

**Assessment of Recent
Changes in Water Quality of the
Bow River Downstream of the
Canada Creosote Site in Calgary**

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SUMMARY

The former Canada Creosote plant was located beside the Bow River in downtown Calgary, Alberta. The plant used tars, creosote and petroleum oils to preserve wood over about 38 years from 1924 to 1962. Pentachlorophenol (PCP) was also used during part of this time period. Drilling at the site in 1988 determined that a liquid mixture of creosote, PCP, dioxins and dibenzofurans and other contaminants was present beneath the former wood treatment plant. In November 1989, a liquid mixture of these contaminants called dense non-aqueous phase liquid (DNAPL), was found seeping into the Bow River adjacent to the Canada Creosote site. A permanent barrier to contaminant flow was installed along the entire shoreline between April 29 and May 3, 1995, and a system designed to prevent the flow of contaminated groundwater to the river around the barrier was fully-operational by February 8, 1996.

Alberta Environmental Protection intensively monitored the Bow River ecosystem from 1989 to March 31, 2002, when the City of Calgary assumed responsibility for the containment system under a formal agreement. Alberta Environment and Sustainable Resource Development (AESRD) resumed monitoring of river water quality in 2011. AESRD contracted Sosiak Environmental Services to undertake a statistical evaluation and graphic summary of changes in river concentrations in recent years of polycyclic aromatic hydrocarbons (PAH) and PCP (together called the target compounds) in support of a risk assessment. The evaluation was also intended to evaluate seasonal variation of these constituents, evaluate 2011-2013 quality assurance/quality control (QAQC) data, conduct a water quality evaluation relative to current guidelines, and determine if there was any evidence of changes in contaminant movement before and after the 2013 Bow River flood.

All carcinogenic PAH and PCP from the Canada Creosote site have remained at or below detection limits since 1998. PCP and these three carcinogens have never been detected in 16 years of monitoring upstream from the Canada Creosote site, which suggests these compounds were mainly associated with DNAPL from the contaminated site. Since all these compounds remain at or below detection limits, this suggests that the containment system continues to effectively prevent movement of the most harmful contaminants from this site.

Concentrations of naphthalene and methylnaphthalene were significantly higher in recent years (2011, 2012) downstream from the Canada Creosote site, compared to the period immediately after site containment (1996-2002). This may be due to the higher than average flows recorded in the Bow River in recent years.

These sampling results provide no evidence that the target compounds occur regularly in river water along the left bank (facing downstream), on the north side of the river. Contaminant movement from the remaining pool of DNAPL in the river bed close to the right bank (facing downstream) remains the likely source of compounds detected on that side of the river downstream from the Canada Creosote site.

Aside from naphthalene, these results suggest that during monitoring all the target compounds at all sites remained well below levels that are likely to cause adverse aquatic effects since site

containment. Although the interim guideline for naphthalene has been exceeded immediately downstream from the Canada Creosote site and concentrations have increased in recent years, naphthalene has remained well below the lowest observed aquatic effects level determined by CCME. Accordingly, harm to aquatic life seems unlikely, and detections of naphthalene appear to be localized based on the available monitoring.

It seems likely that bed movement occurred in at least 1990, 2005, and 2013, when flows greatly exceeding the bed mobility threshold occurred. There were no statistically-significant changes in concentration at any site before and after the 2013 flood, which suggests that there was no change in contaminant levels in the Bow River after the flood had subsided.

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ABBREVIATIONS

AESRD	Alberta Environment and Sustainable Resource Development
CCME	Canadian Council of Ministers of Environment Environmental Quality Guidelines
DL	detection limit
DW	Health Canada Guidelines for Canadian Drinking Water Quality
m ³ /s	cubic metres per second
PAL	CCME Guidelines for the Protection of Aquatic Life
PAH	polycyclic aromatic hydrocarbons
PCP	pentachlorophenol
µg/L	micrograms per litre
USEPA	United States Environmental Protection Agency
WSC	Water Survey of Canada
u/s	upstream
d/s	downstream

1.0 INTRODUCTION

The former Canada Creosote plant was located beside the Bow River in downtown Calgary, Alberta. The former plant has sometimes been called Canada Creosoting, but the simpler term “Canada Creosote Site” will be used in this report. The plant used tars, creosote and petroleum oils to preserve wood over about 38 years from 1924 to 1962. Pentachlorophenol (PCP) was also used during part of this time period. Drilling at the site in 1988 during the H.E.L.P. (Help Eliminate Landfill Pollution) program, determined that a liquid mixture of creosote, PCP, dioxins and dibenzofurans and other contaminants was present beneath the former wood treatment plant.

In November 1989, a liquid mixture of these contaminants called dense non-aqueous phase liquid (DNAPL), was found seeping into the Bow River adjacent to the Canada Creosote site. A temporary berm was built in the river around the seepage area on November 6-9, 1989, and rebuilt on October 9-19, 1990 after flood damage that year. Contaminants were removed from the bermed area. A permanent barrier to contaminant flow was installed along the entire shoreline between April 29 and May 3, 1995, and a system designed to prevent the flow of contaminated groundwater to the river around the barrier was fully-operational by February 8, 1996.

Alberta Environmental Protection intensively monitored the Bow River ecosystem from 1989 to March 31, 2002, when the City of Calgary assumed responsibility for the containment system under a formal agreement. Alberta Environment and Sustainable Resource Development (AESRD) resumed monitoring of river water quality in 2011. The earlier work was designed to determine the distribution of contaminants from the Canada Creosote site in the aquatic ecosystem of the Bow River, to protect domestic water supplies, and to ensure that human consumption of fish was safe. Two previous government reports (Sosiak 1998, 1999) evaluated changes in water quality and fish residues over several years after the containment system was installed. These reports found that the containment system had significantly reduced the movement of contaminants to the Bow River from the Canada Creosote site and improved water quality in the Bow River (Sosiak 1999).

River water quality monitoring by AESRD was resumed in 2011 to augment work being done on a Health Risk Assessment in the West Hillhurst Community, where there was sampling of groundwater and soil vapour. West Hillhurst is the community on the north side of the river directly across from the Canada Creosote site (Figure 1) and adjacent to the Bow River. Because DNAPL is heavier than water, it has the potential to migrate across a river bed. This monitoring was designed to provide a more complete understanding of current conditions related to the presence of the contaminants associated with the Canada Creosote site.

AESRD contracted Sosiak Environmental Services to undertake a statistical evaluation and graphic summary of changes in river concentrations in recent years of polycyclic aromatic hydrocarbons (PAH) and PCP in support of the risk assessment. The evaluation was also intended to evaluate seasonal variation of these constituents, evaluate 2011-2013 quality assurance/quality control (QAQC) data, conduct a water quality evaluation relative to current water quality guidelines, and determine if there was any evidence of recent changes in contaminant movement before and after the 2013 Bow River flood.



Figure 1 Location of Canada Creosote sampling and hydrometric sites on the Bow River

2.0 METHODS

2.1 Data Sources, Study Sites, and Sampling Procedures

All available river water data from four AESRD Canada Creosote sampling sites were downloaded by AESRD from the provincial water quality database (WDS) for the entire period of sampling from 1989 to 2013. Daily Bow River flows for the Water Survey of Canada (WSC) hydrometric station closest to the Canada Creosote site (05BH004, Figure 1) were downloaded from the WSC web site and plotted along with a 1989-2012 (24 year) daily average superimposed. Only flows from 1989 to 2012, which were approved for release, were used to calculate a long-term average flow. Flows for 2013 were provided by AESRD as preliminary information subject to correction.

Site locations are provided in Figure 1, and WDS station names and codes (in parentheses) are as follows:

Bow River upstream Canada Creosote (AB05BH0150): this site is along the right bank (facing downstream) just upstream of storm sewer B-71 and all known impacts of the Canada Creosote site.

Bow River downstream Canada Creosote RB (AB05BH0200): this site is along the right bank just downstream from the boundary of the former Canada Creosote site, below the former berm at this site, but upstream from the 14 Street bridge.

Bow River downstream Canada Creosote LB (AB05BH0190): this site is along the left bank (facing downstream) opposite site AB05BH0190, and also upstream from the 14 Street bridge.

Bow R. at Stier's Ranch (AB05BM0150): this site is about 38 km downstream from the Canada Creosote site at a historic AESRD sampling location.

The three right bank sites above have been sampled throughout the entire sampling period, along with other sites and sampling media that are not part of this study. The site on the left bank downstream from the Canada Creosote site was sampled briefly in 1989, then not again until 2011.

These sites were all sampled daily for part of 1989 (including a brief period at the left bank site downstream Canada Creosote), then the sampling frequency was gradually reduced to monthly from 1992 to 2013 (except weekly during containment system construction work in 1995) as summarized in Table 1. Samples were only collected during February to June 2011, throughout 2012, and during August to December 2013, whereas sampling prior to 2002 was done year-round.

Subsurface grab samples were collected in pre-cleaned glass bottles supplied by the analytical laboratory, without head space, at each sampling location. During the most intensive and frequent sampling period, 1989-1992, each trip a sample of Type 1 laboratory water (treated with reverse osmosis and double distilled to remove all contaminants) was spiked with vials containing a

mixture of PAH and PCP known only to AESRD staff, or left un-spiked and submitted “blind” as a blank for analysis. Laboratory performance against these known concentrations was tracked as a form of QAQC. QAQC samples were collected on most sampling trips in 2011 to 2013. QAQC samples in 2011 to 2013 consisted of three types of samples: (1) river water samples split in half, with one half sent to either the Alberta Innovates Technology Futures (AITF) laboratory in Vegreville, AB or the Maxxam Analytics laboratory in Calgary, and the other half to ALS, (2) samples of Type 1 water submitted as blanks to ALS, and (3) triplicate split samples sent to ALS. These recent QAQC data (2011-2013) were reviewed to identify any sampling concerns.

Table 1 Period of data and sampling frequency for Canada Creosote study sites, 1989 to 2013

Sampling Site	Period of Data (m-d-y)	Sampling Frequency
Bow River u/s Canada Creosote	11/02/89 - 03/30/90	Every other day
	10/03/91 - 11/01/91	Weekly
	08/08/95 - 12/17/98	Monthly
	02/23/99 - 03/26/02	Monthly (4 or 5 in one year)
	02/17/11 - 06/01/11	Monthly (7 in one year)
	01/27/12 - 12/10/12	Monthly
Bow River d/s Canada Creosote Left Bank	08/13/13 - 12/11/13	Tw ice/Month Aug. and Oct, Otherw ise Monthly (7 in one year)
	11/07/89 - 11/10/89	Daily
	02/17/11 - 06/01/11	Monthly (7 in one year)
	01/27/12 - 12/10/12	Monthly
Bow River d/s Canada Creosote Right Bank	08/13/13 - 12/11/13	Tw ice/Month Aug. and Oct, Otherw ise Monthly (7 in one year)
	11/02/89 - 12/29/89	Daily
	01/03/90 - 03/30/90	Every other day
	05/23/90 - 07/26/90	Every other day
	08/02/90 - 12/12/91	Every other day/Weekly
	01/09/92 - 12/07/94	Monthly
	04/07/95 - 07/10/95	Weekly
	08/08/95 - 12/17/98	Monthly
	02/23/99 - 03/26/02	Monthly (4 or 5 in one year)
	02/17/11 - 06/01/11	Monthly (7 in one year)
01/27/12 - 12/10/12	Monthly	
Bow River at Stier's Ranch	08/13/13 - 12/11/13	Tw ice/Month Aug. and Oct, Otherw ise Monthly (7 in one year)
	11/04/89 - 12/21/89	Daily
	01/03/90 - 10/24/90	Every other day
	11/01/90 - 12/12/91	Weekly
	01/09/92 - 12/07/94	Monthly
	04/07/95 - 07/10/95	Weekly
	08/08/95 - 12/17/98	Monthly
	02/23/99 - 03/26/02	Monthly (4 or 5 in one year)
	02/17/11 - 06/01/11	Monthly (7 in one year)
	01/27/12 - 12/10/12	Monthly

Enviro-Test Laboratories (later renamed ALS) conducted all chemical analysis on these samples, except for QAQC samples that were sent to other laboratories.

2.2 Contaminants of Concern and Study Approach

A list of target PAH compounds and PCP (Table 2) was developed in 1989 based on the most abundant and important compounds from a human and aquatic toxicity perspective in several GC/MS scans of DNAPL recovered from the river bed. These target compounds were used for all subsequent chemical analysis. Further details on sample analytical procedures are provided in Sosiak (1999). PCP is no longer used for wood treatment in Alberta, and the presence of this compound in test results was considered a good indication of DNAPL movement from the Canada Creosote site.

As directed by the terms of reference for this project, this study focused on the target PAH and PCP compounds. In addition to these compounds, total hydrocarbons (C6-C10, C10-C16, C16-C34, C34-C50 carbon chain length) and BTEX compounds (benzene, toluene, ethyl-benzene, xylene, and styrene) were individually measured on five sampling days at each of the four sampling sites from March to June 2011, and were screened to determine if these compounds were pertinent to the objectives for this project.

This study was designed to determine if there have been any statistically-significant changes in river concentrations for the target compounds during two time periods:

- (1) In recent years before the 2013 flood. Results from 2011 and 2012 were compared to historic levels during operation of the containment system, namely February 8, 1996 (when the containment system became fully-operational) to March 26, 2002, when regular sampling by AESRD finished. This phase of the project was designed to provide any indication of changes in contaminant movement since the previous study (Sosiak 1999) which provided an analysis of results to 1999,
- (2) Following the large flood on the Bow River that began June 21, 2013. To evaluate whether the flood caused an increase in movement of these contaminants, river concentrations from August 13 to December 11, 2013 were compared statistically to results before the flood, from February 17, 2011 to December 10, 2012.

To determine if river bed movement likely occurred, daily flows were compared to a 413 m³/s bed mobility threshold flow that was developed in Sosiak (2002) for the WSC hydrometric site (05BH004) for which flows were plotted. Sustained flows above this threshold should be enough to initiate river bed movement but amount and magnitude of movement would likely depend on peak flows and the duration of high flows in an individual flood.

