts measured at the closest meteorological monitoring station. For the Reference stations, sampling dates were matched to precipitation amounts recorded at the North Community meteorological station. Sampling histories at the Western Boundary stations were matched to TA-06 meteorological station rainfall amounts.

The plots indicate the samples were collected during a range of rainfall depths, particularly in 2010. Daily rainfall amounts ranged from near 0 to over 1 in. at both the Reference and Western Boundary areas. For some sampling events, no rainfall was recorded at the noted meteorological stations, indicating the storms likely were very localized on those days, but runoff amounts were sufficient to trigger the automated runoff samplers.

Bedrock types found in watersheds for the Western Boundary stations include Bandelier Tuff and dacitic rocks of the Tschicoma Formation (Smith et al. 1970, 009752). Cobbles and gravel largely consisting of tuff, dacite, and pumice in a sandy matrix, rich in quartz and sanidine crystals, dominate the lithology of the canyon sediment. Reference tributary canyons drain areas exposing the Puye Formation, the Bandelier Tuff, and the Tschicoma Formation (Smith et al. 1970, 009752). Cobbles and gravel largely consisting of dacitic and andesitic clasts in a sandy matrix dominate the lithology of the Guaje Canyon sediment. The other Reference tributary canyons drain areas underlain by Bandelier Tuff bedrock.

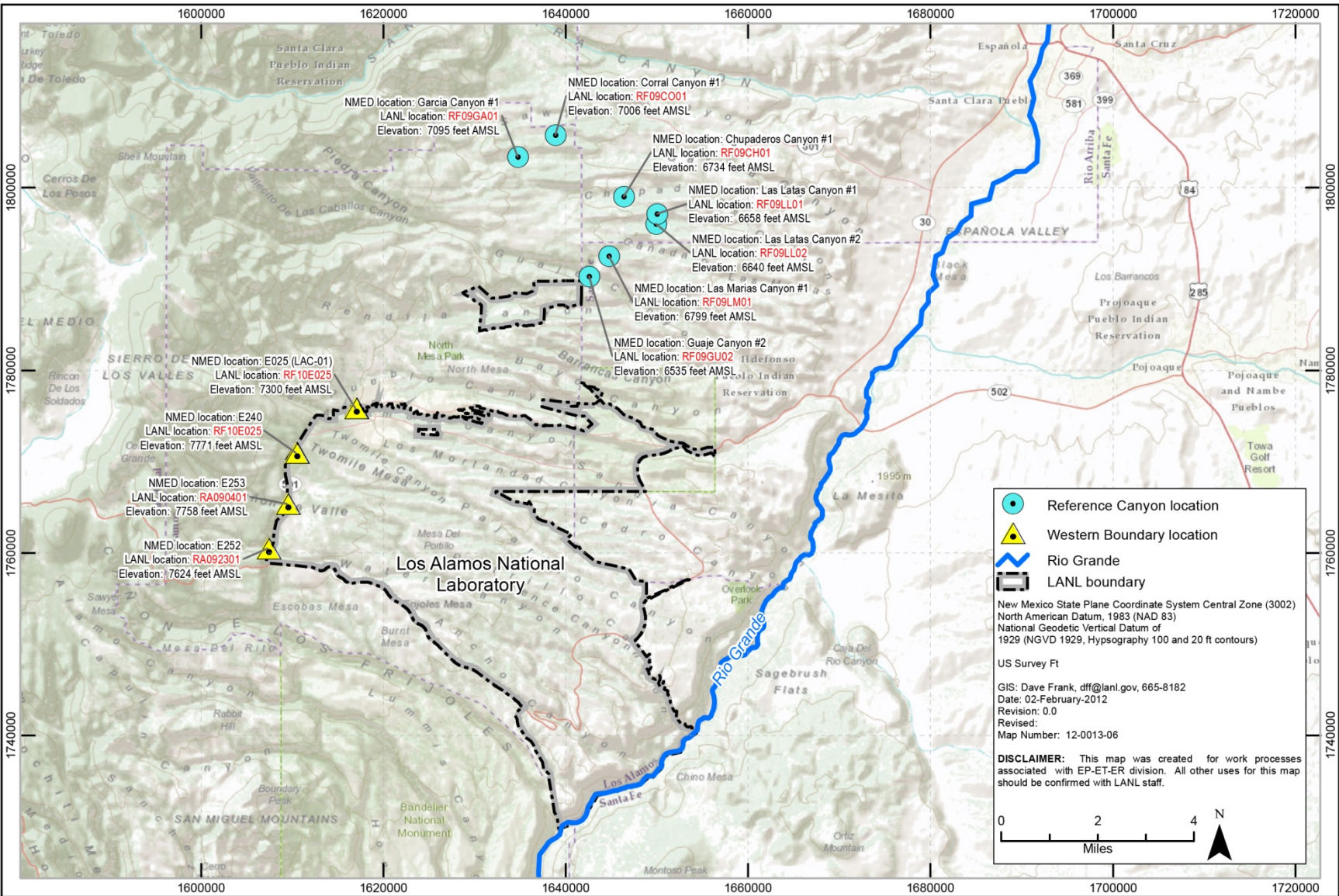
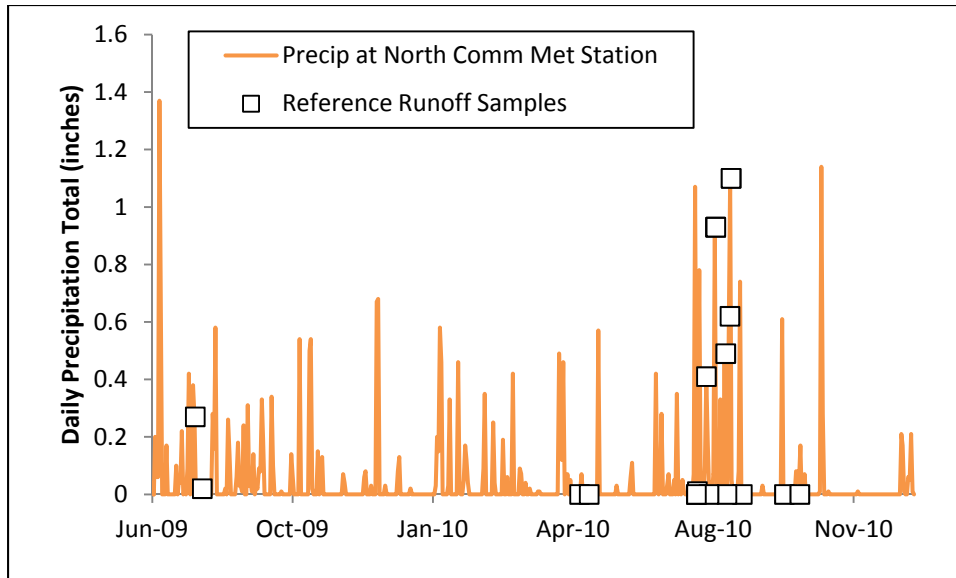
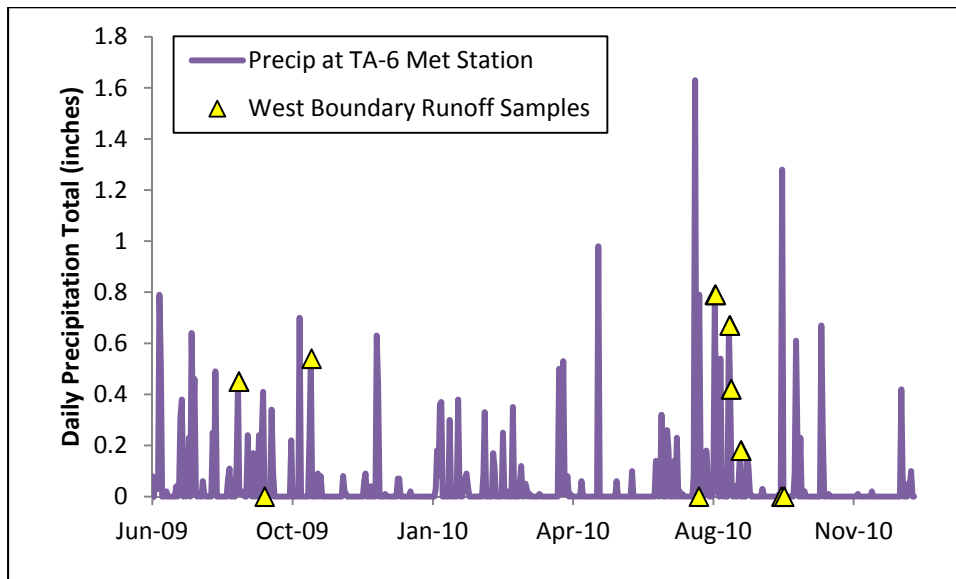


Figure 28 Location map for Reference and Western Boundary stations



Note: Raw precipitation data accessed at <http://environweb.lanl.gov/weathemachine/>.

**Figure 29** Precipitation amounts measured on dates PCB runoff samples were collected in Reference area



Note: Raw precipitation data accessed at <http://environweb.lanl.gov/weathemachine/>.

**Figure 30** Precipitation amounts measured on dates PCB runoff samples were collected in Western Boundary area

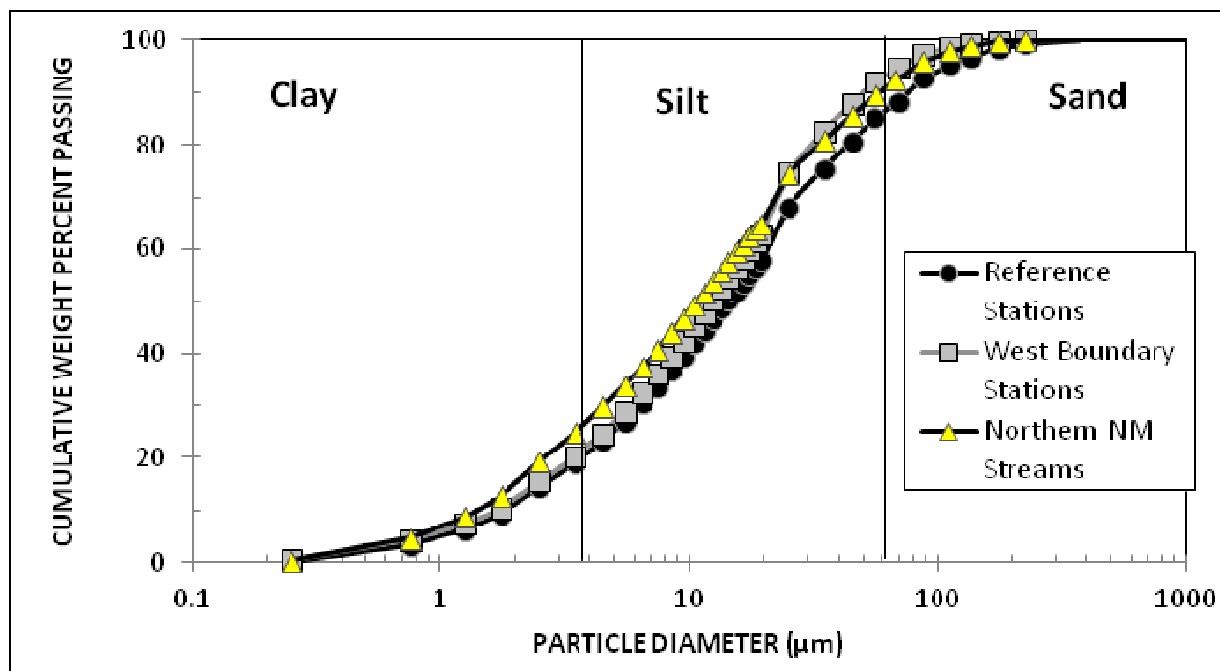
A summary of particle-size analyses is presented in Table 8, and complete results are presented in Appendix B. Particle-size distribution data are available for six of the Reference stations sampled and two of the Western Boundary stations. Suspended sediment collected in the Reference and Western Boundary areas were largely dominated by the silt-size fraction (3.9 to 62.5  $\mu\text{m}$ ), with silt contents averaging 72% and 86% by weight, respectively. The Reference samples on average contained twice the amount of sand than did the Western Boundary stations (15.7% versus 7.9%).

**Table 8**  
**Comparison of Particle-Size Distributions for Suspended Sediment and Stream Bed Sediment**

Location	Area	N	Sand (% wt*)		Silt+Clay (% wt)		Silt (% wt)		Clay (% wt)	
			Mean	SD	Mean	SD	Mean	SD	Mean	SD
<b>Suspended Sediment (Current Study)</b>										
Northern New Mexico	Rio Grande/Rio Chama tributaries	15	10.5	7.8	89.5	7.7	76.9	6.0	12.6	3.5
Pajarito Plateau	Reference stations	8	15.7	19.3	85.1	15.7	75.9	15.9	9.2	3.9
Pajarito Plateau	Western Boundary stations	9	7.9	6.1	92.1	6.1	81.7	3.9	10.4	4.7
Los Alamos Townsite	South Fork Acid Run-on location	8	15.3	4.8	84.9	4.9	76.3	3.5	8.5	2.9
<b>Stream Bed Sediment (McDonald et al. 2003, 076084)</b>										
Pajarito Plateau	Channel sediment	9	81.4	14.2	18.6	14.2	15.6	12.4	3	2.3
Pajarito Plateau	Floodplain sediment	15	71.8	14.5	28.2	14.6	24.4	12.4	3.7	2.8

\*% wt = Percent weight.

Figure 31 shows the mean particle-size distributions for the Reference and Western Boundary stations, along with the northern New Mexico tributary samples for added reference. On average, the suspended sediment sampled at each of the general sampling areas is remarkably similar in texture. The median (D50) suspended sediment sizes for all of the sampling areas were essentially identical, near 12  $\mu\text{m}$ .



**Figure 31** Comparison of mean particle-size distributions for suspended sediment at Reference, Western Boundary and northern New Mexico tributary runoff sampling stations

Particle size-distributions for individual Reference and Western Boundary samples are presented in Figures 32 and 33. With the exception of one sand-rich Reference sample from the Garcia-1 station, the Reference and Western Boundary distribution ranges overlap well with comparable variation.

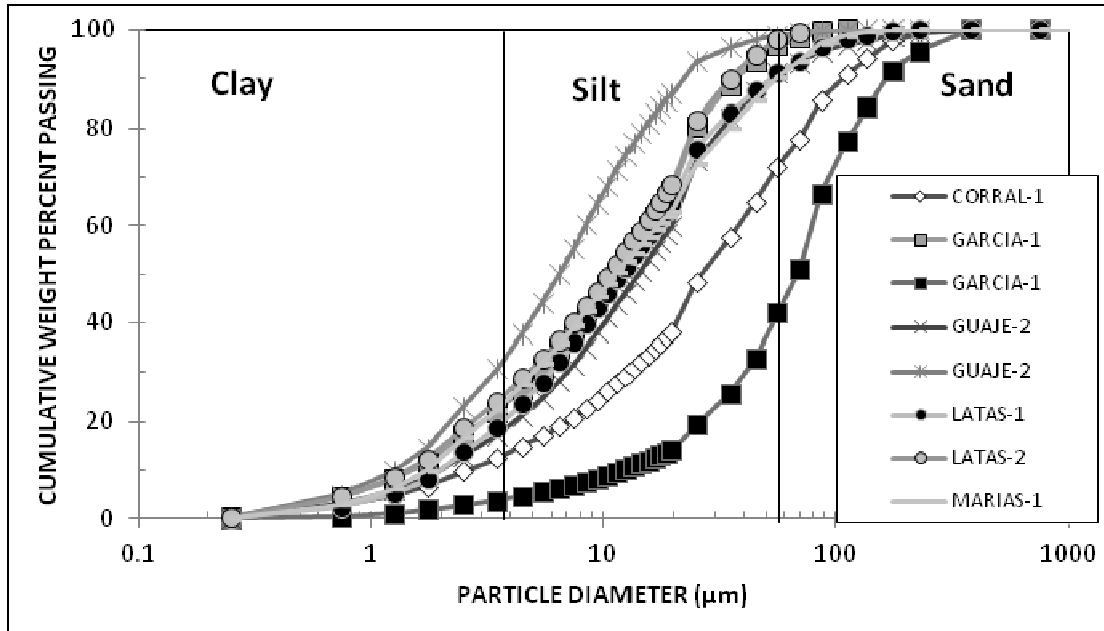


Figure 32 Cumulative frequency plots for particle-size distribution for eight suspended sediment samples in Reference area runoff.

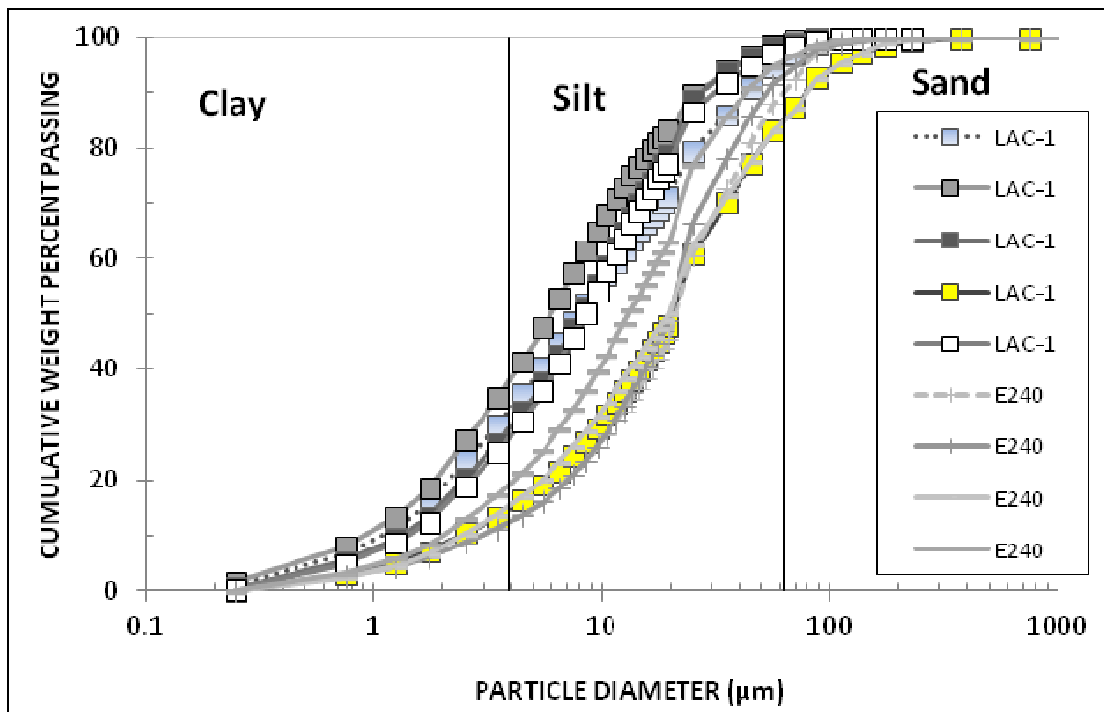


Figure 33 Cumulative frequency plots for particle-size distribution for nine suspended sediment samples from Western Boundary runoff

Examination of Table 8 shows two important elements: first, silts and clays dominate the suspended sediment particles for a wide range of sampling locations and geologic settings across the study area. Second, the abundance of silt+clay in Pajarito Plateau runoff samples is substantially higher than previously measured by McDonald et al. (2003, 076084) for stream channel and floodplain deposits on the Plateau. The earlier study found that sediment deposited in the floor of the stream channels consisted of more than 70% sand on average, while the suspended sediment samples collected in this study contained 15% or less of sand. Therefore, it is inferred that stream power in the present runoff events was not sufficient to mobilize most of the particles heavier than silt from the stream bed, and fine-grained sediment was most prevalent in runoff. The suspended sediment was approximately 3 to 5 times more abundant in the silt and clay fractions than previously found in the stream bed. The tendency towards finer particles is important because the concentrations of most analytes increase as silt and clay contents increase (owing to higher surface area to volume ratios as particle sizes decrease, surface sorption being the driving force).

#### 4.5.1 Baseline PCB Concentrations in Pajarito Plateau Runoff

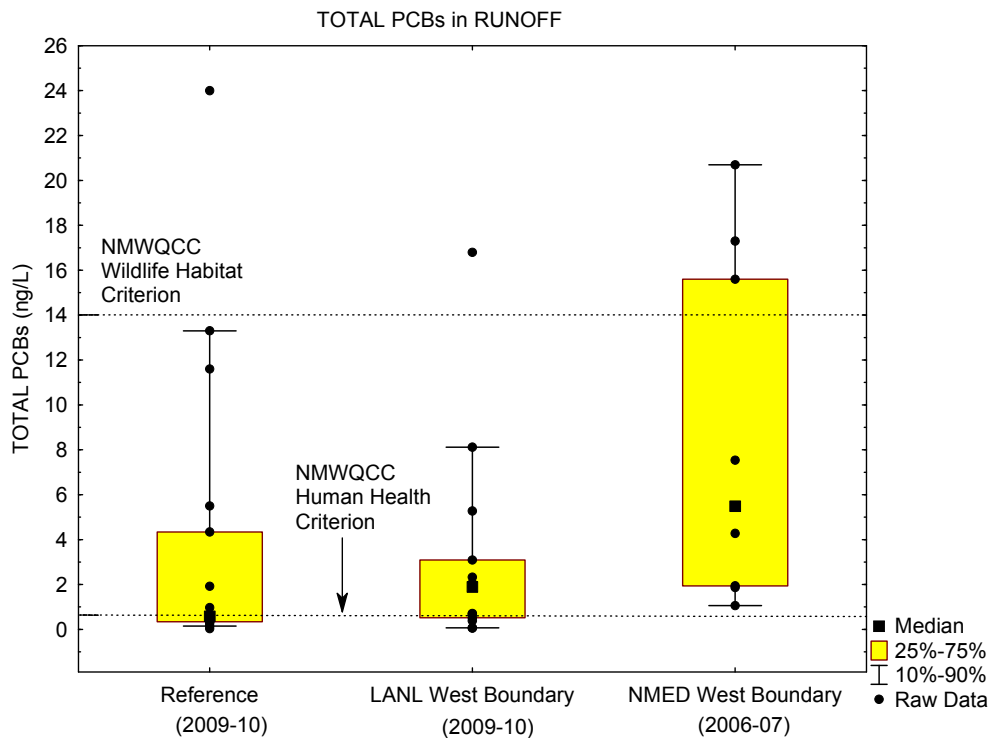
PCB concentration data utilized in this baseline assessment were from this study in 2009–2010 and from NMED-SWQB sampling effort along the Western Boundary in 2006–2007. All the PCB results from Pajarito Plateau runoff were detected at concentrations ranging from 0.02 ng/L to 24 ng/L, well within and on the low end of the range of concentrations detected worldwide (Table 9). The box plots in Figure 34 indicate the largest two or three values were elevated in Reference area samples. Probability plots of total PCB concentrations and of suspended PCB concentrations support the finding that the two largest values of 13.3 ng/L and 24 ng/L appear to be associated with a second higher-concentration population than most of the results. These samples were excluded because of their large influence on summary statistics for Reference area PCBs. A third suspect Reference total PCB concentration of 11.6 ng/L was retained in the UTL calculation because its suspended PCB concentration was consistent with most of the results. After the two largest results were excluded, the remaining Reference area data range from 0.02 ng/L to 11.6 ng/L and appear to originate from a lognormal statistical distribution (the probability plots are presented in Appendix C). All the Western Boundary results were retained because suspended PCB concentrations are consistent with a single population in a probability plot. The Western Boundary total PCB concentrations appear to originate from a gamma distribution.

The box plots show 2006–2007 NMED results are generally larger than those LANL obtained in 2009–2010. The differences are primarily related to greater levels of suspended sediment in the nine NMED samples, perhaps corresponding to larger runoff events or different sampling techniques—NMED samples were from grab or single-stage samplers while LANL samples were collected using automatic samplers. However, because the calculated suspended PCB concentrations from LANL and NMED samples were comparable (see Figure 33), the results from LANL and NMED were combined to produce a more robust description of Western Boundary PCB levels. Western Boundary summary statistics and UTL calculations that follow include the NMED results. The results are summarized in Table 10.

The median concentration in the Reference samples was 0.4 ng/L, and 2.07 ng/L in the Western Boundary samples. At the Reference sites, 5 of 18 (28%) results were above the New Mexico human health WQC, and none were above the wildlife habitat WQC. At the Western Boundary sites, 18 of 23 (78%) were above the human health WQC, and 4 of 23 (17%) were above the wildlife habitat WQC.

**Table 9**  
**Worldwide PCB Concentrations in Stormwater and Runoff**

Location	Site Characterization	Precipitation Type	PCB Concentration (ng/L)	Reference
Bow Lake, Alberta, Canada	Rural	Glacial runoff	0.363–0.480	Lafrenière et al. 2006, 213417
Bow Lake, Alberta, Canada	Rural	Bow River Runoff	0.280–0.410	Lafrenière et al. 2006, 213417
Sarnia, Ontario, Canada	Urban	Stormwater	179	Marsalek and Ng 1989, 213423
Sault Ste. Marie, Ontario, Canada	Urban	Stormwater	26.9	Marsalek and Ng 1989, 213423
Windsor, Ontario, Canada	Urban	Stormwater	88.8	Marsalek and Ng 1989, 213423
Lausanne and Geneva, Switzerland	Urban	Stormwater	<0.24–403	Rossi et al. 2004, 213427
Karlsruhe, Germany	Urban	Stormwater	150	Xanthopoulos and Hahn 1990, 213435
Switzerland	Urban	Stormwater	27–290	Rossi et al. 2004, 213427
New York City and New Jersey water pollution control plants and combined sewer overflows	Urban	Normal-Flow Influent	26–1096	Durell and Lizotte 1998, 213406
New York City and New Jersey water pollution control plants and combined sewer overflows	Urban	Storm-Flow Influent	44–773	Durell and Lizotte 1998, 213406
Creteil, France	Urban	Stormwater	26–2600	Granier et al. 1990, 213411



**Figure 34** Box plots of total PCB concentrations at baseline sampling sites on the Pajarito Plateau



**Table 10**  
**Summary Statistics of Baseline PCB Concentrations in Pajarito Plateau Runoff**

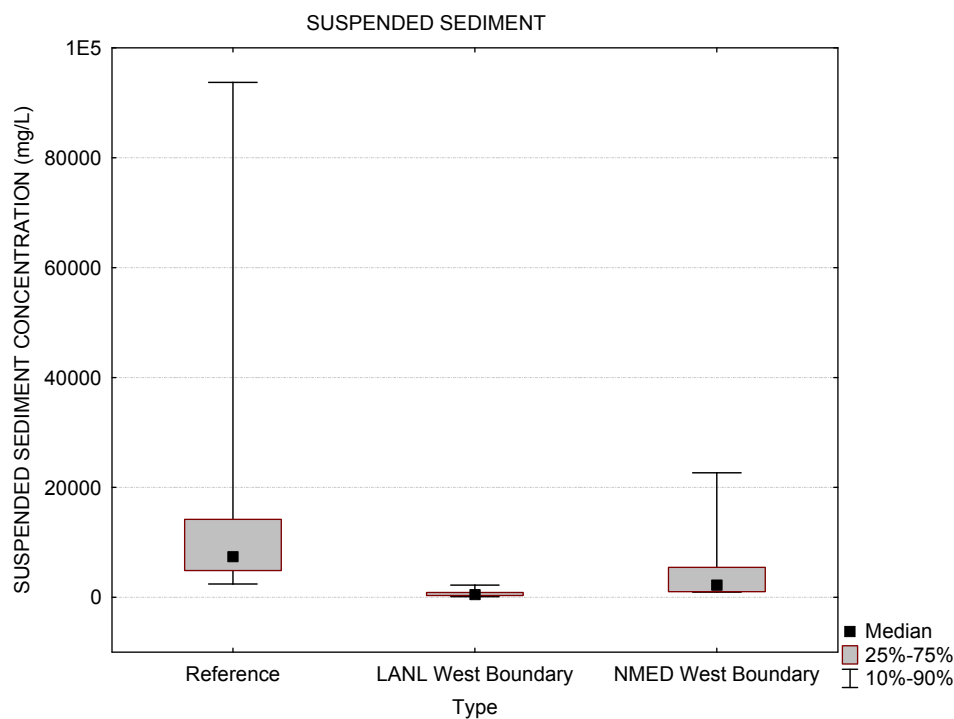
Area	N	Min	Max	Mean	SD	Median	Distribution	UTL <sup>a</sup>
<b>Total PCB Concentration (ng/L)</b>								
Reference	18	0.013	11.6	1.56	2.93	0.40	Lognormal	11.7
Western Boundary	23	0.033	20.7	5.1	6.33	2.07	Gamma	19.5 <sup>b</sup>
Reference and Western Boundary Combined	41	0.23	20.7	3.56	5.38	0.97	Gamma	13.0 <sup>b</sup>
<b>Calculated Suspended PCB Concentration (ng/g)</b>								
Reference	15						Lognormal	1.22
Western Boundary	22						Normal	9.94
Reference and Western Boundary Combined	37	0.01	9.97	2.04	2.42	1.02	Not discernible (used nonparametric UTL)	7.73

<sup>a</sup> 95% UTL with 90% coverage

<sup>b</sup> 95% W-H approximate gamma UTL with 90% coverage.

The UTL for the Reference area is 11.7 ng/L, which is essentially equal to the maximum value. The UTLs for the Western Boundary area are 19.5 ng/L and 21.4 ng/L (depending on calculation method used), which bracket the maximum value.

Unlike the overall similarity in total PCB concentrations between the Reference and the Western Boundary areas, there were significant differences ( $p < 0.001$ ) in the levels of suspended sediment carried by the runoff events sampled (Figure 35). The median SSC in the Reference samples was 17 times larger than the median SSC for the Western Boundary stations (7380 mg/L versus 432 mg/L).



**Figure 35** Box plots of SSC in Pajarito Plateau runoff samples

The large disparity in SSCs between the Reference and Western Boundary areas reflects the nature of the landscapes, particularly the degree of vegetative cover. The general absence of grass cover in the Reference area encourages more erosion than occurs in the Western Boundary vicinity. Given the large differences in the amounts of sediment in runoff samples—and PCBs are commonly associated with sediment—it appears it was only coincidental that the distributions in total PCB concentrations were nearly identical between the two sampling areas. Although the Western Boundary runoff samples contained relatively low sediment content, a sample NMED previously collected in 2006 contained an SSC of 22,000 mg/L, indicating larger values can occasionally be obtained along the Western Boundary under certain conditions. Overall, however, the results from this 2009–2010 study showed a significant disparity between the two sampling areas.

Spearman’s rank correlation analysis for the relation between total PCB concentrations and suspended sediment, suspended solids, and metals showed the Western Boundary stations had a significant positive correlation (increasing PCB concentration with increasing SSC [Table 11]). Correlation coefficients for these constituents at the Western Boundary stations often were greater than 0.7, indicating strong associations. In contrast, the correlation analysis for the Reference stations showed weaker positive associations between PCBs concentrations and SSCs.

