Radionuclides and Inorganics in WIPP Exhaust Air

Introduction

The CEMRC aerosol sampling program for the WIPP EM is designed to study the pathway that is the most likely route by which contaminants from the WIPP site could become rapidly dispersed in the environment. One facet of this comprehensive program is the monitoring of aerosols in the WIPP exhaust shaft. These samples are collected at a location (Station A) that represents the release point of aerosol effluents from the underground to the environment. CEMRC is interested in obtaining information on air quality from Station A because it provides a means for characterizing a source-term that will be needed for the interpretation of future monitoring results from the WIPP EM. For example, if radioactive or hazardous material was released from the WIPP, we would expect to detect it at Station A before it is observed in the local population or environment. In addition, source-term data collected at Station A would be of critical importance for the determination of public or worker dose in the event of an accident at the WIPP.

Another objective of the sampling program at Station A is to provide a gross check of emissions on a short resolution time-scale (e.g. weeks). For example, many of the WIPP EM analyses require many months to complete once the samples are collected. Such time is needed because of the specificity and sensitivity of the analyses. At Station A, gross monitoring results (less specific and sensitive) are provided within three weeks of sample collection and are used to trigger more detailed investigations if necessary.

Methods

A detailed description of the sampling protocol, aerosol sampler, analytical methods and detection limits are provided in the CEMRC 1999 and 2000 Reports. These reports and continually updated results can be found at the CEMRC website (http://www.cemrc.org). In summary, the monitoring program consists of daily aerosol sampling, gravimetric and gross alpha/beta analyses of individual filters, elemental and gamma-ray analysis of weekly filter composites and actinide analysis of quarterly filter composites.

Some changes to effluent sampling and analytes measured were made during this reporting period. Specifically, changes were made to the sampling location within Station A and ^{241}Pu was added to the suite of actinides analyzed as part of the quarterly composite.

At Station A, there are three shrouded-probe aerosol samplers, located on three separate sampling skids (skids 1-3). On each skid, aerosols are split into three sampling legs such that three concurrent samples can be collected from a single skid. CEMRC had sampled on skid 3, leg 2. The Environmental Evaluation Group (EEG) and Westinghouse TRU Solutions (WTS) sample concurrently on the remaining legs of skid 3. In April 2001, the entire sampling apparatus from skid 3 was exchanged with that at skid 1. Sampling was moved to this location to reduce problems associated with water infiltration into the exhaust shaft, which was most prevalent at the previous skid location.

Results and Discussion

Routine Monitoring

Aerosol sampling has been conducted continuously at Station A by CEMRC since 12 December 1998. Monitoring results from 1 July 2000 through 1 July 2001 are discussed herein. Tables presenting aerosol data summarized herein are available on the CEMRC web site at http://www.cemrc.org. For measurements of radioactivity, data reported during the current period are considered operational monitoring, since radioactive waste was received in March 1998. For measurements of elemental constituents, data reported herein constitute baseline and operational monitoring since WIPP received mixed waste on September 9, 2000.

Values of gross alpha activity concentration and density ranged from < MDC (≈ 0.03) to 0.7 mBq m^{-3} and < MDC (≈ 0.4) to 4.5 Bq g^{-1}, respectively. Values of gross beta

activity concentration and density ranged from < MDC (≈ 0.07) to 58 mBq m^{-3} and < MDC (≈ 1) to 92 Bq g^{-1}, respectively. In general, values of gross alpha and beta concentration and density are either unchanged or have decreased since the WIPP began receiving waste in March 1998. (Table 6, Figs 17 and 18).

In January 2001, the CEMRC monitoring program identified elevated gross beta radioactivity for filters collected on January 9, 2001 (Fig. 18). CEMRC notified the DOE, and the elevated measurements were later confirmed by EEG and WTS. While investigating these results, it was noted that on this day a fire retardant, trade name Purple K, was accidentally released in the WIPP underground. The primary constituent of Purple K is potassium bicarbonate, which includes the naturally occurring radioactive K isotope (^{40}K) that decays by beta emission 89% of the time. Follow-up measurements verified that the fire retardant containing ^{40}K was the cause of the elevated results and that WIPP waste had not been released. In addition, it is important to note that EEG confirmed the absence of beta emitting ^{90}Sr (WIPP waste constituent) on these filters.

The release of the fire retardant provided an excellent opportunity for the organizations sampling at Station A to intercompare analytical results and evaluate the efficacy of the sampling apparatus. For all three filters containing the fire retardant, results reported by CEMRC, EEG and WTS compared very well (Table 7) and demonstrates the quality of monitoring efforts at Station A.