2.3 Data Analysis

Some of the target compounds were infrequently or never detected at some sites (detections summarized in Table 3). Because these compounds were skewed towards the lower end of the distribution, tests that evaluate and correct for seasonality were used for this analysis. This was

Table 2 Summary of target compounds, detection limits, dates and available water quality guidelines for PAH and PCP, 1989 to 2013

Variable	Guidelines (µg/L) (CCME 2014, HC 2012, USEPA 2014)	Detection Limit (µg/L)	DL Dates (d-m-y)	Number of Samples
Naphthalene	1.1 (CCME PAL)	L0.1	11/89 - 08/90	299
		L0.01	23/08/90 - 03/02	416
		L0.03, L0.02	21/02/97	2
		L0.05	17/02/11	4
		L0.01	28/02/11	4
		L0.05	09/03/11	4
		L0.05	22/03/11	4
		L0.06	08/04/11	4
		L0.07	06/05/11	1
		L0.05	06/05/11	3
		L0.3	01/06/11	1
		L0.03	01/06/11	3
		L0.05	01/12 - current	75
L0.2	03/08/12	1		
Methylnaphthalene		L0.1	11/89 - 08/90	299
		L0.01	23/08/90 - 03/02	416
		L0.07	21/02/97	1
		L0.05	17/02/11	4
		L0.01	28/02/11	4
		L0.05	09/03/11	4
		L0.07	22/03/11	4
		L0.1	08/04/11	4
		L0.04	06/05/11	4
		L0.01	01/06/11	4
		L0.02	01/12 - current	72
		L0.03	03/08/12	4
Dimethylnaphthalene		L0.1	11/89 - 08/90	299
		L0.01	23/08/90 - current	418
Acenaphthylene		L0.1	11/89 - 08/90	298
		L0.01	23/08/90 - 06/11	446
		L0.02	01/12 - current	76
Acenaphthene	5.8 (CCME PAL) 20 (USEPA PAL)	L0.1	11/89 - 08/90	299
		L0.01	23/08/90 - 04/11	441
		L0.09	21/02/97	1
		L0.04	06/05/11	4
		L0.01	01/06/11	4
		L0.02	01/12 - current	75
		L0.03	03/08/12	1
Fluorene	3.0 (CCME PAL)	L0.1	11/89 - 08/90	299
		L0.01	23/08/90 - 04/11	437
		L0.04	21/02/97	1
		L0.05	06/05/11	4
		L0.01	01/06/11	4
		L0.02	01/12 - current	73
		L0.03	03/08/12	3
Phenanthrene/ Anthracene	Phenanthrene 0.4 (CCME PAL) Anthracene 0.012 (CCME PAL)	L0.1	11/89 - 08/90	299
		L0.03	21/02/97	1
		L0.01	09/90 - current	521

Table 2 Continued

Variable	Guidelines (µg/L) (CCME 2014, HC 2012, USEPA 2014)	Detection Limit (µg/L)	DL Dates (d-m-y)	Number of Samples
Dibenzofuran		L0.1	11/89 - 15/08/90, 30/08/90	299
		L0.01	23/08/90, 09/90 - 04/11	437
		L0.04	21/02/97	1
		L0.05	06/05/11	4
		L0.01	01/06/11	4
		L0.02	01/12 - 07/12	28
		L0.03	03/08/12	4
		L0.02	09/12 - current	44
Carbazole		L0.2	11/89 - 15/08/90, 30/08/90	300
		L0.02	23/08/90	1
		L0.01	09/90 - 06/11	445
		L0.02	01/12 - current	76
Methyl Phenanthrene/ Anthracene		L0.1	11/89 - 15/08/90, 30/08/90	297
		L0.01	27/06/90, 29/06/90	2
		L0.01	09/1990 - 06/11	447
		L0.02	01/12 - current	76
Benzo(a)Pyrene	0.015 (CCME PAL) 0.01 (HC DW)	L0.01	11/89 - 09/90	304
		L0.005	23/08/90, 27/09/90 - 08/94	210
		L0.01	09/94 - current	306
Benzo(b) Fluoranthene		L0.01	08/90 - 20/09/90	9
		L0.005	27/09/90 - 02/08/94	208
		L0.01	19/09/94 - current	306
Benzo(a) Anthracene	0.018 (CCME PAL)	L0.01	08/90 - 20/09/90	9
		L0.005	27/09/90 - 02/08/94	206
		L0.01	23/05/91, 19/09/94 - current	307
Pentachlorophenol	0.5 (CCME PAL) 60 (HC DW) 15 (USEPA) PAL 30 (USEPA) TASTE/ODOR	L0.1	11/89 - 08/90	298
		L0.01	23/08/90 - 05/12	454
		L0.1	13/06/12	4
		L0.01	07/12 - current	52

Sites Monitored:

Bow River upstream Canada Creosote

Bow River downstream Canada Creosote (right bank, left bank)

Bow River at Stier's Ranch

Bold italics denote detection limits used for substitution of values <detection limits

Guidelines: CCME PAL (Canadian Council Ministers of the Environment, Protection of Aquatic Life), HC DW (Health Canada, Drinking Water), USEPA (United States Environmental Protection Agency)

Table 3 Summary of PAH and PCP detection frequency, 1989 to 2013 (units in µg/L)

Station No. (AB05)	Station Name	Variable:	Naphthalene	Methyl Naphthalenes	2-Methyl naphthalene	Acenaphthylene	Acenaphthene	Fluorene	Anthracene
BH0150	Bow River u/s Canada Creosote	No. Of Samples	144	144	118	144	144	144	144
		No. Of Detections	14	11	9	0	2	1	1
		% Det. Frequency	9.7	7.6	7.6	0	1.4	0.7	0.7
BH0190	Bow River d/s Canada Creosote Left Bank	No. Of Samples	30	30	4	30	30	30	30
		No. Of Detections	0	2	0	0	0	0	0
		% Det. Frequency	0	6.7	0	0	0	0	0
BH0200	Bow River d/s Canada Creosote Right Bank	No. Of Samples	315	315	289	314	315	315	315
		No. Of Detections	268	198	99	17	107	101	98
		% Det. Frequency	85.1	62.9	34.3	5.4	34.0	32.1	31.1
BM0150	Bow River at Stier's Ranch	No. Of Samples	332	332	306	332	332	332	332
		No. Of Detections	119	65	38	2	11	20	32
		% Det. Frequency	35.8	19.6	12.4	0.6	3.3	6.0	9.6
Station No. (AB05)	Station Name	Variable:	Dibenzofuran	Carbazole	Methyl Anthracenes	Benzo(a) Pyrene	Benzo (b or k) Fluoranthene	Benzo(a) Anthracene	Penta chloro phenol
BH0150	Bow River u/s Canada Creosote	No. Of Samples	144	144	144	144	86	86	141
		No. Of Detections	1	1	2	0	0	0	0
		% Det. Frequency	0.7	0.7	1.4	0	0	0	0
BH0190	Bow River d/s Canada Creosote Left Bank	No. Of Samples	30	30	30	30	26	26	27
		No. Of Detections	0	0	0	0	1	0	0
		% Det. Frequency	0	0	0	0	3.8	0	0
BH0200	Bow River d/s Canada Creosote Right Bank	No. Of Samples	315	315	315	314	206	206	312
		No. Of Detections	68	49	26	11	10	13	134
		% Det. Frequency	21.6	15.6	8.3	3.5	4.9	6.3	43.0
BM0150	Bow River at Stier's Ranch	No. Of Samples	332	332	332	332	205	205	329
		No. Of Detections	7	8	12	5	3	4	19
		% Det. Frequency	2.1	2.4	3.6	1.5	1.5	2.0	5.8

done to ensure that results would be comparable with previous work to assess contaminant movement from this site (Sosiak 1998, 1999).

To permit numerical analysis, values less than analytical detection limits were first replaced by values one-half the detection limit. Substitution with values half the detection limit is acceptable for the nonparametric methods of analysis used in this study, but would not be appropriate for parametric statistics such as linear regression, mean, or standard deviation (Helsel and Hirsch 2002), which are not needed for this study. Another challenge with this dataset is that detection limits have fluctuated considerably over time at the same analytical lab, and these are summarized in Table 2. Changing detection limits can create a false trend in a dataset, especially since they generally decline over time with improvements in analytical methods. However, in this dataset, variables such as naphthalene had much higher detection limits in 2011 to 2013 (Table 2).

A common method of dealing with multiple detection limits in trend analysis is to use the highest detection limit encountered over the period of analysis (Aroner 2012, Helsel and Hirsch 2002). This approach was also used in Sosiak (1999). However, in 2011-2013, some relatively high detection limits were only used for a single sample. Accordingly half the highest detection limit that was repeatedly used for sample analysis (marked with bold italics in Table 2) was substituted for values less than analytical detection limits. Files with a uniform higher detection limit were used for all statistical analysis, while the plotted values contain half the actual detection limit in the database.

Variables were first tested with the Kruskal-Wallis test for seasonality for the time periods specified in Section 2.2, before testing for changes in concentration, using procedures in the computer program WQHYDRO (Aroner, 2012). Significant seasonality may also provide some indication of the mechanisms of contaminant transport to the river at these sites. Step trend analysis detects abrupt changes in concentration related to some intervention or change in a watershed, such as the 2013 flood or a release of contaminants from the Canada Creosote site in recent years. Step trend analysis was used instead of monotonic trend analysis for this project because there was a nine years gap in the monitoring records, and there was concern about whether there were compounds leaking from the Canada Creosote site in recent years. A substance release report that described an oily sheen in the vicinity of the Canada Creosote site in November 2008 was investigated by City of Calgary scientific staff (W. Koning, pers. comm).

Changes in concentration over time that exhibited significant seasonality were tested using the Seasonal Wilcoxon-Mann-Whitney rank sum test, and changes in concentration were calculated using the Seasonal Hodges-Lehman estimator. This seasonal step trend test is about 15% less sensitive when used to test datasets that do not display significant seasonality (E. Aroner. 2014. WQHydro, pers. comm.). Accordingly, for data without significant seasonal variation, step trends were tested using the Anderson-Darling K-sample analysis of variance (ANOVA) followed by a Pairwise Wilcoxon-Mann-Whitney multiple comparison tests where the ANOVA was significant. This procedure was used to evaluate other water quality variables in the Bow River in Sosiak (2002). The Anderson-Darling ANOVA is not adversely affected by differences in variance between samples, which often occurred in such data. This procedure was also used to test for differences between right and left bank results downstream from the Canada Creosote site.

Furthermore, it was able to detect significant differences between individual pairs of years, while the seasonal test compared only two time periods. As recommended by Ward et al. (1990), a 0.10 level of statistical significance was used to assess the results of all step trend tests.

The concentrations of the graphed target compounds were compared to the most sensitive and recent Canadian Environmental Quality Guidelines (CCME) (Table 2) (CCME 2014) as specified in the terms of reference. To determine if these values were the most stringent environmental guidelines of those widely-used in Canada, the web site for the United States Environmental Protection Agency (USEPA) was also consulted, and aquatic criteria and taste and odour criteria from USEPA are included in Table 2. In each case CCME guidelines were lower than the corresponding USEPA criteria, and were used in this evaluation. The most recent Health Canada Guidelines for Canadian Drinking Water Quality (HC 2012) are also included for information in Table 2, because the Bow River supplies municipal drinking water supplies to various downstream communities. However, these guidelines apply to finished drinking water, not the river concentrations in this report.

3.0 RESULTS AND DISCUSSION

Recent changes in flow, PAH, and PCP concentrations in the Bow River over time are discussed in the following sections. A continuous line plot of Bow River flows from 1989 to 2013 with a bed mobility threshold and long-term daily averages superimposed is presented in Figure 2. A summary of changes in sampling frequencies over the monitoring program is in Table 1. Changes in detection limits and water quality guidelines are in Table 2. A summary of detection frequency is in Table 3. All step trend test results (both spatial and temporal comparisons) are summarized in Tables 4 and 5. Lastly, QAQC results from 2011-2013 are in Table 6, and these results are discussed in Appendix II.

Line plots of each PAH and PCP from 1989 to 2013 at all sampling sites are in Figure 3 to 15. Note that results for the left and right bank sites downstream from the Canada Creosote site are plotted in different colours on the same axes to facilitate comparisons, and the most stringent water quality guidelines are superimposed on each plot. A significant increase in naphthalene in recent years is in Figure 16. A plot of one PAH that has fluctuated seasonally (naphthalene) is in Figure 17. All seasonality tests are in Table 1 and 2, Appendix I.

3.1 Temporal and Spatial Variation

Concentrations of naphthalene (Figure 3) and methylnaphthalene were significantly higher in recent years (2011, 2012, Figure 16) downstream from the Canada Creosote site, compared to the period immediately after site containment (1996-2002) (Table 4). Throughout this report the term significant refers to statistical significance. As discussed in more detail in Section 3.2, naphthalene sometimes exceeded the CCME PAL guideline in recent years, but not during 1996-2002 (Figure 3). There were also small but statistically-significant increases in acenaphthene and phenanthrene at this site, but no change over time for any compound at the upstream site or further downstream at Stier's Ranch (Table 4).