**Table 11**  
**Results of Spearman’s Correlation Analysis for Relation between**  
**Total PCB Concentrations and Other Total Constituents in Runoff from the Pajarito Plateau**

Analyte	Reference Sites			Western Boundary Sites		
	N	Correlation Coefficient	p-Level	N	Correlation Coefficient	p-Level
Aluminum	19	0.502	<b>0.029</b>	12	0.797	<b>0.002</b>
Antimony	19	0.168	0.492	12	0.109	0.736
Arsenic	19	0.589	<b>0.008</b>	12	0.632	<b>0.027</b>
Barium	19	0.519	<b>0.023</b>	12	0.839	<b>0.001</b>
Beryllium	19	0.632	<b>0.004</b>	12	0.880	<b>&lt;0.001</b>
Boron	19	0.468	<b>0.043</b>	12	0.473	0.120
Cadmium	19	0.659	<b>0.002</b>	12	0.803	<b>0.002</b>
Calcium	19	0.584	<b>0.009</b>	12	0.469	0.124
Chromium	19	0.387	0.102	12	0.760	<b>0.004</b>
Cobalt	19	0.525	<b>0.021</b>	12	0.804	<b>0.002</b>
Copper	19	0.670	<b>0.002</b>	12	0.804	<b>0.002</b>
Gross alpha	14	-0.015	0.958	13	0.698	<b>0.008</b>
Hardness	19	0.626	<b>0.004</b>	12	0.441	0.152
Iron	19	0.504	<b>0.028</b>	12	0.755	<b>0.005</b>
Lead	19	0.575	<b>0.010</b>	12	0.928	<b>&lt;0.001</b>
Magnesium	19	0.546	<b>0.016</b>	12	0.434	0.159
Manganese	19	0.528	<b>0.020</b>	12	0.909	<b>&lt;0.001</b>
Mercury	19	0.089	0.718	10	na*	na
Nickel	19	0.681	<b>0.001</b>	12	0.858	<b>&lt;0.001</b>

Table 11 (continued)

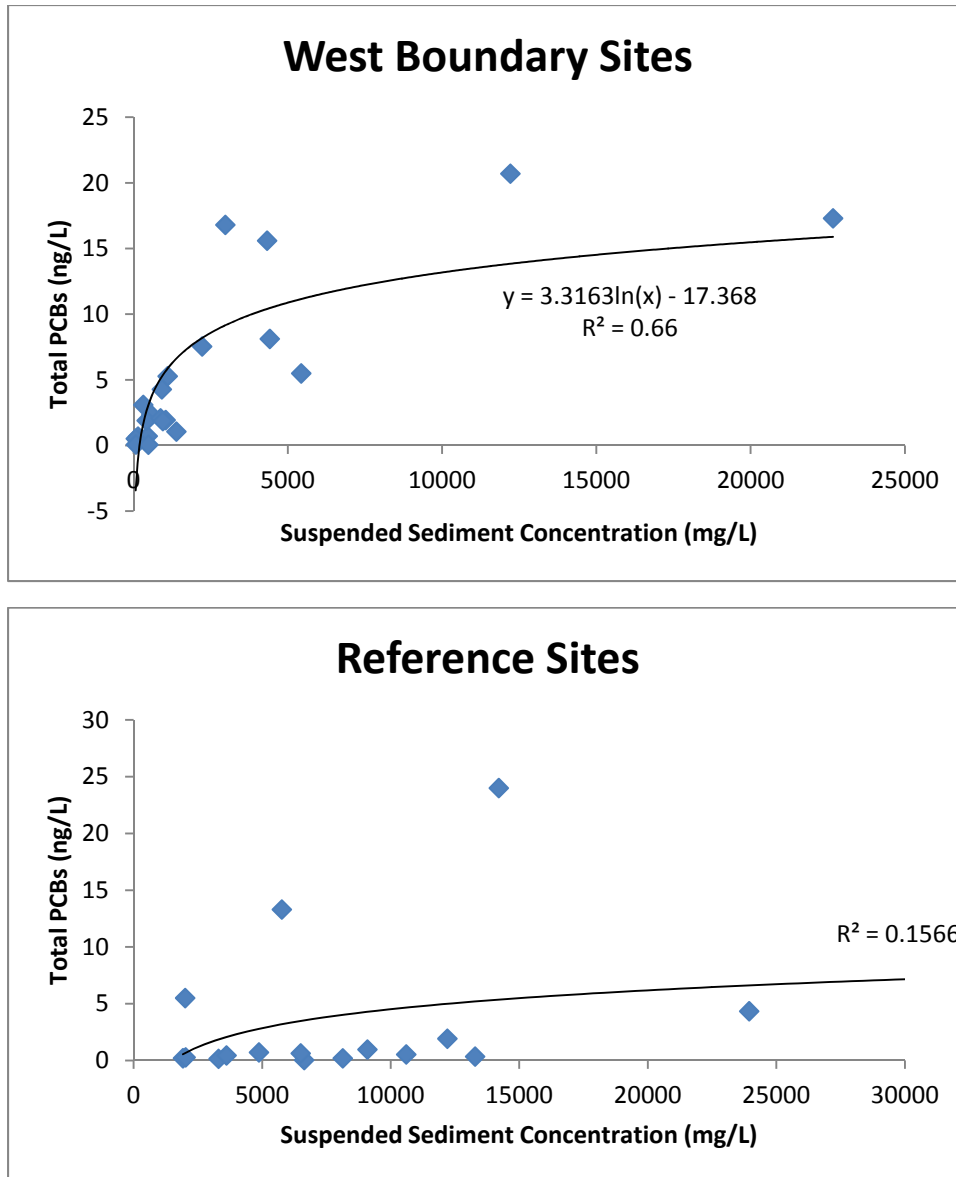
Analyte	Reference Sites			Western Boundary Sites		
	N	Correlation Coefficient	p-Level	N	Correlation Coefficient	p-Level
Potassium	19	0.572	<b>0.011</b>	12	0.650	<b>0.022</b>
Radium-226	10	0.067	0.855	9	0.817	<b>0.007</b>
Radium-226+228	8	0.214	0.610	5	0.400	0.505
Radium-228	10	0.358	0.310	9	0.450	0.224
Selenium	19	0.410	0.082	12	na	na
Silver	19	0.079	0.748	12	0.480	0.114
Sodium	19	-0.291	0.226	12	0.217	0.499
Thallium	19	0.315	0.189	12	0.524	0.080
Uranium	19	0.391	0.098	12	0.846	<b>0.001</b>
Vanadium	19	0.450	0.053	12	0.776	<b>0.003</b>
Zinc	19	0.368	0.121	12	0.741	<b>0.006</b>
TOC	19	0.399	0.090	15	0.389	0.152
Total Suspended Solids	17	0.402	0.110	11	0.900	<b>&lt;0.001</b>
SSC	10	0.576	0.082	13	0.797	<b>0.001</b>
Clay	8	0.000	1.000	9	-0.367	0.332
Sand	8	0.190	0.651	9	0.267	0.488
Silt	8	-0.190	0.651	9	0.233	0.546
Silt+Clay	8	-0.190	0.651	9	-0.267	0.488

Note: Bold values indicate statistically significant correlation ( $p < 0.05$ ).

\*na = Not available. Detections of mercury or selenium were too few to calculate correlation coefficients.

At both baseline areas, positive correlations between TOC and PCB concentrations were weak, near 0.4, and not statistically significant. The TOC correlations were substantially stronger than those for sediment texture (e.g., %clay, %silt, %sand). Previous studies elsewhere often showed PCBs were most often associated with TOC and fine-grained sediment (Ghosh et al. 2003, 213410; Ilyas et al. 2011, 213415).

Figure 36 shows that PCBs at the Western Boundary stations increase with increasing SSC or metal concentrations, apparently logarithmically ( $R^2 = 0.66$ ). In such a setting, PCB concentrations are mainly controlled by the sediment-carrying capacity of the runoff streams. For the Reference stations, a much different PCB-to-sediment relationship was found in that PCB concentrations do not show a predictable relationship with suspended sediment. As was seen in the northern New Mexico tributary samples, the PCB concentrations appear to follow two distinctly different tracks. Along one track, PCB concentrations track upward as SSCs increase. Along the second track, however, PCB concentrations show minimal correspondence to SSCs.

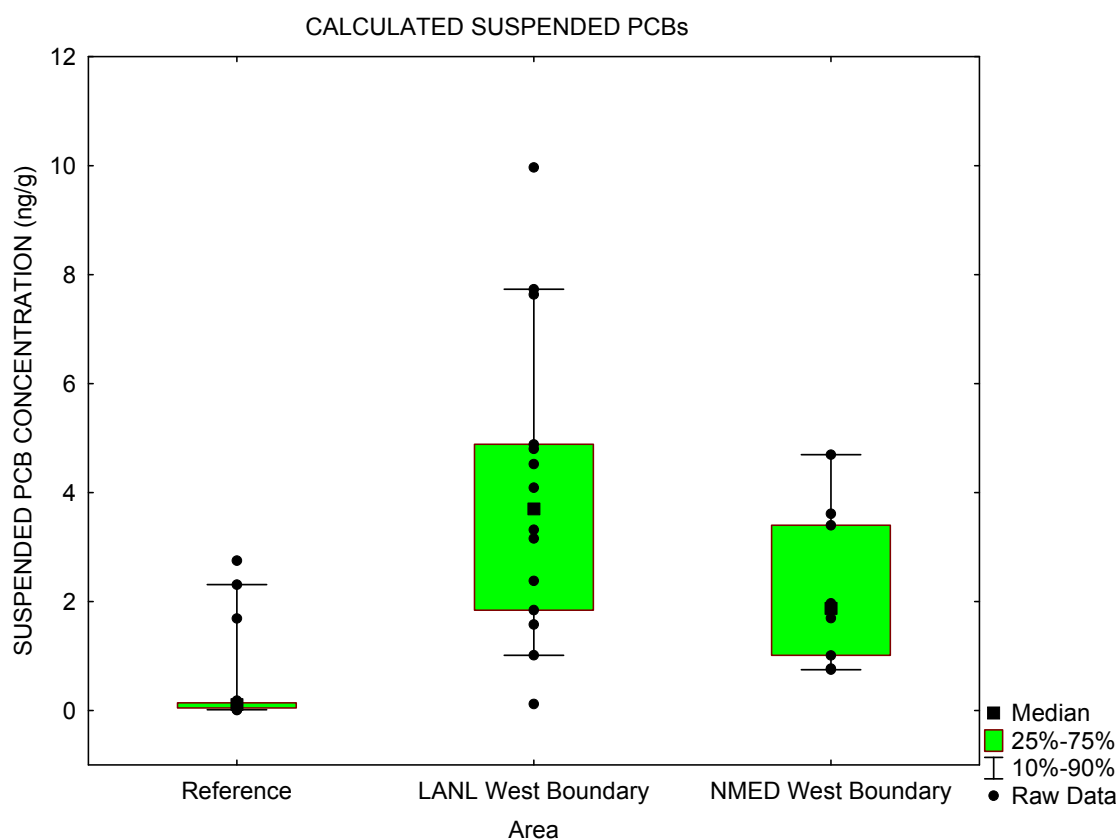


**Figure 36** Relation between total PCB concentration and SSC in Pajarito Plateau runoff at Western Boundary (top) and Reference (bottom) baseline areas

The differences between the two tributary sampling groups may be associated with different sediment sources and transport modes. The Western Boundary tributary results reflect what may occur in drainages in relatively stable landscapes. The PCBs measured in Western Boundary tributary runoff samples are primarily derived from the surface of the landscape rather than from eroding bed materials. This phenomenon is apparent for the Western Boundary stations because increasing PCB concentrations had moderately strong correlations with increasing SSCs. In contrast, the Reference tributaries tend to have more incised channels that erode and transport bed materials, which are likely much lower in sediment PCB concentrations than in surficial deposits. In these conditions, the intact surface soil—that exposed to atmospheric deposition for long periods—can be mixed with older or subsurface sediments that have not been regularly exposed to fallout derived PCBs, and the overall

PCB concentrations decreased as a result of dilution. As a result, sediment carried in Western Boundary runoff generally would be more enriched in PCBs than that carried in runoff from the Reference area tributaries.

Box plots of calculated suspended PCB concentrations for the two groups of baseline tributaries are shown in Figure 37. Most of the Western Boundary results are an order of magnitude larger than those calculated for the Reference stations. However, three results from the Reference area, two from station Las Latas-2, and one from Chup-1 are comparable. These three Reference samples fall on the “upward” track identified earlier. The calculations show that while suspended PCB concentrations above 1 ng/g were common in the Western Boundary samples, concentrations of that magnitude also were detected in some of the Reference area samples. The degree of PCB enrichment found in baseline area runoff samples may be a function of the geomorphology in the drainage and the level of mixing of young (post-PCB production) and old (pre-PCB production) sediment.



**Figure 37** Box plots of calculated suspended PCB concentrations in Pajarito Plateau runoff samples

Calculated suspended PCB concentrations at the Reference sites were comparable with those measured for the northern New Mexico ephemeral streams. A noted difference between the Reference and Western Boundary suspended PCB results can be discerned. However, the correlation analyses presented in the following section indicate the congener profiles between the two baseline areas are strongly associated, and consequently the data sets can be combined to determine overall baseline concentrations for Pajarito Plateau runoff. Further study is needed to determine the exact cause of the

PCB enrichment in the Western Boundary samples. With this in mind, UTL calculations were performed for each baseline area as well as for a tentatively combined data set.

#### 4.5.2 Fingerprint of PCBs in Pajarito Plateau Baseline Areas Runoff

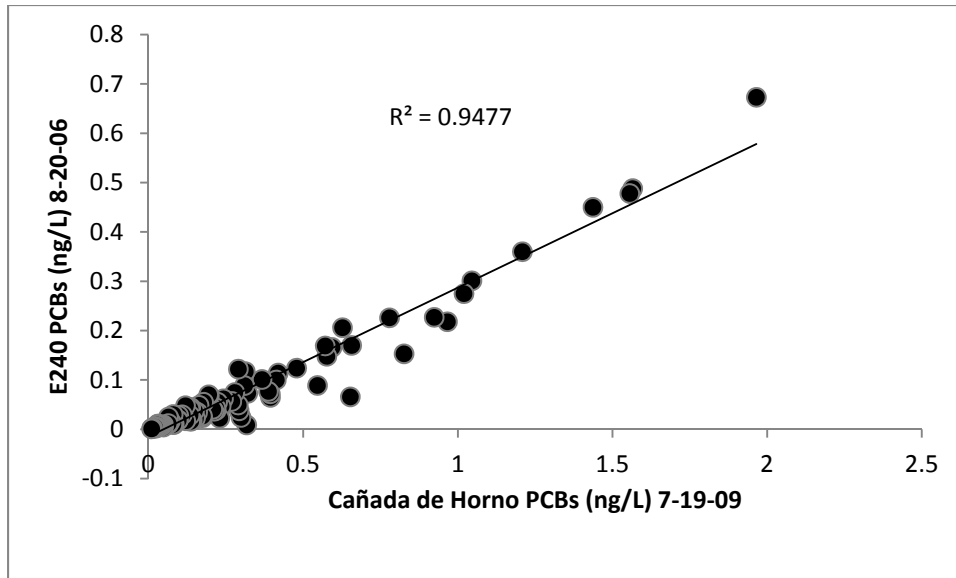
The similarities of Pajarito Plateau baseline PCB congener profiles were examined using correlation analyses. Table D-3 of Appendix D lists  $R^2$  values when Pajarito Plateau profiles are compared with each other. Table D-4 of Appendix D shows  $R^2$  values when Pajarito Plateau profiles are compared with those from northern New Mexico tributaries off of the Plateau.  $R^2$  values for profiles from stations Garcia-1 and E252 were not included in the tables because fewer than 10 congeners were detected in common with the other profiles.

Profiles in stormwater collected across the Pajarito Plateau generally correlated well. Of the 380 intersample comparisons, the median  $R^2$  value was 0.76, indicating minimal overall variation across the Pajarito Plateau. Among comparisons involving Western Boundary station profiles, 80% were strongly associated, as were 60% of comparisons with Reference area stations. A particularly strong uniformity can be seen in profiles collected along the Western Boundary. More variability in profiles was evident in samples from the Reference area sites, yet a majority of the results were consistent with those found in Western Boundary samples. Samples from the Las Latas drainage in the Reference area showed weak associations with the other Pajarito Plateau locations, but not consistently.

As was seen in some samples from the northern New Mexico tributaries, evidence indicates PCBs are stable in the landscape of the Pajarito Plateau. The samples NMED collected in 2006 using single-stage samplers showed similar congener profiles as samples LANL collected in 2009 and 2010 with automatic sampling equipment. This was evident in samples collected in Guaje Canyon within the Reference tributary group and in Pajarito Canyon (E240) within the Western Boundary tributary group.

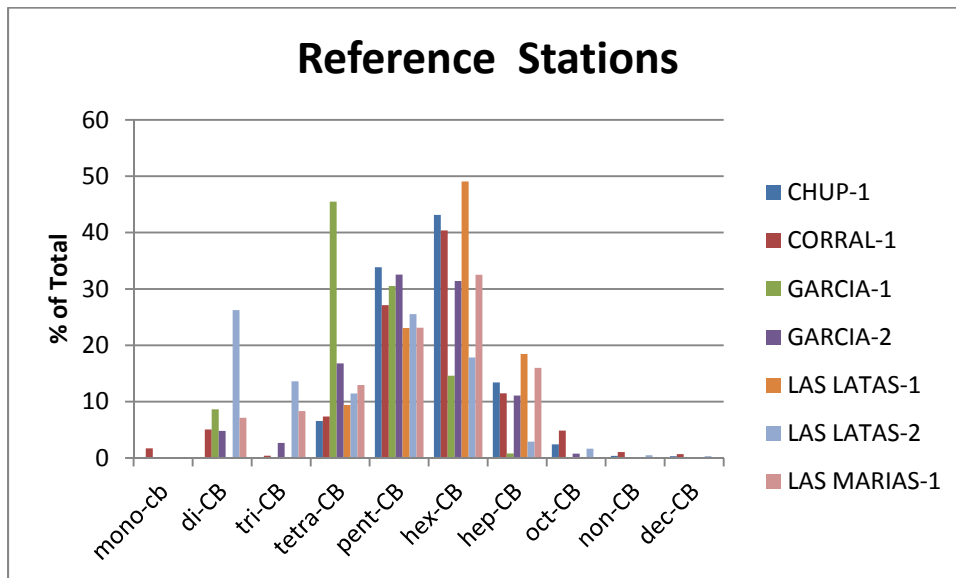
On a broader perspective, the correlation analyses indicate that baseline PCB profiles are generally consistent across the landscape on a regional scale. For this analysis, 29 PCB profiles in stormwater samples from northern New Mexico tributaries were compared with 27 profiles from the Pajarito Plateau ephemeral drainages. The median  $R^2$  value for the entire matrix of comparisons was 0.73 (see Table D-4 of Appendix D), indicating a large percentage of the variability in PCB makeup can be attributed to a common source—background. It also supports the selection of the Reference and Western Boundary stations as baseline locations. The PCB congener profiles at the Pajarito Plateau baseline stations match well with stations located distant from Los Alamos—many tens of miles away—with no indication of substantial industrial impacts.

Figure 38 presents an example of a comparison of two PCB congener profiles. The scatter plot illustrates the correlation of PCB congener concentration results in a stormwater sample NMED collected at Cañada de Horno in 2009 with congener concentrations measured in a stormwater sample from station E240 in 2006. Cañada de Horno is located within the Rio Chama valley, and E240 is located in Pajarito Canyon on the Pajarito Plateau. Deviation away from the best fit regression line is minor. With an  $R^2$  value of 0.95 and a probability less than 0.05, the two congener profiles are strongly associated. Furthermore, because the samples were collected 3 yr apart, the association additionally indicates considerable stability in the regional PCB signature.

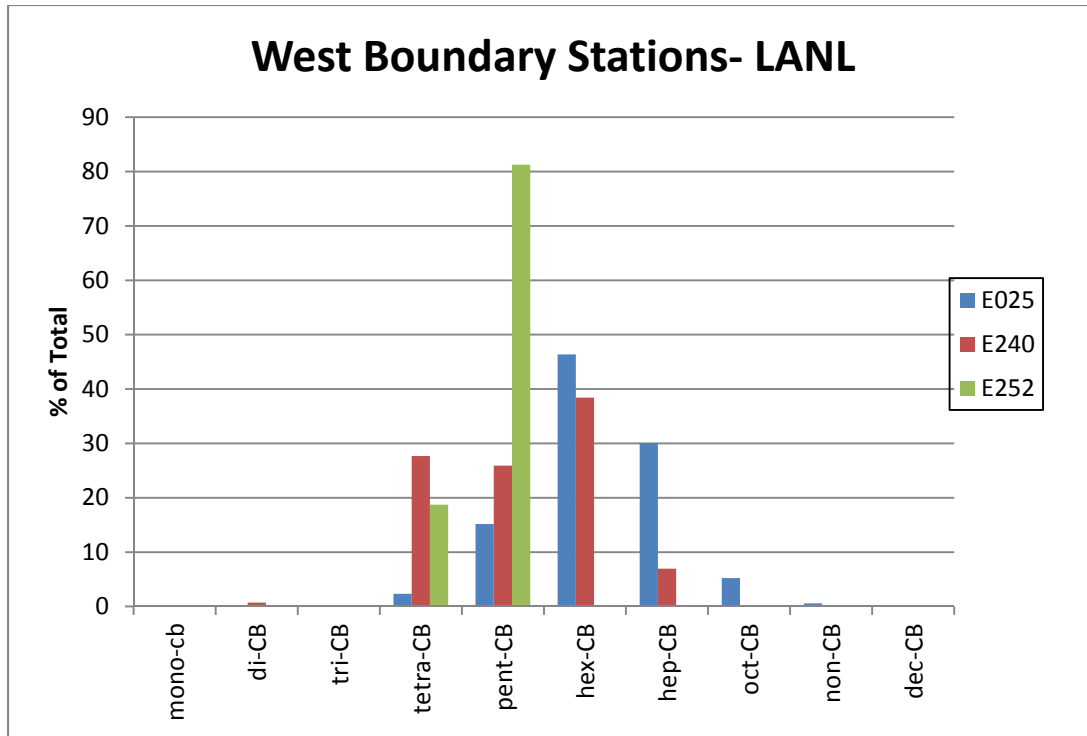


**Figure 38 Comparison of PCB congener concentrations in storm runoff samples from Pajarito Plateau (E240) and from Rio Chama tributary (Cañada de Horno)**

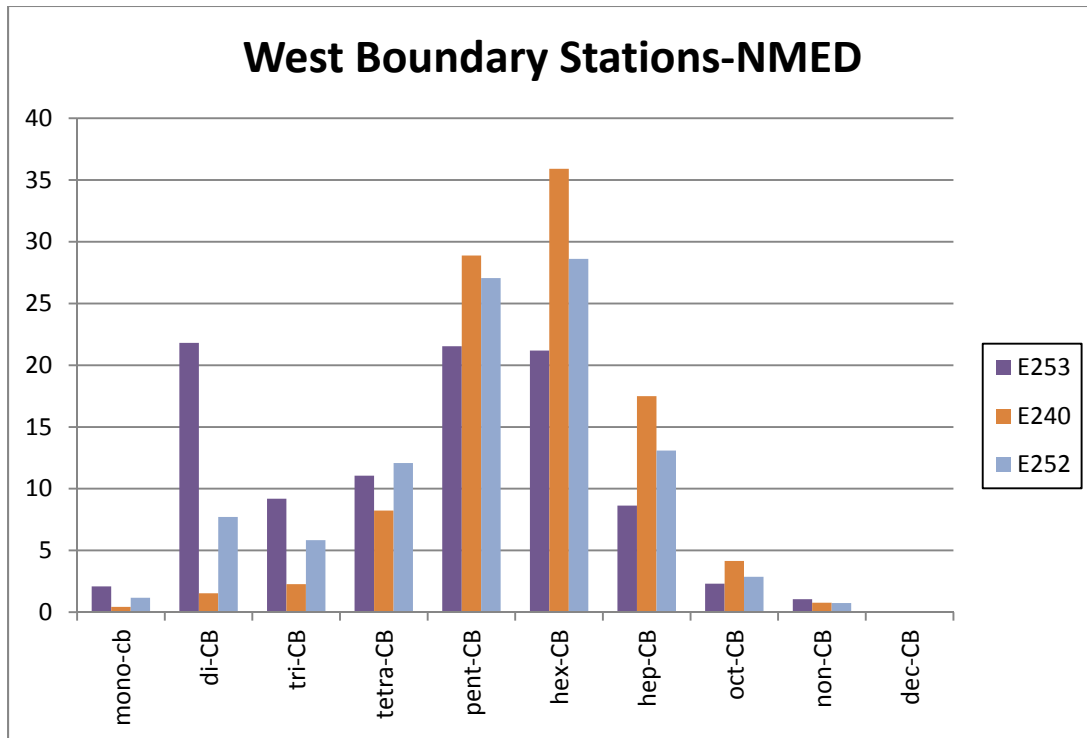
A more general perspective of Pajarito Plateau baseline PCB makeup is presented with homolog plots. Figures 39 to 41 show the average homolog distributions for the Pajarito Plateau baseline areas stormwater samples. The homolog distributions in the Pajarito Plateau samples are centered near the hexa-CB homolog, as were the northern New Mexico tributary samples. Considerable variability occurs in the amount of the low-chlorinated CB homologs. The bimodal distribution noted in precipitation and regional soil samples is evident in most of the Reference area samples but is largely absent in Western Boundary samples. Of the PCBs in the samples, 80% is contained in the moderately chlorinated penta-, hexa-, and hepta-CB homologs; the low-chlorinated CB homologs comprised less than 10% of the total.



**Figure 39 Average PCB homolog distribution in 20 samples from Reference area storm runoff**



**Figure 40** Average PCB homolog distribution in 15 samples LANL collected in 2009–2010 from the Western Boundary area storm runoff



**Figure 41** Average PCB homolog distribution in 13 samples NMED collected in 2006–2007 from the Western Boundary area storm runoff



In an attempt to better understand the relationships between Reference and Western Boundary sample results, a more in-depth evaluation of the homolog distributions was conducted using multivariate statistical methods. These methods have successfully been used elsewhere to refine understanding of PCB sources (Scrimshaw and Lester 2001; Howel 2007; Huang et al. 2007, 213413). The analyses were performed using only the 2009–2010 data to ensure consistency in analytical laboratories and sampling periods. All data were used in the assessment, including those earlier identified as possibly belonging to a higher-concentration population.

Principal component factor analysis (PCFA) reduced the number of variables (PCB percent abundances for 10 homologs) to four and found relationships among the originally measured variables. In total, the first four factors explained 88% of the system's variation. Table 12 presents the rotated factor loadings for the 10 homologs. The first rotated factor explains 32% of the system's variation and is primarily related to the abundance of the lowest and highest chlorinated homologs, as it presents high factor loadings (above 0.7) for the mono-, octa-, nona-, and deca-CBs. The second factor explains 21% of the variation with high factor loadings for the low-chlorinated di- and tri-CB homologs. The third factor explains 18% of the variation and is mainly controlled by tetra- and hexa-CBs. The fourth factor explains 17% of the variation and presents high factor scores for penta-CBs. Because nearly every sample is abundant in the moderately chlorinated hexa- and hepta-CB homologs, relatively small variation occurs in the PCB profiles within this range. Instead, the less abundant low-chlorinated and high-chlorinated homologs help refine the signatures of the PCBs.

**Table 12**  
**Rotated Factor Loadings for PCB Homologs in Baseline Runoff**

Homolog	Factor 1	Factor 2	Factor 3	Factor 4
mono-CB	<b>0.797</b>	-0.036	-0.030	-0.079
di-CB	0.104	<b>-0.955</b>	-0.112	-0.027
tri-CB	-0.116	<b>-0.951</b>	-0.019	0.119
tetra-CB	-0.139	0.090	<b>-0.977</b>	0.126
penta-CB	-0.130	0.241	0.102	<b>-0.929</b>
hexa-CB	-0.001	0.395	<b>0.727</b>	0.372
hepta-CB	0.177	0.244	0.509	<b>0.689</b>
octa-CB	<b>0.773</b>	0.123	0.215	0.355
nona-CB	<b>0.965</b>	0.004	0.085	0.147
deca-CB	<b>0.947</b>	-0.027	0.059	0.075
<b>Variation</b>	3.153	2.116	1.823	1.668
<b>Percentage</b>	31.5%	21.2%	18.2%	16.7%

Note: Values in bold indicate significant loading terms.

After the principal component analysis, the PCFA scores for the four variables were entered into cluster analyses (CA). The CA groups samples according to similarities in the PCFA scores. In essence, the combination of the PCFA and CA allows for a numerical determination of which samples are most alike.

The CA identified three broad groups of samples. Table 13 summarizes within-group averages, and Table 14 lists the cluster assignments for the 34 specific samples. Cluster 1 consists of 6 of the 34 samples that characteristically contain abundant di- and tri-CB homologs. This cluster has the lowest average concentrations for total PCBs, SSC, and suspended PCB concentrations, indicating this cluster is more

greatly influenced by precipitation, which tends to be dominated by homologs with less chlorine substitution. Cluster 2 consists of 21 samples, and characteristically is dominated (>50%) by hexa-CB homologs. The lowest and highest chlorinated homologs are largely absent in samples within this cluster. Total PCB, SSC, and suspended PCB concentrations within this cluster are slightly larger than in Cluster 1 samples. Cluster 3 is the most anomalous of the clusters. It consists of seven samples that characteristically contain significant proportions of the highest chlorinated octa, nona-, and deca-CB homologs. Samples in this cluster have the highest average total PCB, SSC, and suspended PCB concentrations.

**Table 13**  
**Characteristics of Clusters Derived for Pajarito Plateau Baseline Runoff Samples**

Cluster	No. of Samples	Average Total PCB Conc. (ng/L)	Average SSC (mg/L)	Average Calculated Suspended PCB Conc. (ng/g)	Characteristics of Cluster
1	6	1.10	3118	0.81	Abundant di- and tri-CBs. Often tetra-CBs. Little octa-, nona-, deca-CBs. Peak at hepta-CB.
2	21	1.46	4335	1.79	Often >50% of PCBs of hexa-CBs. Little mono, di-, tri-, octa-, nona-, or deca-CBs.
3	7	10.04	29,993	3.36	Octa-, nona-, deca-CB homologs present. Little di- or tri-. Peak at hexa-, hepta-CBs.