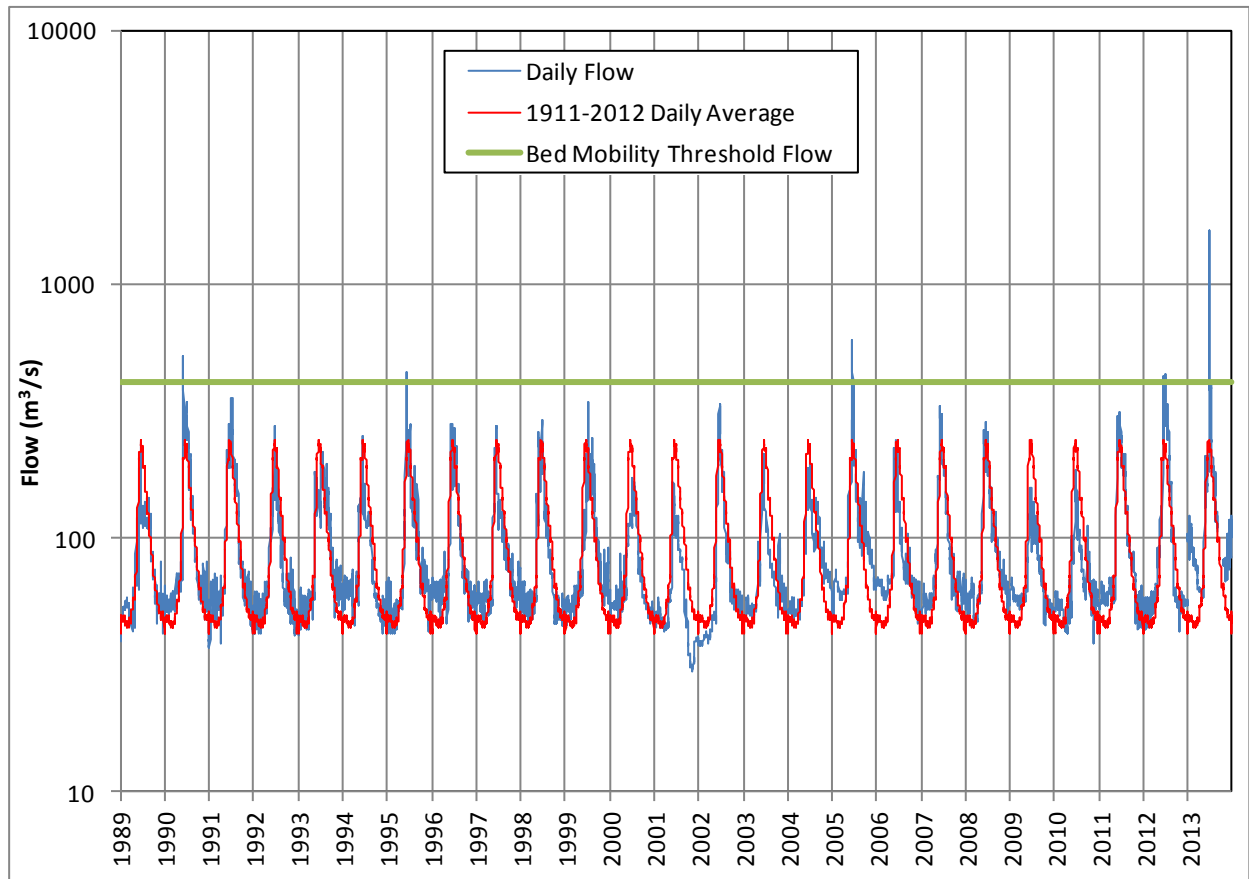


Figure 2 Mean daily flows in the Bow River at WSC Hydrometric Station 05BH004 with 24 year mean daily flows superimposed, along with a bed mobility threshold flow for this station

Table 4 Summary of significant step trends in PAH and PCP ($\mu\text{g/L}$) prior to the 2013 flood at Canada Creosote Project sites (1996-2012)

Constituents	Bow River u/s Canada Creosote	Bow River d/s Canada Creosote, Right ^d Bank	Bow River at Stier's Ranch
Naphthalene	ns	$\uparrow 0.081^a$, $P=0.073$	ns
Methylnaphthalene	ns	$\uparrow 0.01^b$ 2011, $P=0.003$	ns
Acenaphthylene	-	na	-
Acenaphthene	ns	$\uparrow < 0.0001^b$ 2012, $P=0.006$	ns
Fluorene	na	ns	ns
Phenanthrene/Anthracene	ns	ns	ns
Dibenzofuran	na	$\uparrow < 0.0001^b$ 2012, $P=0.001$	ns
Carbazole	ns	ns	-
Methylphenanthrene/Anthracene	ns	na	-
Benzo(a)Pyrene	-	-	-
Benzo(b or k)Fluoranthene	-	ns	-
Benzo(a)Anthracene	-	ns	-
Pentachlorophenol	-	ns	-

^a Seasonal Wilcoxon-Mann-Whitney test and Seasonal Hodges-Lehmann estimate of change in mean concentration, comparing 1996-2002 to 2011- 2012

^b Anderson-Darling ANOVA followed by Pairwise Wilcoxon-Mann-Whitney multiple comparison test and estimate of difference in median concentration comparing 1996-2002 to 2011- 2012

^c Abbreviations: \uparrow statistically-significant increasing ns: no significant change ($P>0.1$), na: could not be tested with the available data, hyphen: variable not tested at this location because all measurements during the specified time intervals were less than the detection limit

^d Facing downstream

Table 5 Comparison of right and left bank sites, and summary of step trends results for PAH and PCP after the 2013 flood at the Canada Creosote Project sites, during 2011-2013

Constituents	Bow River u/s Canada Creosote	Bow River d/s Canada Creosote, Right ^c Bank	Comparison of Right and Left Bank Sites d/s Canada Creosote	Bow River d/s Canada Creosote, Left ^c Bank	Bow River at Stier's Ranch
Naphthalene	ns	ns	RDB>LDB ^a : 2012,+0.21 2013,+0.735	-	ns
Methylnaphthalene	ns	ns	RDB>LDB ^a : 2012,+0.0075 2013,+0.115	ns	ns
Acenaphthylene	-	ns	-	-	ns
Acenaphthene	-	ns	RDB>LDB ^a : 2013,+0.05	-	ns
Fluorene	na	ns	ns	-	ns
Phenanthrene/Anthracene	-	ns	-	-	ns
Dibenzofuran	na	ns	ns	-	ns
Carbazole	ns	ns	ns	-	ns
Methylphenanthrene/Anthracene	-	-	-	-	ns
Benzo(a)Pyrene	-	-	-	-	-
Benzo(b or k)Fluoranthene	-	-	ns	ns	-
Benzo(a)Anthracene	-	-	-	-	-
Pentachlorophenol	-	-	-	-	-

^a Anderson-Darling ANOVA followed by Pairwise Wilcoxon-Mann-Whitney multiple comparison test and estimate of difference in median concentration between right and left bank sites 2011- 2013

^b Abbreviations: ns: no significant change (P>0.1), hyphen: variable not tested at this location because all measurements during the specified time interval were less than the detection limit, RDB: right downstream bank, LDB: left downstream bank

^c Facing downstream.

Table 6 Blank samples, split, and triplicate samples at the Bow River d/s Canada Creosote RB site (AB05BH0200), 2011-2013

Comment	Date	Naphthalene	Methyl Naphthalenes	2-Methyl naphthalene	Acenaphthylene	Acenaphthene	Fluorene	Anthracene
Routine sample	22-Mar-11	L0.05	L0.07		L0.01	L0.01	L0.01	L0.01
Trip. Split rep 2	22-Mar-11	L0.05	L0.1		L0.01	L0.01	L0.01	L0.01
Trip. Split rep 3	22-Mar-11	L0.05	L0.07		L0.01	L0.01	L0.01	L0.01
	% Difference	na	na	na	na	na	na	na
Routine sample	1-Jun-11	L0.3	0.04		L0.01	L0.01	0.01	L0.01
Trip. Split rep 2	1-Jun-11	L0.3	0.04		L0.01	L0.01	L0.01	L0.01
	% Difference	na	0	na	na	na	na	na
Trip. Split rep 3	1-Jun-11	L0.3	0.04		L0.01	L0.01	0.01	L0.01
	% Difference	na	0	na	na	na	na	na
Split sample	1-Jun-11	L0.01	L0.01	L0.01	L0.01	L0.01	L0.01	L0.01
Routine sample	17-Oct-12	0.52	0.03		L0.02	0.04	L0.02	L0.01
Split sample	17-Oct-12	0.18	0.055	0.022	0.004	0.066	0.032	L0.01
	% Difference	-65.4	83.3	na	na	65.0	na	na
Routine sample	8-Nov-12	1.27	0.18		L0.02	0.08	0.04	L0.01
Split sample	8-Nov-12	0.52	0.09	0.06	0.006	0.089	0.043	0.004
	% Difference	-59.1	-50.0	na	na	11.3	7.5	na
Routine sample	10-Dec-12	0.4	0.08		L0.02	0.03	L0.02	L0.01
Split sample	10-Dec-12	0.34	0.034	0.026	L0.01	0.023	0.012	L0.01
	% Difference	-15.0	-57.5	na	na	-23.3	na	na
Routine sample	11-Dec-13	2.52	0.48		L0.02	0.21	0.1	L0.01
Maxxam Split	11-Dec-13	2.6		0.32	L0.1	0.21	0.1	L0.01
	% Difference	3.2	na	na	na	0	na	na
<i>Routine sample</i>	<i>11-Dec-13</i>	<i>L0.05</i>	<i>L0.02</i>		<i>L0.02</i>	<i>L0.02</i>	<i>L0.02</i>	<i>L0.01</i>
<i>Maxxam Split</i>	<i>11-Dec-13</i>	<i>L0.1</i>		<i>L0.1</i>	<i>L0.1</i>	<i>L0.1</i>	<i>L0.05</i>	<i>L0.01</i>
	% Difference	<i>na</i>	<i>na</i>	<i>na</i>	<i>na</i>	<i>na</i>	<i>na</i>	<i>na</i>
Blank	22-Mar-11	L0.05	L0.07		L0.01	L0.01	L0.01	L0.01
Blank	1-Jun-11	L0.03	L0.01		L0.01	L0.01	L0.01	L0.01
Blank	23-Feb-12	L0.05	L0.02		L0.02	L0.02	L0.02	L0.01
Trip blank	1-Jun-11	L0.03	L0.01		L0.01	L0.01	L0.01	L0.01
Trip blank	23-Feb-12	L0.05	L0.00002		L0.02	L0.02	L0.02	L0.01

Table 6 Continued

Comment	Date	Dibenzo furan	Carbazole	Methyl Anthracenes	Benzo(a) Pyrene	Benzo (b or k) Fluoranthene	Benzo(a) Anthracene	Penta chloro phenol
Routine sample	22-Mar-11	L0.01	L0.01	L0.01	L0.01	L0.01	L0.01	L0.01
Trip. split rep 2	22-Mar-11	L0.01	L0.01	L0.01	L0.01	L0.01	L0.01	L0.01
Trip. split rep 3	22-Mar-11	L0.01	L0.01	L0.01	L0.01	L0.01	L0.01	L0.01
	% Difference	na	na	na	na	na	na	na
Routine sample	1-Jun-11	L0.01	L0.01	L0.01	L0.01	L0.01	L0.01	L0.01
Trip. split rep 2	1-Jun-11	L0.01	L0.01	L0.01	L0.01	L0.01	L0.01	L0.01
	% Difference	na	na	na	na	na	na	na
Trip. split rep 3	1-Jun-11	0.01	L0.01	L0.01	L0.01	L0.01	L0.01	L0.01
	% Difference	na	na	na	na	na	na	na
Split sample	1-Jun-11				L0.01		L0.01	
Routine sample	17-Oct-12	0.02	0.03	L0.02	L0.01	L0.01	L0.01	L0.01
Split sample	17-Oct-12				L0.01		L0.01	
	% Difference	na	na	na	na	na	na	na
Routine sample	8-Nov-12	0.04	0.05	L0.02	L0.01	L0.01	L0.01	L0.01
Split sample	8-Nov-12				L0.01		L0.01	
	% Difference	na	na	na	na	na	na	na
Routine sample	10-Dec-12	0.02	L0.02	L0.02	L0.01	L0.01	L0.01	L0.01
Split sample	10-Dec-12				L0.01		L0.01	
	% Difference	na	na	na	na	na	na	na
Routine sample	11-Dec-13	0.1	0.06	L0.02	L0.01	L0.01	L0.01	L0.01
Maxxam split	11-Dec-13				L0.0075	L0.0085	L0.0085	L0.1
	% Difference	na	na	na	na	na	na	na
<i>Routine sample</i>	<i>11-Dec-13</i>	<i>L0.02</i>	<i>L0.02</i>	<i>L0.02</i>	<i>L0.01</i>	<i>L0.01</i>	<i>L0.01</i>	<i>L0.01</i>
<i>Maxxam split</i>	<i>11-Dec-13</i>				<i>L0.0075</i>	<i>L0.0085</i>	<i>L0.0085</i>	<i>L0.1</i>
	% Difference	na	na	na	na	na	na	na
Blank	22-Mar-11	L0.01	L0.01	L0.01	L0.01	L0.01	L0.01	L0.01
Blank	1-Jun-11	L0.01	L0.01	L0.01	L0.01	L0.01	L0.01	L0.01
Blank	23-Feb-12	L0.02	L0.02	L0.02	L0.01	L0.01	L0.01	
Trip blank	1-Jun-11	L0.01	L0.01	L0.01	L0.01	L0.01	L0.01	L0.01
Trip blank	23-Feb-12	L0.02	L0.02	L0.00002	L0.01	L0.01	L0.01	

Note: Italics indicates a Left Bank Sample

Definition of Comments: Routine sample – river water sample collected during routine sampling; Trip. split rep (2 and 3) – triplicate split of river water sampled in intermediate container, then poured in series of aliquots to three pre-cleaned bottles after agitation; Split sample - duplicate split of river water sampled in intermediate container, then poured to two pre-cleaned bottles after agitation; Blank – Type 1 water sample submitted to laboratory with other samples, with labelling similar to real sites. Trip blanks – Blank sample carried to field and opened briefly on site.