**Table 14**  
**Samples in Clusters Derived for Pajarito Plateau Stormwater**

Area	Station Name	Date	Cluster	Total PCBs (ng/L)	SSC or TSS (mg/L)	Suspended PCB Conc. (ng/g)
Reference	CHUP-1	8/4/09	3	24	14,200	1.690
Reference	CHUP-1	8/16/10	2	0.534	10,600	0.050
Reference	CORRAL-1	8/5/10	2	1.92	12,200	0.157
Reference	CORRAL-1	8/16/10	3	11.6	163,550	0.071
Reference	GARCIA-1	4/30/10	1	0.023	2.7	nc <sup>a</sup>
Reference	GARCIA-1	8/5/10	1	0.038	6630	0.006
Reference	GARCIA-1	8/24/10	2	0.201	1915	0.105
Reference	GUAJE-2	5/7/10	2	0.071	na <sup>b</sup>	na
Reference	GUAJE-2	8/12/10	2	0.345	13,280	0.026
Reference	GUAJE-2	8/13/10	2	0.967	9090	0.106
Reference	GUAJE-2	9/23/10	1	0.273	2020	0.135
Reference	LAS LATAS-1	7/30/09	2	0.6275	6495	0.097
Reference	LAS LATAS-1	7/30/10	2	0.149	3300	0.045
Reference	LAS LATAS-1	8/15/10	2	0.19	8130	0.023
Reference	LAS LATAS-2	7/22/10	1	5.5	2000	2.750
Reference	LAS LATAS-2	7/23/10	2	13.3	5760	2.309
Reference	LAS LATAS-2	7/31/10	3	4.34	23,940	0.181
Reference	LAS MARIAS-1	7/22/10	2	0.193	na	na
Reference	LAS MARIAS-1	8/5/10	2	0.445	3610	0.123

Table 14 (continued)

Area	Station Name	Date	Cluster	Total PCBs (ng/L)	SSC or TSS (mg/L)	Suspended PCB Conc. (ng/g)
Reference	LAS MARIAS-1	10/4/10	1	0.711	4870	0.146
Western Boundary	E025	7/24/10	2	0.684	140	4.886
Western Boundary	E025	8/5/10	3	3.09	310	9.968
Western Boundary	E025	8/15/10	3	2.33	570	4.088
Western Boundary	E025	8/16/10	3	8.12	4410	1.841
Western Boundary	E025	8/23/10	3	16.8	2970	5.657
Western Boundary	E240	8/30/09	2	0.388	123	3.154
Western Boundary	E240	9/18/09	2	0.713	452	1.577
Western Boundary	E240	10/21/09	2	0.518	67	7.731
Western Boundary	E240	8/5/10	2	5.28	1100	4.800
Western Boundary	E240	8/15/10	2	1.9	420	4.524
Western Boundary	E240	8/16/10	2	2.07	870	2.379
Western Boundary	E240	9/21/10	1	0.072	71	1.015
Western Boundary	E252	8/30/09	2	0.057	474	0.120
Western Boundary	E252	8/23/10	2	0.033	na	na

<sup>a</sup> nc=Ratio not calculated because TSS value small and not representative of typical storm runoff event.

<sup>b</sup> na = Not available.

It is noteworthy that Clusters 2 and 3 include samples from both the Reference and Western Boundary tributary groups. This supports the interpretation that the two study areas share similar PCB compositions.

#### 4.6 Urban Runoff Near Los Alamos

The basic footprint of the developed portions of the Los Alamos townsite has changed little over decades. Retail stores, county government operations, and businesses are concentrated together in the downtown and situated on a mesa top within a zone roughly 2 to 3 mi across. Away from the commercial center, land use transitions to a residential mix of apartment complexes and single-family houses. The townsite has been laid out in this general configuration since the 1960s. A portion of this development was built on ground that once housed research activities of the Manhattan Project. Buildings from that earlier era were removed, and several rounds of remediation of the surface have been performed; remaining SWMUs and AOCs have been delineated and are under investigation by LANL. Most of the townsite area has long been covered with imported fill dirt, new buildings, pavement or park land, in essence forming caps over the original ground.

Stormwater sample collection was conducted in the townsite vicinity to measure PCB concentrations in locations representing storm runoff from a relatively small urban environment. Samplers were placed in ephemeral tributary channels around the edge of the urban development; no urban runoff samplers were placed below any known areas of concentrated contamination. A majority of samplers were located to collect stormwater samples from housing developments, schools, and a golf course. In addition to monitoring the townsite perimeter, sampling was also conducted in drainage channels downstream from the administrative offices of LANL. The sampling locations are shown in Figure 42.

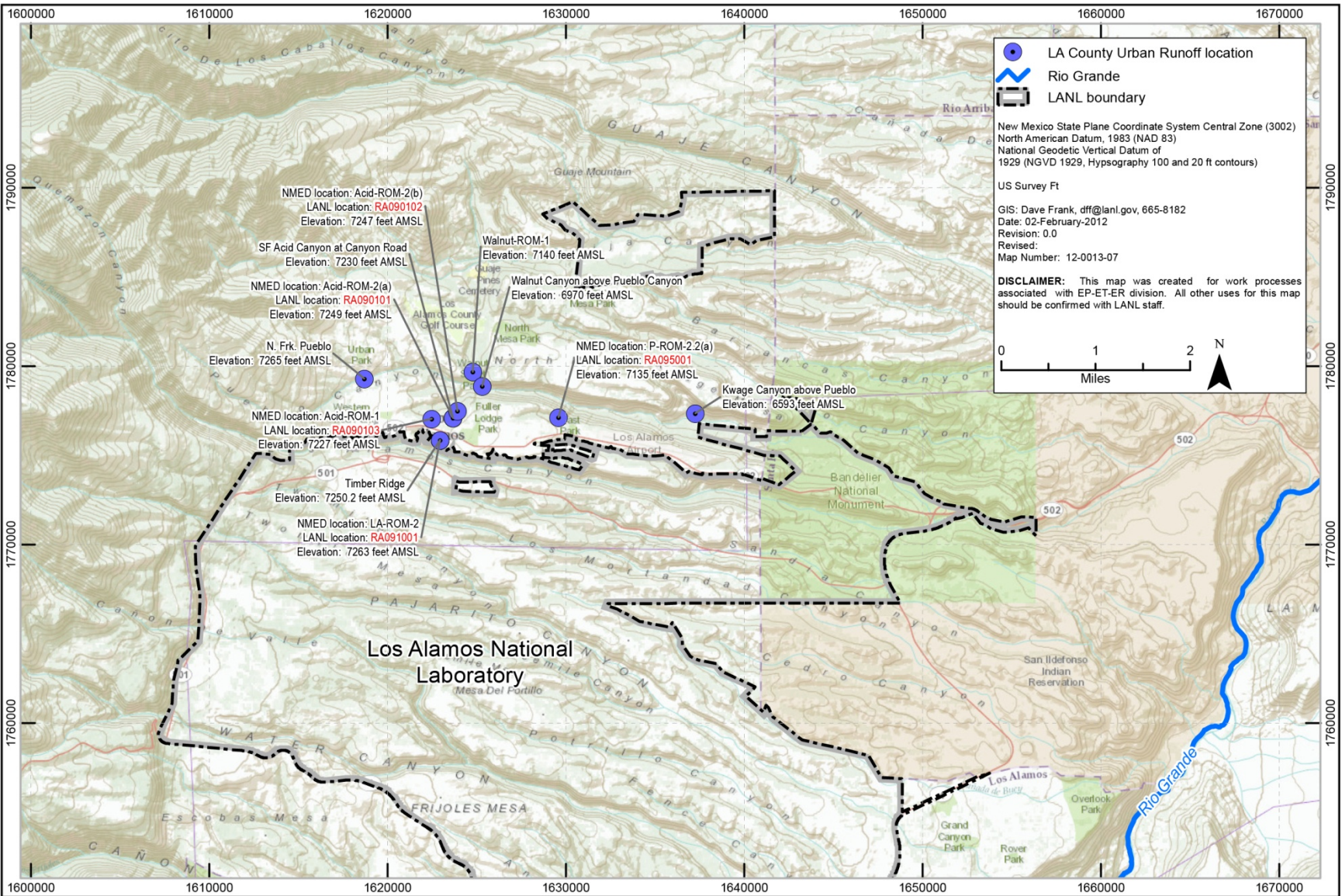


Figure 42 Locations of urban runoff monitoring stations

PCB congener data are available from two phases of monitoring: NMED performed the first phase in 2006–2007 and 2009 using single-stage samplers, and LANL performed the second phase in 2009–2010 using automated-pump samplers. A total of 47 sample results were assessed for this report, 26 samples from NMED and 21 samples from LANL.

#### 4.6.1 PCB Concentrations in Urban Runoff Near Los Alamos

A box plot in Figure 43 displays individual total PCB concentration results and median values obtained at each sampling station; the calculated suspended PCB concentrations are shown in a companion plot (Figure 44). Median total PCB concentrations measured by NMED were slightly above those in the LANL data set, but that value reflects higher sediment concentrations in the NMED samples probably because of the sampling device rather than more enriched contamination.

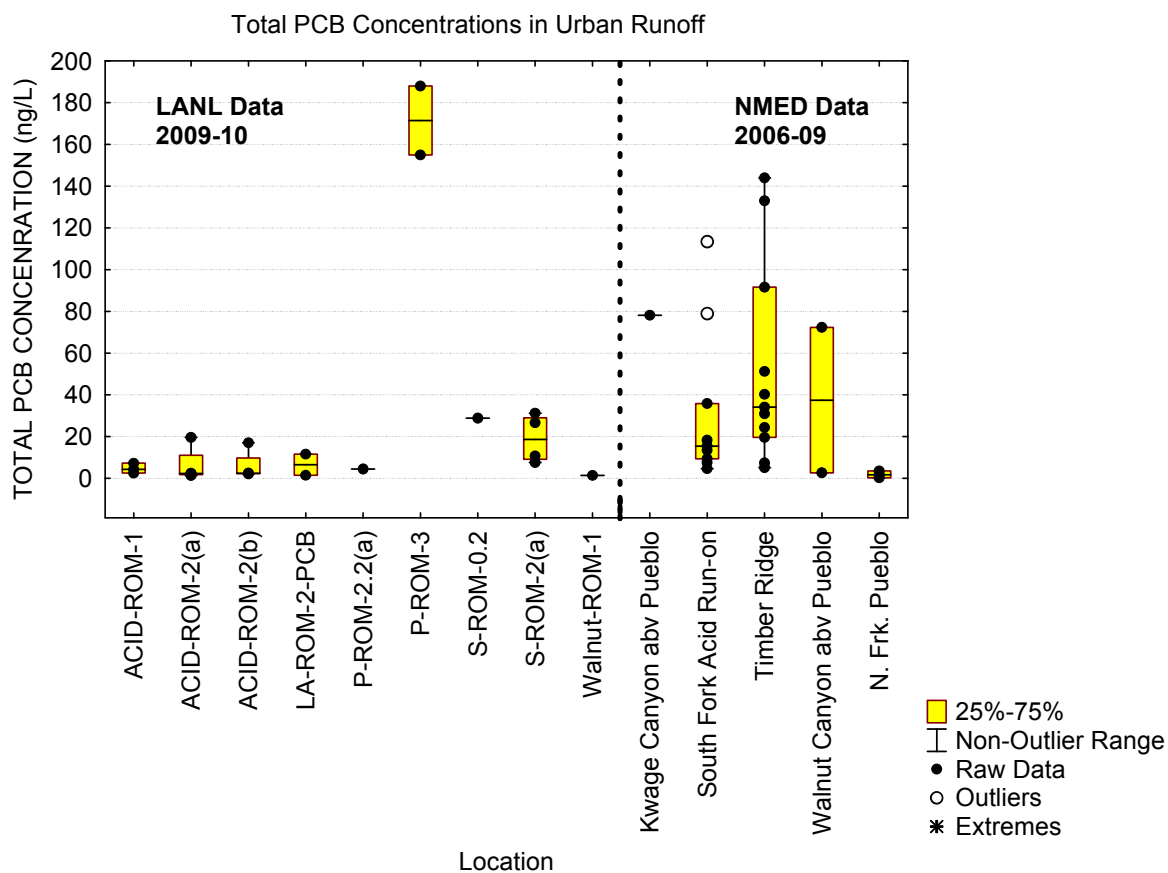
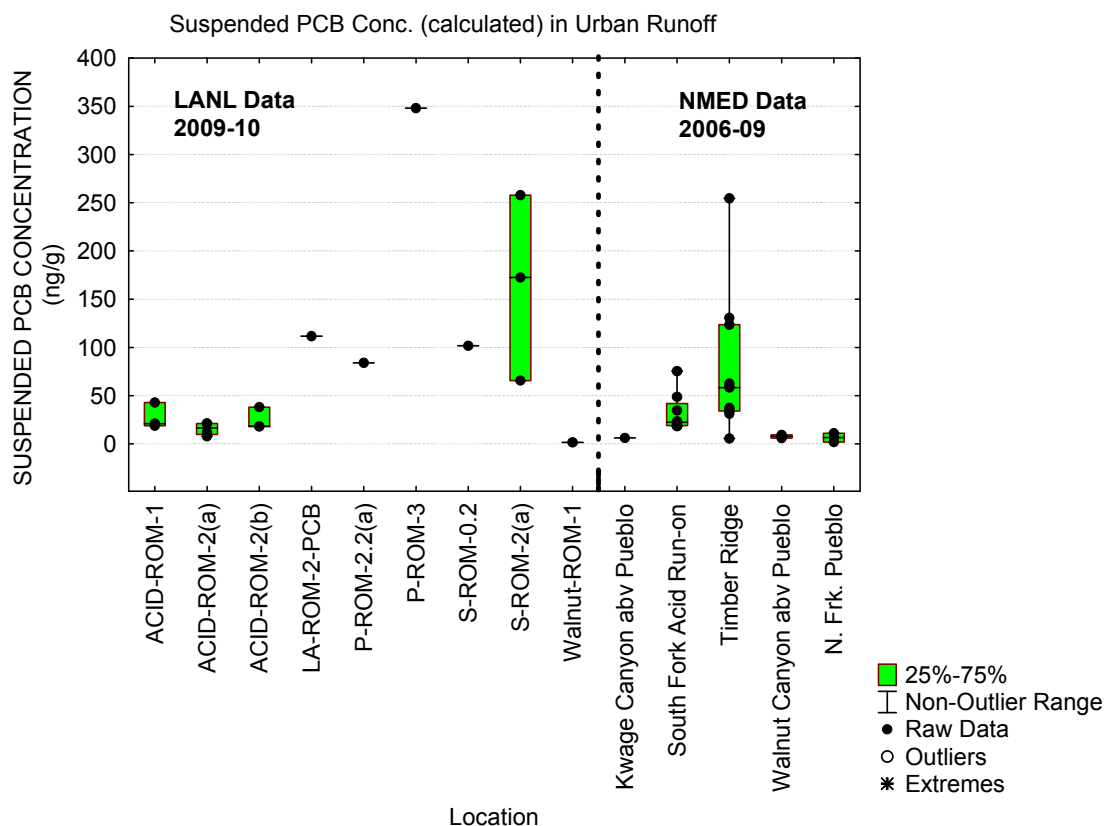


Figure 43 Box plot of total PCB concentrations in Los Alamos urban runoff

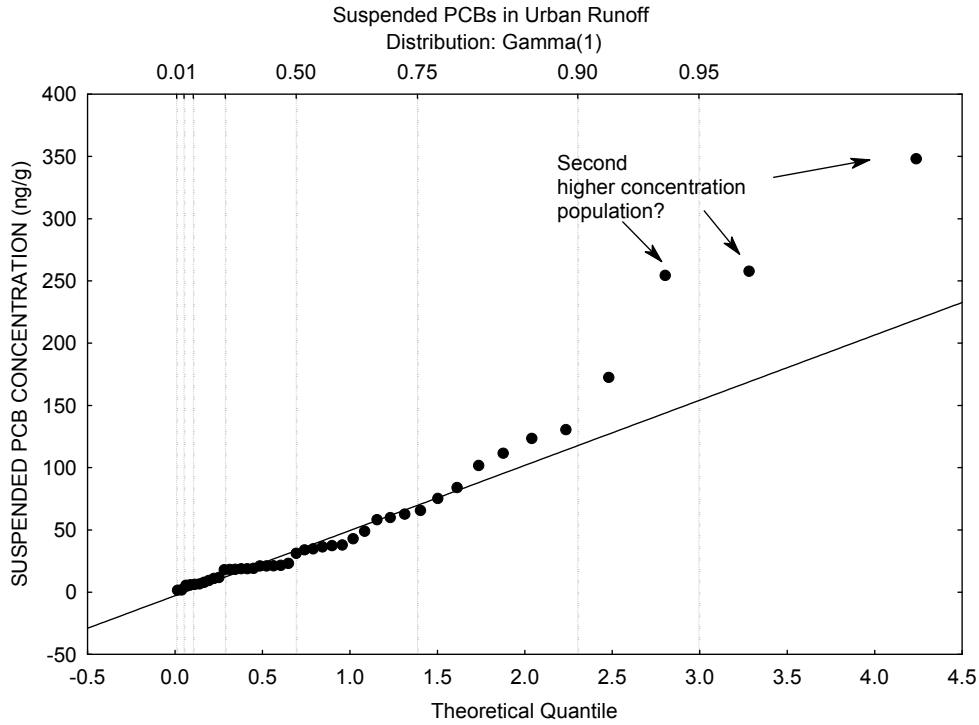


**Figure 44** Box plot of calculated suspended PCB concentrations in Los Alamos urban runoff

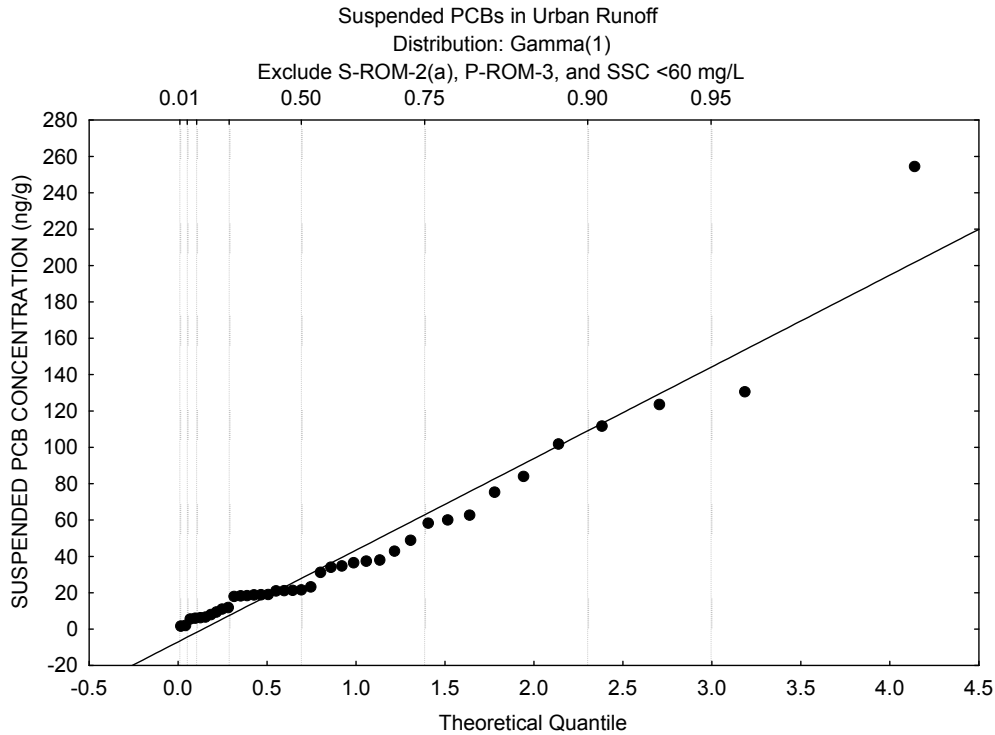
A preliminary examination of the plots indicates suspended PCB concentrations may be elevated at two stations: P-ROM-3 and S-ROM-2(a). This possibility was confirmed through a probability plot of suspended PCB concentrations for the combined NMED and LANL data (Figure 45). The majority of results plot along a single population line until concentrations approach about 150 ng/g. At higher levels, P-ROM-3 and S-ROM-2(a) results substantially deviate from the line, indicating they were derived from a higher-concentration source. Results from those stations were removed from the data set because of uncertainty as to the source(s) for the elevated PCB concentrations. Figure 46 shows the remaining data, plotted without the two stations, conform to a single population that describes widespread baseline PCB concentrations in Los Alamos urban runoff.

After excluding the two suspect stations, the remaining urban runoff data range from 0.01 ng/L to 144 ng/L and appear to originate from a gamma statistical distribution (Table 15). The median concentration was 12 ng/L. All but 1 of the 41 (98%) results were above the New Mexico human health WQC, and 19 of 41 (46%) were above the wildlife habitat WQC. The UTL for the area is 98.0 ng/L, which is within the measured values.

Perhaps most indicative of the impacts of urbanization on PCB levels is the suspended PCB concentrations, which are summarized statistically in Table 15. The median calculated suspended PCB concentration in the urban runoff samples was 21 ng/g. Suspended PCBs carried by urban runoff from the Los Alamos townsite were 10 to 200 times more enriched than at the Pajarito Plateau baseline sites. However, the actual environmental impact of this enrichment is tempered somewhat by the low to moderate SSCs measured in the townsite runoff, which typically were below 1000 mg/L.



**Figure 45** Probability plot of calculated suspended PCB concentrations in Los Alamos urban runoff



**Figure 46** Probability plot of calculated suspended PCB concentrations in Los Alamos urban runoff, excluding results from stations P-ROM-3 and S-ROM-2(a)

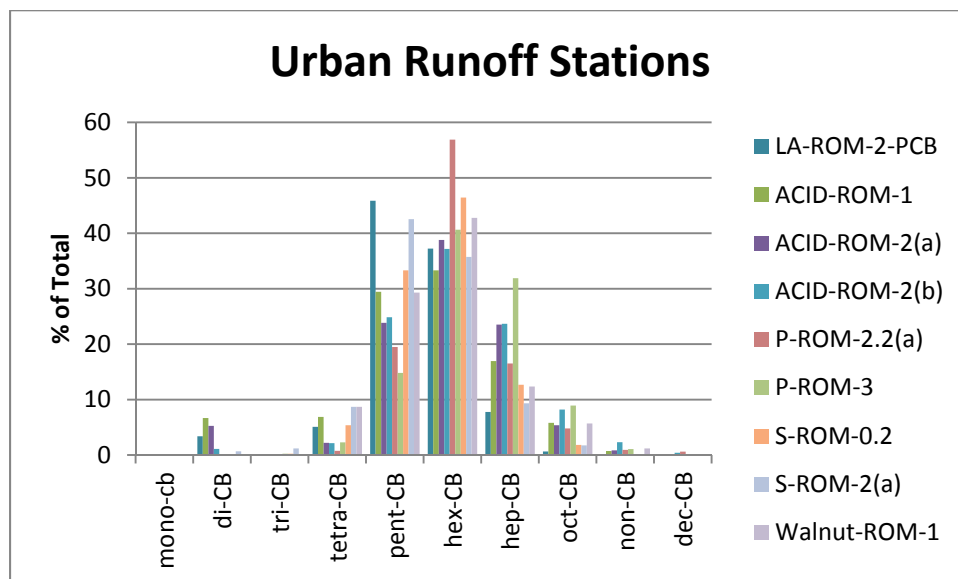
**Table 15**  
**Summary Statistics of Urban Runoff PCB Concentrations in Los Alamos**

	N	Min	Max	Mean	SD	Median	Distribution	UTL*
Total PCB Concentration (ng/L)	41	0.01	144	27.7	37.7	12	Gamma	98.0
Calculated Suspended PCB Concentration (ng/g)	37	2	131	36.7	35.0	21	Gamma	106.3

\*95% W-H approximate gamma UTL with 90% coverage.

#### 4.6.2 Fingerprint of PCBs in Los Alamos Area Urban Runoff

Figure 47 shows the average homolog distributions for Los Alamos townsite urban runoff. The homolog distributions were centered near the penta- and hexa-CBs. The bimodal distribution noted in precipitation and regional soil samples is evident in about one-third of the urban runoff samples, particularly those from channels draining apartment complexes [LA-ROM-2, Acid-ROM-1, Acid-ROM-2(a)].



**Figure 47** Average PCB homolog distributions in Los Alamos urban runoff

## 5.0 SUMMARY AND DISCUSSION

Studies around the world confirm that PCBs have been released into the environment from a wide variety of sources, including industrial processes, appliance sealants, leaking electrical transformers, hazardous waste accidents, and improper waste disposal practices. Because of the unique chemical properties of PCBs, they can persist in the environment for decades, usually adsorbed to soil, stream sediment, or organic matter. With time, a portion of the lighter PCB molecules volatilizes and is distributed globally through the atmosphere and from precipitation events. Consequently, PCBs are found in the landscape not only near industrial centers but also in residential areas, on undeveloped lands, and even in remote polar regions and mountain snow packs. A compounding problem with PCBs is their toxicity and their ability to bioaccumulate in the food chain; thus, regulations set stringent action levels for PCBs in surface water to protect wildlife, aquatic organisms, and human health.



In northern New Mexico, sediment transport by stormwater is believed to be the predominant mechanism for redistributing PCBs. This study was designed to characterize PCB levels in precipitation and stormwater in the nonindustrialized portions of the upper Rio Grande watershed. The principal objectives of the study were to determine (1) baseline levels of PCB concentrations in precipitation and snowpack in northern New Mexico; (2) baseline levels of PCB concentrations stormwater in northern New Mexico streams and arroyos that are tributaries to the Rio Grande and Rio Chama; (3) the range of PCB concentrations found in the Rio Grande during base-flow and storm-flow conditions; (4) baseline levels of PCBs in stormwater from undeveloped watersheds of the Pajarito Plateau; (5) the concentrations of PCBs in urban runoff from the Los Alamos townsite that flow onto LANL, and (6) how these findings may be used to target significant pollution sources.

The sampling locations used to determine baseline levels of PCBs in stormwater on the Pajarito Plateau were selected to avoid any known contamination and to provide reasonable estimates of baseline concentrations, including a wide variety of bedrock source areas and sediment texture. Although it was hypothesized that the sites would contain only baseline concentrations of PCBs, several statistical, graphical, and analytical methods were used to monitor for the presence of anomalous contamination. These same techniques were used to evaluate PCB results from the upper Rio Grande and contributing tributaries as well as to quantify PCB concentrations in urban runoff from developed areas in Los Alamos. The data do not indicate distinct contributions of PCBs from local industrial pollution sources at most locations.

Total PCB concentrations for precipitation and stormwater are summarized in Table 16. The concentrations in precipitation were generally low, probably reflecting the rural nature of the study area. Levels in precipitation and snowpack samples from the upper Rio Grande watershed rank among the lowest when compared with those reported in the scientific literature for other “nonpollution” locations. With the possible exception of near Albuquerque, samples of snowpack from alpine mountains in northern New Mexico did not show a clear PCB airborne impact from the nearest municipality.

**Table 16**  
**Summary of Total PCB Concentrations in Upper Rio Grande Watershed**

Category	Median (ng/L)	UTL (ng/L)	Max Conc. (ng/L)	Percentage of Results Greater Than NM Health Standard (0.64 ng/L)	Percentage of Results Greater Than NM Wildlife Standard (14 ng/L)
Precipitation	0.12	0.68	0.61	0	0
Snowpack	0.14	0.7	0.65	8	0
Rio Grande/Rio Chama					
Base flow	0.01	—*	1.36	6	0
Stormwater (runoff)	0.24	—	51.4	39	3
Northern New Mexico Tributaries Stormwater	5.5	24	30.6	91	22
Baseline Pajarito Plateau Stormwater					
Reference Sites (Flows originating on Pajarito Plateau)	0.4	11.7	11.6	28	0
Western Boundary Sites (Flows Originating in Jemez Mountains)	2.1	19.5	20.7	78	17
Reference and Western Boundary Combined	0.97	13	20.7	56	10
Urban Runoff Los Alamos Townsite	12	98	144	98	46

\*— = Not available.

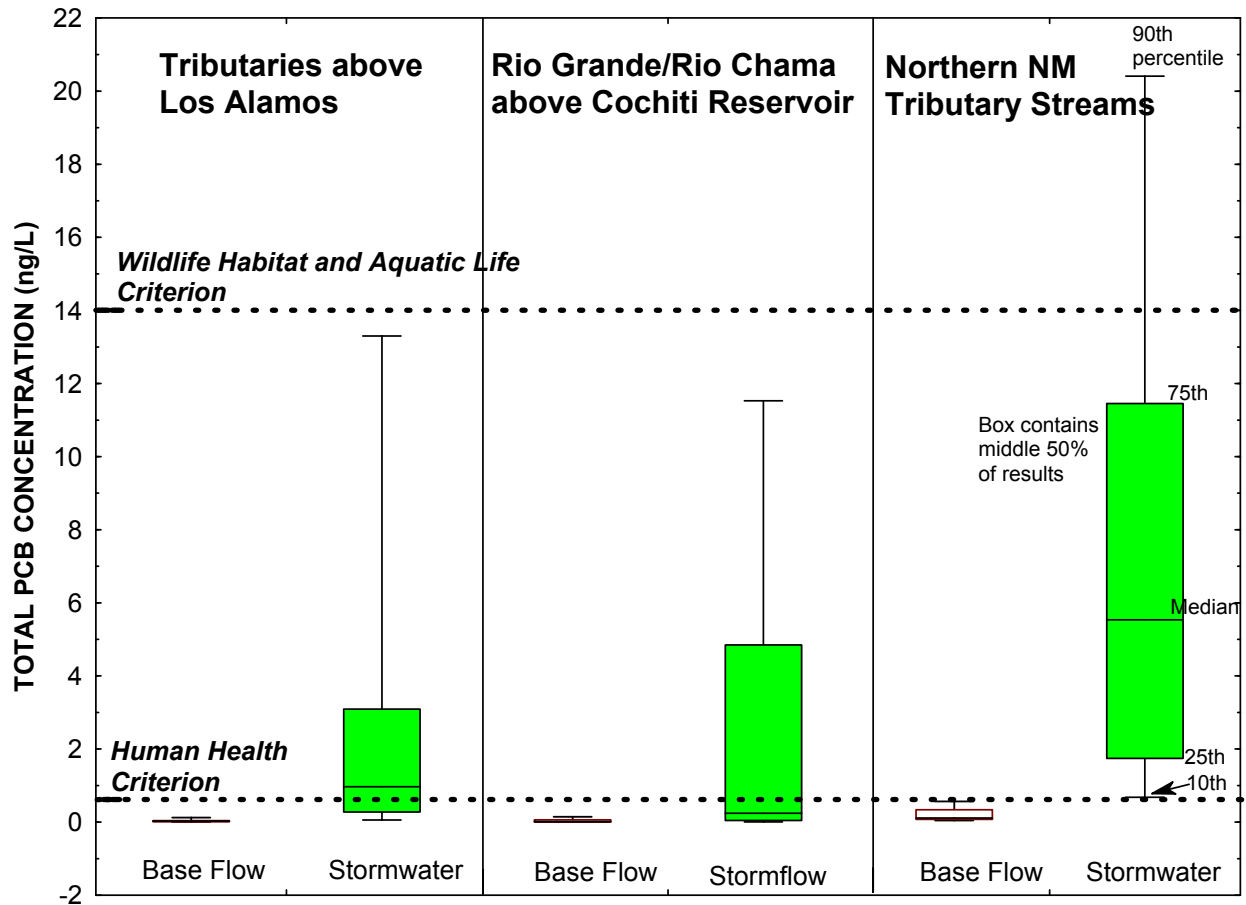
Although PCB concentrations in precipitation and snowpack are relatively low, those sources still play a major indirect role in impacting surface-water quality. Over long periods of time—perhaps decades—precipitation events leave behind an inventory of PCBs on surface soil. The quality of nearby surface water deteriorates once the surface soil is eroded and carried by runoff into watercourses. Temporary deterioration of water quality is observed in drainages both small and large. Storm flow occurs infrequently. These flow events are generally very short lived, with flows lasting from less than an hour to—rarely—several days.

The magnitude of the impact on water quality can be gauged by comparing measured PCB concentrations in surface water with NMWQCC criteria for total PCBs in water of 0.64 ng/L (0.64 ppt) for the protection of human health and 14 ng/L for the protection of wildlife habitat. Environmental monitoring results show that small tributaries carrying a moderate amount of suspended soil/sediment likely will have total PCB concentrations above human health WQC and occasionally the wildlife habitat WQC, even in the absence of industrial pollution. PCB concentrations above the WQC would be expected in the most remote parts of the drainage system because of the high sediment load carried by small tributaries during periods of storm runoff. Table 16 shows that concentrations greater than the New Mexico human health WQC were measured in 91% of stormwater samples collected from tributaries to the Rio Chama and Rio Grande, in 28% to 78% in ephemeral channels on the Pajarito Plateau, and in 38% of stormwater samples from the Rio Grande or Rio Chama.

Sources of PCBs detected in water may include recognizable discrete local-scale PCB sources as well as ubiquitously dispersed sources. The upper ranges of PCB concentrations in baseline or Rio Grande storm runoff were approximately an order of magnitude larger than those for precipitation (less than 1 ng/L in precipitation and 10 ng/L to 50 ng/L in storm runoff). This increase was primarily from the presence of PCBs associated with suspended sediment in runoff. Similarly, another order of magnitude increase in PCB concentrations was evident when upper ranges in urban runoff (above 100 ng/L) were compared with upper ranges in baseline or Rio Grande storm runoff. The higher concentrations associated with the urban runoff likely resulted from the contribution of additional diffuse local sources in the urban environment. This finding is consistent with information in the toxicological profile for PCBs published by the Agency for Toxic Substances and Disease Registry as well numerous studies that report PCB concentrations in stormwater in urban areas are higher than in rural locations (Table 9) (ATSDR 2000, 209548).

The disparity between PCB concentrations during base-flow (ambient) and storm-flow periods because of suspended sediment is significant. While concentrations are elevated during storm runoff events in perennial or intermittent segments, they may recover quickly to lower levels during the intervening periods of base flow (unless impacted by a significant pollution source). On a time-weighted basis, average exposure levels in the water column would be relatively low, yet the perennial segment could exceed NMWQCC criteria if the assessment data set includes samples collected when runoff was occurring.

To illustrate the role of suspended sediment in affecting PCB concentrations in surface water, data for base-flow periods were compiled for these same drainage areas. Figure 48 shows that PCB concentrations were only rarely above the New Mexico human health WQC under base-flow conditions because suspended sediment concentrations associated with base flow were very low, typically less than 100 mg/L. For perennial or intermittent surface waters, base flow predominates perhaps 90% or more of the time. Consequently, on any given day, the PCB concentrations in the water column of perennial or intermittent surface water would be relatively small.



**Figure 48** Box plots of base flow and storm runoff PCB concentrations for various drainages in the upper Rio Grande system

To appropriately target the significant pollution sources, decisions on remedy should not be based solely on water column concentration results. This study illustrates the utility of also considering the suspended sediment PCB concentrations as an indicator of a significant pollution source. The use of suspended sediment PCB concentrations allows discrimination between the need for focused, point-source-based best management practices (BMPs) to control source-term contributions to contaminant loading, or watershed-scale BMPs to reduce excessive erosion of baseline sediments.

## 6.0 REFERENCES AND MAP DATA SOURCES

### 6.1 References

The following list includes all documents cited in this report. Parenthetical information following each reference provides the author(s), publication date, and ER ID. This information is also included in text citations. ER IDs are assigned by the Environmental Programs Directorate's Records Processing Facility (RPF) and are used to locate the document at the RPF and, where applicable, in the master reference set.

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## 6.2 Map Data Sources

LANL Areas Used and Occupied; Los Alamos National Laboratory, Site Planning & Project Initiation Group, Infrastructure Planning Office; 19 September 2007; as published 13 August 2010.

Watercourse; Los Alamos National Laboratory, ENV Water Quality & Hydrology Group; 05 April 2005.

# **Appendix A**

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*Acronyms and Abbreviations and Metric Conversion Table*



## A-1.0 ACRONYMS AND ABBREVIATIONS

% wt	percent weight
A-D	Anderson-Darling
AOC	area of concern
AQA	Analytical Quality Associates, Inc.
ASTM	American Society for Testing and Materials
BMP	best management practice
CA	cluster analysis
CB	chlorobiphenyl
DOE	Department of Energy (U.S.)
dw	dry weight
EF	enrichment factor
EPA	Environmental Protection Agency (U.S.)
HPLC	high-performance liquid chromatography
HW	Hawkins-Wixley
IUPAC	International Union of Pure and Applied Chemistry
IP	Individual Permit
K-S	Kolmogorov-Smirnov
LANL	Los Alamos National Laboratory
LASO	Los Alamos Area Office (DOE)
LOWESS	locally weighted scatter plot smoothing (method)
MBCR	method blank corrected result
MBCV	method blank corrected value
NM	New Mexico
NMAC	New Mexico Administrative Code
NMWQCC	New Mexico Water Quality Control Commission
NPDES	National Pollutant Discharge Elimination System
Oversight Bureau	New Mexico Environment Department–U.S. Department of Energy Oversight Bureau
PCB	polychlorinated biphenyl
PCFA	principal component factor analysis
QC	quality control
RG	Rio Grande
RPD	relative percent difference
RPF	Records Processing Facility
SD	standard deviation
SSC	suspended sediment concentration

SWMU	solid waste management unit
SWQB	Surface Water Quality Bureau (NMED)
S-W	Shapiro-Wilk
TA	technical area
TMDL	total maximum daily load
TOC	total organic carbon
TSCA	Toxic Substances Control Act
USGS	U.S. Geological Survey
UTL	upper tolerance limit
W-H	Wilson-Hilferty
WMW	Wilcoxon-Mann-Whitney
WQC	water-quality criteria
WQS	water-quality standard
ww	wet weight

**A-2.0 METRIC CONVERSION TABLE**

Multiply SI (Metric) Unit	by	To Obtain U.S. Customary Unit
kilometers (km)	0.622	miles (mi)
kilometers (km)	3281	feet (ft)
meters (m)	3.281	feet (ft)
meters (m)	39.37	inches (in.)
centimeters (cm)	0.03281	feet (ft)
centimeters (cm)	0.394	inches (in.)
millimeters (mm)	0.0394	inches (in.)
micrometers or microns ( $\mu\text{m}$ )	0.0000394	inches (in.)
square kilometers ( $\text{km}^2$ )	0.3861	square miles ( $\text{mi}^2$ )
hectares (ha)	2.5	acres
square meters ( $\text{m}^2$ )	10.764	square feet ( $\text{ft}^2$ )
cubic meters ( $\text{m}^3$ )	35.31	cubic feet ( $\text{ft}^3$ )
kilograms (kg)	2.2046	pounds (lb)
grams (g)	0.0353	ounces (oz)
grams per cubic centimeter ( $\text{g}/\text{cm}^3$ )	62.422	pounds per cubic foot ( $\text{lb}/\text{ft}^3$ )
milligrams per kilogram ( $\text{mg}/\text{kg}$ )	1	parts per million (ppm)
micrograms per gram ( $\mu\text{g}/\text{g}$ )	1	parts per million (ppm)
liters (L)	0.26	gallons (gal.)
milligrams per liter ( $\text{mg}/\text{L}$ )	1	parts per million (ppm)
nanograms per liter ( $\text{ng}/\text{L}$ )	1	parts per trillion (ppt)
nanograms per liter ( $\text{ng}/\text{L}$ )	0.001	parts per quadrillion (ppq)
degrees Celsius ( $^{\circ}\text{C}$ )	$9/5 + 32$	degrees Fahrenheit ( $^{\circ}\text{F}$ )

## **Appendix B**

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*Analytical Results*  
*(on CD included with this document)*





# **Appendix C**

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## *Probability Plots*



This appendix contains probability plots for polychlorinated biphenyl (PCB) concentrations on three scales: (1) untransformed (normal distribution), (2) gamma transformation, and (3) natural logarithmic transformation.

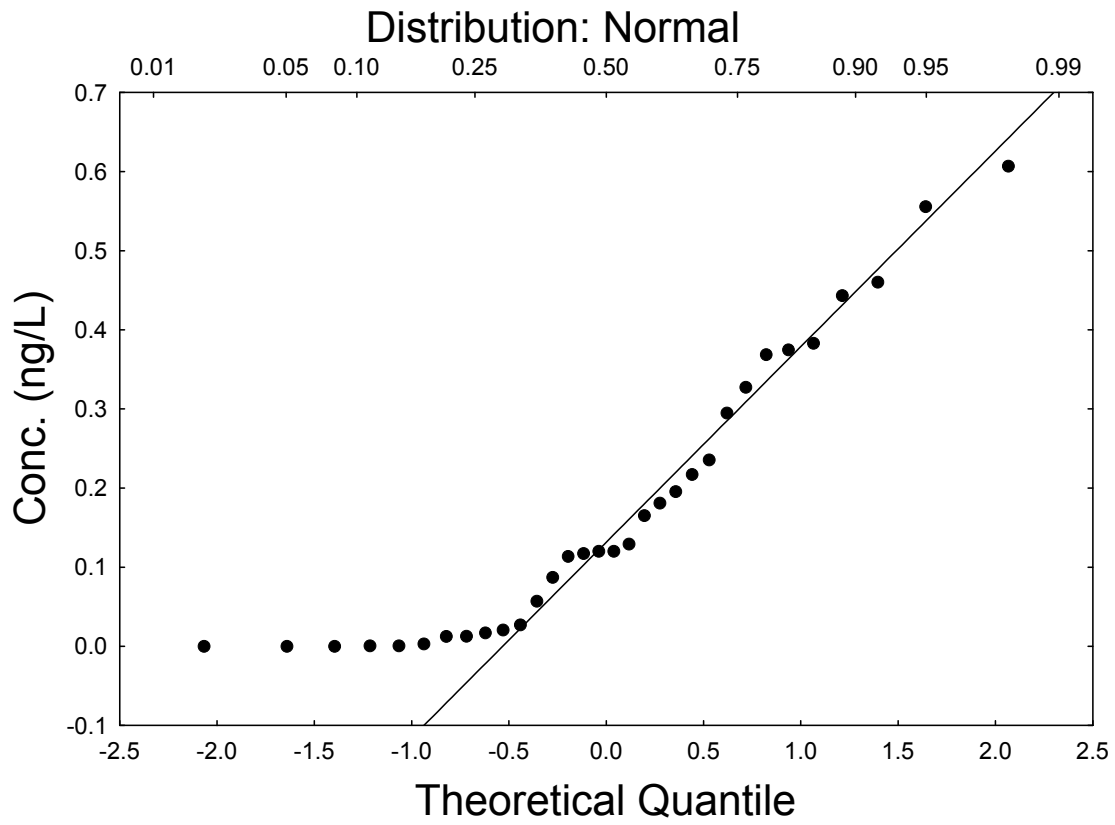
The probability plots show each analytical result ordered from lowest to highest. The x-axis is the standard normal quantile scale. The units of the standard normal quantile are in standard deviation, where 1 represents 1 standard deviation. The y-axis of the probability plot is the PCB concentration in ng/L or ng/g. The purpose of the plots is twofold. First, they are a succinct way to present all data for each analyte at a specific location. Second, they provide a way to assess the statistical distribution of each group of results. Specifically, if the data follow a straight line when plotted on an untransformed or standard normal scale, these data are considered to originate from a normal distribution. One can assess the fit to other statistical distributions by transforming the y-axis to another scale. For example, chemicals frequently follow a lognormal distribution, and transforming the y-axis into a logarithmic scale assesses the fit to a lognormal distribution.

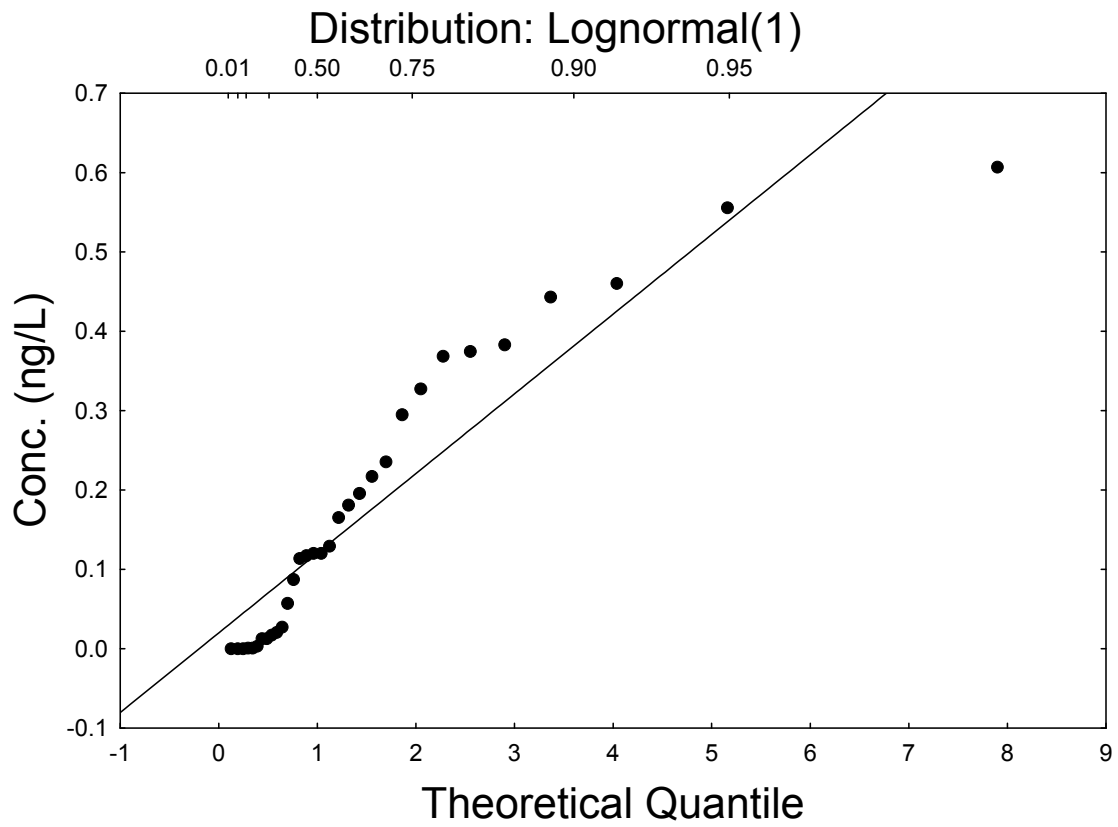
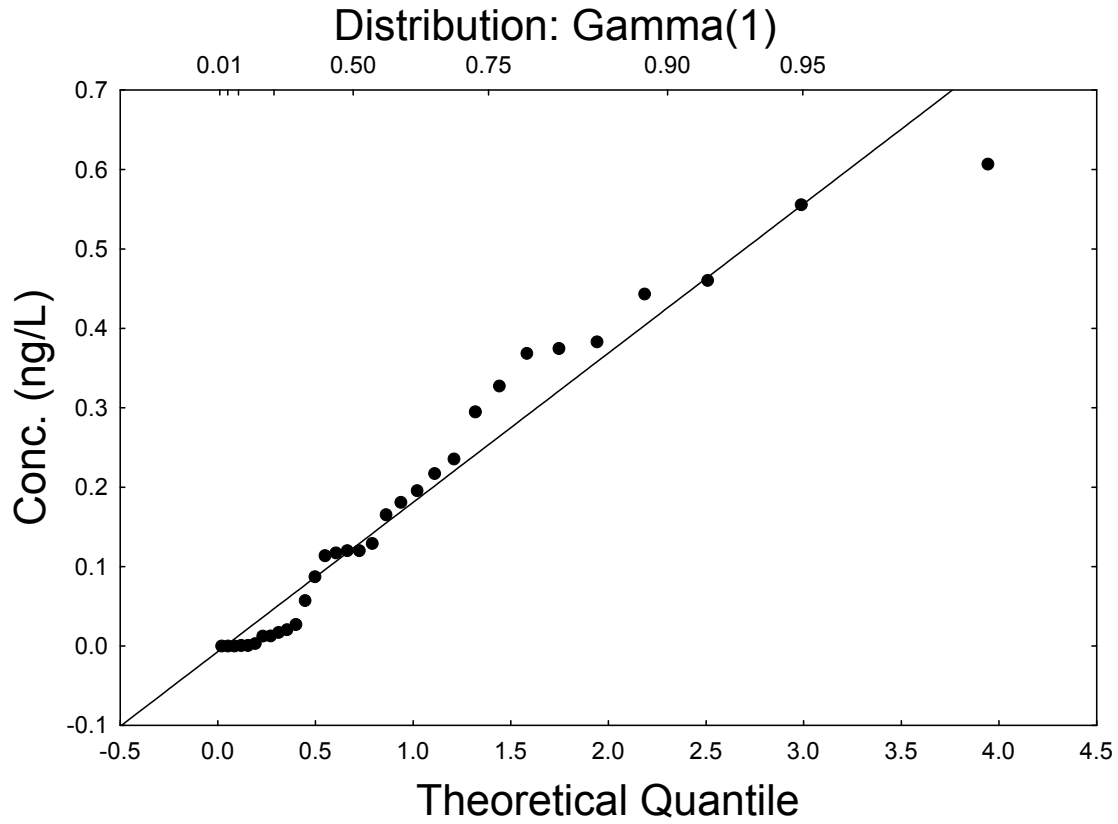
Generally, probability plots of background concentration data for soils, sediments, and dissolved constituents plot on a line after some form of transformation, indicating environmental levels of many constituents vary within a limited statistical range. Outliers or anomalous results are often identified by their deviation from the line. However, for total PCB concentrations in stormwater, it is not clear if this approach works to identify outliers because stormwater total PCB variations are controlled more by the carrying capacity of the flow event rather than by actual variation in the PCB concentrations. Consequently, to identify possible outlier or anomalous results, the probability plots of the suspended PCB concentrations were analyzed because they generally vary within a relatively limited range unless contamination is present.

Several outliers were readily identified in the probability plots. Examples of clear probable outliers are shown in the probability plot for Reference station suspended PCB concentrations. Three high concentration values plot considerably away from the line formed by the remaining values. Other potential outliers express themselves more subtly in the plots and must be identified through complementary lines of evidence. For example, four potential outliers are suggested in the suspended PCB concentration plots for urban runoff. P-ROM-3 was identified as a likely outlier because the suspended PCB concentration was elevated and the total PCB concentrations were among the highest measured. S-ROM-2(a) was identified as a likely outlier because multiple values of elevated suspended PCBs were measured, indicating repeated presence. In contrast, Timber Ridge was not identified as a station with anomalous concentrations because only 1 of 11 suspended PCB sample results for the stations appeared as an outlier.

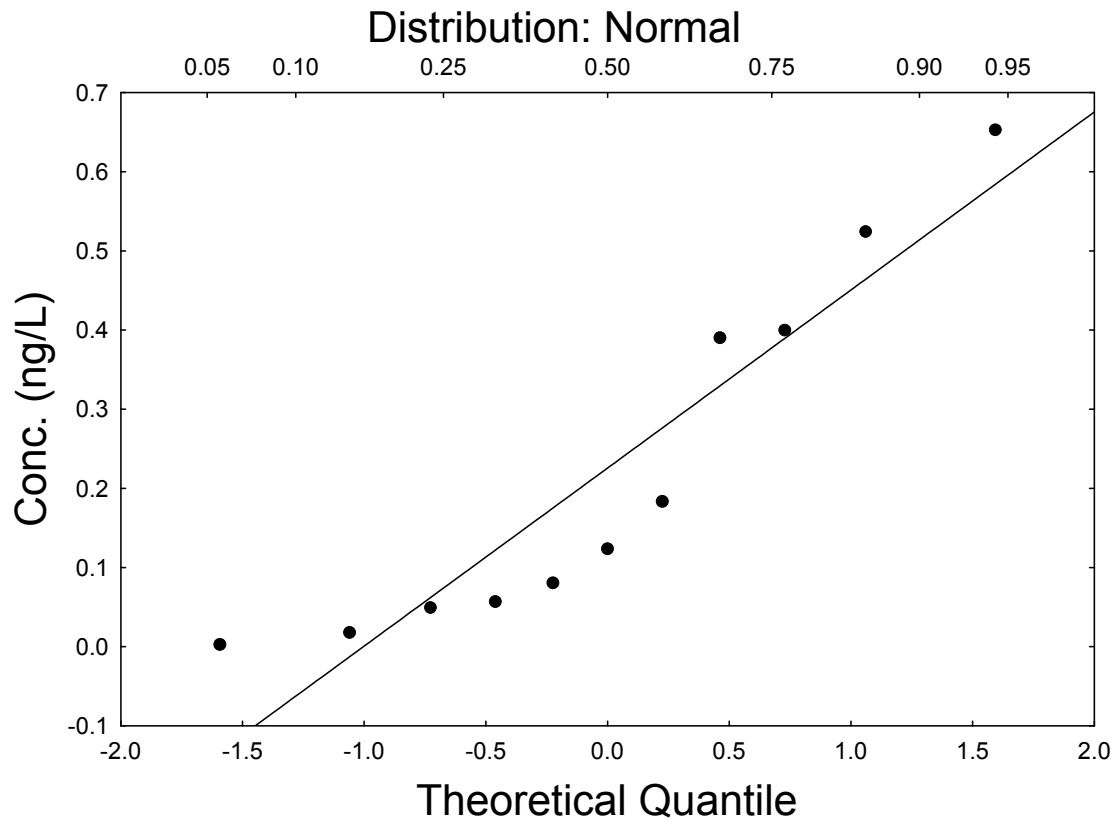


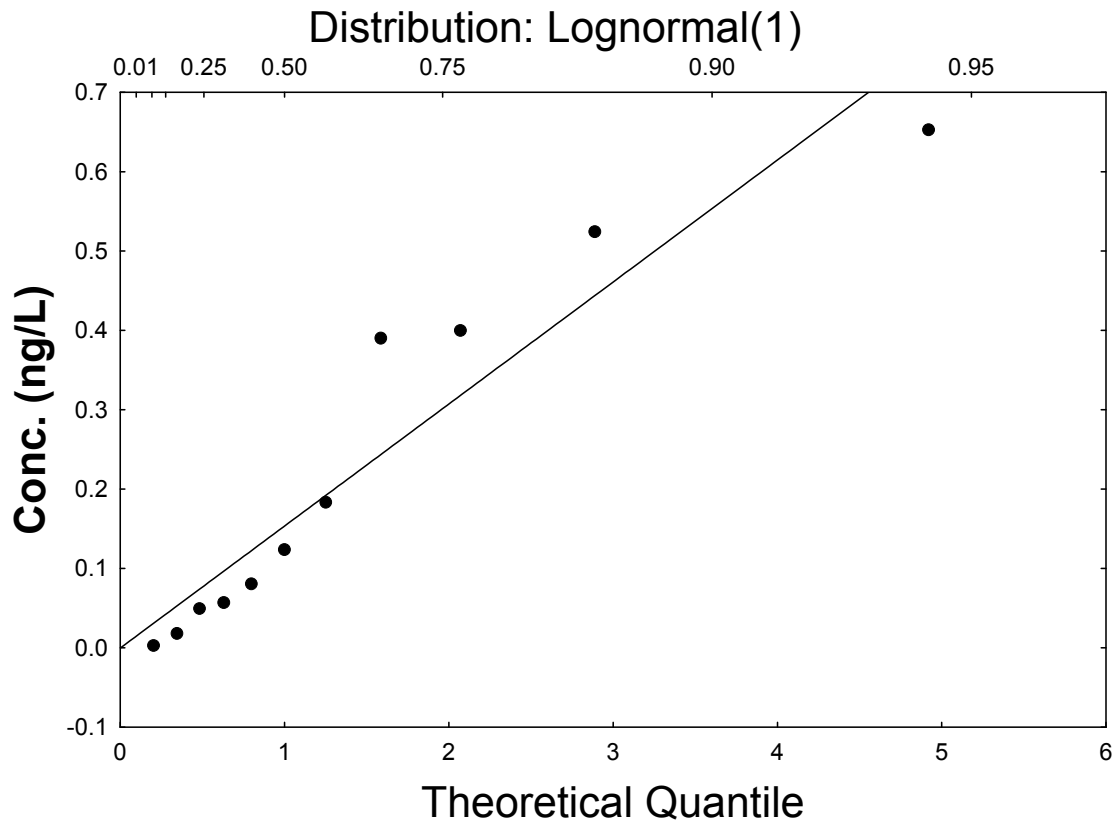
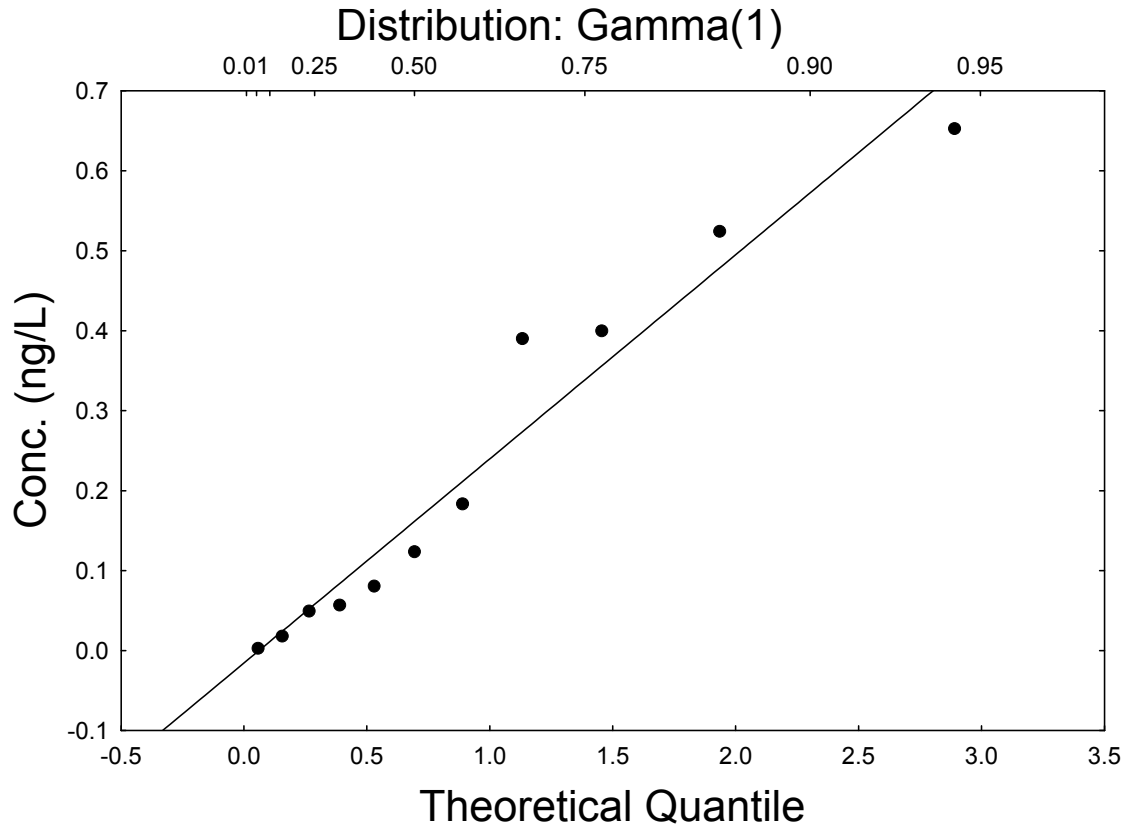
Precipitation





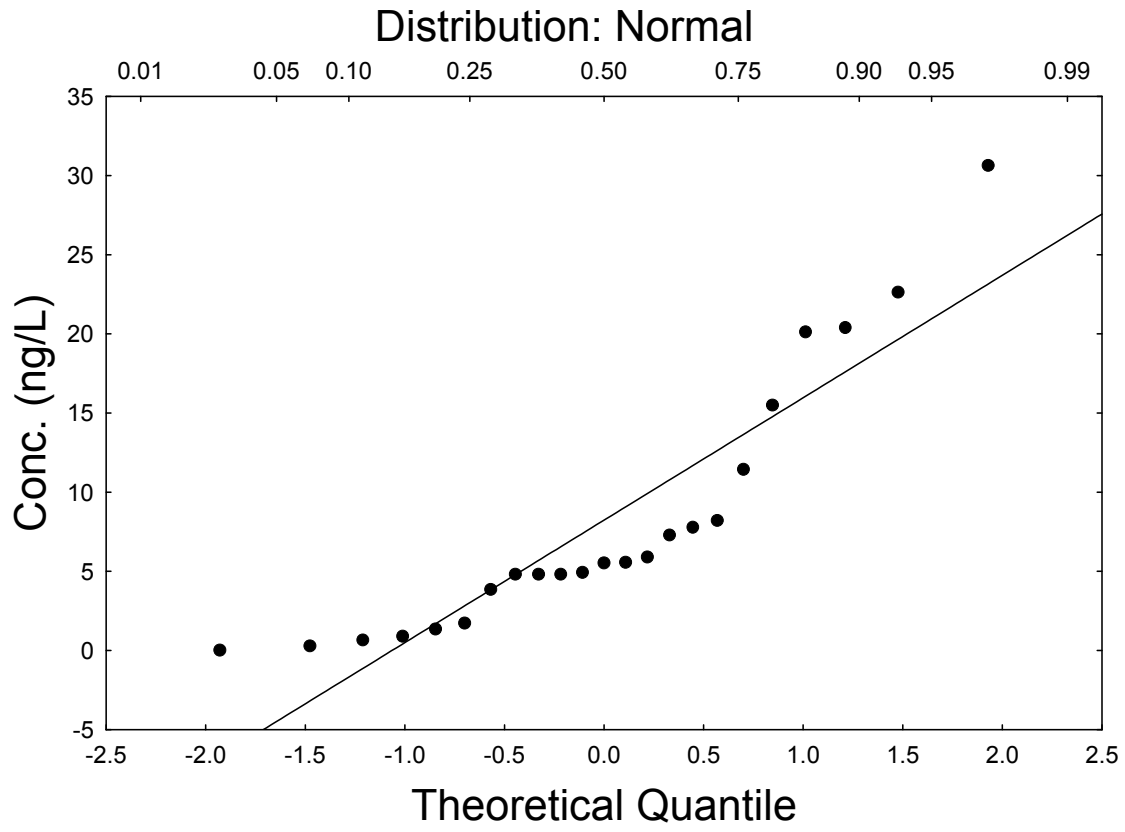
Snowpack

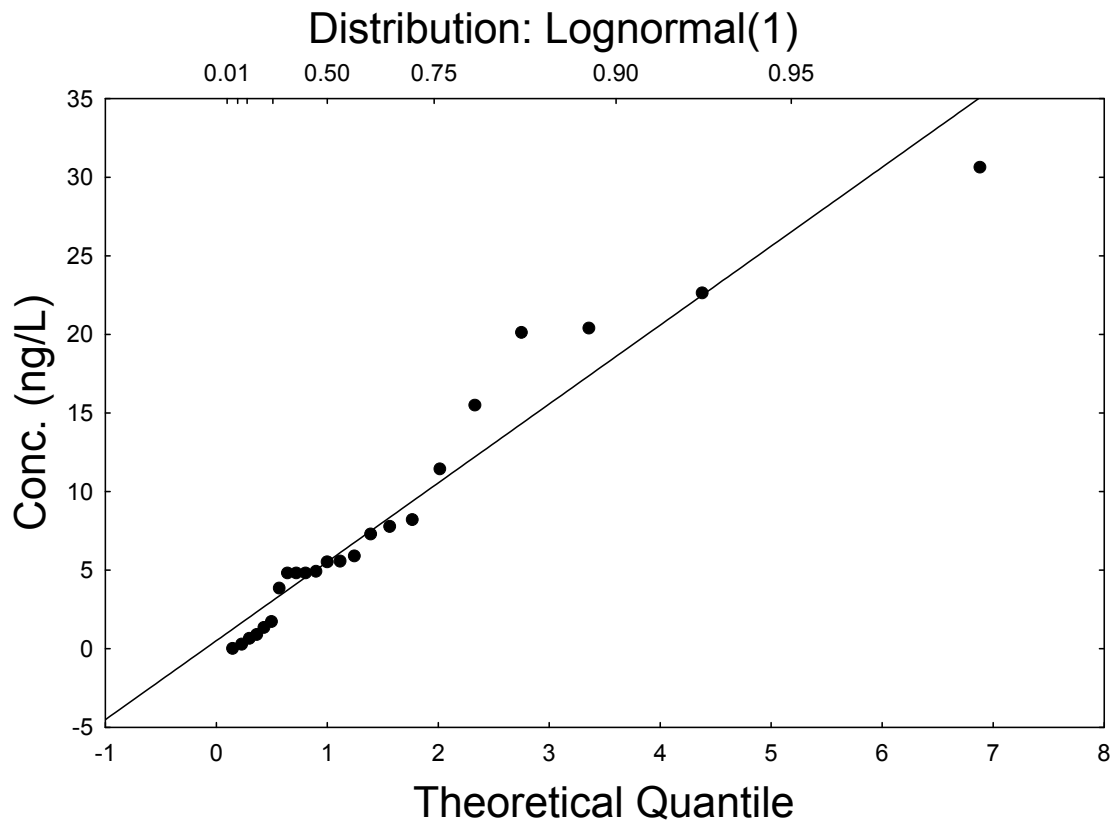
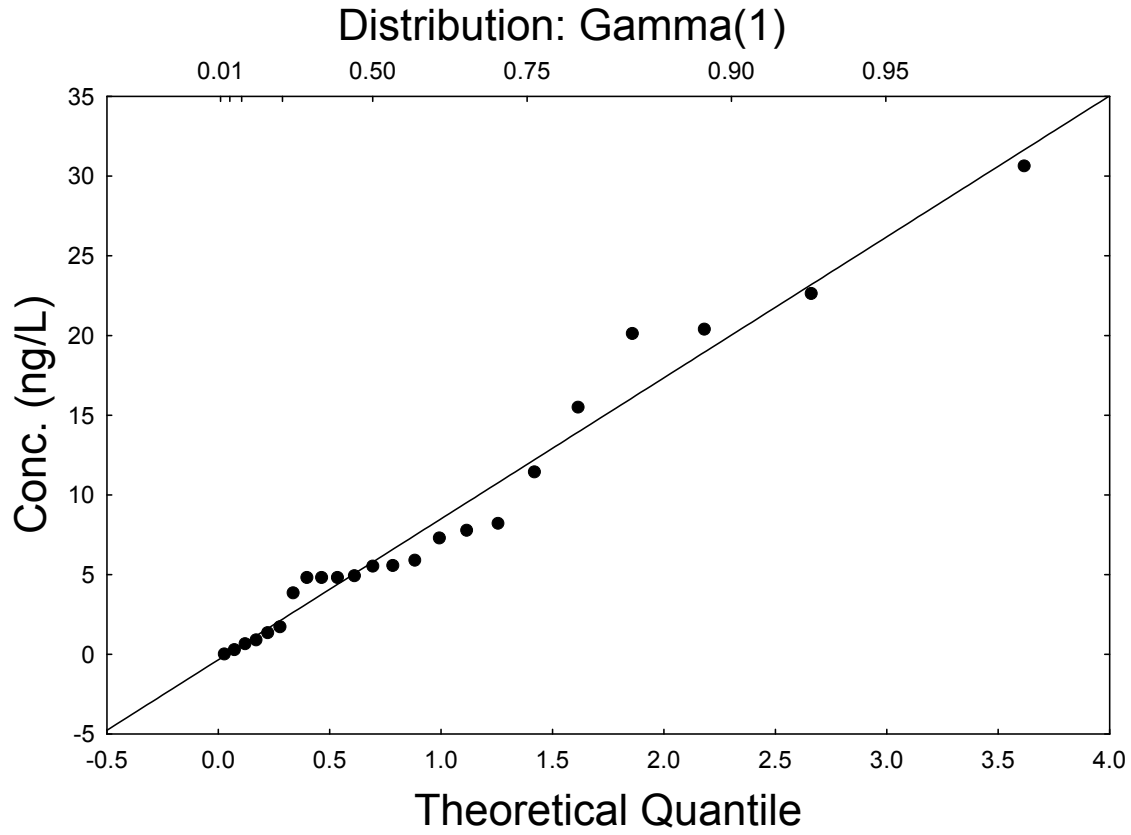