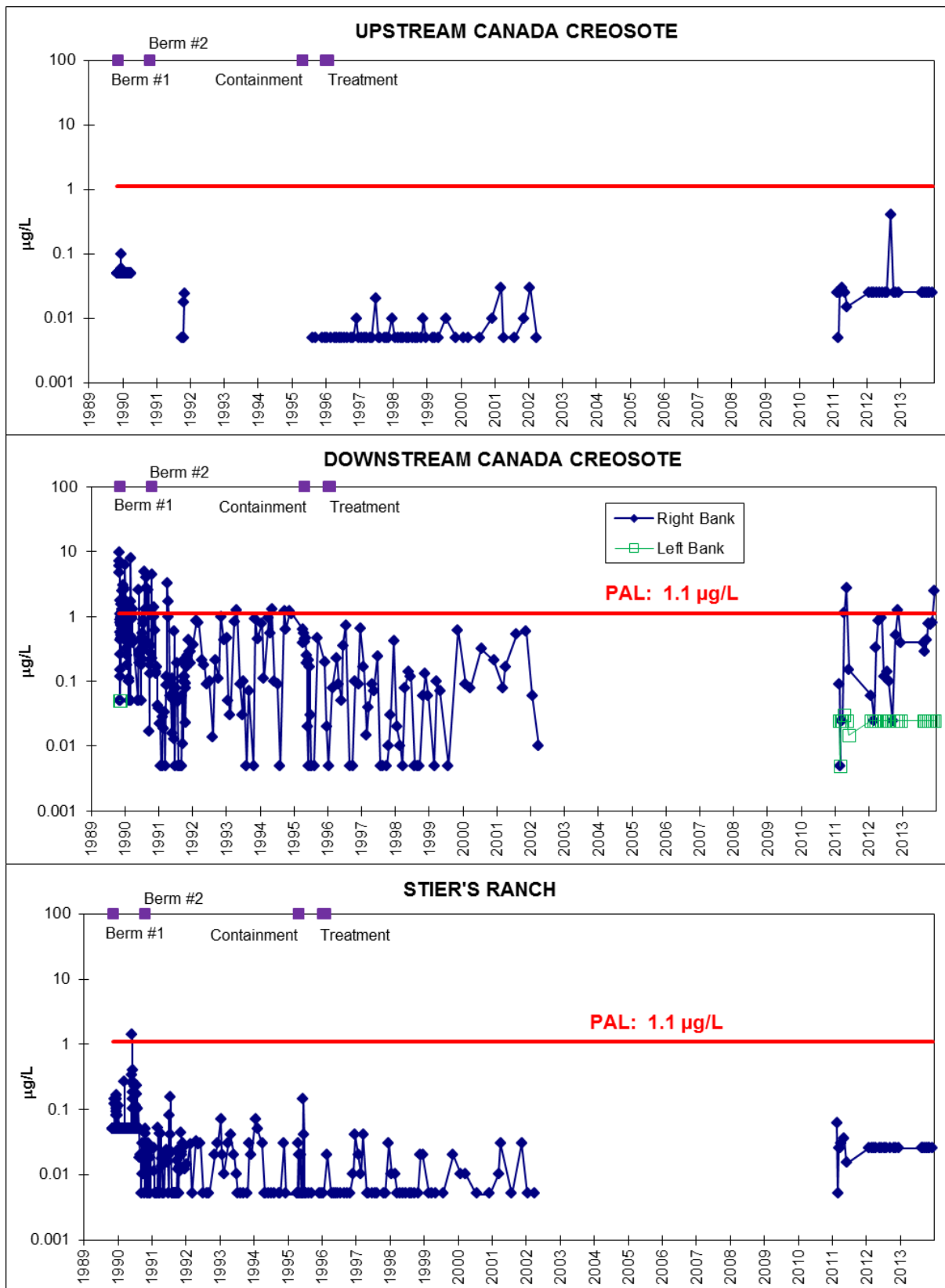


Figure 3 Concentrations of naphthalene at four sites on the Bow River, November 1989 to December 2013. Note: logarithmic scale used

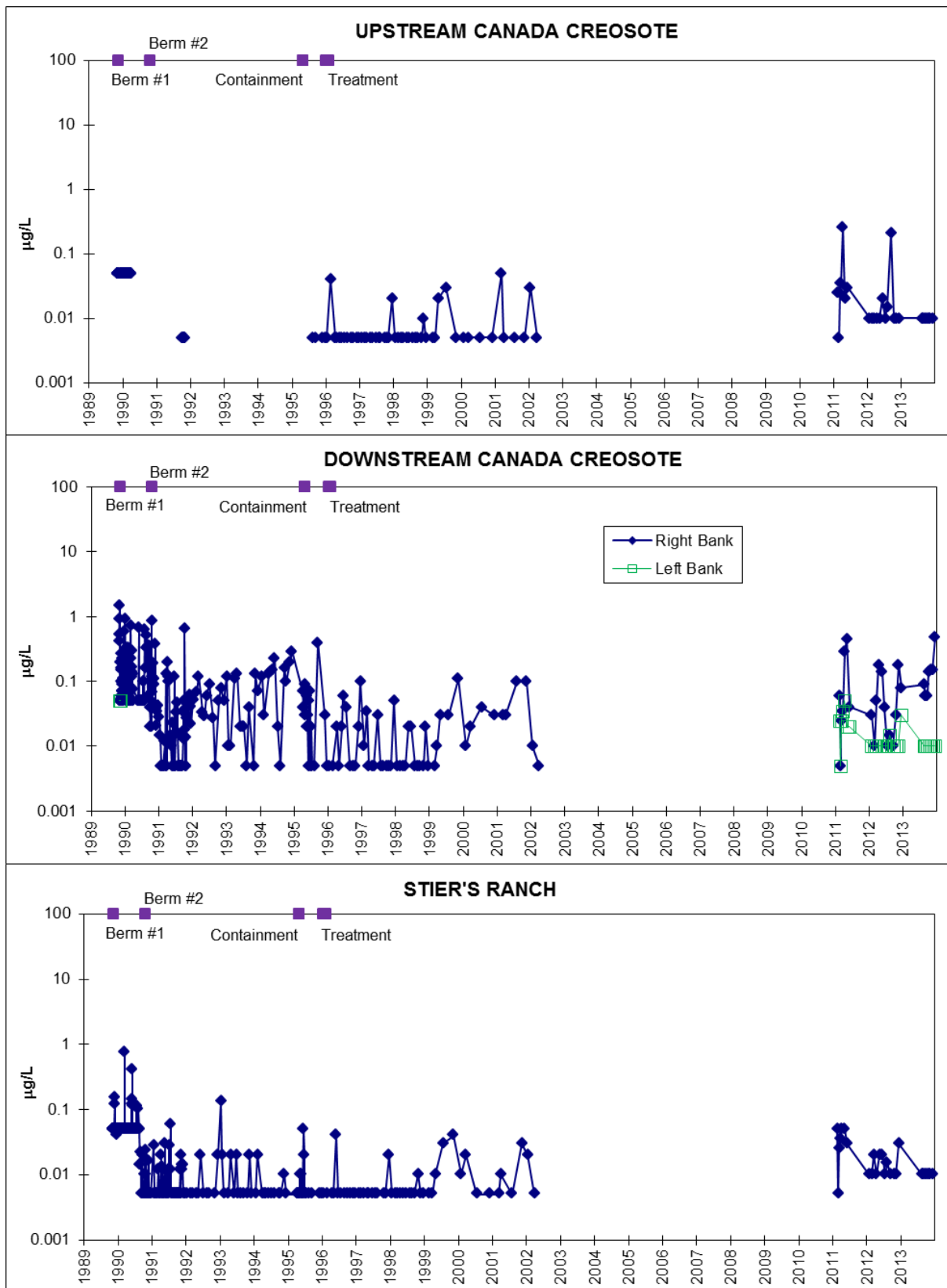


Figure 4 Concentrations of methyl naphthalene at four sites on the Bow River, November 1989 to December 2013. Note: logarithmic scale used

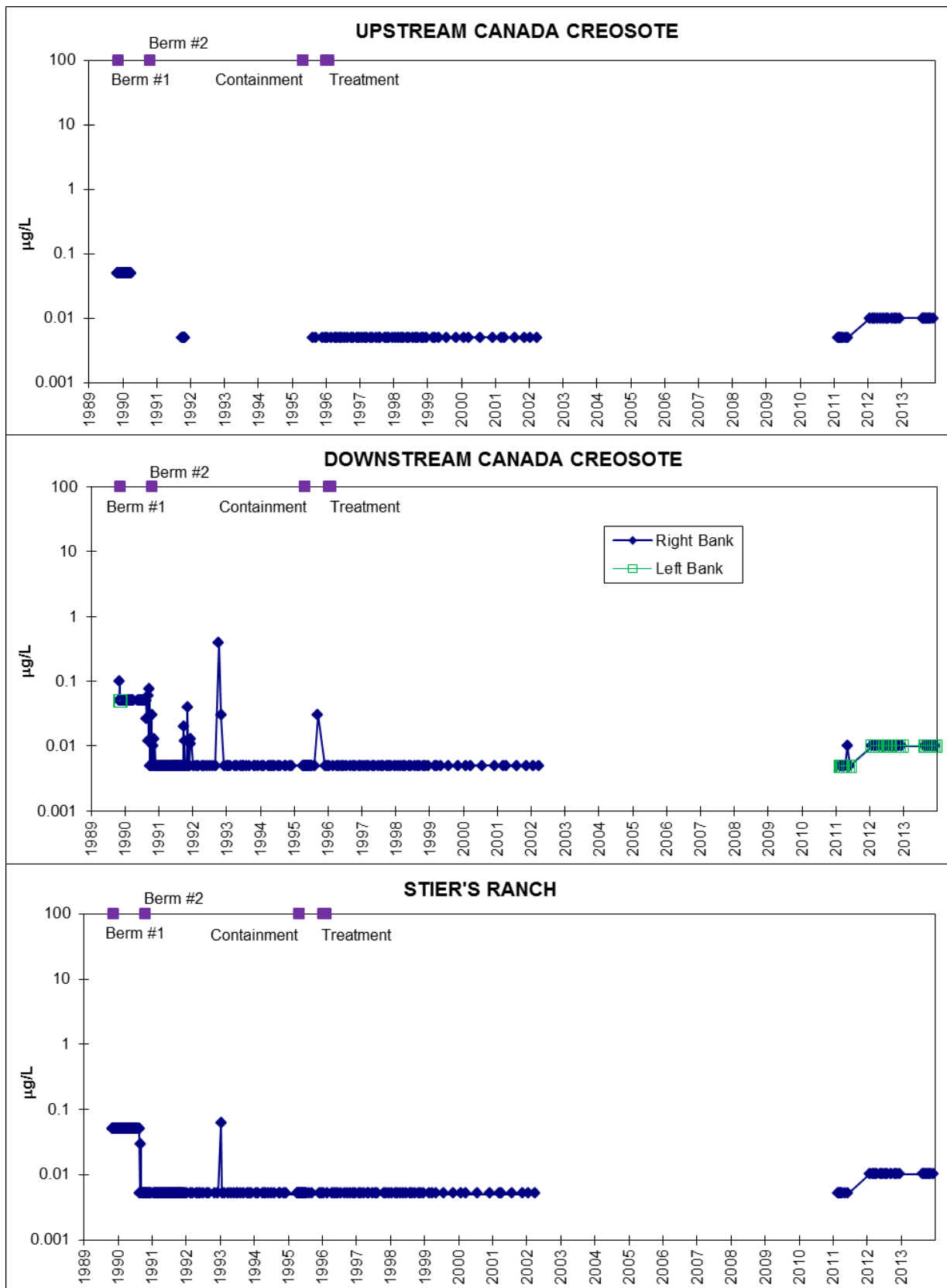


Figure 5 Concentrations of acenaphthylene at four sites on the Bow River, November 1989 to December 2013. Note: logarithmic scale used

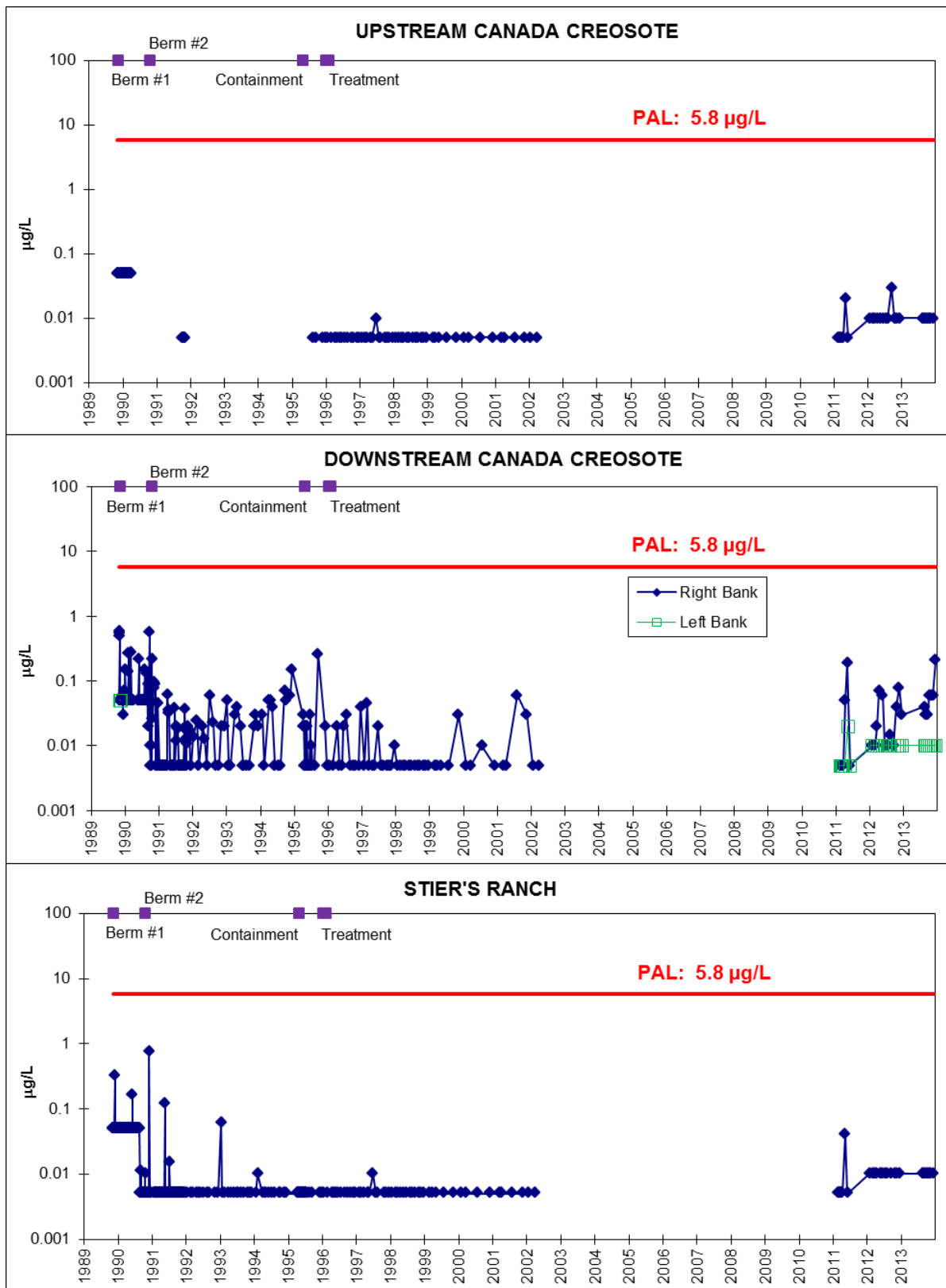


Figure 6 Concentrations of acenaphthene at four sites on the Bow River, November 1989 to December 2013. Note: logarithmic scale used

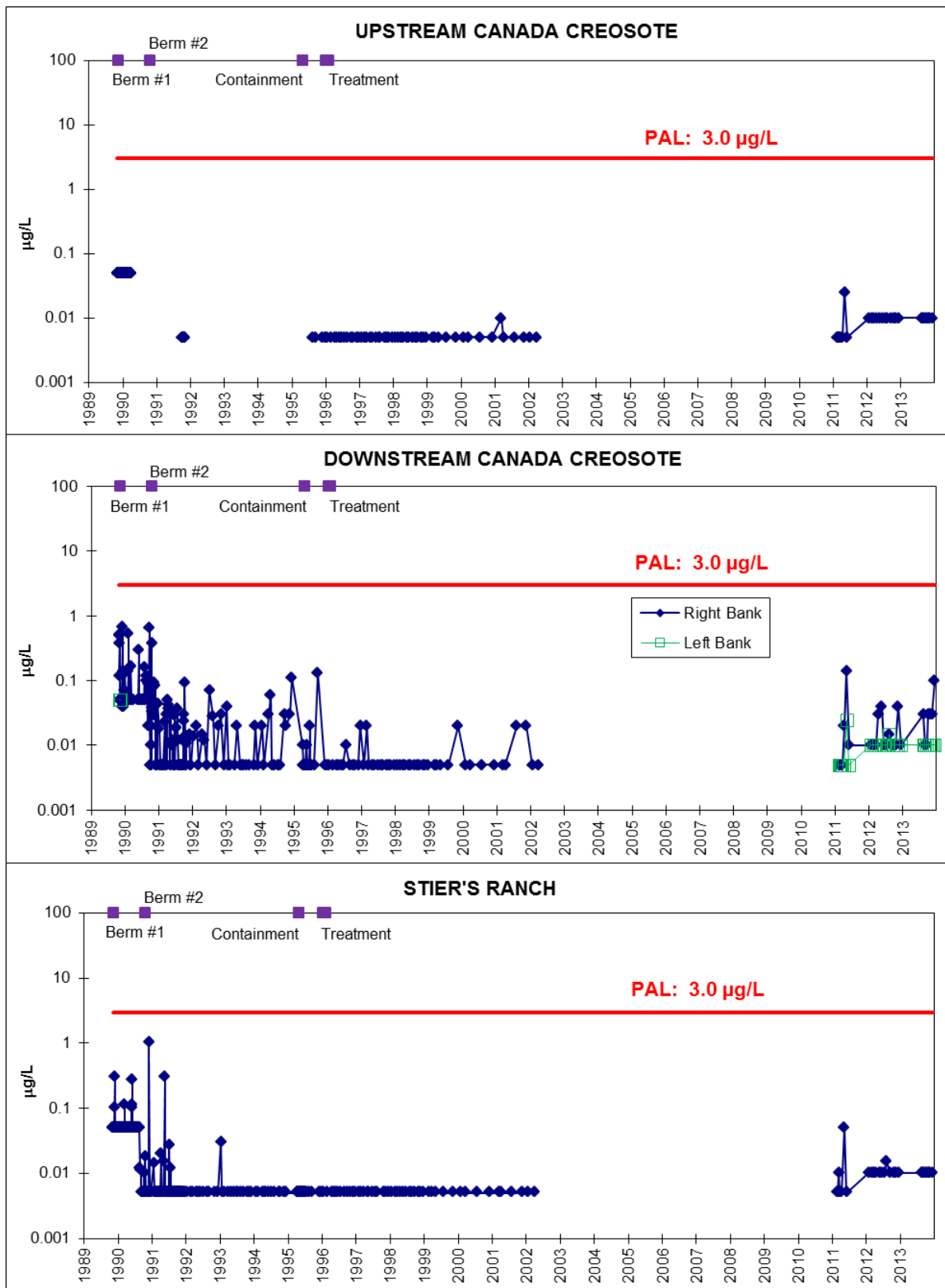


Figure 7 Concentrations of fluorene at four sites on the Bow River, November 1989 to December 2013. Note: logarithmic scale used

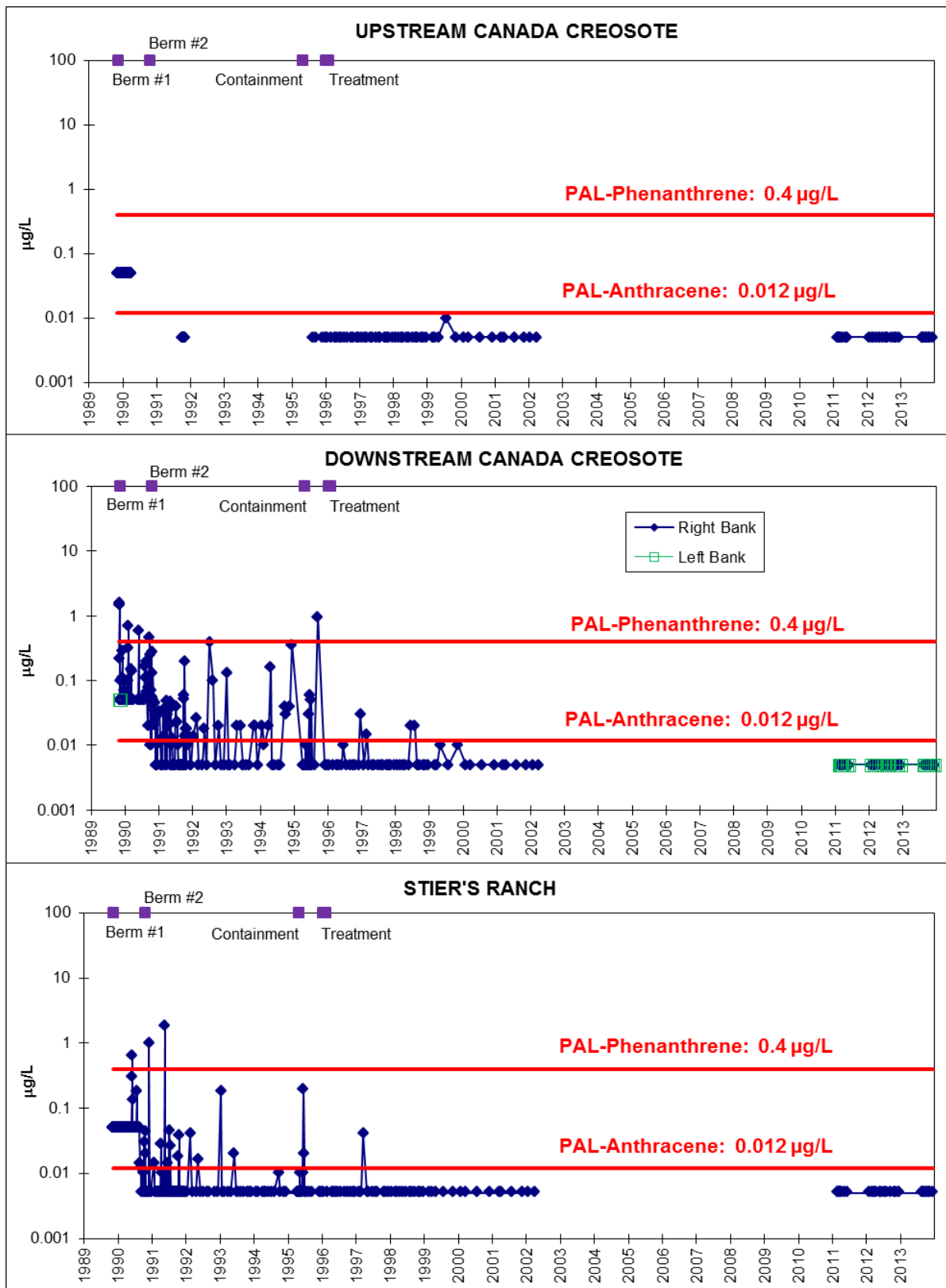


Figure 8 Concentrations of phenanthrene/anthracene at four sites on the Bow River, November 1989 to December 2013. Note: logarithmic scale used

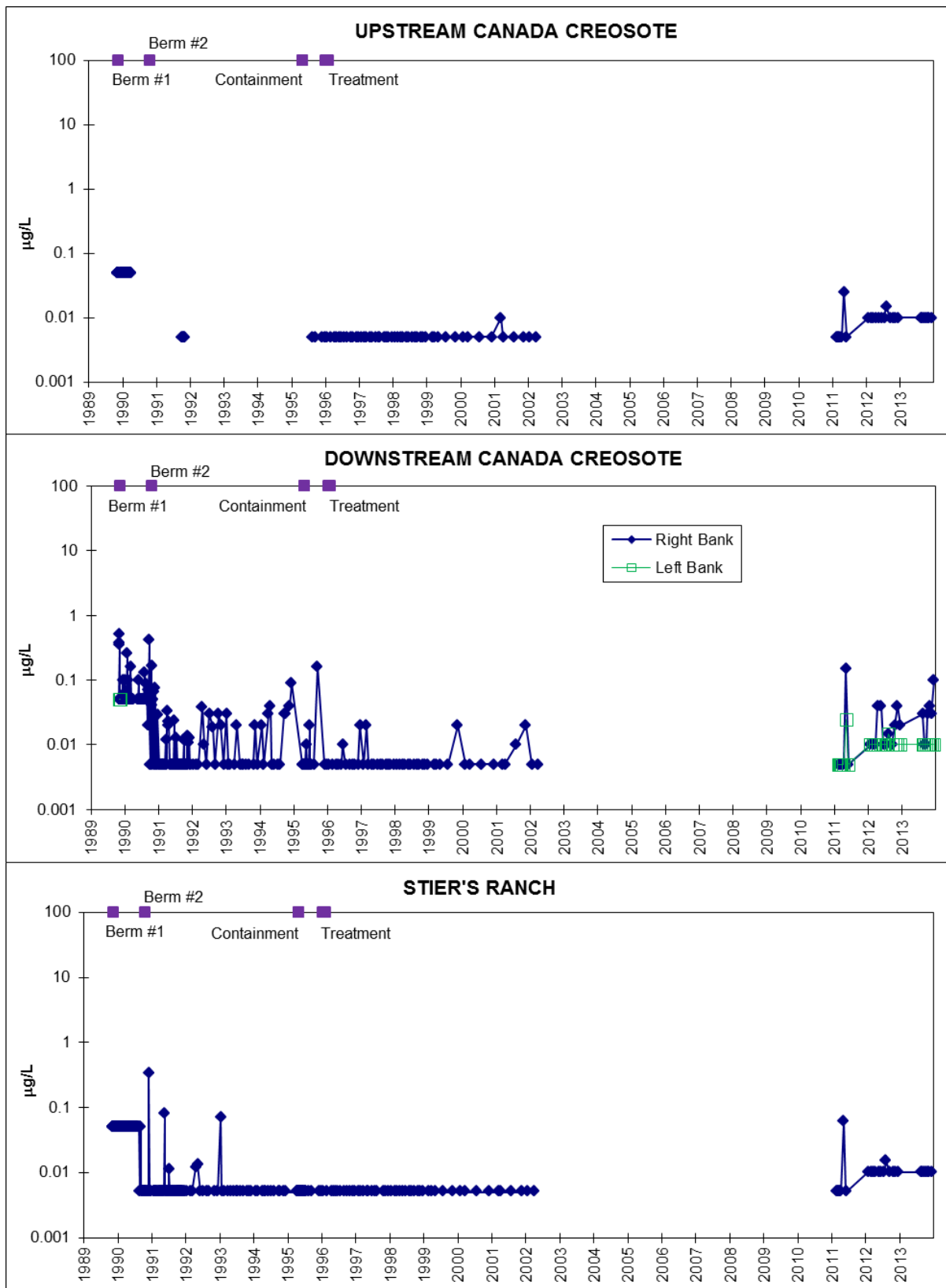


Figure 9 Concentrations of dibenzofuran at four sites on the Bow River, November 1989 to December 2013. Note: logarithmic scale used

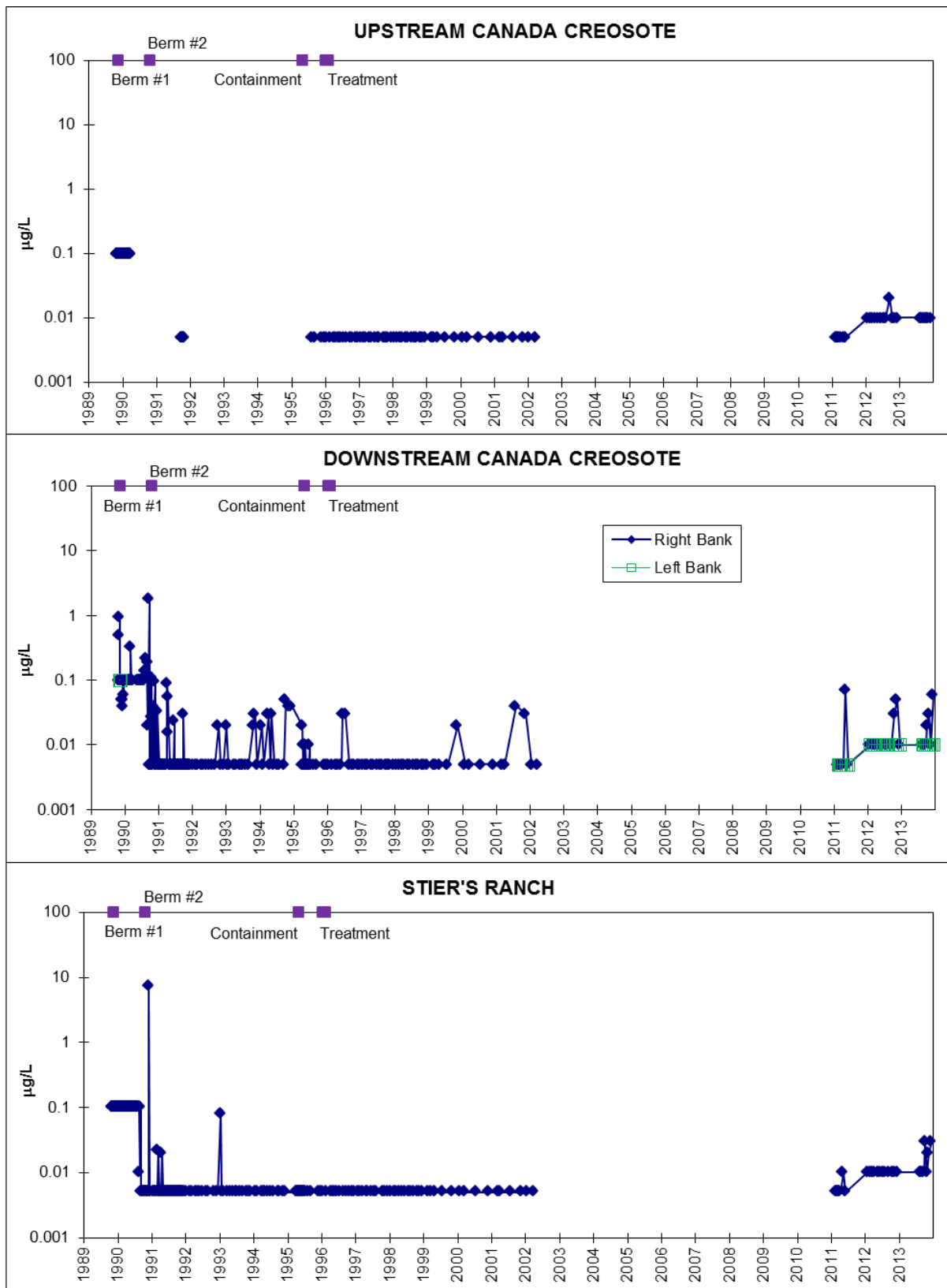


Figure 10 Concentrations of carbazole at four sites on the Bow River, November 1989 to December 2013. Note: logarithmic scale used