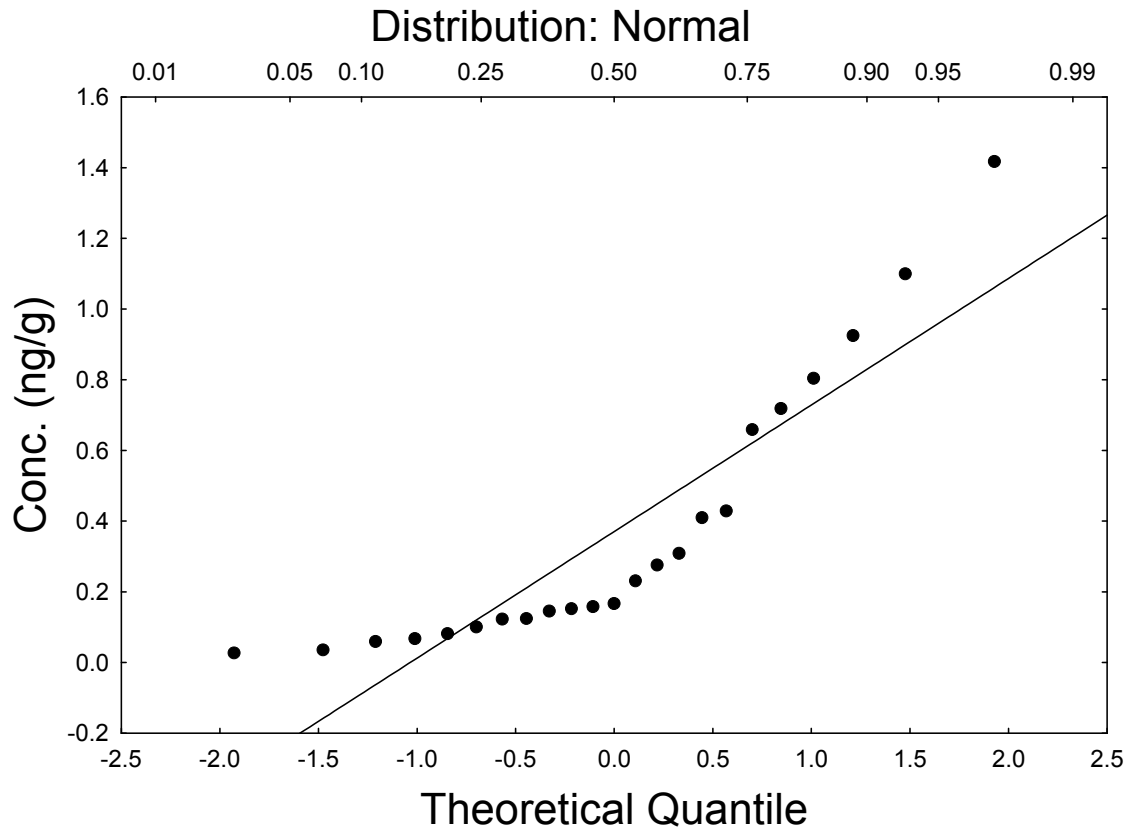


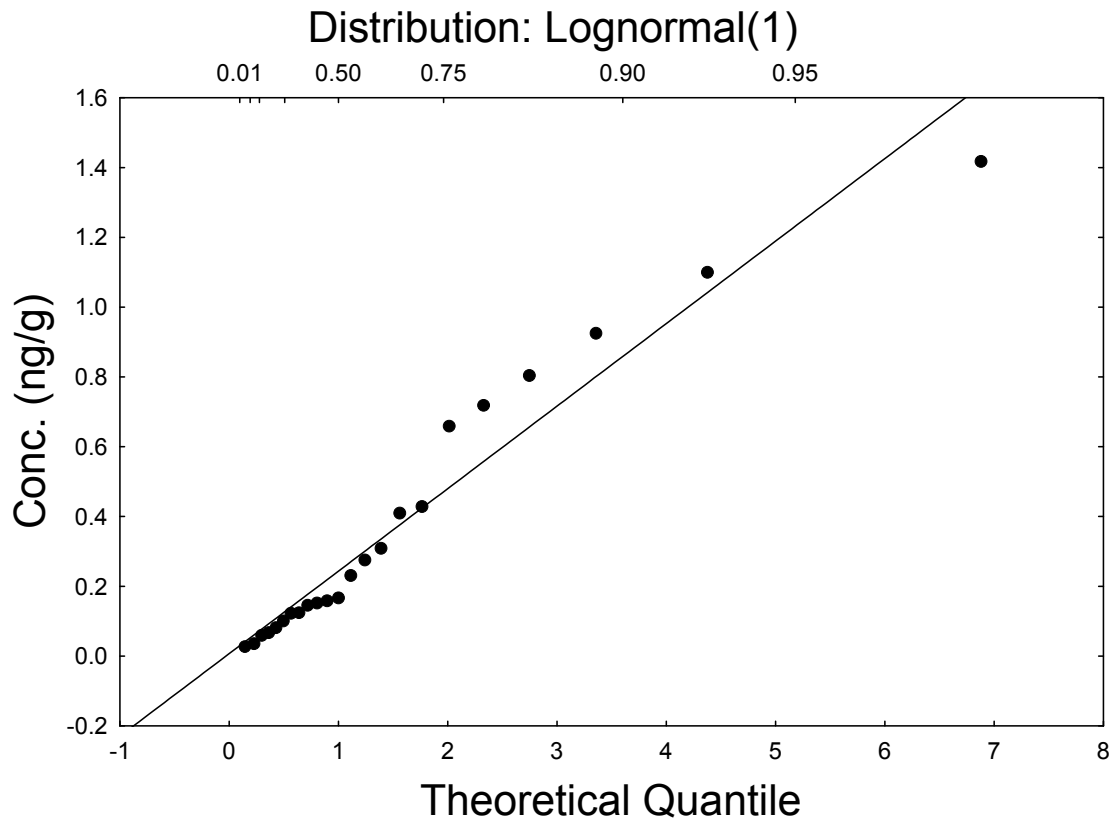
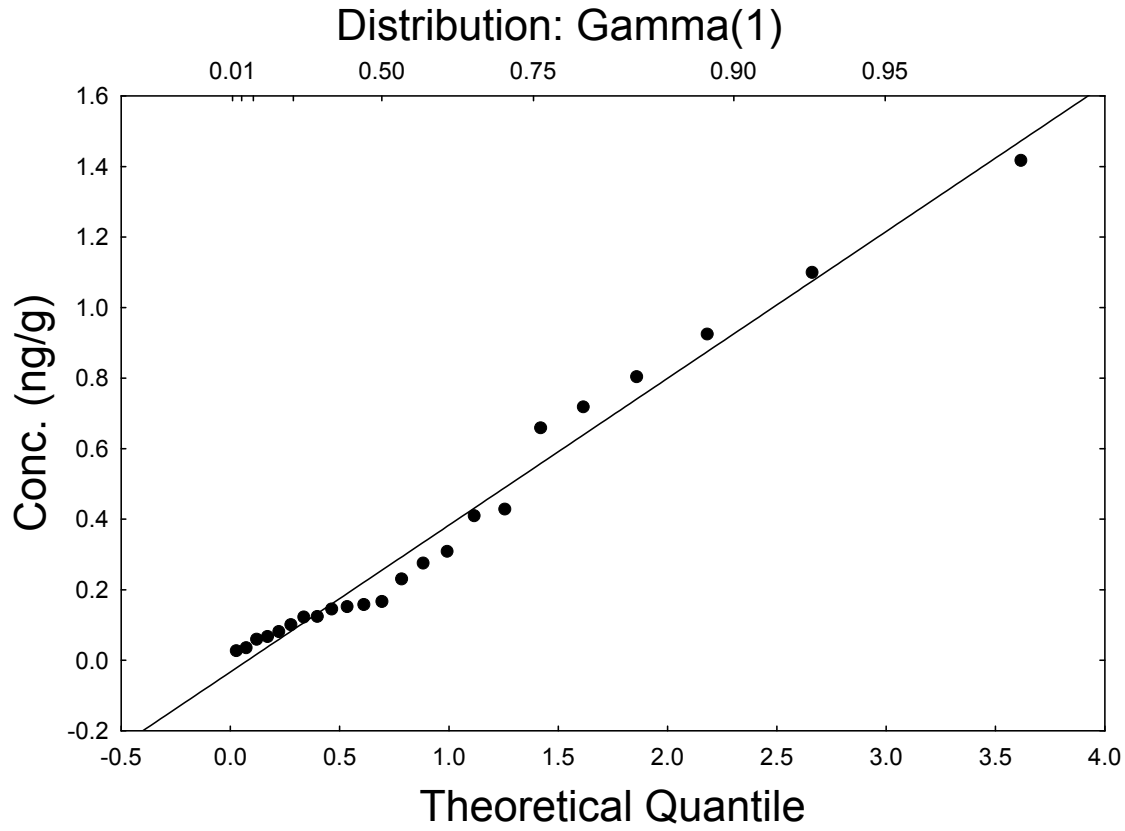
Northern New Mexico Tributaries Stormwater PCBs



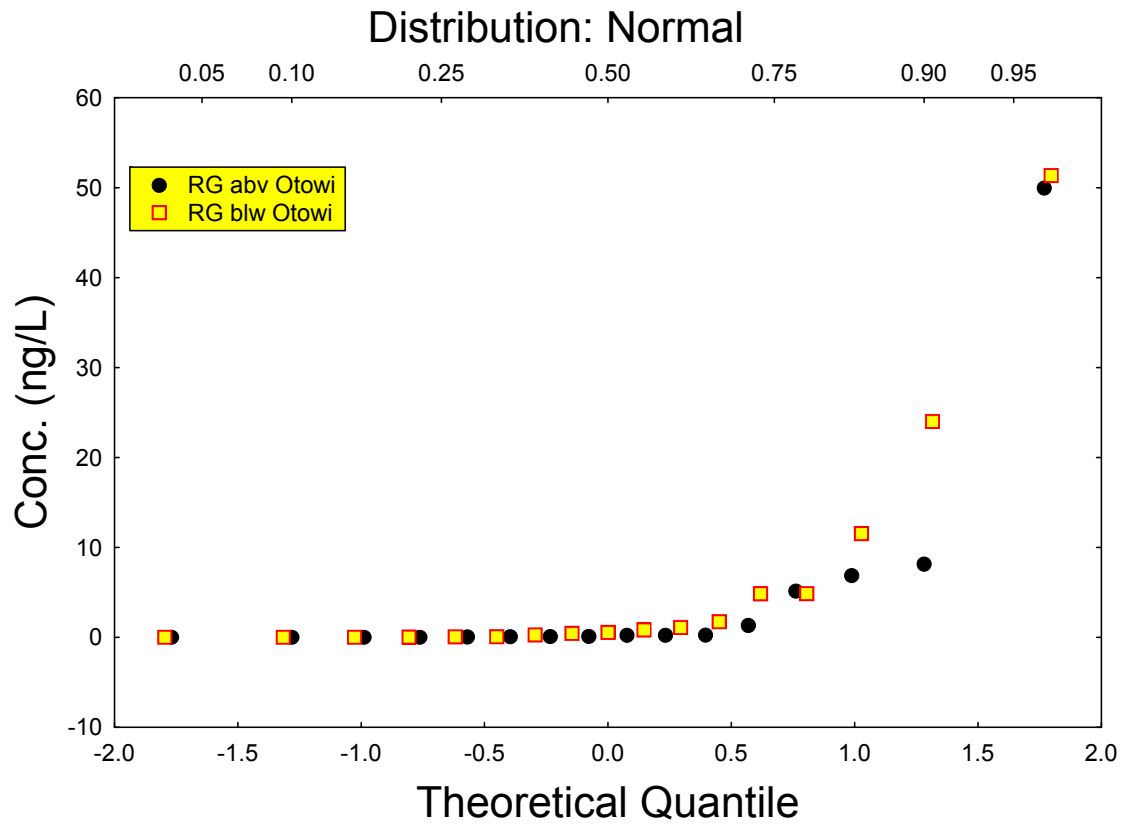


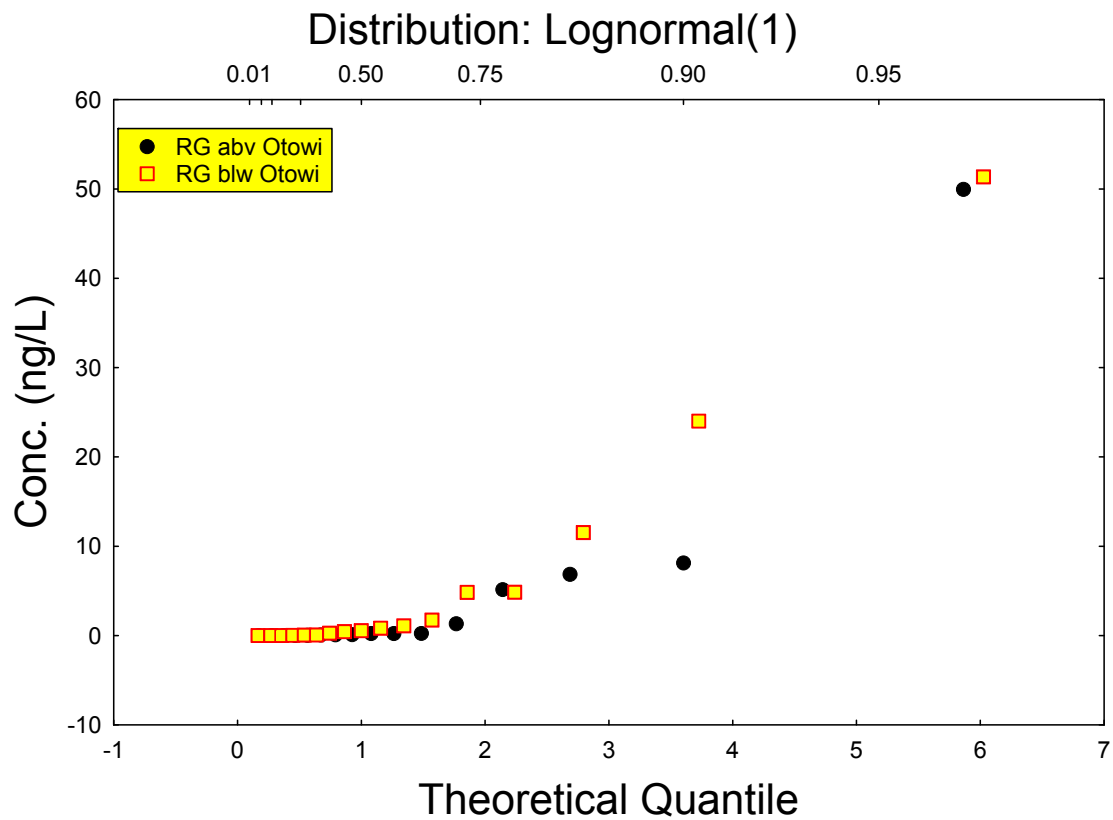
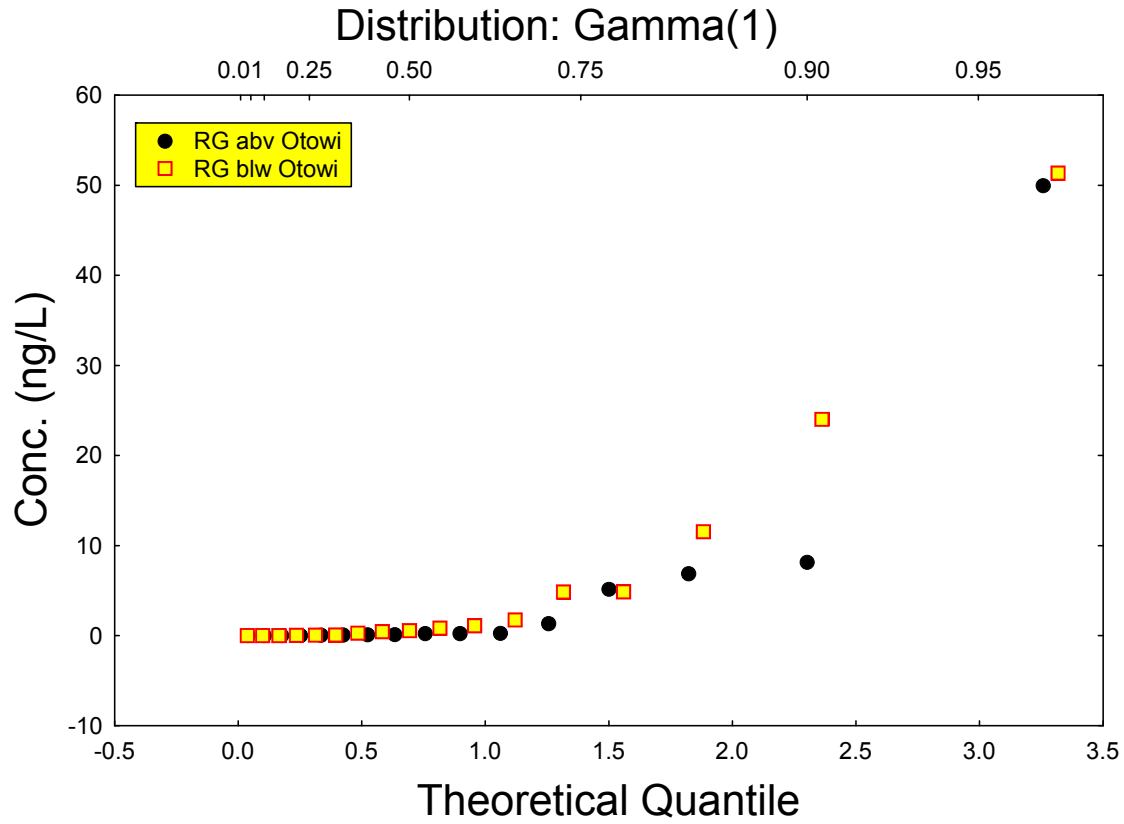
Northern New Mexico Tributaries Suspended PCBs



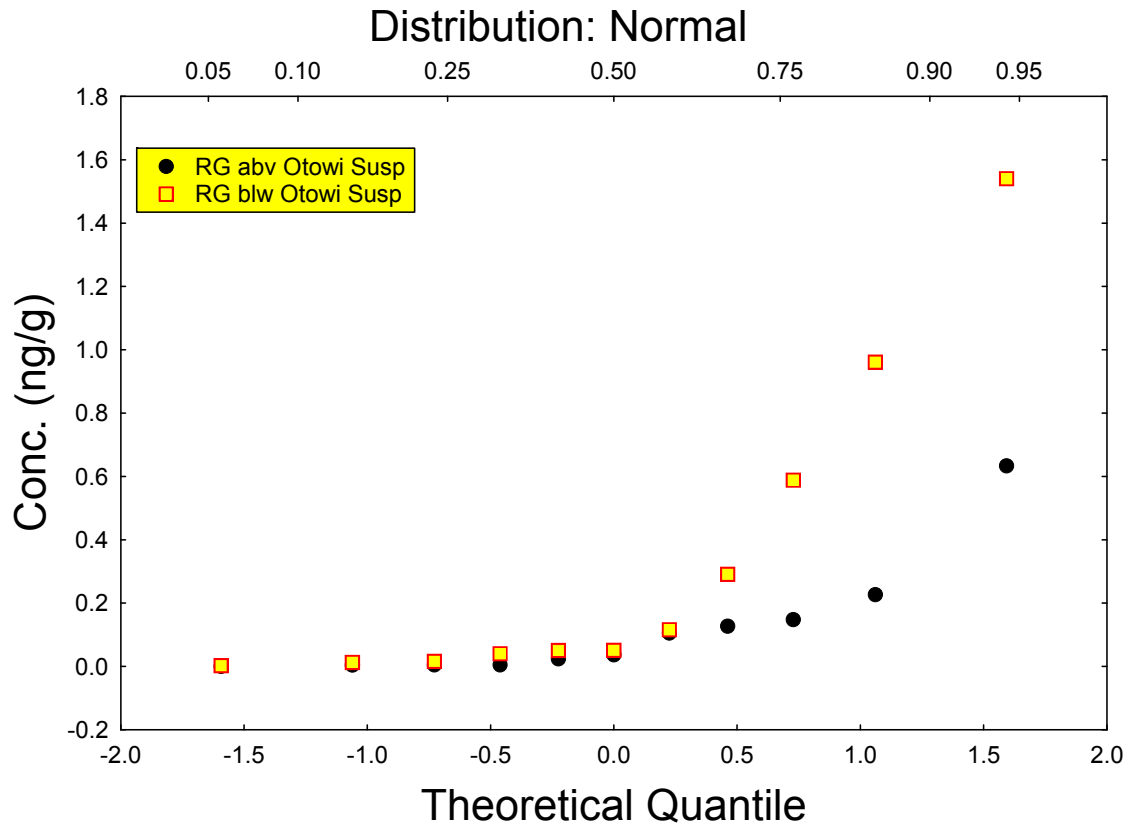


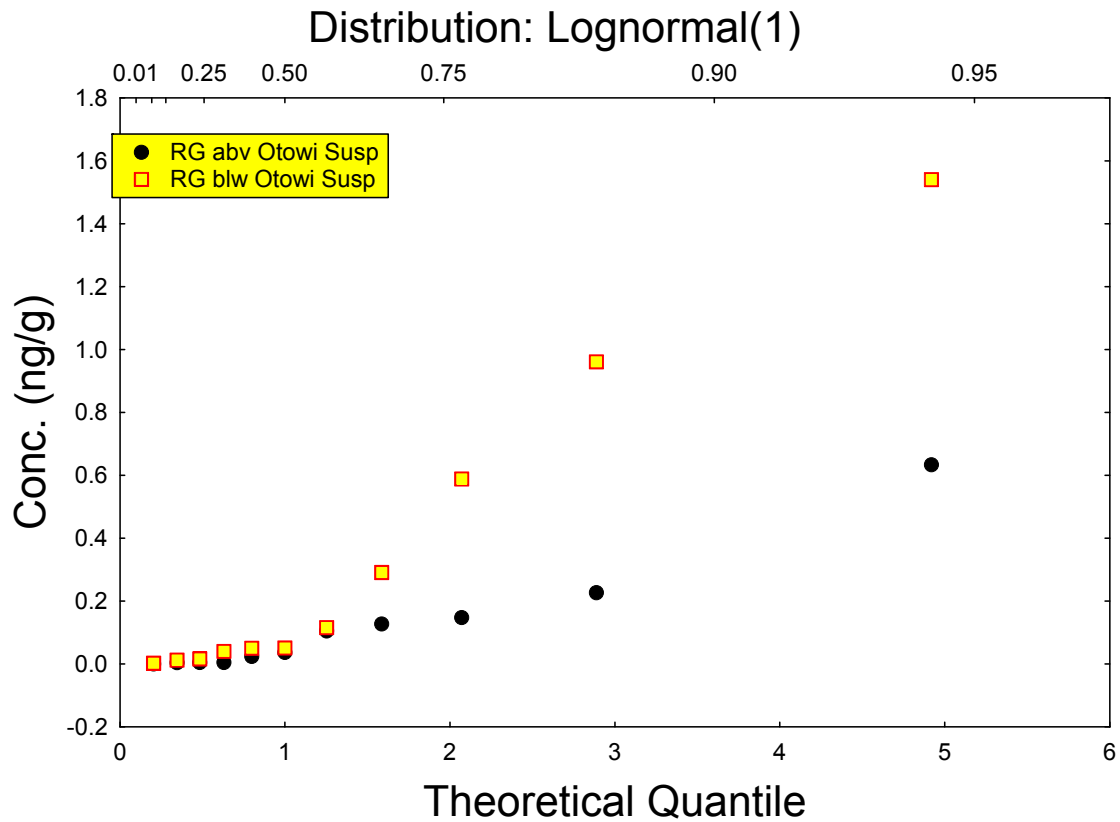
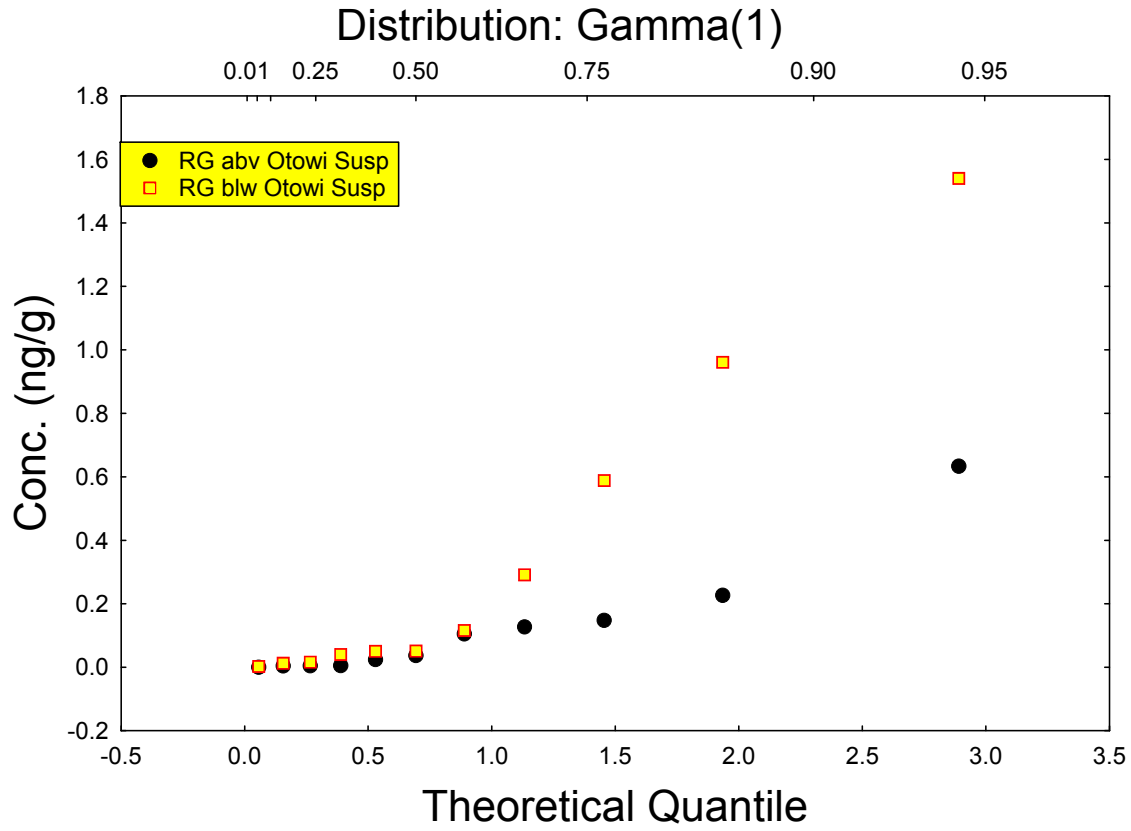
Rio Grande/Rio Chama Stormwater PCBs