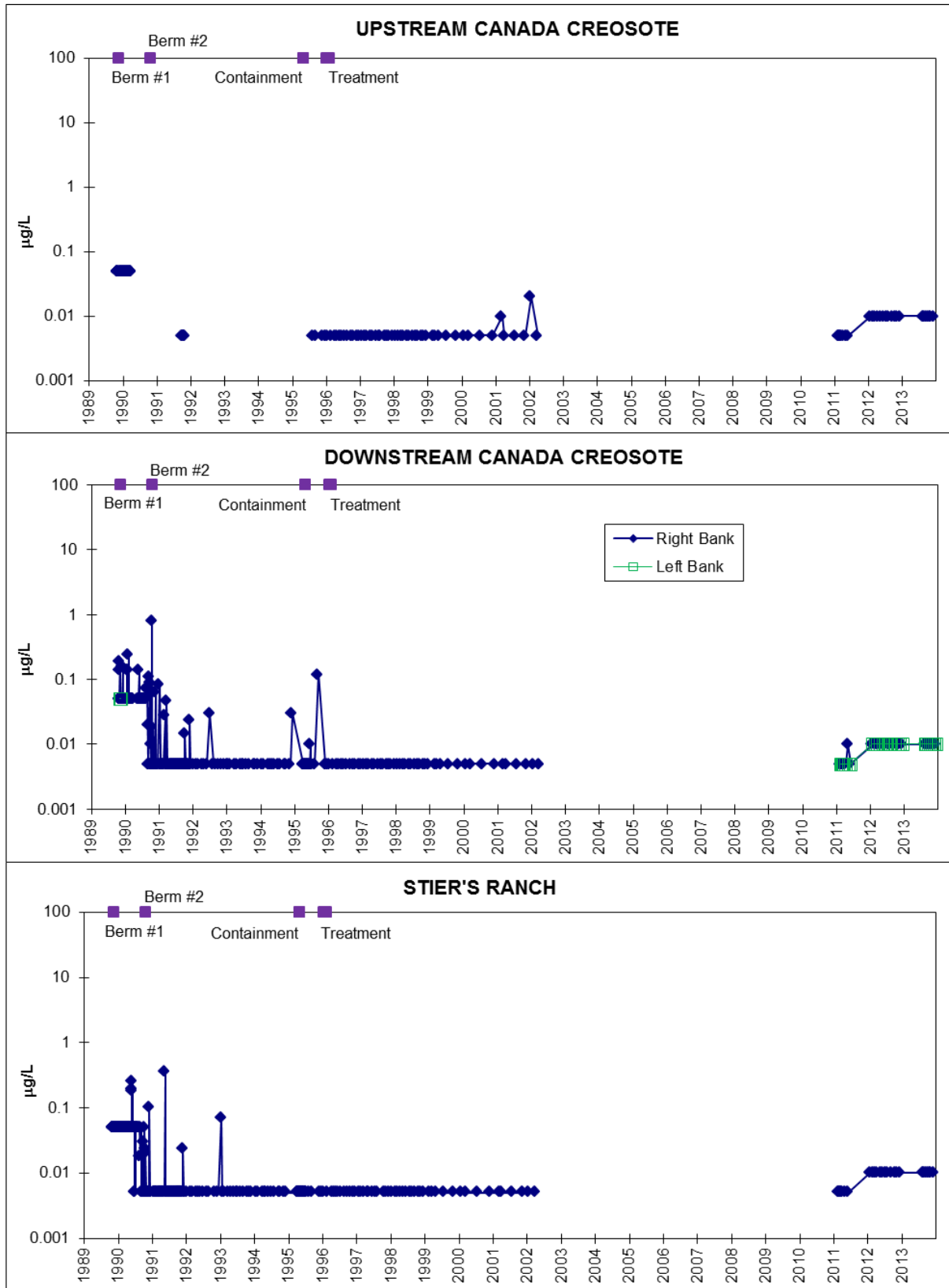


Figure 11 Concentrations of methylphenanthrene/anthracene at four sites on the Bow River, November 1989 to December 2013. Note: logarithmic scale used

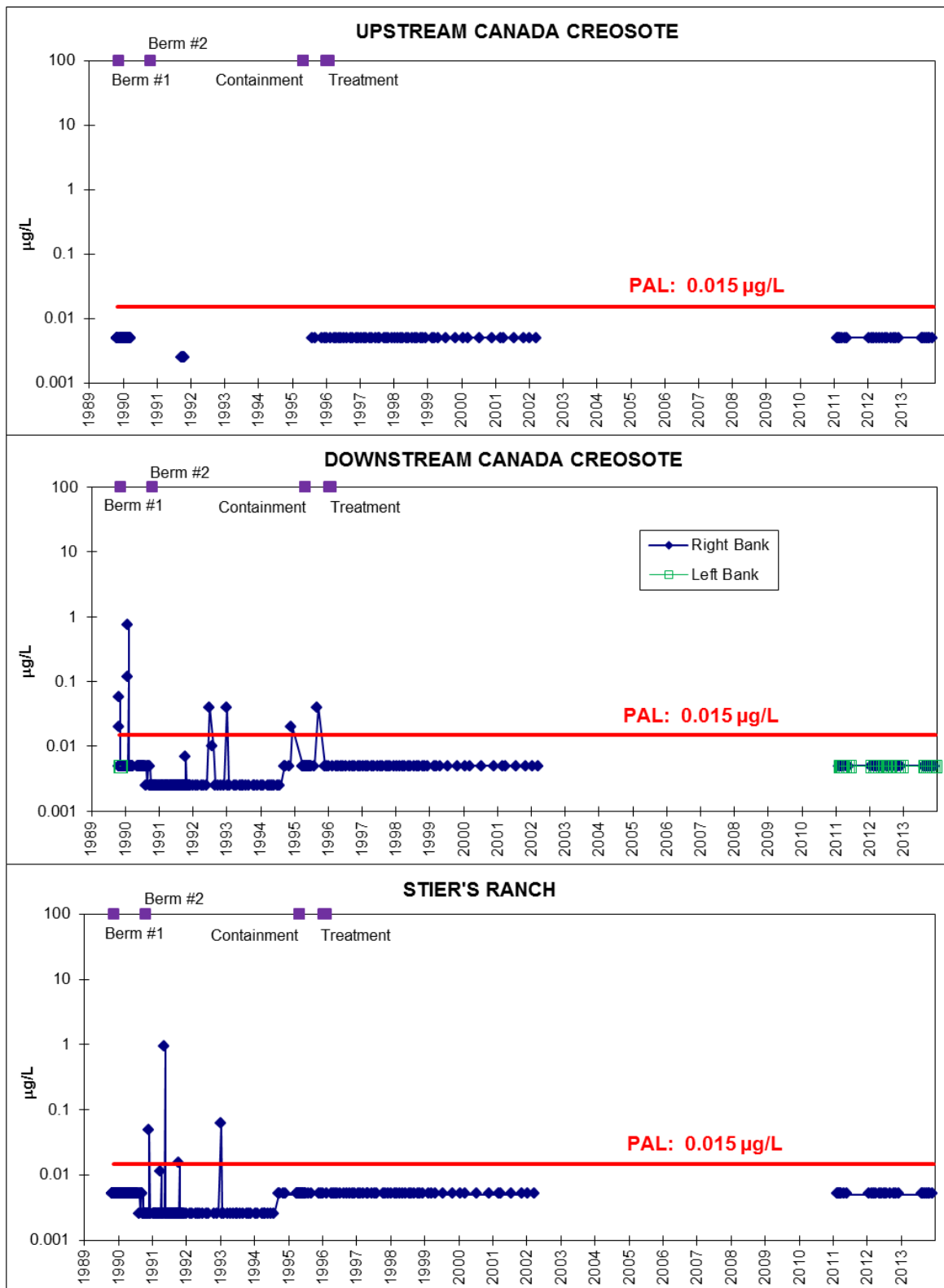


Figure 12 Concentrations of benzo(a)pyrene at four sites on the Bow River, November 1989 to December 2013. Note: logarithmic scale used

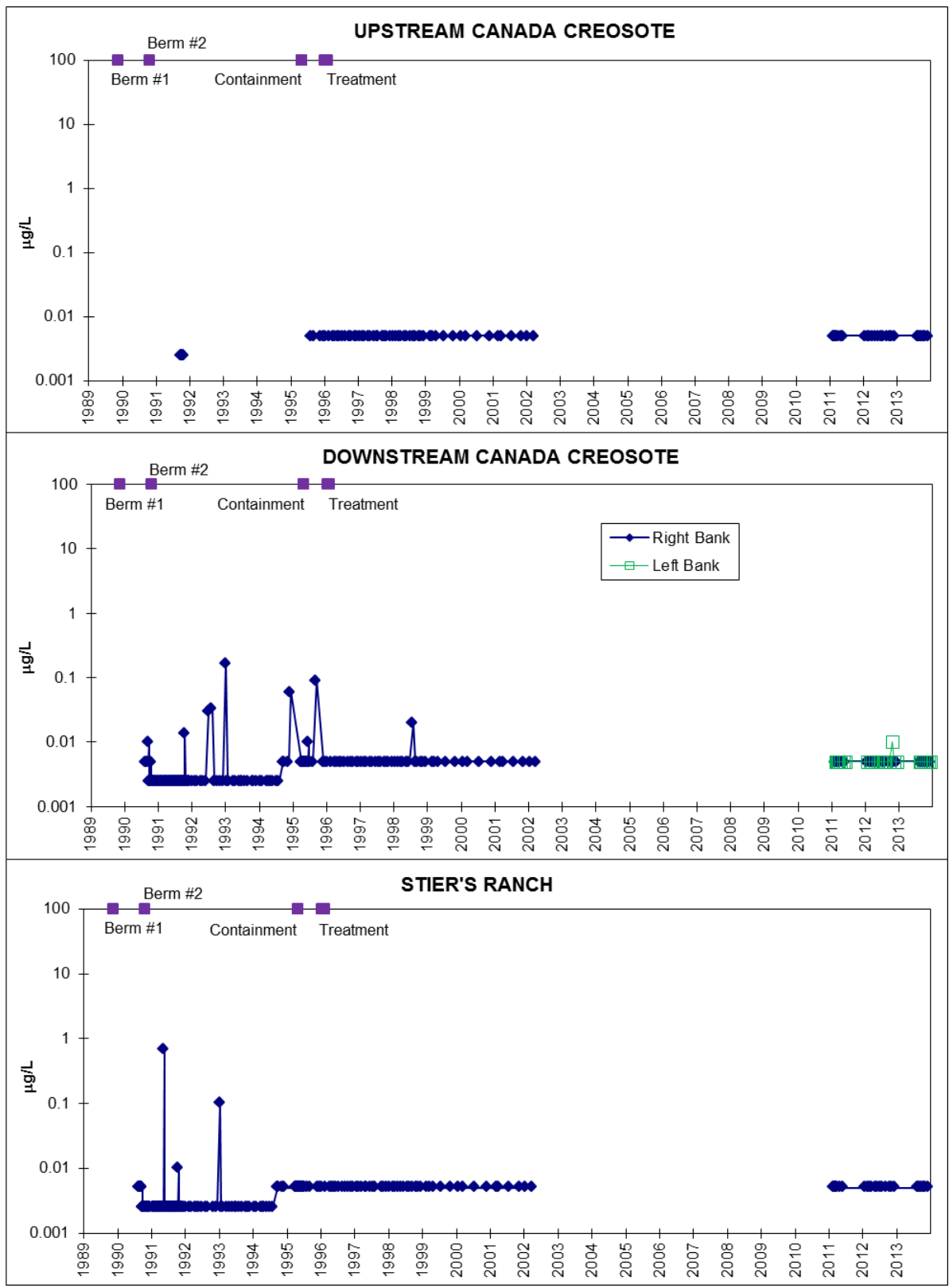


Figure 13 Concentrations of benzo(b or k)fluoranthene at four sites on the Bow River, November 1989 to December 2013. Note: logarithmic scale used