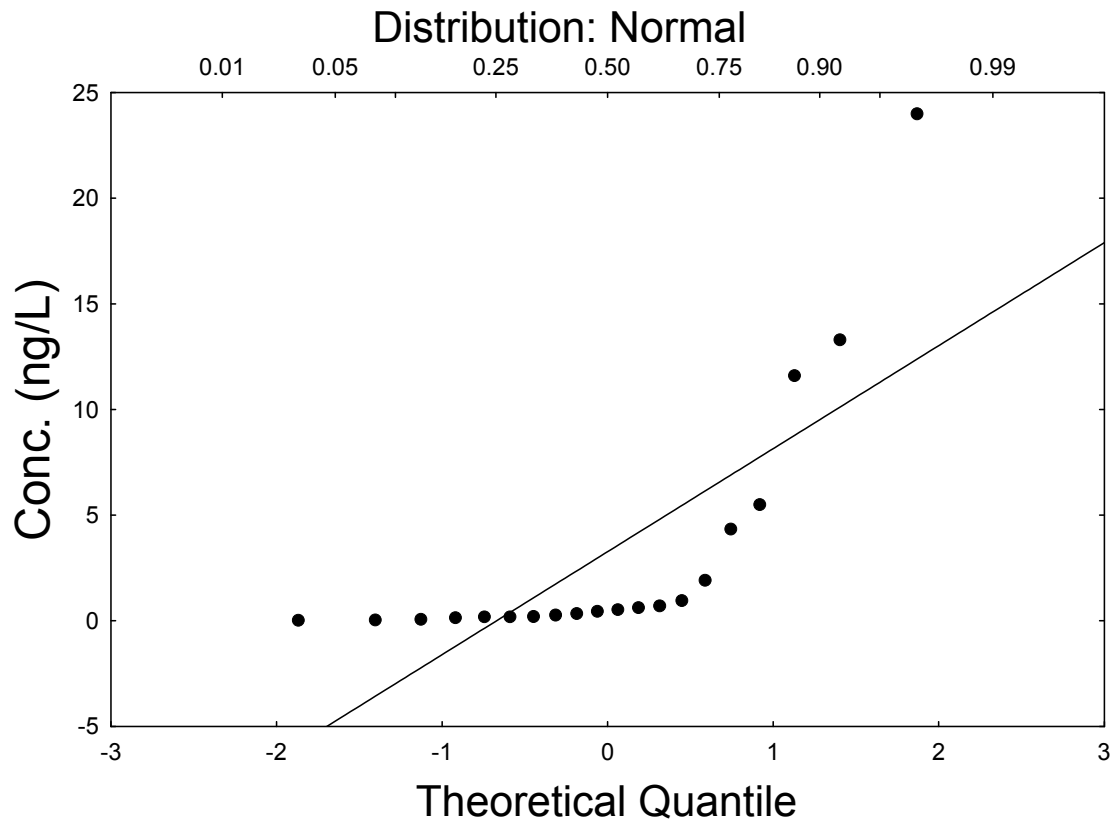
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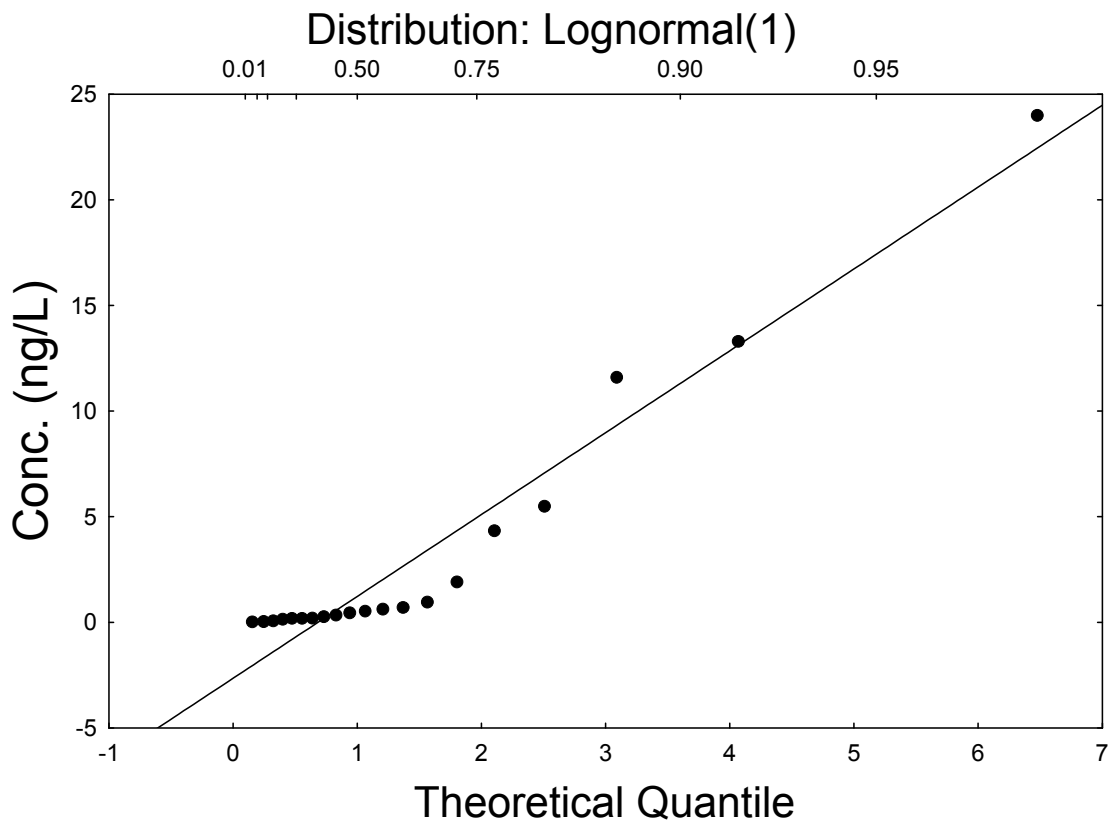
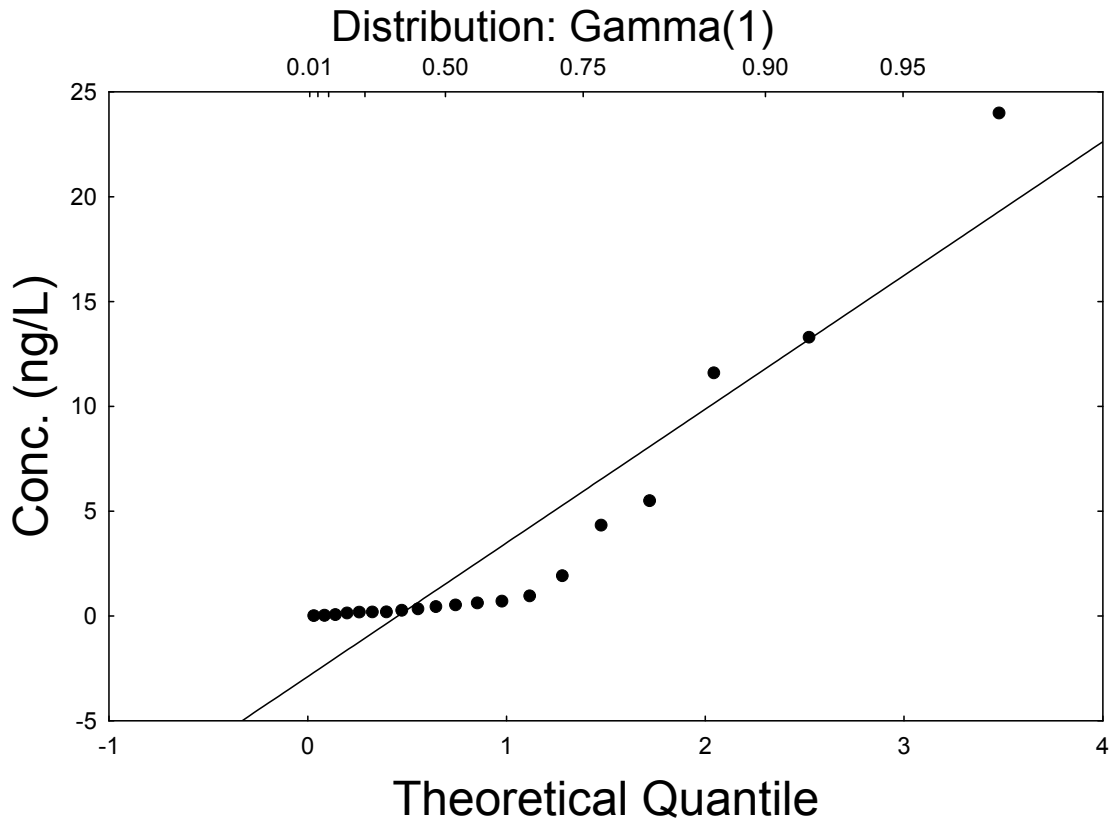




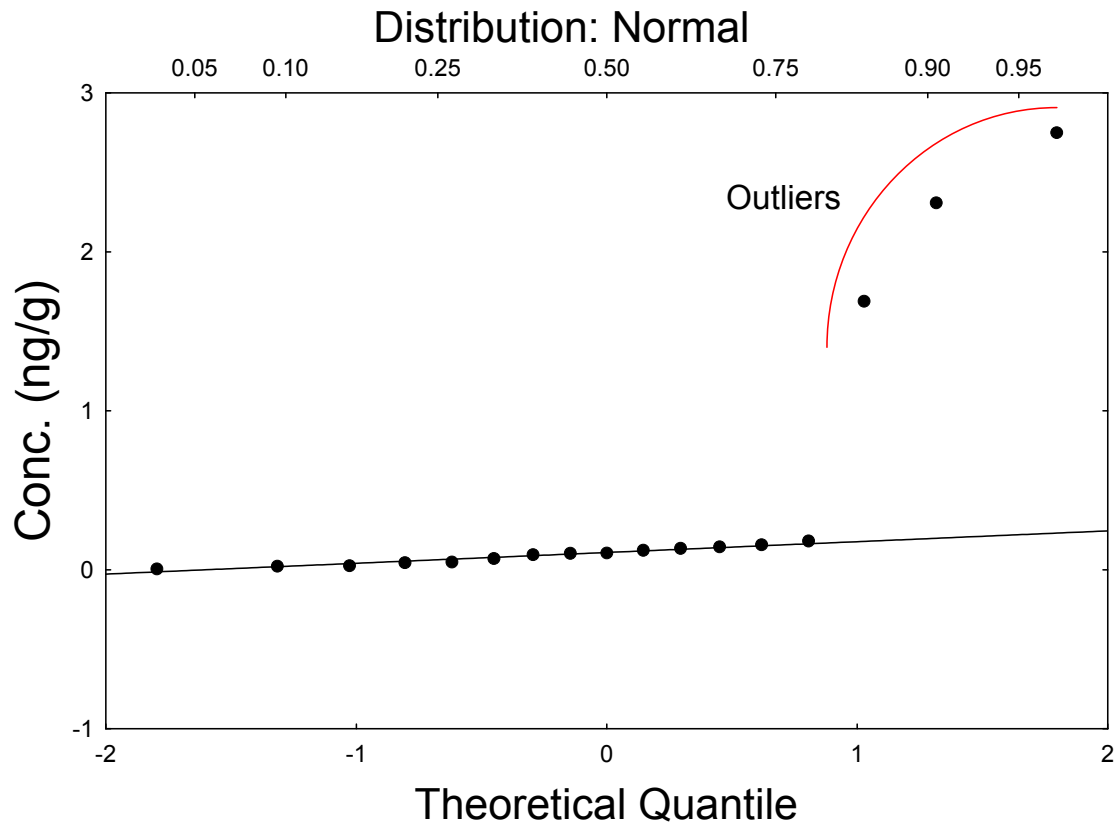


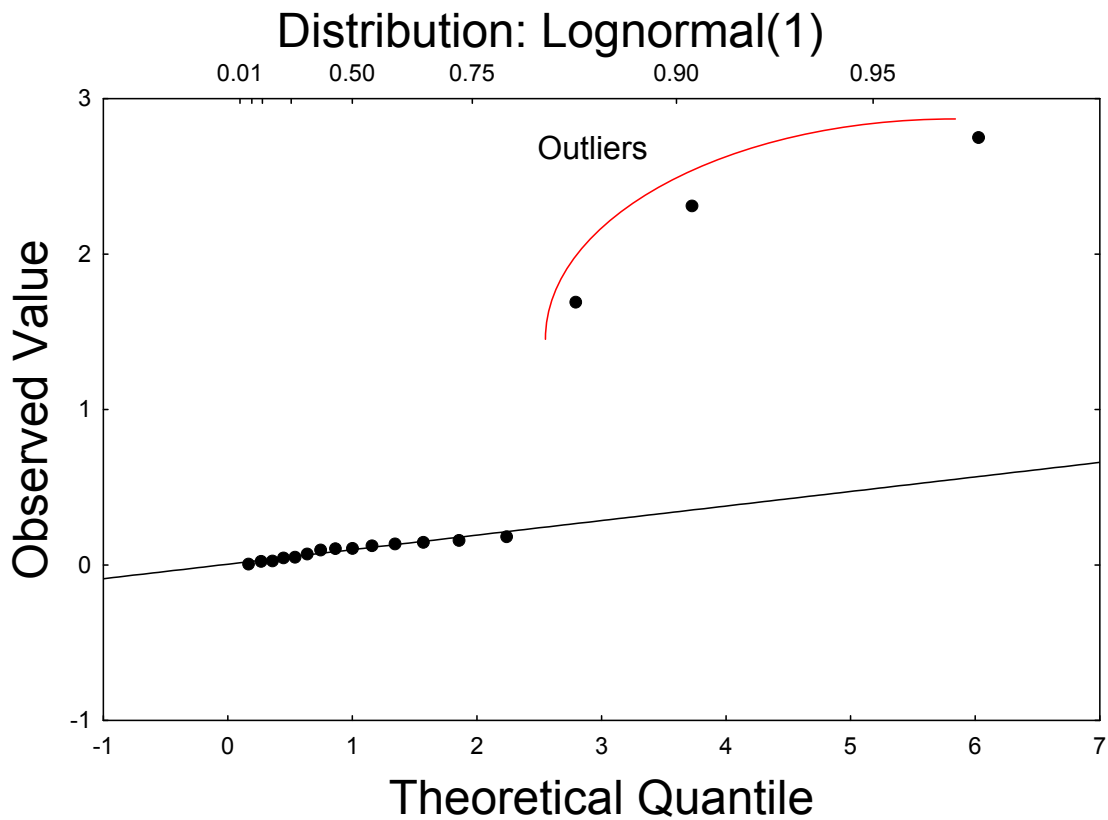
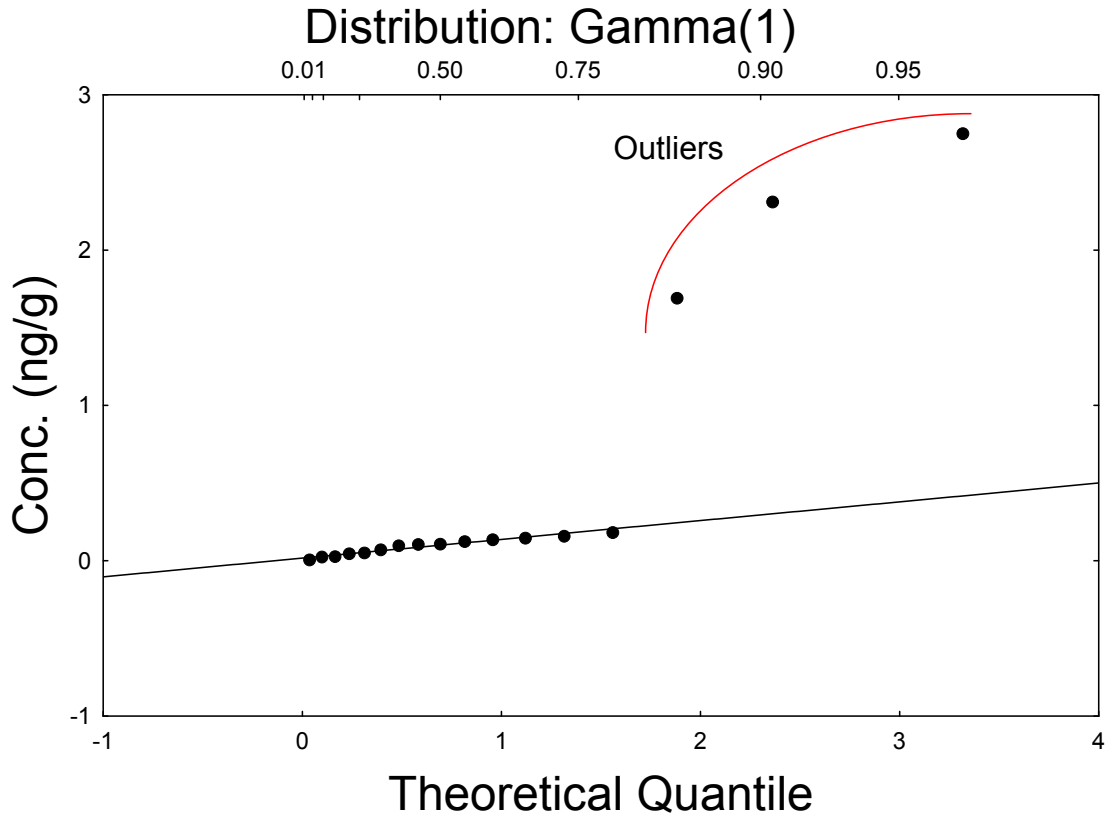
Reference Stations Stormwater PCBs



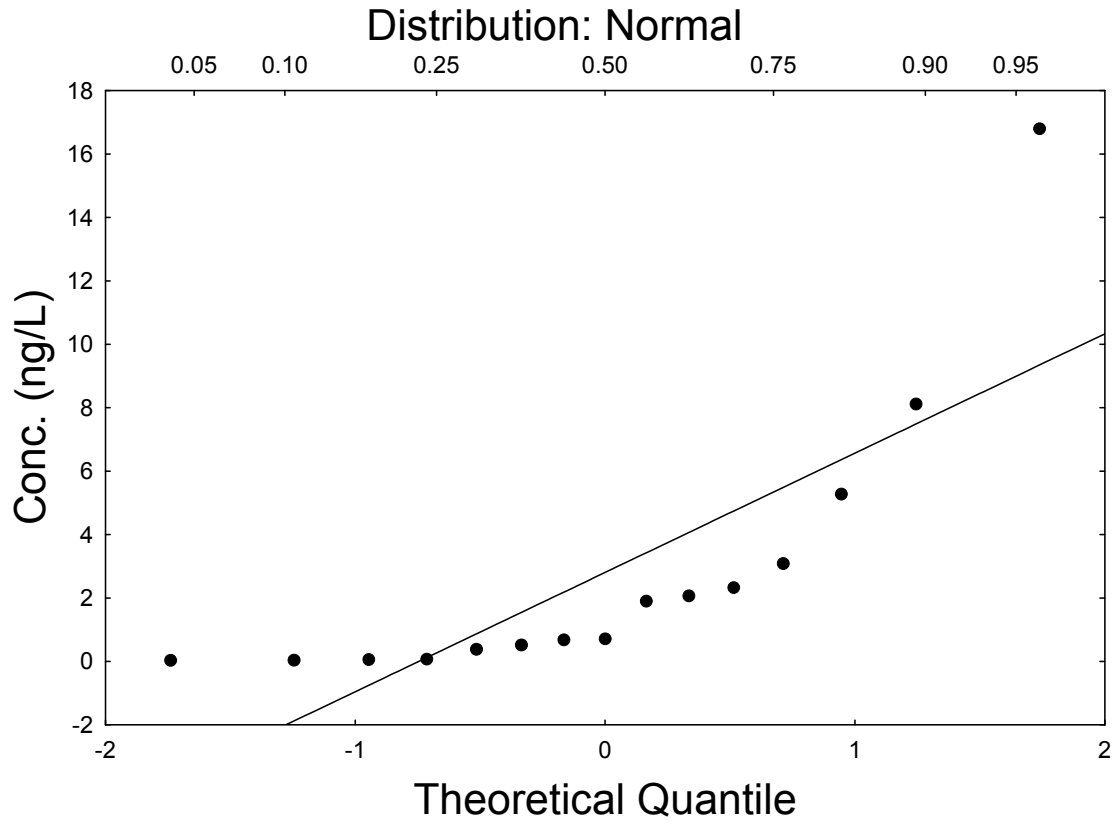


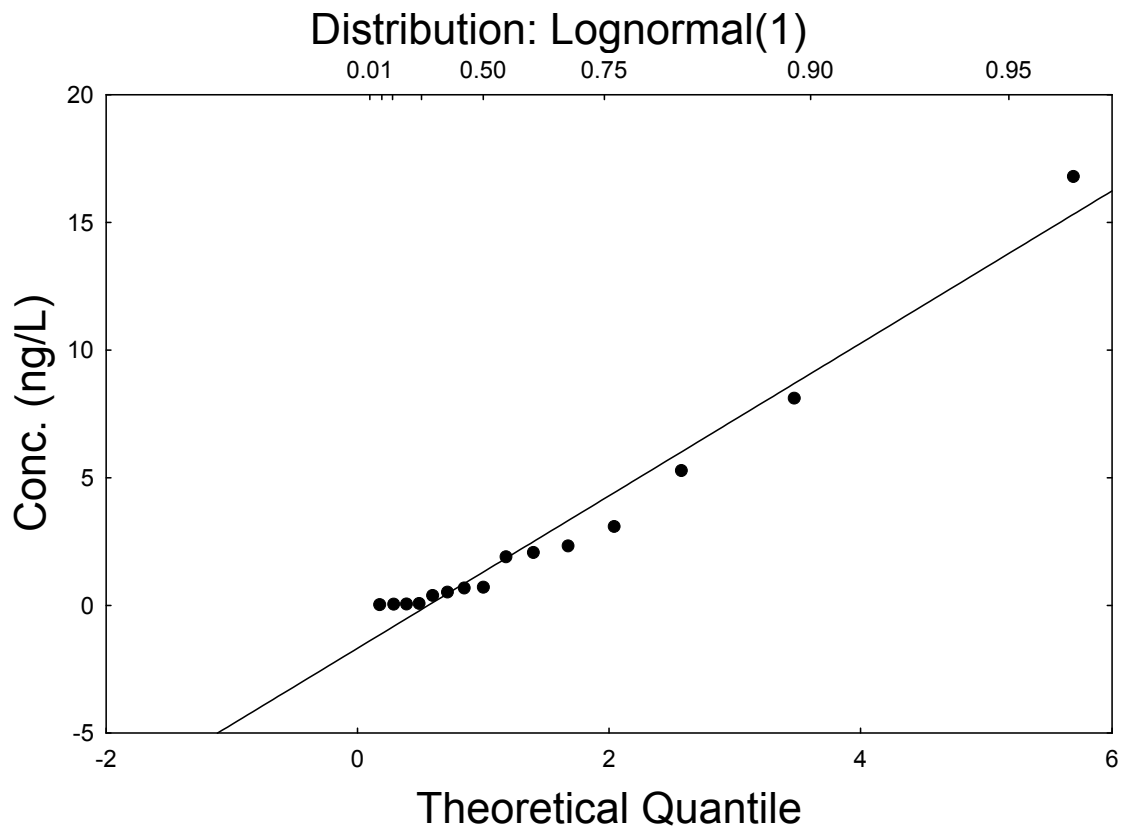
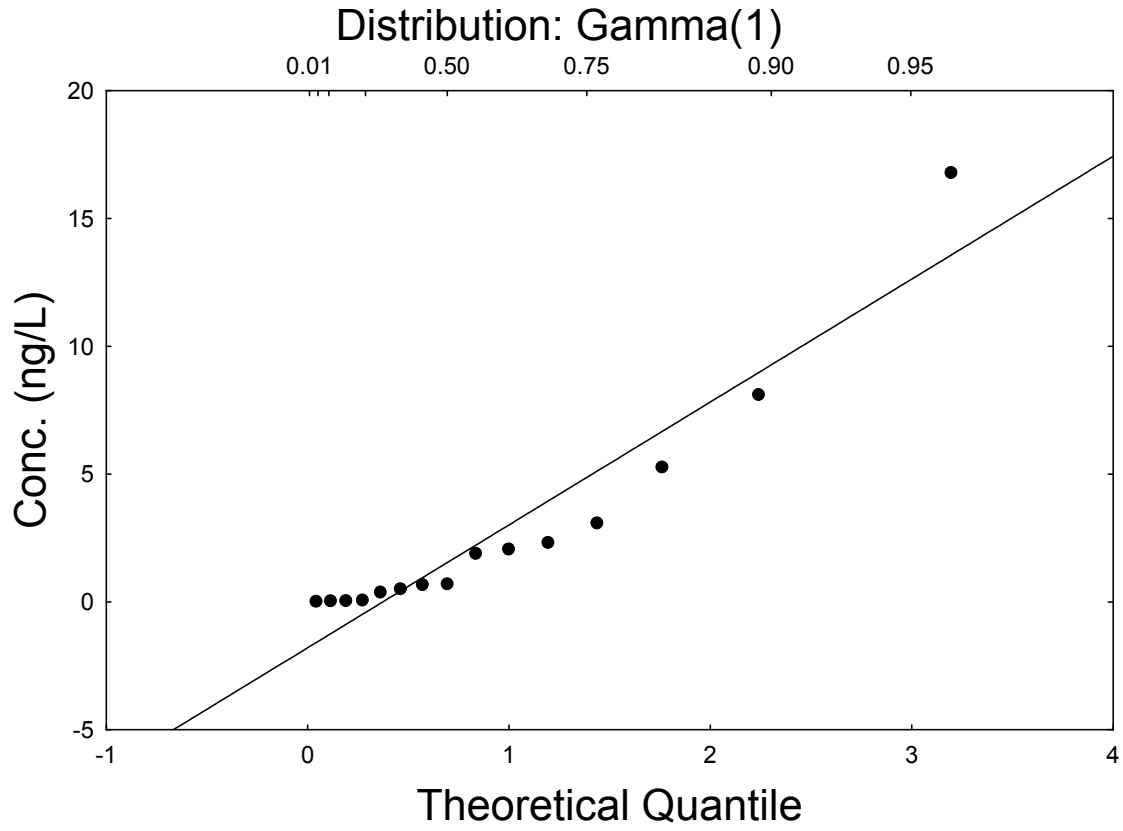
Reference Stations Suspended PCBs



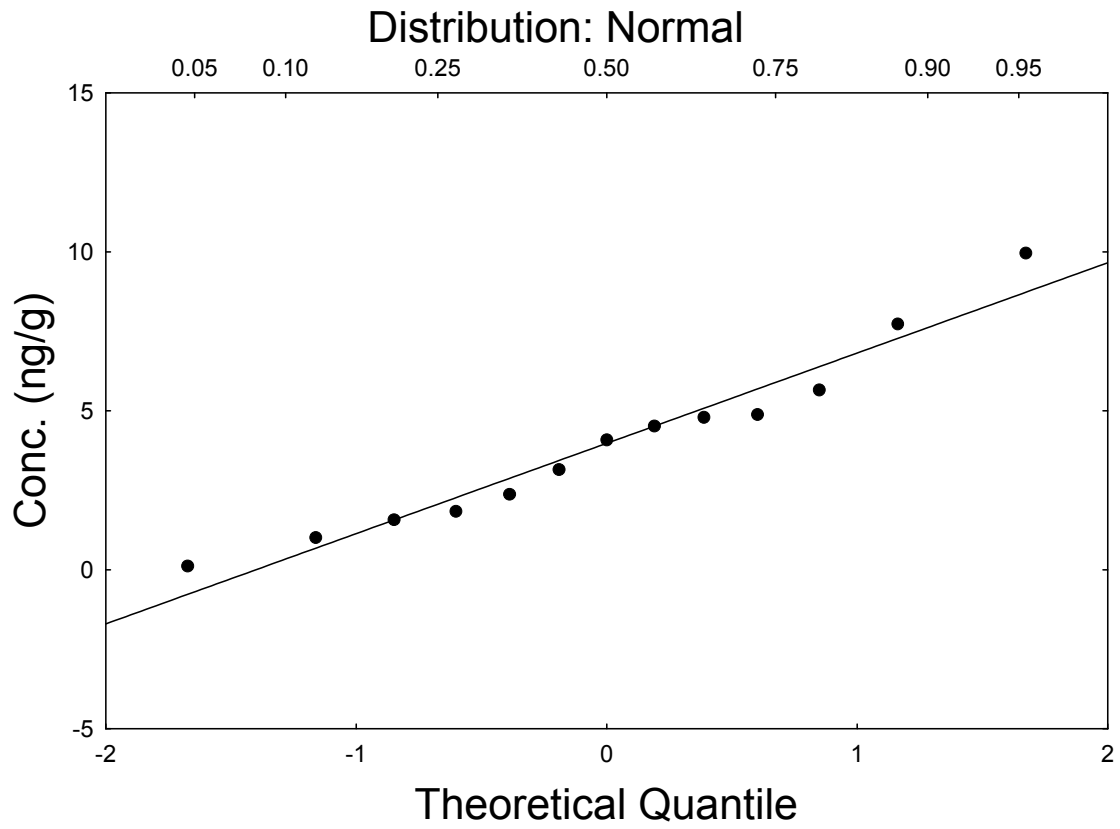


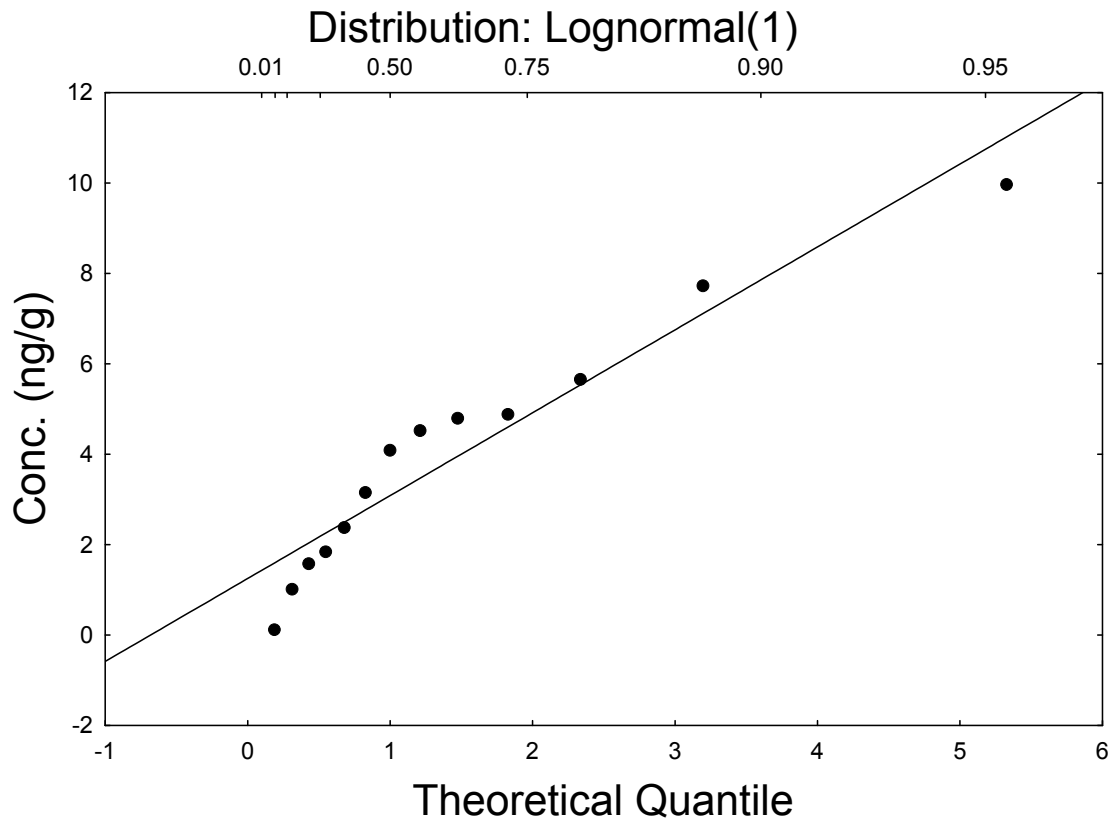
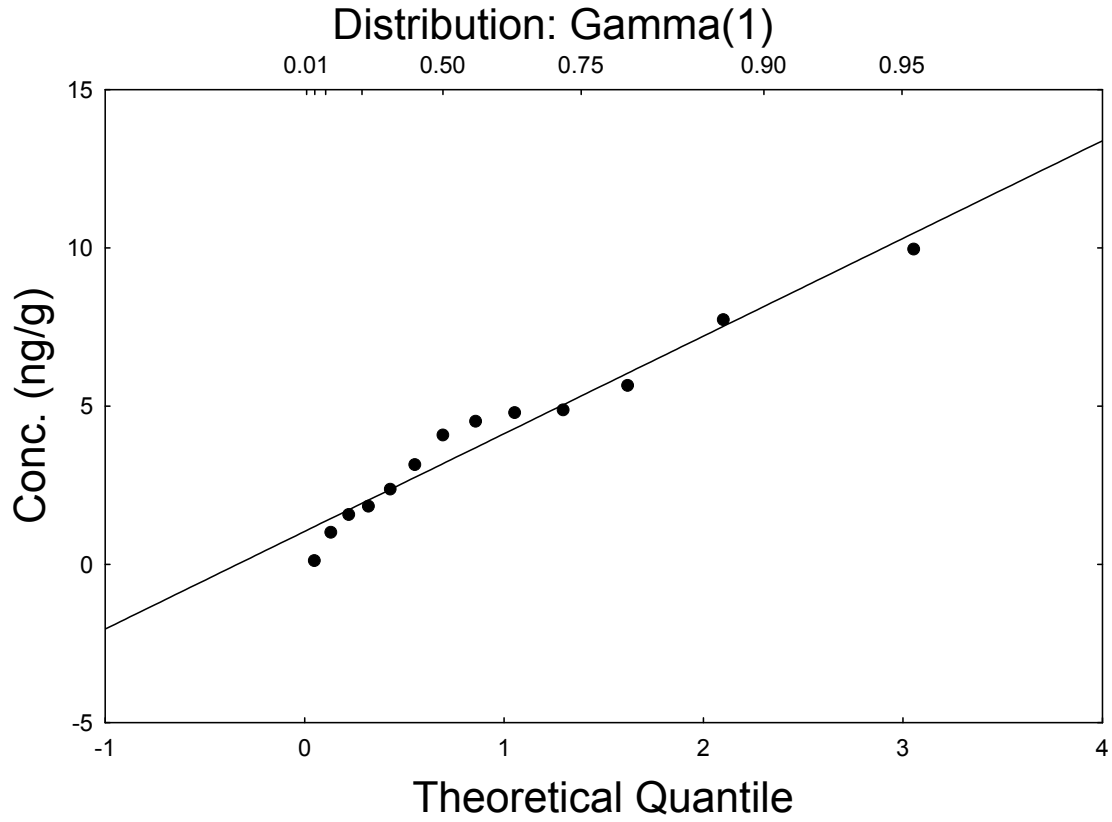
Western Boundary Stations Stormwater PCBs