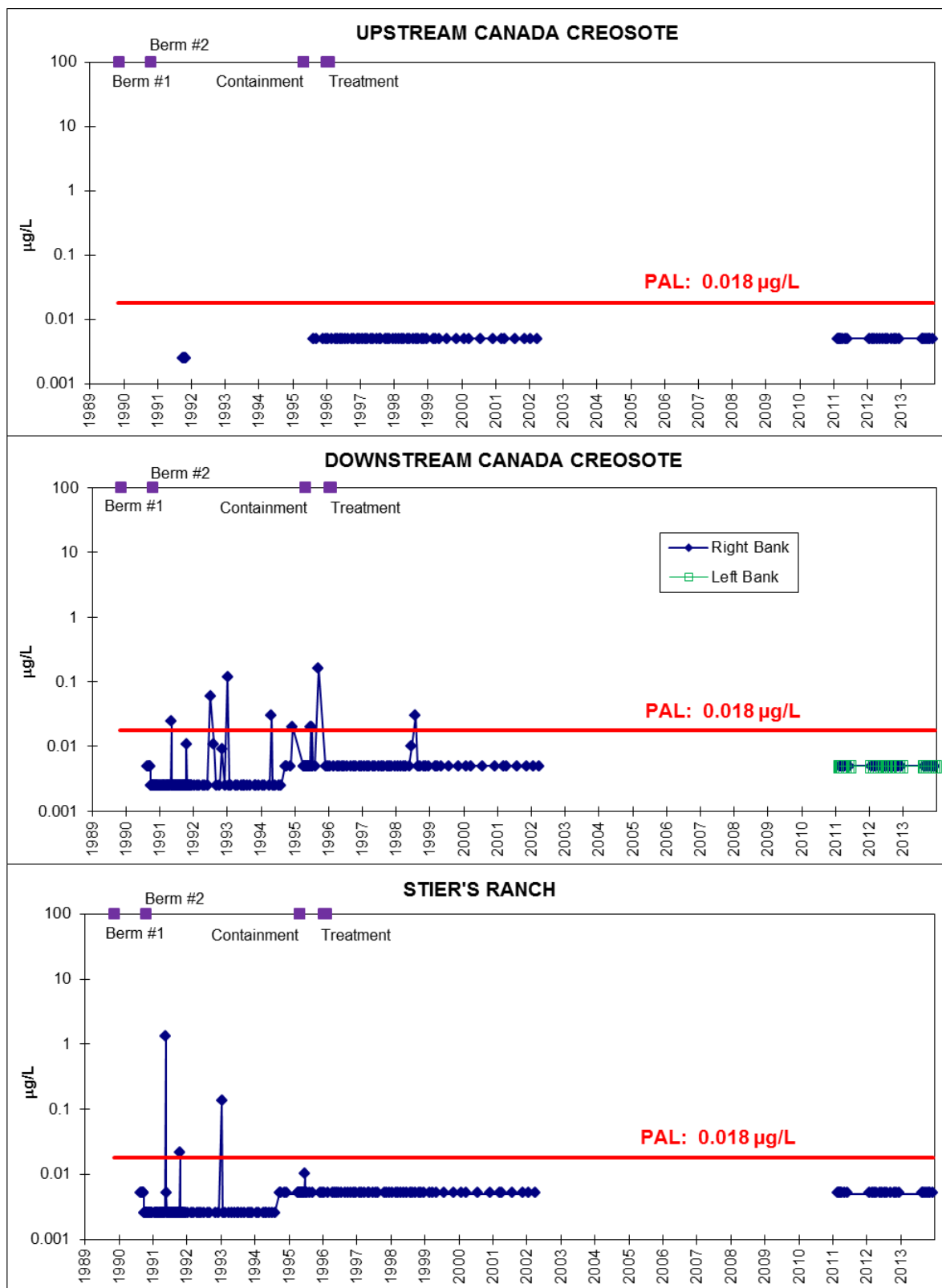


Figure 14 Concentrations of benzo(a)anthracene at four sites on the Bow River, November 1989 to December 2013. Note: logarithmic scale used

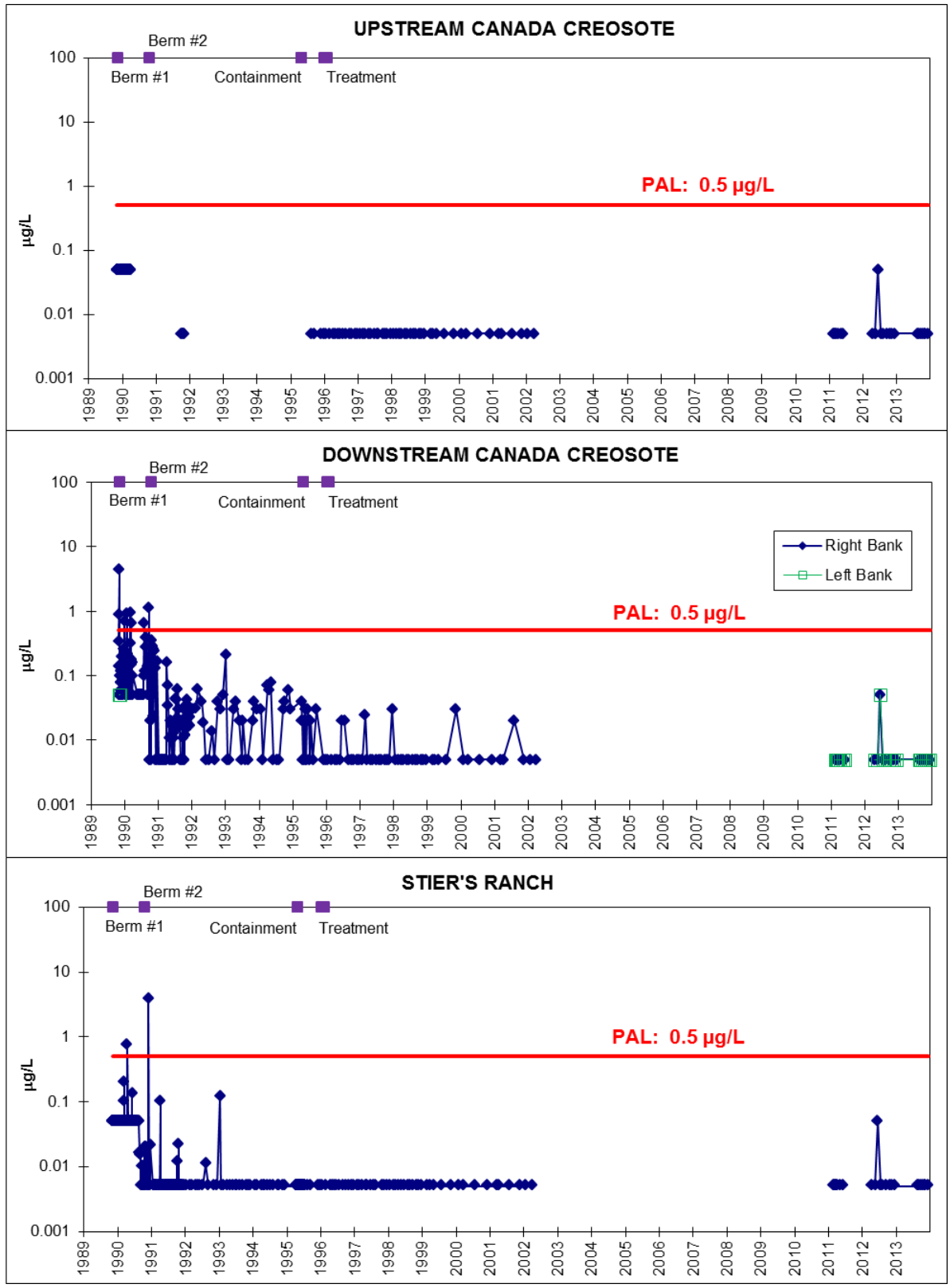


Figure 15 Concentrations of pentachlorophenol at four sites on the Bow River, November 1989 to December 2013. Note: logarithmic scale used

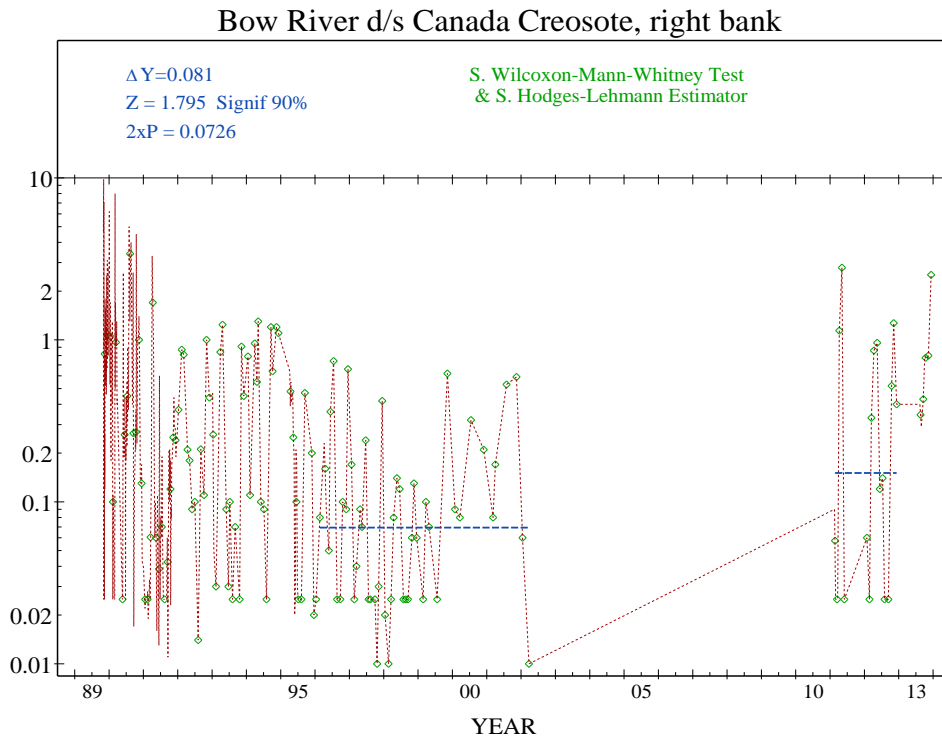


Figure 16 Significant increase in naphthalene along the right bank of the Bow River downstream from the Canada Creosote site in 2011-2012, compared to 1996-2002

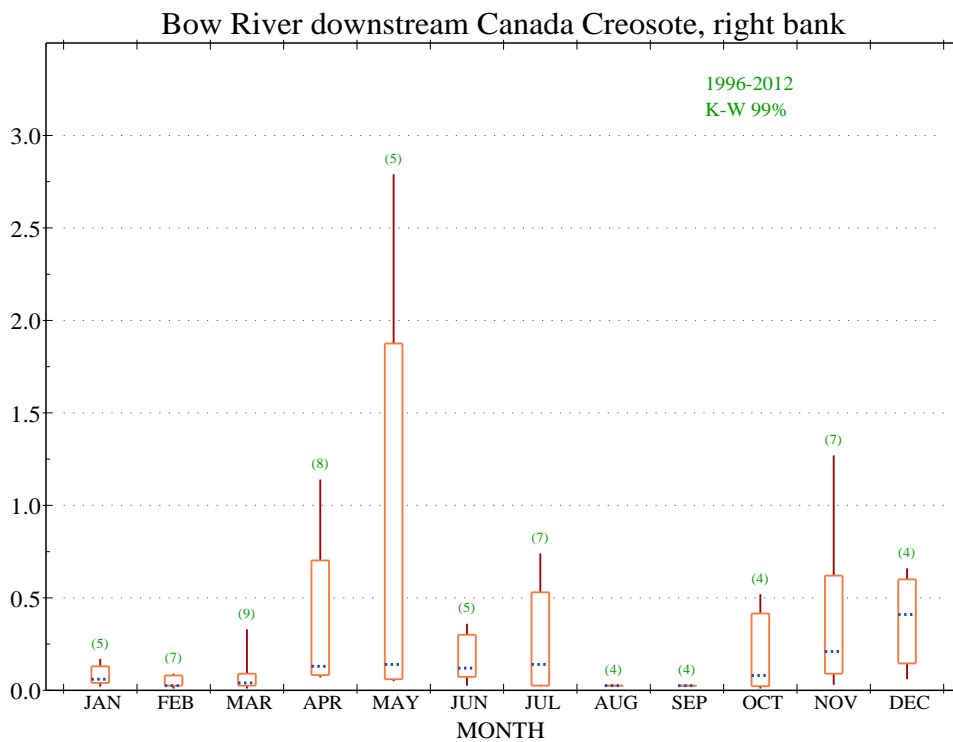


Figure 17 Statistically-significant seasonality for naphthalene along the right bank of the Bow River downstream from the Canada Creosote site, 1996-2012

The reason for higher levels of some of these compounds downstream from the Canada Creosote site in recent years is not known. However, the effects seem localized as no significant change was detected further downstream at Stier's Ranch. One possible explanation could be release of more soluble PAH such as naphthalene from the pool of DNAPL that remained in the river bed after site containment, associated with higher flows in recent years (Figure 2), rather than leakage from the Canada Creosote site. If the site was leaking, various carcinogens and PCP should also be detected.

Occasional detections of naphthalene and a few other PAH at low levels upstream from the site (Table 3, Figure 3-15) may reflect the contribution of these compounds from upstream sources, either from urban or rural areas. PAH occur widely in the aquatic environment throughout the world, generally at low concentrations (CCME 1999). Some major sources in the aquatic environments include (in order) petroleum spillage, atmospheric deposition, wastewater, and surface land runoff (Eisler 1987, cited in Nagpal 1993). Contributions from all these sources may occur upstream from the Canada Creosote site.

There was no change over time in the concentration of more hazardous compounds such as PCP, and three carcinogens (benzo(a)pyrene, benzo(b or k)fluoranthene, benzo(a)anthracene), which remained at or below detection limits (Table 4, Figure 3-15). As explained later (Appendix II) apparent spikes in the concentration of PCP in Figure 15 in recent years were merely temporary increases in detection limits, rather than any change in contaminant movement from the Canada Creosote site. The three carcinogens were below detection limits at all sites since 1999, except for a single benzo(b or k)fluoranthene value that was at the detection limit of 0.01 µg/L downstream from the Canada Creosote site, on the left bank, on October 17, 2012 (Figure 13). PCP and these three carcinogens have never been detected in 16 years of monitoring upstream from the Canada Creosote site, which suggests these compounds were mainly associated with DNAPL from the contaminated site (Figure 12-15). Since all these compounds remain at or below detection limits, this suggests that the containment system continues to effectively prevent their movement from the site.

Most compounds were detected only along the right bank immediately downstream from the Canada Creosote site (Table 3), and only two were detected at the left bank site. Only methylnaphthalene (twice) and benzo(b or k)fluoranthene (once) were detected at very low levels at the left bank site downstream from the Canada Creosote site (Table 3, Figure 4 and 13). Although a variety of compounds including PCP and the carcinogens were detected prior to site containment at Stier's Ranch, few compounds aside from naphthalene and methylnaphthalene were detected at this site in recent years (Figure 3-15).

Although early work at the site found that DNAPL had migrated across the river bed, these sampling results provide no evidence that the target compounds occur regularly in river water along the left bank. Contaminant movement from the remaining pool of DNAPL in the river bed close to the right bank remains the likely source of compounds detected at the right bank site downstream from the Canada Creosote site.

Only naphthalene, dimethylnaphthalene, and acenaphthene exhibited statistically-significant seasonal variation at any site, mostly at the site immediately downstream Canada Creosote

(Appendix I, Table 1 and 2). Acenaphthene only displayed significant seasonality in the shorter dataset (2011-2013) and only naphthalene displayed significant seasonality upstream from the Canada Creosote site in the longer dataset (Appendix I, Table 1, 1996-2012). Dibenzofuran also exhibited seasonal variation in concentration, but this change was not statistically-significant. (Appendix I, Table 1). Figure 17 presents significant seasonality for naphthalene, with highest levels in May and November.