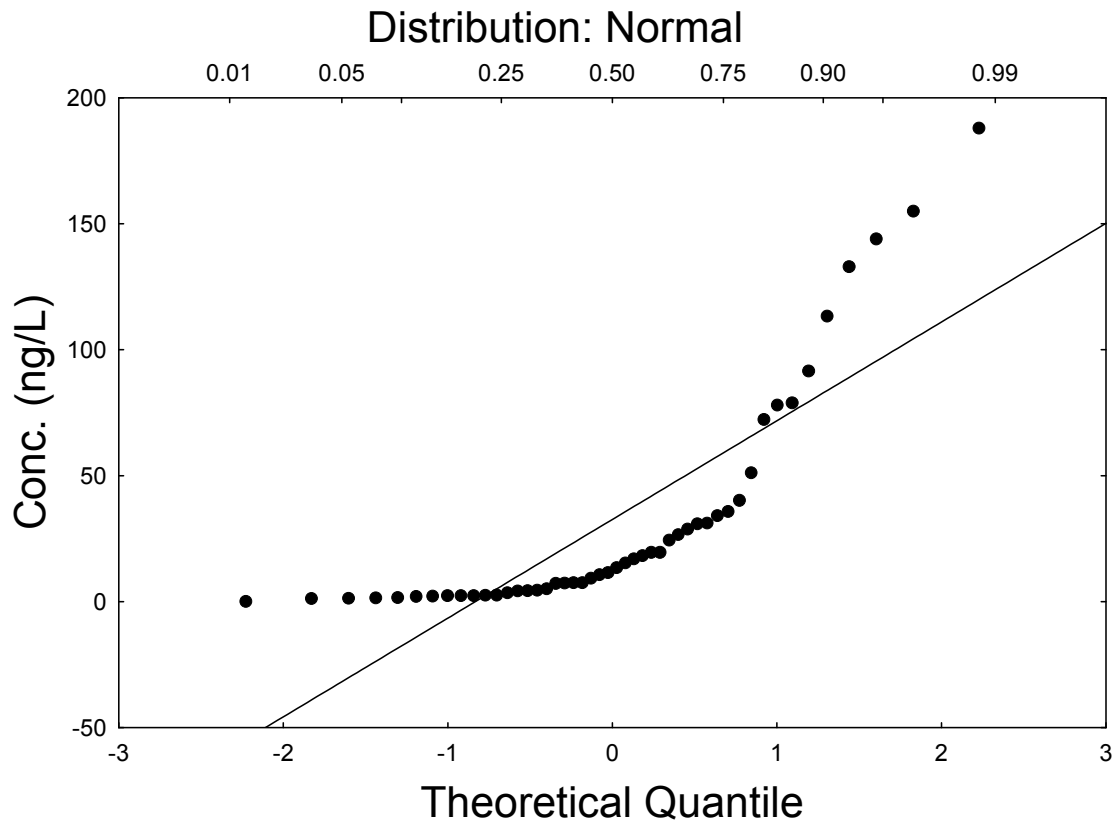
Western Boundary Stations Suspended PCBs

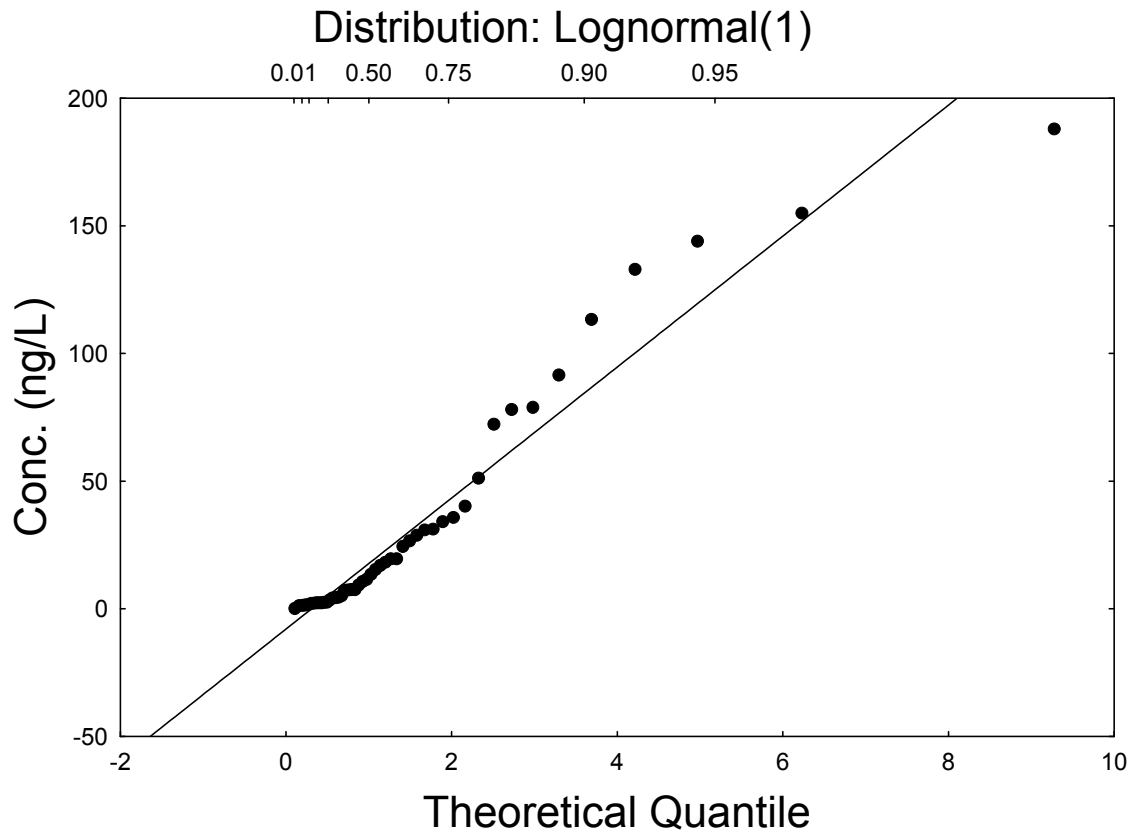
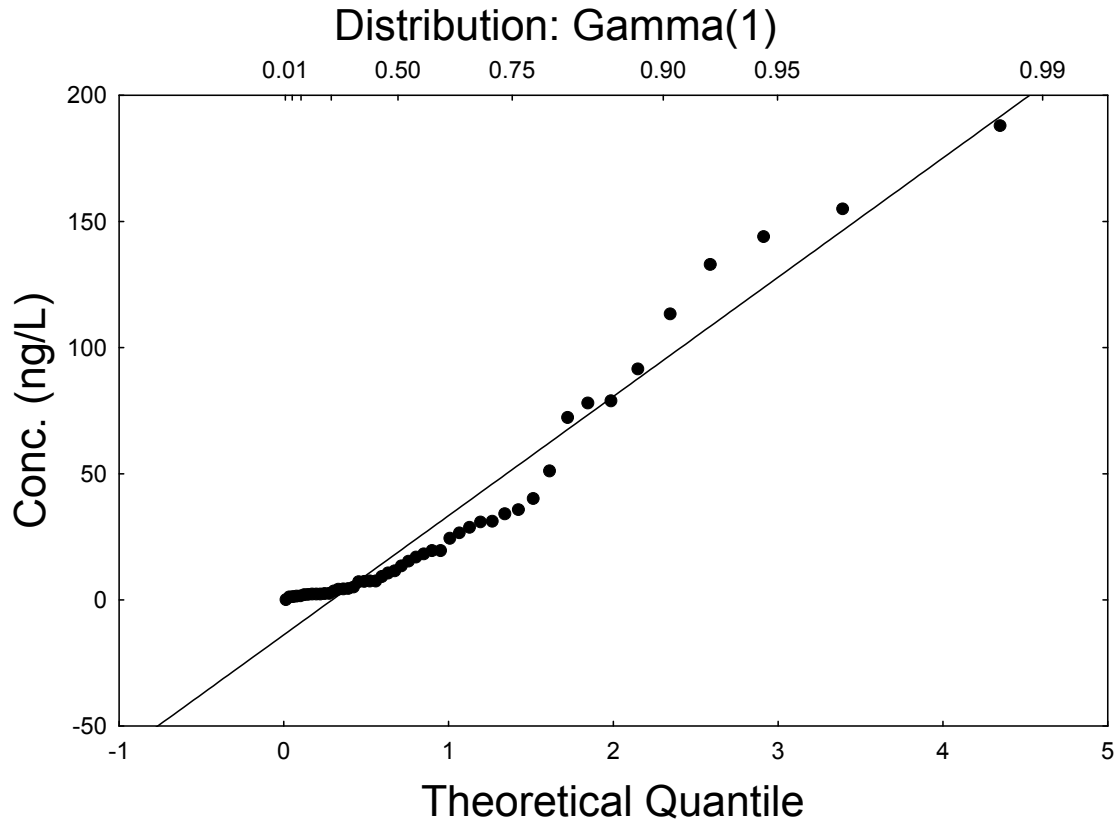




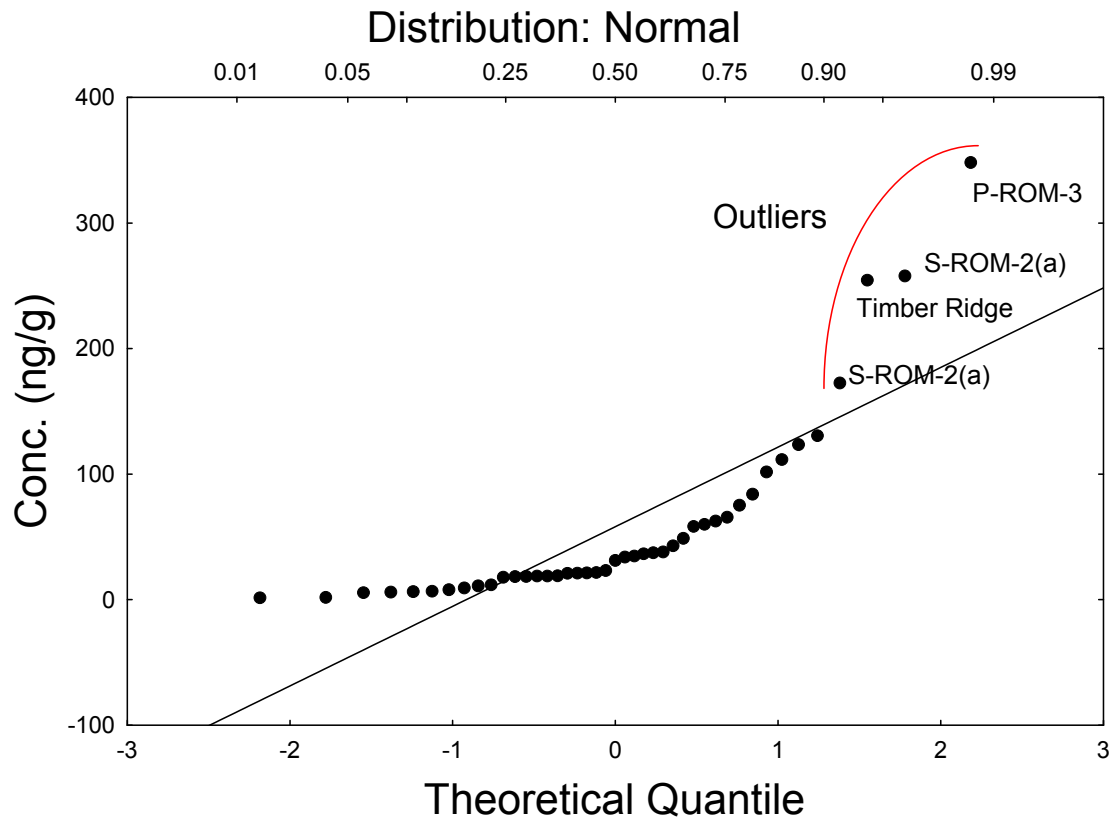


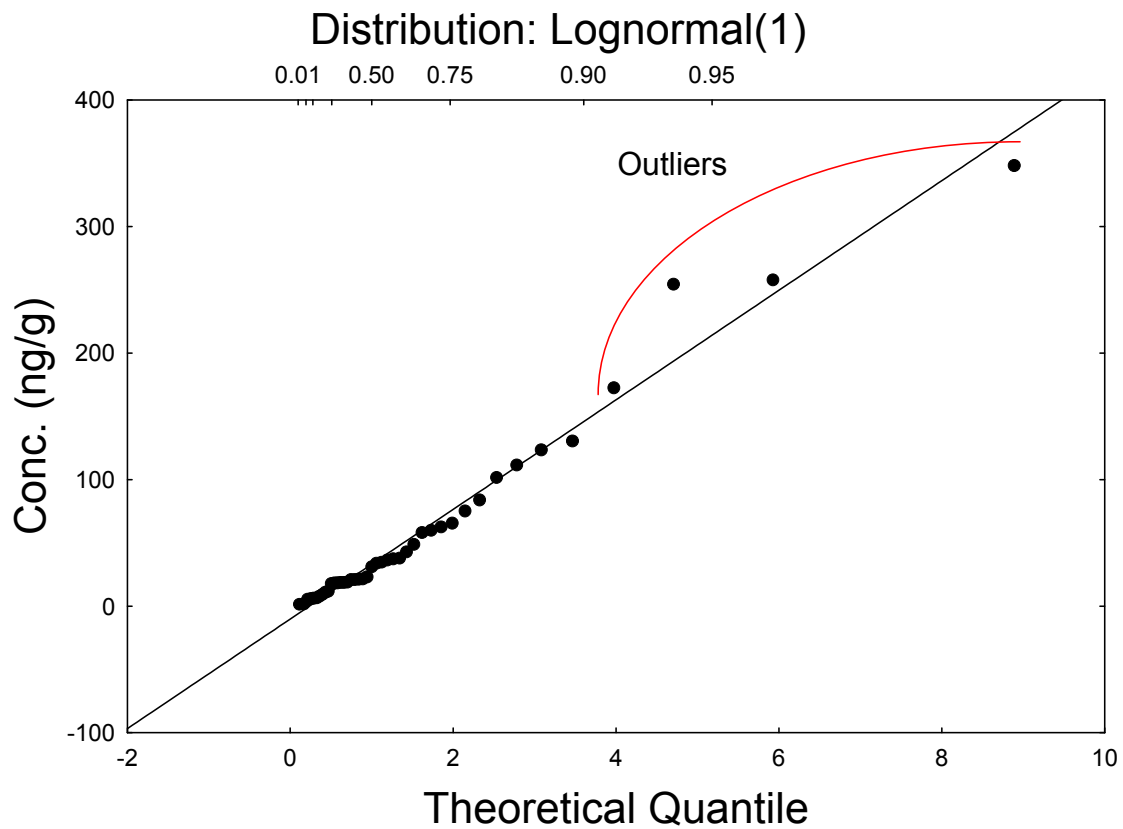
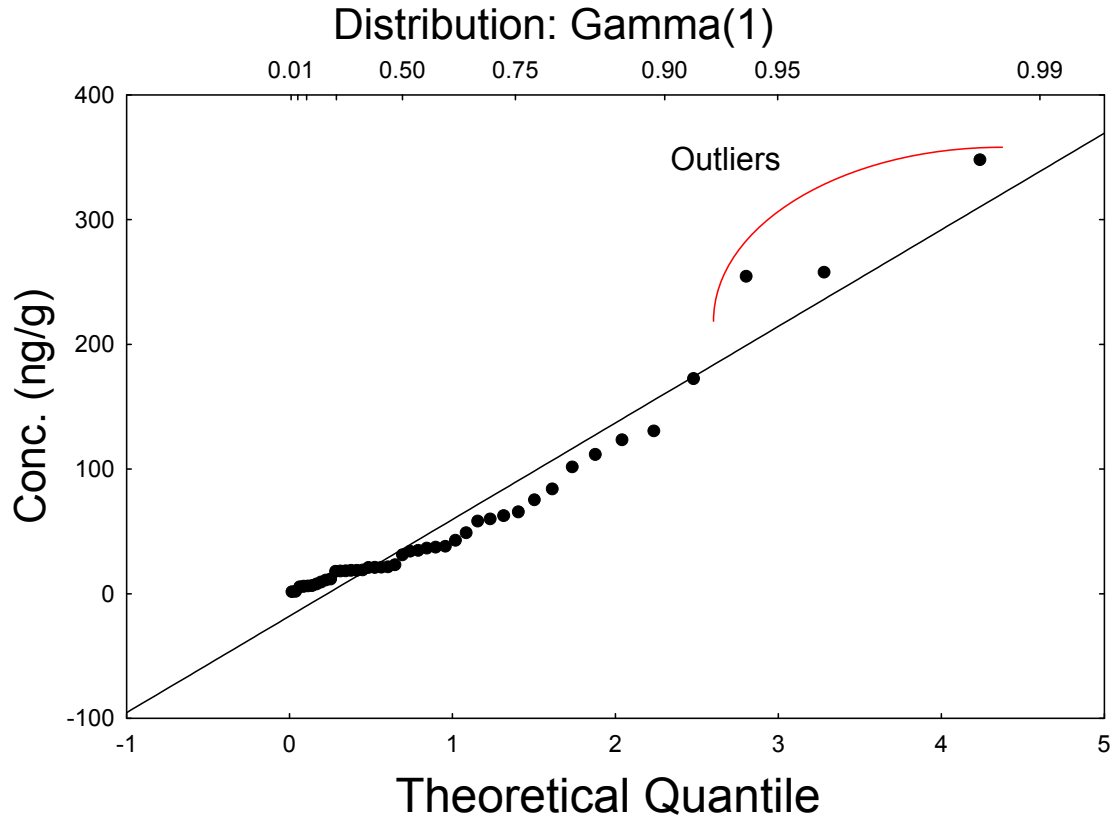
Urban Runoff Stormwater PCBs





Urban Runoff Suspended PCBs





## **Appendix D**

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### *Quantitative Comparison of Congener Profiles*



Tables D-1 through D-4 examine the similarities of congener profiles for polychlorinated biphenyls (PCBs) across the northern New Mexico region.

Similarities in PCB congener profiles across study areas were evaluated by correlation analyses. Congener profiles, or concentration patterns, were compared across an area on a sample-by-sample basis by calculating the coefficient of determination ( $R^2$ ) and associated probability value.  $R^2$  is a measure of the strength of association between each sample, and the probability value is a measure of the significance (the odds that the association is caused by random chance).  $R^2$  is the square of the Pearson product moment correlation coefficient,  $r$ . It ranges from zero to 1 and is the fraction of the variance in the two variables that is shared. For example, if  $R^2$  was 0.63, then 63% of the variance in Sample A can be explained by variation in Sample B, and vice versa. The greater the proportion of explained variation, the closer are the sample values, hence the stronger the linear relationship. Samples with a  $R^2$  greater than 0.64 ( $r = 0.8$ ) and a probability of 0.05 or less were assumed to be strongly associated.

Concentrations of PCBs detected in one sample were matched to same-congener concentrations detected in the comparison sample. For example, if PCB-52 was detected in both samples, the two PCB-52 results would be paired together and included in the analysis, along with pairs for other PCBs also detected in both samples. This typically resulted in a group of several tens of congener data pairs that were jointly detected. If the congener profiles in the two samples were closely associated, there would be minimal overall variation, reflected with a  $R^2$  value close to 1.

The similarity in congener profiles in stormwaters was examined across geographic areas: northern New Mexico arroyos, Rio Grande and Rio Chama drainages, and Pajarito Plateau background arroyos. Lastly, the Pajarito Plateau results were compared with the northern New Mexico arroyo results to gain a broader regional perspective.

The tables present  $R^2$  values for each sample to sample comparison. Results with  $p$  values less than or equal to 0.05 are underlined. Samples with a high degree of association ( $R^2 > 0.64$  and  $p < 0.05$ ) are shaded. Blank values indicate fewer than 10 congener pairs were detected in the samples being compared, and  $R^2$  values were not calculated for those samples.





**Table D-1**  
**Comparison of Congener Profiles in Stormwater from Northern New Mexico Arroyos**

	Ancha 10/13/09	Aqua Caliente 7/15/08	Aqua Caliente 7/15/08 (D)	Arroyo Pino 9/2/08	Canada Agua 10/13/09	Canada Agua 8/3/09	Canada Agua 9/13/09	Embudo 8/18/08	Hondo 7/21/08	Horno 7/19/09	Horno 8/5/09	Oso 7/19/09	Oso 10/13/09	Oso 7/7/09	Oso 8/24/09	Palacio 10/13/09	Palacio 8/18/08	Palacio 8/24/08	Palacio 8/24/08 (D)	Poj River 10/13/09	Poj River 9/2/09	Poj River 8/5/09	Poj River (N Bank) 8/13/09	Poj River (S bank) 8/13/09	Santa Cruz 7/9/08	Santa Cruz 8/20/08	Toro 8/17/09	Toro 8/24/09	Truchas 7/28/09
Ancha 10/13/09		0.50	0.45	0.84	0.91	0.88	0.90	0.38	0.48	0.92	0.91	0.76	0.85	0.86	0.88	0.92	0.90	0.54	0.66	0.89	0.87	0.84	0.62	0.34	0.05	0.78	0.85	0.90	0.84
Aqua Caliente 7/15/08	0.50		0.98	0.73	0.48	0.42	0.75	0.18	0.75	0.68	0.68	0.87	0.66	0.66	0.75	0.43	0.59	0.57	0.66	0.67	0.74	0.73	0.85	0.72	0.03	0.84	0.76	0.69	0.69
Aqua Caliente 7/15/08 (D)	0.45	0.98		0.67	0.48	0.38	0.73	0.17	0.69	0.61	0.62	0.82	0.60	0.64	0.71	0.38	0.53	0.53	0.62	0.63	0.72	0.67	0.79	0.72	0.04	0.82	0.70	0.64	0.64
Arroyo Pino 9/2/08	0.84	0.73	0.67		0.79	0.83	0.96	0.51	0.69	0.96	0.95	0.93	0.96	0.88	0.97	0.85	0.93	0.58	0.72	0.91	0.95	0.94	0.83	0.59	0.08	0.88	0.97	0.95	0.95
Canada Agua 10/13/09	0.91	0.48	0.48	0.79		0.82	0.80	0.64	0.37	0.82	0.78	0.66	0.77	0.71	0.80	0.89	0.80	0.44	0.55	0.84	0.82	0.76	0.55	0.60	0.16	0.64	0.73	0.82	0.78
Canada Agua 8/3/09	0.88	0.42	0.38	0.83	0.82		0.88	0.57	0.44	0.88	0.87	0.70	0.82	0.80	0.84	0.91	0.90	0.53	0.64	0.84	0.88	0.82	0.58	0.40	0.09	0.61	0.80	0.85	0.84
Canada Agua 9/13/09	0.90	0.75	0.73	0.96	0.80	0.88		0.43	0.73	0.98	0.99	0.95	0.96	0.94	0.98	0.87	0.96	0.69	0.82	0.92	0.97	0.98	0.86	0.58	0.08	0.91	0.97	0.97	0.97
Embudo 8/18/08	0.38	0.18	0.17	0.51	0.64	0.57	0.43		0.11	0.48	0.43	0.31	0.50	0.38	0.45	0.61	0.54	0.20	0.27	0.49	0.56	0.42	0.27	0.40	0.03	0.23	0.42	0.43	0.49
Hondo 7/21/08	0.48	0.75	0.69	0.69	0.37	0.44	0.73	0.11		0.67	0.73	0.84	0.72	0.75	0.71	0.43	0.63	0.67	0.75	0.53	0.60	0.79	0.90	0.55	0.03	0.83	0.75	0.67	0.68
Horno 7/19/09	0.92	0.68	0.61	0.96	0.82	0.88	0.98	0.48	0.67		0.98	0.92	0.95	0.90	0.98	0.88	0.96	0.64	0.77	0.93	0.97	0.95	0.82	0.56	0.09	0.87	0.97	0.98	0.96
Horno 8/5/09	0.91	0.68	0.62	0.95	0.78	0.87	0.99	0.43	0.73	0.98		0.94	0.95	0.95	0.97	0.88	0.97	0.72	0.84	0.89	0.96	0.98	0.85	0.56	0.06	0.91	0.97	0.96	0.96
Oso 7/19/09	0.76	0.87	0.82	0.93	0.66	0.70	0.95	0.31	0.84	0.92	0.94		0.91	0.90	0.95	0.72	0.87	0.72	0.84	0.84	0.91	0.95	0.94	0.66	0.05	0.96	0.97	0.92	0.92
Oso 10/13/09	0.85	0.66	0.60	0.96	0.77	0.82	0.96	0.50	0.72	0.95	0.95	0.91		0.88	0.96	0.83	0.94	0.55	0.70	0.90	0.95	0.93	0.84	0.66	0.09	0.90	0.96	0.95	0.96
Oso 7/7/09	0.86	0.66	0.64	0.88	0.71	0.80	0.94	0.38	0.75	0.90	0.95	0.90	0.88		0.90	0.83	0.90	0.78	0.89	0.78	0.88	0.97	0.84	0.55	0.03	0.90	0.89	0.87	0.90
Oso 8/24/09	0.88	0.75	0.71	0.97	0.80	0.84	0.98	0.45	0.71	0.98	0.97	0.95	0.96	0.90		0.85	0.95	0.65	0.78	0.92	0.96	0.96	0.86	0.62	0.09	0.93	0.99	0.98	0.97
Palacio 10/13/09	0.92	0.43	0.38	0.85	0.89	0.91	0.87	0.61	0.43	0.88	0.88	0.72	0.83	0.83	0.85		0.93	0.54	0.65	0.84	0.90	0.83	0.58	0.38	0.04	0.71	0.82	0.85	0.83
Palacio 8/18/08	0.90	0.59	0.53	0.93	0.80	0.90	0.96	0.54	0.63	0.96	0.97	0.87	0.94	0.90	0.95	0.93		0.69	0.80	0.89	0.97	0.93	0.75	0.53	0.08	0.84	0.94	0.93	0.93
Palacio 8/24/08	0.54	0.57	0.53	0.58	0.44	0.53	0.69	0.20	0.67	0.64	0.72	0.72	0.55	0.78	0.65	0.54	0.69		0.97	0.49	0.59	0.78	0.74	0.57	0.04	0.92	0.65	0.60	0.61
Palacio 8/24/08 (D)	0.66	0.66	0.62	0.72	0.55	0.64	0.82	0.27	0.75	0.77	0.84	0.84	0.70	0.89	0.78	0.65	0.80	0.97		0.63	0.74	0.89	0.83	0.60	0.04	0.93	0.79	0.73	0.74
Poj River 10/13/09	0.89	0.67	0.63	0.91	0.84	0.84	0.92	0.49	0.53	0.93	0.89	0.84	0.90	0.78	0.92	0.84	0.89	0.49	0.63		0.93	0.86	0.73	0.60	0.09	0.85	0.91	0.93	0.89
Poj River 9/2/09	0.87	0.74	0.72	0.95	0.82	0.88	0.97	0.56	0.60	0.97	0.96	0.91	0.95	0.88	0.96	0.90	0.97	0.59	0.74	0.93		0.95	0.81	0.67	0.03	0.86	0.96	0.95	0.96
Poj River 8/5/09	0.84	0.73	0.67	0.94	0.76	0.82	0.98	0.42	0.79	0.95	0.98	0.95	0.93	0.97	0.96	0.83	0.93	0.78	0.89	0.86	0.95		0.91	0.64	0.08	0.93	0.96	0.93	0.94
Poj River (N Bank) 8/13/09	0.62	0.85	0.79	0.83	0.55	0.58	0.86	0.27	0.90	0.82	0.85	0.94	0.84	0.84	0.86	0.58	0.75	0.74	0.83	0.73	0.81	0.91		0.78	0.06	0.93	0.87	0.81	0.85
Poj River (S bank) 8/13/09	0.34	0.72	0.72	0.59	0.60	0.40	0.58	0.40	0.55	0.56	0.56	0.66	0.66	0.55	0.62	0.38	0.53	0.57	0.60	0.60	0.67	0.64	0.78		0.04	0.93	0.59	0.52	0.64
Santa Cruz 7/9/08	0.05	0.03	0.04	0.08	0.16	0.09	0.08	0.03	0.03	0.09	0.06	0.05	0.09	0.03	0.09	0.04	0.08	0.04	0.04	0.09	0.03	0.08	0.06	0.04		0.03	0.05	0.12	0.07
Santa Cruz 8/20/08	0.78	0.84	0.82	0.88	0.64	0.61	0.91	0.23	0.83	0.87	0.91	0.96	0.90	0.90	0.93	0.71	0.84	0.92	0.93	0.85	0.86	0.93	0.93	0.93	0.03		0.95	0.88	0.90
Toro 8/17/09	0.85	0.76	0.70	0.97	0.73	0.80	0.97	0.42	0.75	0.97	0.97	0.97	0.96	0.89	0.99	0.82	0.94	0.65	0.79	0.91	0.96	0.96	0.87	0.59	0.05	0.95		0.96	0.96
Toro 8/24/09	0.90	0.69	0.64	0.95	0.82	0.85	0.97	0.43	0.67	0.98	0.96	0.92	0.95	0.87	0.98	0.85	0.93	0.60	0.73	0.93	0.95	0.93	0.81	0.52	0.12	0.88	0.96		0.95
Truchas 7/28/09	0.84	0.69	0.64	0.95	0.78	0.84	0.97	0.49	0.68	0.96	0.96	0.92	0.96	0.90	0.97	0.83	0.93	0.61	0.74	0.89	0.96	0.94	0.85	0.64	0.07	0.90	0.96	0.95	