Factors that vary over the year such as higher flow through the river bed, scouring, volatility, and mobility in the aquatic environment may account for seasonal variation in these compounds. PAH tend to be hydrophobic, and readily adsorb to sediments in aquatic environments (CCME 1999). However, of the target PAH included in this study, naphthalene has the lowest molecular weight and octanol-water partitioning coefficient (K_{ow}) (Nagpal 1993), and is the most volatile and soluble in water. These factors likely explain some of the strong seasonality that is exhibited by naphthalene in the Bow River. This seasonality was a consideration in the selection of statistical procedure (Section 2.3), and from a monitoring perspective. Concentrations were generally low in the middle of winter (January, February) late summer (August, September) and monitoring then would be less likely to detect naphthalene (Figure 17).

None of the total hydrocarbons listed by carbon chain length in Section 2.2, or BTEX, were detected in any sample collected in 2011. Accordingly these compounds were not considered further in this study. Some BTEX monitoring was done before site containment in 1989-1996. However, none of these results were present in the download from the WDS database, and none of the more recent results provide evidence that BTEX or these hydrocarbons were contributed to the Bow River from the Canada Creosote site in recent years.

3.2 Water Quality Evaluation

Four of 26 naphthalene samples exceeded the CCME PAL guideline during 2011 to 2013 at the site immediately downstream from the Canada Creosote site, but no other sample has exceeded any PAH or PCP guideline at any other sampling location since containment in 1996 aside from a single benzo(a)anthracene sample in 1998 (Figure 3-15). The single benzo(a)anthracene value over the guideline in 1998 may reflect scouring of the river bed, and release of sediments with attached benzo(a)anthracene. However, various PAH (including naphthalene, phenanthrene/anthracene, benzo(a)pyrene, benzo(a)anthracene) and PCP frequently exceeded their respective CCME PAL guidelines before containment (Figure 3-15).

Aside from naphthalene, these results suggest that during monitoring all the target compounds remained well below levels that are likely to cause adverse aquatic effects since site containment. It is important to note that all three carcinogenic forms of PAH monitored in this study have remained below detection limits in recent years aside from a single benzo(b or k)fluoranthene measurement. Accordingly these results suggest that, in contrast to naphthalene, these most potentially hazardous compounds remained quite low since the installation of the containment system.

The interim CCME PAL guideline for naphthalene of 1.1 $\mu\text{g/L}$ is based on multiplying the lowest observed effects level (LOEL) of 11 $\mu\text{g/L}$ by a safety factor of 0.1 (CCME 1999). The LOEL

level was based on a variety of aquatic organisms that are common in the Bow River. Accordingly, although this interim guideline has been exceeded, the naphthalene values over the guideline (all $\leq 2.79 \mu\text{g/L}$) were all well below the LOEL level, and harm to aquatic life seems unlikely. Furthermore, this guideline for naphthalene was not exceeded at Stier's Ranch, so effects appear to be localized. However, the recent exceedance of the naphthalene guideline below the Canada Creosote site is a potential concern, and continued monitoring and evaluation is warranted to confirm this compound is being released from DNAPL in the river bed and does not represent leakage from the site. Since PCP is a good indicator for contaminant flux from the Canada Creosote site, it should be routinely included in all sampling along with the target PAH.

3.3 Flood Impact on Contaminant Movement

The flood of 2013 was clearly the largest in recent decades. Preliminary flows at WSC Hydrometric Station 05BH004 exceeded $1000 \text{ m}^3/\text{s}$ over three days starting on June 21, 2013, and peaked at $1630 \text{ m}^3/\text{s}$ (Figure 2), well above the bed mobility threshold and other flood levels of this 25 year period of record. However, this bed mobility threshold was also exceeded in four other years during the 25 year period (20% of years, overall) in Figure 2. Furthermore, peak flows were above average during the most recent monitoring from 2011 to 2013, and the bed mobility threshold was also just exceeded in 2012. The 2013 record also contains some unusually high early winter and fall flows, perhaps indicative of some inaccuracies in the preliminary flows for 2013. The 2013 preliminary flows were the only record that was available in time for this study, and are subject to change by WSC. Records for other years are approved final flows.

It seems likely that some bed movement occurred at least in 1990, 2005, and 2013, when the highest flows occurred, greatly exceeding the bed mobility threshold. During the 2013 flood, flows were large enough to cause appreciable bed movement just downstream from the Centre Street Bridge, between the hydrometric station and Canada Creosote site in Figure 1. There is now a major gravel bar along the north shore of the Bow River just downstream from this bridge, where none occurred before the flood. Major movement of the river bed at the Canada Creosote site would likely have caused some release of contaminants, since a pool of DNAPL remained in the river bed after containment of the site. It was decided at the time that excavation and removal of this pool of DNAPL would have been too risky and expensive. However, since there has been no sampling during any of the recent floods (since site containment), the magnitude and duration of any contaminant release is unknown.

There were no statistically-significant changes in concentration at any site before and after the 2013 flood (2011-2013, Table 5). This suggests that there was no change in contaminant levels in the Bow River after the flood had subsided.

Sampling after the 2013 flood occurred on August 13, 2013, over seven weeks after the start of the flood. On August 13, the preliminary mean daily flow had declined to $154 \text{ m}^3/\text{s}$, or less than a tenth of the peak flood flow that year.

4.0 CONCLUSIONS

1. All carcinogenic PAH and PCP have remained at or below detection limits downstream from the Canada Creosote site since 1998, but were found previously. Since these compounds have never been detected in 16 years of monitoring upstream from the Canada Creosote site, they were likely associated with DNAPL from the contaminated site. This suggests that the containment system, which became fully operational in 1996, continues to effectively prevent movement of the most harmful contaminants from this site.
2. Concentrations of naphthalene and methylnaphthalene were significantly higher in recent years (2011, 2012) downstream from the Canada Creosote site, compared to the period immediately after site containment (1996-2002). One possible explanation for this recent increase in naphthalene levels immediately below the site could be release of more soluble PAH from the pool of DNAPL that remained in the river bed after site containment, associated with higher flows in recent years.
3. These sampling results provide no evidence that the target compounds occur regularly in river water along the left bank. Contaminant movement from the remaining pool of DNAPL in the river bed close to the right bank remains the likely source of compounds detected on that side of the river downstream from the Canada Creosote site.
4. Although the interim guideline for naphthalene has been exceeded immediately downstream from the Canada Creosote site and concentrations have increased in recent years, naphthalene has remained well below the lowest observed aquatic effects level determined by CCME. Accordingly, harm to aquatic life seems unlikely, and effects appear to be localized based on the available monitoring.
5. Aside from naphthalene, these results suggest that during monitoring all the target compounds remained well below levels that are likely to cause adverse aquatic effects since site containment.
6. It seems likely that bed movement has occurred in at least 1990, 2005, and 2013, when flows greatly exceeded the bed mobility threshold. There were no statistically-significant changes in concentration at any site before and after the 2013 flood, which suggests that there was no change in contaminant levels in the Bow River after the flood had subsided.

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Appendix I, Table 1 Summary of significant seasonality in PAH and PCP ($\mu\text{g/L}$) prior to the 2013 flood at Canada Creosote Project sites (1996-2012)

Constituents	Bow River u/s Canada Creosote	Bow River d/s Canada Creosote, Right Bank ^c	Bow River at Stier's Ranch
Naphthalene	* $P=0.018^a$	* $P=0.003^a$	ns
Methylnaphthalene	ns	ns	ns
Dimethylnaphthalene	ns	* $P=0.043^a$	ns
Acenaphthylene	ns	ns	ns
Acenaphthene	ns	ns	ns
Fluorene	ns	ns	ns
Phenanthrene/Anthracene	ns	ns	ns
Dibenzofuran	ns	ns, $P=0.053^a$	ns
Carbazole	ns	ns	ns
Methylphenanthrene/Anthracene	ns	ns	ns
Benzo(a)Pyrene	ns	ns	ns
Benzo(b or k)Fluoranthene	ns	ns	ns
Benzo(a)Anthracene	ns	ns	ns
Pentachlorophenol	ns	ns	ns

^a Kruskal-Wallis test for seasonality 1996-2012

^b Abbreviations: * statistically-significant seasonality; ns: no significant seasonality ($P>0.05$)

^c Facing downstream

Appendix I, Table 2 Summary of significant seasonality in PAH and PCP after the 2013 flood at Canada Creosote Project sites during 2011-2013

Constituents	Bow River u/s Canada Creosote	Bow River d/s Canada Creosote, Right Bank ^c	Bow River d/s Canada Creosote, Left Bank ^c	Bow River at Stier's Ranch
Naphthalene	ns	* $P=0.048^a$	ns	ns
Methylnaphthalene	ns	ns	ns	ns
Acenaphthylene	ns	ns	ns	ns
Acenaphthene	ns	* $P=0.036^a$	ns	ns
Fluorene	ns	ns, $P=0.090^a$	ns	ns
Phenanthrene/Anthracene	ns	ns	ns	ns
Dibenzofuran	ns	ns, $P=0.051^a$	ns	ns
Carbazole	ns	ns	ns	ns
Methylphenanthrene/Anthracene	ns	ns	ns	ns
Benzo(a)Pyrene	ns	ns	ns	ns
Benzo(b or k)Fluoranthene	ns	ns	ns	ns
Benzo(a)Anthracene	ns	ns	ns	ns
Pentachlorophenol	ns	ns	ns	ns

^a Kruskal-Wallis test for seasonality 2011-2013

^b Abbreviations: * statistically-significant seasonality; ns: no significant seasonality ($P>0.05$)

^c Facing downstream

Appendix II

A1.0 Analysis and QAQC

A1.1 Sample and Data Analysis Methods

The frequent changes in detection limits in recent years that are summarized in Table 2 created various challenges in data analysis, graphics, and interpretation of results for this project. To put these frequent changes in detection limits in historical context, there were 11 different changes in detection limits for naphthalene in the three years from 2011 to 2013, compared to four over the previous 14 years of sample analysis by ALS (sometimes daily) during 1989 to 2002.

These fluctuating detection limits caused problems with graphics and statistical analysis. Some of the apparent fluctuation in PAH and PCP in Figures 3-15 in recent years were actually caused by variation in detection limits (Table 2) rather than any real change in concentration. For example, distinctive spikes in PCP occurred in results for 2012 that are plotted in Figure 15. Samples collected June 13, 2012 were reported by ALS with a detection limit of 0.1 µg/L that day and half this detection limit (0.05) has been plotted, while other PCP samples collected during 2011-2013 had a much lower detection limit of 0.01 µg/L (Table 2).

Reasons provided by ALS for the unusual increases in the detection limits over time for organic compounds included: (1) Review of methodology can cause increases in detection limit to make it more defensible, (2) Sometimes they used a theoretical formula instead of deriving from existing detection limits, even if the methodology stayed the same, (3) Detection limits can be recalculated based on baseline noise, which is dependent on various factors (C. Chung, AESRD, pers. comm.).

These fluctuating detection limits were resolved by substituting values half the most frequently used higher detection limit. The practice of using the highest detection limit is not entirely satisfactory, as some values that were at trace levels with a very low detection limit are then below the adjusted higher detection limit. This practice also forces one to revert to the least sensitive measurements in the record. However, Helsel and Hirsch (2002) note that there is really no alternative for a water quality dataset with multiple detection limits.

Resolution of this issue is well outside the terms of reference for this project. AESRD should determine if commercial laboratories can consistently maintain some realistic detection limit for these target PAH and PCP, as laboratories do for most inorganic analysis and long-term pesticide analysis. Sometimes it is necessary to lower detection limits as methods improve. However it is very unusual for detection limits to fluctuate in both directions over a sampling program, over a relatively short period of time.

The statistical analysis procedure was enhanced compared to methods used in Sosiak (1999). In particular a more sensitive procedure was used to test for step trends, based on a procedure for nonseasonal datasets that was used in a previously published water quality study on the Bow River (Sosiak 2002). As mentioned earlier, this was done because the seasonal step trend test that was used uniformly in 1999 is about 15% less sensitive when used to test datasets that do not display significant seasonality (E. Aroner. 2014. WQHydro, pers. comm.). For this study, datasets were first tested for significant seasonality, and then either a seasonal or nonseasonal step trend test procedure was selected.

A1.2 QAQC Samples

Comments on the different types of QAQC samples collected during recent AESRD sampling (Table 6) are as follows:

(1) River water samples split in half, with one half sent to the AITF or Maxxam, and the other half to ALS:

There was close agreement between Maxxam and ALS results for 2013 (Table 6). However, results from AITF and ALS labs in 2012 were different for three of the four samples that had detectable concentrations, and both labs did not quantify all compounds. Naphthalene results varied by 15 to 65%,

with ALS usually higher, methylnaphthalene results varied by 50 to 83%, and acenaphthene results from by 11 to 65% (Table 6). Also, some compounds were not done at both laboratories, including 2-methyl naphthalene, dibenzofuran, carbazole, methyl anthracenes, benzo(b or k)fluoranthene, and PCP (Table 6). PCP is a good indicator for contaminant flux from the Canada Creosote site, and should be included in all QAQC sampling, along with these other compounds. The reasons for this poor agreement between laboratories can't be determined from the information that has been provided. Since a bucket was used to split samples, there is a possibility that some compounds adsorbed to the bucket and may have caused different concentrations in the split samples, if the bucket was made out of a material that readily adsorbs organic compounds. Teflon intermediate sampling containers are sometimes used to avoid adsorption of organic compounds.

(2) Samples of Type 1 water were submitted as blanks to ALS:

All compounds were below detection limits for these five blanks that were tested in 2011 and 2012, which suggests no contamination from sampling equipment and techniques occurred. Notes for the samples indicated that one sample was poured at the "Bow River downstream Canada Creosoting RDB", and included a bucket used to split samples. The only concern identified is that PCP was not included in the results for two of the blanks.

(3) Triplicate split samples of river water sent to ALS:

There was good agreement among the triplicate split samples in 2011, as all but two of the compounds were less than the detection limit, and those two were at the detection limit. The two river samples that were triplicate split were labelled "Bow River downstream Canada Creosote". It is surprising that so little was detected in two samples from this site. One would usually expect at least some naphthalene higher than the detection limit.

Certified spikes and certified reference materials are available for most of these compounds, and would be a useful addition to this program. These would be useful when samples are submitted to multiple laboratories, and to evaluate the performance of a single laboratory. Lastly, PCP should be included in all sample analysis for the Canada Creosote site. In past, this compound has been used as an indicator of contaminant movement from the Canada Creosote site (Section 2.2).