**Table D-2**  
**Comparison of Congener Profiles in Stormwater from Rio Grande and Rio Chama**

	Chama at Chamita 6/26/09	Chama at Chamita 7/13/09	Chama at Chamita 7/21/09	RG at Lyden 10/13/09	RG at Lyden 3/15/10	RG at Otowi 10/13/09/12:16	RG at Otowi 6/26/09	RG at Otowi 7/22/09	RG at Otowi 8/13/09	RG at Otowi 7/23/10	RG at Otowi 7/31/10	RG at Otowi 8/21/10	RG at Otowi 9/22/10	RG at Buckman 10/11/08 Dup	RG at Buckman 10/11/08/1943	RG at Buckman 10/13/09/10:40	RG at Buckman 10/13/09/13:38	RG at Buckman 6/27/09	RG at Buckman 7/19/09	RG at Buckman 7/30/09	RG at Otowi 7/31/10	RG at Otowi 8/21/10	RG at Otowi 9/22/10	RG at Buckman 10/11/08 Dup	RG at Buckman 10/11/08/1943	RG at Buckman 10/13/09/10:40	RG at Buckman 10/13/09/13:38	RG at Buckman 6/27/09	RG at Buckman 7/19/09	RG at Buckman 7/30/09
Chama at Chamita 6/26/09				0.26		0.61	1.00	0.87	0.31	0.03	0.37		0.07	0.63	0.54	0.64	0.56	0.96		0.31	0.37		0.07	0.63	0.54	0.64	0.56	0.96		0.31
Chama at Chamita 7/13/09				0.59		0.14	0.98	0.81		0.06	0.06		0.05	0.11	0.10	0.07	0.09	0.85		0.12	0.06		0.05	0.11	0.10	0.07	0.09	0.85		0.12
Chama at Chamita 7/21/09																														
RG at Lyden 10/13/09	0.26	0.59				0.45	0.42	0.18	0.53	0.49	0.25		0.34	0.64	0.67	0.61	0.37	0.53		0.28	0.25		0.34	0.64	0.67	0.61	0.37	0.53		0.28
RG at Lyden 3/15/10																														
RG at Otowi 10/13/09/12:16	0.61	0.14		0.45		0.25	0.35	0.44	0.18	0.77	0.55	0.95	0.58	0.46	0.74	0.95	0.83		0.59	0.77	0.55	0.95	0.58	0.46	0.74	0.95	0.83		0.59	
RG at Otowi 6/26/09	1.00	0.98		0.42		0.25		0.85	0.32	0.00	0.29	0.00	0.00	0.17	0.17	0.25	0.30	0.91		0.22	0.29	0.00	0.00	0.17	0.17	0.25	0.30	0.91		0.22
RG at Otowi 7/22/09	0.87	0.81		0.18		0.35	0.85		0.28	0.00	0.40		0.03	0.11	0.07	0.16	0.40	0.88		0.41	0.40		0.03	0.11	0.07	0.16	0.40	0.88		0.41
RG at Otowi 8/13/09	0.31			0.53		0.44	0.32	0.28		0.06	0.51		0.29	0.65	0.68	0.76	0.49	0.38		0.52	0.51		0.29	0.65	0.68	0.76	0.49	0.38		0.52
RG at Otowi 7/23/10	0.03	0.06		0.49		0.18	0.00	0.00	0.06		0.17	0.00	0.25	0.17	0.37	0.19	0.17	0.00		0.04	0.17	0.00	0.25	0.17	0.37	0.19	0.17	0.00		0.04
RG at Otowi 7/31/10	0.37	0.06		0.25		0.77	0.29	0.40	0.51	0.17		0.56	0.85	0.37	0.28	0.64	0.83	0.68		0.65		0.56	0.85	0.37	0.28	0.64	0.83	0.68		0.65
RG at Otowi 8/21/10						0.55	0.00			0.00	0.56		0.46	0.10	0.12	0.15	0.63				0.56		0.46	0.10	0.12	0.15	0.63			
RG at Otowi 9/22/10	0.07	0.05		0.34		0.95	0.00	0.03	0.29	0.25	0.85	0.46		0.56	0.45	0.74	0.96	0.01		0.49	0.85	0.46	0.56	0.45	0.74	0.96	0.01		0.49	
RG at Buckman 10/11/08 Duplicate	0.63	0.11		0.64		0.58	0.17	0.11	0.65	0.17	0.37	0.10	0.56		0.92	0.87	0.52	0.76		0.35	0.37	0.10	0.56		0.92	0.87	0.52	0.76		0.35
RG at Buckman 10/11/08/1943	0.54	0.10		0.67		0.46	0.17	0.07	0.68	0.37	0.28	0.12	0.45	0.92		0.79	0.40	0.62		0.23	0.28	0.12	0.45	0.92		0.79	0.40	0.62		0.23
RG at Buckman 10/13/09/10:40	0.64	0.07		0.61		0.74	0.25	0.16	0.76	0.19	0.64	0.15	0.74	0.87	0.79		0.75	0.88		0.52	0.64	0.15	0.74	0.87	0.79		0.75	0.88		0.52
RG at Buckman 10/13/09/13:38	0.56	0.09		0.37		0.95	0.30	0.40	0.49	0.17	0.83	0.63	0.96	0.52	0.40	0.75		0.86		0.67	0.83	0.63	0.96	0.52	0.40	0.75		0.86		0.67
RG at Buckman 6/27/09	0.96	0.85		0.53		0.83	0.91	0.88	0.38	0.00	0.68		0.01	0.76	0.62	0.88	0.86			0.32	0.68		0.01	0.76	0.62	0.88	0.86		0.32	
RG at Buckman 7/19/09																														
RG at Buckman 7/30/09	0.31	0.12		0.28		0.59	0.22	0.41	0.52	0.04	0.65		0.49	0.35	0.23	0.52	0.67	0.32			0.65		0.49	0.35	0.23	0.52	0.67	0.32		
RG at Buckman 7/4/09				0.55				0.29	0.12	0.12			0.08		0.54	0.37		0.27		0.24	0.12		0.08		0.54	0.37		0.27		0.24
RG at Buckman 7/23/10	0.11	0.14		0.39		0.93	0.00	0.03	0.43	0.22	0.91	0.64	0.94	0.56	0.45	0.79	0.91	0.05		0.67	0.91	0.64	0.94	0.56	0.45	0.79	0.91	0.05		0.67
RG at Buckman 7/26/08				0.49		0.34				0.86			0.94										0.94							
RG at Buckman 8/13/09		0.34		0.13		0.01	0.23	0.40	0.40	0.03	0.31		0.12	0.07	0.13	0.22	0.18	0.29		0.45	0.31		0.12	0.07	0.13	0.22	0.18	0.29		0.45
RG at Buckman 8/1/10				0.49		0.77	0.63	0.82	0.73	0.08	0.65		0.68	0.57	0.46	0.66	0.82	0.89		0.75	0.65		0.68	0.57	0.46	0.66	0.82	0.89		0.75
RG at Buckman 8/15/10	0.05	0.09		0.54		0.69	0.00	0.01	0.57	0.21	0.69	0.06	0.65	0.84	0.75	0.96	0.68	0.06		0.51	0.69	0.06	0.65	0.84	0.75	0.96	0.68	0.06		0.51
RG at Buckman 8/24/08				0.43		0.66				0.43	0.63		0.64	0.71	0.65	0.88	0.64	0.86		0.60	0.63		0.64	0.71	0.65	0.88	0.64	0.86		0.60
RG at Buckman 9/9/08/2225 Dup		0.52		0.56		0.43	0.70			0.24	0.39		0.56	0.93	0.90	0.89	0.50	0.83		0.42	0.39		0.56	0.93	0.90	0.89	0.50	0.83		0.42
RG at Buckman 9/9/08/22:25	0.05	0.52		0.01		0.39	0.30	0.40	0.04	0.16	0.22		0.46	0.03	0.01	0.07	0.38	0.08		0.24	0.22		0.46	0.03	0.01	0.07	0.38	0.08		0.24
RG at Buckman 8/23/10	0.03	0.06		0.62		0.74	0.00	0.01	0.58	0.25	0.64	0.10	0.78	0.91	0.84	0.97	0.73	0.06		0.42	0.64	0.10	0.78	0.91	0.84	0.97	0.73	0.06		0.42
RG at Buckman 9/22/10	0.14	0.04		0.32		0.96	0.00	0.03	0.03	0.15	0.84	0.61	0.95	0.31	0.21	0.69	0.90	0.04		0.25	0.84	0.61	0.95	0.31	0.21	0.69	0.90	0.04		0.25

**Table D-3**  
**Comparison of Congener Profiles in Stormwater from Pajarito Plateau Arroyos**

	Chup-1 8/4/09	Chup-1 8/16/10	Corral-1 8/5/10	Corral-1 8/16/10	Guaje avb Rendija (E089) - 8/8/06	Guaje-2 8/13/10	Las Latas-1 7/30/09	Las Latas-2 7/22/10	Las Latas-2 7/23/10	Las Latas-2 7/31/10	Canada de las Marias 8/4/09	Las Marias-1 8/5/10	Las Marias-1 10/4/10	E025 7/24/10	E025 8/5/10	E025 8/15/10	E025 8/16/10	E025 8/23/10	E240 7/5/06	E240 8/13/06	E240 8/20/06	E240 8/25/06	E240 9/18/09	E240 8/5/10	E240 8/15/10	E240 8/16/10	E240 8/16/10 Dup	
Chup-1 8/4/09		0.50	0.87	0.83	0.77	0.88	0.95		0.66	0.85	0.71	0.83	0.15	0.88	0.85	0.77	0.77	0.70	0.98	0.95	0.96	0.97	0.97	0.76	0.85	0.83	0.87	
Chup-1 8/16/10	0.50		0.75	0.51	0.17	0.79			0.53	0.75	0.11				0.24	0.31	0.19	0.14	0.50	0.40	0.38	0.44		0.47	0.83	0.77	0.81	
Corral-1 8/5/10	0.87	0.75		0.71	0.56	0.98			0.83	0.90	0.44	0.98			0.59	0.65	0.46	0.40	0.85	0.74	0.75	0.78		0.65	0.92	0.85	0.95	
Corral-1 8/16/10	0.83	0.51	0.71		0.76	0.78			0.37	0.34	0.75	0.66	0.04	0.87	0.84	0.82	0.80	0.77	0.78	0.79	0.77	0.77		0.80	0.76	0.82	0.74	
Guaje avb Rendija (E089) - 8/8/06	0.77	0.17	0.56	0.76		0.50	0.73	0.00	0.32	0.07	0.96	0.44	0.00	0.82	0.90	0.90	0.89	0.89	0.84	0.91	0.90	0.87	0.64	0.76	0.57	0.60	0.56	
Guaje-2 8/13/10	0.88	0.79	0.98	0.78	0.50				0.76		0.42	0.99			0.56	0.57	0.46	0.40	0.85	0.73	0.74	0.78		0.63	0.93	0.85	0.94	
Las Latas-1 7/30/09	0.95				0.73				0.35		0.59						0.70		0.96	0.93	0.94	0.93	0.94					
Las Latas-2 7/22/10					0.00						0.03								0.11	0.00	0.00	0.00						
Las Latas-2 7/23/10	0.66	0.53	0.83	0.37	0.32	0.76	0.35			0.73	0.24	0.81	0.40	0.21	0.31	0.26	0.25	0.18	0.70	0.57	0.59	0.63	0.44	0.33	0.63	0.49	0.67	
Las Latas-2 7/31/10	0.85	0.75	0.90	0.34	0.07				0.73		0.09				0.77	0.62	0.62	0.52	0.25	0.16	0.16	0.15		0.59	0.83	0.77	0.85	
Canada de las Marias 1A 8/4/09	0.71	0.11	0.44	0.75	0.96	0.42	0.59	0.03	0.24	0.09		0.35	0.00	0.80	0.93	0.93	0.91	0.94	0.79	0.88	0.86	0.84	0.52	0.72	0.50	0.55	0.48	
Las Marias-1 8/5/10	0.83		0.98	0.66	0.44	0.99			0.81		0.35				0.46	0.46	0.36	0.30	0.81	0.69	0.70	0.74		0.66	0.93	0.84	0.94	
Las Marias-1 10/4/10	0.15				0.00				0.40		0.00						0.00	0.00	0.08	0.01	0.03	0.03			0.12			
E025 7/24/10	0.88			0.87	0.82				0.21		0.80				0.92	0.83	0.86	0.78	0.92	0.96	0.96	0.95		0.80	0.72	0.77	0.71	
E025 8/5/10	0.85	0.24	0.59	0.84	0.90	0.56			0.31	0.77	0.93	0.46		0.92		0.98	0.99	0.97	0.89	0.94	0.94	0.92		0.77	0.60	0.65	0.63	
E025 8/15/10	0.77	0.31	0.65	0.82	0.90	0.57			0.26	0.62	0.93	0.46		0.83	0.98		0.99	0.99	0.82	0.90	0.90	0.87		0.85	0.62	0.72	0.66	
E025 8/16/10	0.77	0.19	0.46	0.80	0.89	0.46	0.70		0.25	0.62	0.91	0.36	0.00	0.86	0.99	0.99		0.99	0.82	0.90	0.89	0.87	0.70	0.76	0.52	0.59	0.53	
E025 8/23/10	0.70	0.14	0.40	0.77	0.89	0.40			0.18	0.52	0.94	0.30	0.00	0.78	0.97	0.99	0.99		0.78	0.87	0.85	0.83		0.73	0.47	0.54	0.49	
E240 7/5/06	0.98	0.50	0.85	0.78	0.84	0.85	0.96	0.11	0.70	0.25	0.79	0.81	0.08	0.92	0.89	0.82	0.82	0.78		0.97	0.98	0.98	0.99	0.79	0.84	0.83	0.87	
E240 8/13/06	0.95	0.40	0.74	0.79	0.91	0.73	0.93	0.00	0.57	0.16	0.88	0.69	0.01	0.96	0.94	0.90	0.90	0.87	0.97		0.99	0.99	0.93	0.87	0.78	0.83	0.80	
E240 8/20/06	0.96	0.38	0.75	0.77	0.90	0.74	0.94	0.00	0.59	0.16	0.86	0.70	0.03	0.96	0.94	0.90	0.89	0.85	0.98	0.99		0.99	0.94	0.85	0.78	0.81	0.80	
E240 8/25/06	0.97	0.44	0.78	0.77	0.87	0.78	0.93	0.00	0.63	0.15	0.84	0.74	0.03	0.95	0.92	0.87	0.87	0.83	0.98	0.99	0.99		0.96	0.85	0.82	0.84	0.83	
E240 9/18/09	0.97				0.64		0.94		0.44		0.52						0.70		0.99	0.93	0.94	0.96						
E240 8/5/10	0.76	0.47	0.65	0.80	0.76	0.63			0.33	0.59	0.72	0.66		0.80	0.77	0.85	0.76	0.73	0.79	0.87	0.85	0.85			0.81	0.90	0.80	
E240 8/15/10	0.85	0.83	0.92	0.76	0.57	0.93			0.63	0.83	0.50	0.93	0.12	0.72	0.60	0.62	0.52	0.47	0.84	0.78	0.78	0.82		0.81		0.98	0.98	
E240 8/16/10	0.83	0.77	0.85	0.82	0.60	0.85			0.49	0.77	0.55	0.84		0.77	0.65	0.72	0.59	0.54	0.83	0.83	0.81	0.84		0.90	0.98		0.96	
E240 8/16/10 Dup	0.87	0.81	0.95	0.74	0.56	0.94			0.67	0.85	0.48	0.94		0.71	0.63	0.66	0.53	0.49	0.87	0.80	0.80	0.83		0.80	0.98	0.96		

**Table D-4**  
**Comparison of Congener Profiles in Northern New Mexico Arroyos and Pajarito Plateau Arroyos**

	Chup-1 8/4/09	Chup-1 8/16/10	Corral-1 8/5/10	Corral-1 8/16/10	Guaje abv Rendija (E089) - 8/8/06	Guaje-2 8/13/10	Las Latas-1 7/30/09	Las Latas-2 7/22/10	Las Latas-2 7/23/10	Las Latas-2 7/31/10	Canada de las Marias 1A 8/4/09	Las Marias-1 8/5/10	Las Marias-1 10/4/10	E025 7/24/10	E025 8/5/10	E025 8/15/10	E025 8/16/10	E025 8/23/10	E240 7/5/06	E240 8/13/06	E240 8/20/06	E240 8/25/06	E240 9/18/09	E240 8/5/10	E240 8/15/10	E240 8/16/10	E240 8/16/10 Dup
Ancha 10/13/09	0.92	0.46	0.84	0.69	0.65	0.82	0.92	0.28	0.73	0.32	0.60	0.84	0.22		0.75	0.65	0.65	0.58	0.87	0.80	0.83	0.81		0.56	0.71	0.64	0.75
Aqua Caliente 7/15/08	0.49	0.11	0.41	0.62	0.87	0.38	0.45	0.00	0.13	0.03	0.88	0.29	0.00	0.65	0.69	0.69	0.71	0.76	0.61	0.70	0.68	0.66	0.42	0.50	0.43	0.47	0.41
Aqua Caliente 7/15/08 (D)	0.42	0.12	0.39	0.55	0.81	0.39	0.50	0.00	0.10	0.03	0.82	0.31	0.02	0.66	0.61	0.62	0.63	0.69	0.55	0.63	0.61	0.60	0.44	0.45	0.46	0.50	0.44
Arroyo Pino 9/2/08	0.93	0.28	0.75	0.71	0.91	0.67	0.91	0.01	0.56	0.15	0.86	0.63	0.02	0.92	0.93	0.88	0.87	0.82	0.95	0.96	0.97	0.96	0.87	0.76	0.69	0.71	0.72
Embudo 8/18/08	0.36	0.14	0.57	0.15	0.33	0.48	0.38	0.05	0.80	0.02	0.24	0.48	0.08	0.17	0.17	0.11	0.15	0.13	0.52	0.44	0.46	0.48	0.42	0.17	0.35	0.13	0.42
Hondo 7/21/08	0.54	0.06	0.32	0.68	0.83	0.28	0.49	0.88	0.11	0.25	0.89	0.23	0.01	0.63	0.89	0.90	0.84	0.92	0.63	0.71	0.69	0.65	0.36	0.66	0.35	0.43	0.36
Horno 7/19/09	0.95	0.36	0.76	0.73	0.85	0.72	0.93	0.16	0.62	0.26	0.81	0.68	0.09	0.96	0.90	0.85	0.84	0.79	0.95	0.93	0.95	0.93	0.94	0.71	0.71	0.71	0.75
Horno 8/5/09	0.95	0.36	0.74	0.77	0.85	0.66	0.95	0.42	0.58	0.36	0.82	0.65	0.13	0.94	0.92	0.87	0.86	0.82	0.95	0.93	0.93	0.92	0.93	0.78	0.72	0.74	0.75
Canada Agua (Dixon) 10/13/09	0.85	0.30	0.77	0.62	0.59	0.75	0.77	0.07	0.70	0.22	0.53	0.82	0.15	0.58	0.59	0.45	0.51	0.48	0.80	0.72	0.75	0.75	0.81	0.49	0.64	0.56	0.70
Canada Agua 8/3/09	0.81	0.37	0.72	0.50	0.61	0.74	0.91	0.10	0.72	0.35	0.55	0.77	0.18	0.79	0.78	0.72	0.55	0.49	0.84	0.76	0.79	0.78	0.90	0.53	0.59	0.55	0.65
Canada Agua 9/13/09	0.94	0.32	0.73	0.80	0.88	0.70	0.93	0.32	0.56	0.30	0.84	0.65	0.09	0.94	0.93	0.89	0.88	0.85	0.95	0.94	0.95	0.93	0.89	0.79	0.72	0.74	0.75
Oso 7/19/09	0.83	0.26	0.62	0.80	0.95	0.58	0.81	0.36	0.38	0.22	0.94	0.51	0.03	0.92	0.93	0.92	0.92	0.91	0.88	0.92	0.91	0.90	0.77	0.76	0.64	0.69	0.65
Oso 10/13/09	0.93	0.29	0.73	0.75	0.89	0.67		0.05	0.54	0.20	0.84	0.66	0.03	0.87	0.93	0.92	0.88	0.84	0.95	0.96	0.97	0.95		0.84	0.73	0.76	0.77
Oso 7/7/09	0.87	0.11	0.60	0.73	0.80	0.57			0.49	0.44	0.78	0.49	0.08	0.86	0.91	0.84	0.85	0.84	0.87	0.84	0.85	0.82		0.71	0.61	0.62	0.61
Oso 8/24/09	0.95	0.35	0.73	0.80	0.90	0.71	0.91	0.12	0.56	0.23	0.87	0.67	0.07	0.94	0.90	0.85	0.85	0.82	0.95	0.96	0.97	0.96	0.90	0.78	0.74	0.76	0.76
Palacio 10/13/09	0.91	0.48	0.91	0.64	0.62	0.88	0.86	0.21	0.86	0.38	0.55	0.90	0.22	0.59	0.69	0.62	0.59	0.54	0.91	0.81	0.83	0.84	0.90	0.60	0.77	0.69	0.81
Palacio 8/18/08	0.97	0.54	0.89	0.76	0.79	0.86	0.95	0.31	0.73	0.38	0.74	0.83	0.14	0.86	0.85	0.84	0.78	0.73	0.97	0.93	0.94	0.94	0.96	0.81	0.86	0.86	0.90
Palacio 8/24/08	0.72	0.25	0.53	0.57	0.58	0.56	0.67	0.85	0.33	0.75	0.60	0.46	0.33	0.90	0.86	0.85	0.89	0.89	0.61	0.58	0.58	0.55	0.72	0.65	0.60	0.63	0.60
Palacio 8/24/08 (D)	0.80	0.29	0.58	0.69	0.71	0.61	0.75	0.80	0.39	0.67	0.73	0.53	0.25	0.95	0.92	0.91	0.93	0.92	0.75	0.73	0.72	0.70	0.78	0.73	0.66	0.70	0.66
Poj River 10/13/09	0.94	0.43	0.82	0.71	0.81	0.78		0.00	0.64	0.10	0.74	0.73	0.04	0.91	0.87	0.81	0.78	0.75	0.90	0.89	0.91	0.90		0.72	0.76	0.74	0.77
Poj River 9/2/09	0.94		0.82	0.77	0.84			0.18	0.72	0.14	0.79		0.09		0.91	0.85	0.88	0.83	0.96	0.94	0.94	0.94		0.86	0.88	0.87	0.89
Poj River 8/5/09	0.90	0.23	0.65	0.80	0.89	0.61	0.84	0.50	0.48	0.38	0.87	0.57	0.12	0.94	0.95	0.90	0.92	0.89	0.92	0.92	0.92	0.90	0.81	0.77	0.66	0.68	0.67
Poj River (North bank) 8/13/09	0.65	0.13	0.45	0.73	0.93	0.42	0.62	0.63	0.23	0.20	0.93	0.36	0.03	0.81	0.89	0.89	0.89	0.92	0.76	0.82	0.81	0.78	0.55	0.72	0.50	0.52	0.50
Poj River (South bank) 8/13/09	0.29	0.15	0.51	0.41	0.71	0.46	0.69	0.41	0.18	0.05	0.64	0.40	0.01	0.83	0.40	0.36	0.43	0.50	0.52	0.55	0.54	0.53	0.60	0.47	0.54	0.32	0.54
Santa Cruz 7/9/08	0.17	0.07	0.21	0.12	0.05	0.34	0.23	0.23	0.00	0.23	0.03	0.40	0.03	0.15	0.25	0.28	0.21	0.07	0.05	0.05	0.05	0.04	0.15	0.19	0.14	0.15	0.21
Santa Cruz/8/20/08	0.90		0.76	0.94	0.96	0.87			0.45	0.66	0.94				0.91	0.92	0.89	0.88	0.88	0.94	0.92	0.91		0.86	0.78	0.81	0.79
Toro 8/17/09	0.94	0.37	0.73	0.79	0.92	0.70	0.91	0.11	0.54	0.20	0.90	0.65	0.03	0.96	0.94	0.92	0.91	0.87	0.96	0.98	0.98	0.97	0.91	0.81	0.74	0.77	0.76
Toro 8/24/09	0.95	0.37	0.75	0.75	0.85	0.73	0.94	0.08	0.56	0.21	0.82	0.69	0.06	0.96	0.91	0.86	0.86	0.81	0.93	0.93	0.94	0.93	0.94	0.75	0.73	0.74	0.76
Truchas 7/28/09	0.92	0.36	0.74	0.74	0.89	0.70	0.97	0.16	0.56	0.22	0.82	0.65	0.06	0.91	0.84	0.80	0.79	0.75	0.93	0.93	0.93	0.92	0.89	0.77	0.74	0.73	0.77

# **Appendix E**

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*Goodness of Fit Test Results*



Tests were run to determine which statistical distribution, if any, the polychlorinated biphenyl data collected for this study best fit. The U.S. Environmental Protection Agency software package ProUCL 4.1 was used to perform all the formal tests. Tests were performed against the standard normal distribution, the gamma distribution, and the (natural) lognormal distribution. Possible outlier or anomalous concentrations identified from review of the probability plots were removed from the data sets before the goodness of fit tests were run. For the normal and lognormal distributions, the Shapiro Wilk (S-W) test was performed. For the gamma distribution, the Anderson-Darling (A-D) and the Kolmogorov-Smirnov (K-S) tests were performed. The final column in the Table E-1 presents the best-fit statistical distribution selected for use in subsequent calculations.

For each test, two pairs of numbers are presented. The test statistic is calculated specifically for that particular data set. The critical value, sometimes referred to as the “table” value, is a look-up value depending on sample size and significance factor. For the S-W test, the data set is considered to be normally or lognormally distributed if the test statistic is greater than the critical value. In tests run by ProUCL for the gamma distribution, the data set is considered to be gamma distributed if the test statistic is less than the critical value. The probability plots in Appendix B in most cases illustrate what distribution fits the line best. For example, precipitation follows a gamma distribution and fits the line better than normal or lognormal distributions.





**Table E-1**  
**Results of Goodness-of-Fit Tests for Various Statistical Distributions**

Media or Location	Analyte	Normal Distribution Test			Gamma Distribution Test [ProUCL]					Lognormal Distribution Test			Data Distribution Test
		S-W Test Statistic	S-W Critical Value	Outcome at 5% Significance Level	A-D Test Statistic	5% A-D Critical Value	K-S Test Statistic	5% K-S Critical Value	Outcome at 5% Significance Level	S-W Test Statistic	S-W Critical Value	Outcome at 5% Significance Level	
Precipitation	Total PCBs	0.871	0.931	Not normal	0.795	0.804	0.164	0.161	Data appear gamma	0.853	0.931	Not lognormal	Data follow approximate gamma distribution
Snowpack	Total PCBs	0.867	0.859	Data appear normal	0.198	0.763	0.156	0.254	Data appear gamma	0.914	0.859	Data appear lognormal	Data appear to follow normal distribution
Northern New Mexico Tributaries	Total PCBs	0.777	0.924	Not normal	0.476	0.775	0.119	0.17	Data appear gamma	0.965	0.924	Data appear lognormal	Data appear gamma distributed
Northern New Mexico Tributaries	Suspended PCBs	0.811	0.914	Not normal	0.485	0.768	0.172	0.186	Data appear gamma	0.972	0.914	Data appear lognormal	Data appear gamma distributed
Rio Grande/Rio Chama above Otowi	Total PCBs	0.413	0.887	Not normal	0.758	0.872	0.269	0.237	Data follow approximate gamma	0.975	0.887	Data appear lognormal	Data follow approximate gamma distribution
Rio Grande/Rio Chama above Otowi	Suspended PCBs	0.676	0.85	Not normal	0.247	0.793	0.168	0.271	Data appear gamma	0.939	0.85	Data appear lognormal	Data appear gamma distributed
Rio Grande at Buckman	Total PCBs	0.524	0.892	Not normal	0.453	0.856	0.154	0.228	Data appear gamma	0.966	0.892	Data appear lognormal	Data appear gamma distributed
Rio Grande at Buckman	Suspended PCBs	0.717	0.85	Not normal	0.386	0.788	0.223	0.27	Data appear gamma	0.968	0.85	Data appear lognormal	Data appear gamma distributed
Reference Stations	Total PCBs	0.569	0.897	Not normal	0.928	0.8	0.222	0.215	Not gamma	0.976	0.897	Data appear lognormal	Data appear Lognormal
Reference Stations	Suspended PCBs	0.354	0.881	Not normal	1.956	0.788	0.366	0.233	Not gamma	0.887	0.881	Data appear lognormal	Data appear lognormal
Western Boundary Stations	Total PCBs	0.675	0.874	Not normal	0.24	0.791	0.139	0.241	Data appear gamma	0.953	0.874	Data appear lognormal	Data appear gamma distributed

Table E-1 (continued)

Media or Location	Analyte	Normal Distribution Test			Gamma Distribution Test [ProUCL]					Lognormal Distribution Test			Data Distribution Test
		S-W Test Statistic	S-W Critical Value	Outcome at 5% Significance Level	A-D Test Statistic	5% A-D Critical Value	K-S Test Statistic	5% K-S Critical Value	Outcome at 5% Significance Level	S-W Test Statistic	S-W Critical Value	Outcome at 5% Significance Level	
Western Boundary Stations	Susp. PCBs	0.953	0.866	Data appear Normal	0.312	0.75	0.16	0.241	Data appear gamma	0.837	0.866	Not lognormal	Data appear normal
Los Alamos Townsite Urban Runoff	Total PCBs	0.831	0.928	Not normal	0.363	0.772	0.117	0.147	Data appear gamma	0.959	0.938	Data appear lognormal	Data appear gamma distributed
Los Alamos Townsite Urban Runoff	Suspended PCBs	0.791	0.929	Not normal	0.533	0.773	0.183	0.162	Data follows approximate gamma	0.962	0.929	Data appear lognormal	Data follow approximate gamma distribution