WIPP received mixed waste on September 9, 2000. For elemental constituents, samples collected prior to this date represent a baseline and samples collected thereafter represent operational monitoring. Numerous elemental constituents were observed in weekly composites (Table 8) prior to and after the receipt of mixed waste. Greater than 85% of all of the 36 elements were observed in 75-100% of the weekly composites. Many of the hazardous elements (e.g. Pb, Be, Cd, etc.) expected to be contained in WIPP mixed waste were already present in WIPP aerosol effluents prior to the receipt of mixed waste. A high degree of variability in weekly concentrations was observed for most elements prior to and after receipt of mixed waste. For example, the ratio between the maximum and minimum Na concentration exceeded 200 and strong temporal peaks in concentration were observed (Fig 19). These peaks appeared during time periods when significant mining was occurring in the repository (e.g. panel excavation). This level of variability was an essential aspect of baseline characterization and should be considered when evaluating operational monitoring results.

With the exception of ^{7}Be, no detectable gamma-emitting radionuclides were observed during this monitoring period. ^{7}Be was detected in approximately 20% of samples, ranging in activity concentration and density from 4 to 18 mBq m^{-3} and 29 to 148 Bq g^{-1}, respectively. For detectable results, mean values (± SE) of activity concentration and density were 9.5 (± 0.4) mBq m^{-3} and 99 (± 8) Bq g^{-1}, respectively. ^{7}Be values during this monitoring period were consistent with those reported in the CEMRC 1999 and 2000 Reports. These results indicate that the aerosols entering through the WIPP air intake eventually reach the exhaust system and are released as exhaust effluents. The presence of ^{7}Be in the exhaust is an indicator of this mechanism because ^{7}Be is a short-lived radionuclide ($T_{1/2}$ = 53 days) that is produced in the stratosphere through spallation of atmospheric gases (not occurring naturally in the WIPP underground). This finding may be of importance because other aerosols containing radionuclides of concern (e.g. Pu, ^{137}Cs) may follow a similar process and be detected in the exhaust in the absence of a WIPP-related contamination event. Therefore, ^{7}Be may be a useful tracer for understanding aerosol residence times in the WIPP.

Isotopes of naturally occurring U and Th isotopes were detected in all quarterly composites reported for this monitoring period with the exception of the fourth quarter 2000 (Table 9). For this quarter, all U and Th analyses were invalidated due to concerns regarding weekly digestate preservation. Concentrations and activity densities of U and Th isotopes for all quarters reported here in

were consistent with that reported in the CEMRC 1999 and 2000 Reports.

No detectable concentrations of ^{238}Pu, $^{239,240}Pu$, ^{241}Pu, or ^{241}Am (Table 9) were observed in any operational quarter reported herein. These results are consistent with that reported in the CEMRC 1999 and 2000 Reports. The analysis for ^{241}Pu was first implemented in the first quarter of 2001, yielding MDCs of approximately 25 $\mu Bq\ m^{-3}$ and 80 $mBq\ g^{-1}$. The ^{241}Pu analysis failed for the second quarter of 2001 because of difficulties in preparing the alpha spectrometry source for liquid scintillation counting.

Table 6. Summary Statistics for Gross Alpha/Beta Analyses of Daily FAS Filters

Gross Emission	[a]N	% ≥ [b]MDC	Activity Concentration ($Bq\ m^{-3}$)			Activity Density ($Bq\ g^{-1}$)		
			[c]Mean	[d]SE	[e]Max	Mean	SE	Max
Pre-Operations Baseline								
Alpha	71	100	3.1E-04	3.1E-05	1.5E-03	3.6E+00	5.8E-01	3.7E+01
Beta	71	100	1.1E-03	9.1E-05	4.9E-03	1.4E+01	1.9E+00	1.2E+02
Operational Monitoring April 1999 – June 2000								
Alpha	427	60	9.8E-05	3.3E-06	3.9E-04	9.9E-01	1.5E-01	9.2E+00
Beta	427	97	9.6E-04	2.1E-05	3.3E-03	1.0E+01	1.0E+00	4.8E+01
Operational Monitoring June 2000 – June 2001								
Alpha	454	35	6.8E-05	2.8E-06	7.3E-04	6.1E-01	3.7E-02	4.5E+00
Beta	454	94	1.1E-03	1.4E-05	5.8E-02	9.5E+00	6.0E-01	9.1E+01

[a]N = number of samples
[b]MDC = minimum detectable concentration
[c]Mean = arithmetic mean
[d]SE = standard error
[e]Max = maximum

Table 7. An Intercomparison of Gross Beta Results following the Release of Fire Retardant Containing ^{40}K on January 9, 2001

Filter	Gross Beta Radioactivity (Bq) per Filter Mean ± 2 [a]SD			Gross Beta Radioactivity Concentration ($mBq\ m^{-3}$) Mean ± 2 SD		
	EEG	WTS	CEMRC	EEG	WID	CEMRC
1 (morning)	0.30 ± 0.04	0.37 ± 0.08	0.35 ± 0.02	44 ± 6	55 ± 13	58 ± 3
2 (afternoon)	0.46 ± 0.10	0.38 ± 0.09	0.38 ± 0.02	35 ± 8	27 ± 6	31 ± 1
3 (evening)	0.31 ± 0.08	0.32 ± 0.08	0.33 ± 0.02	5 ± 1	5 ± 1	5 ± 1

[a] SD = Standard deviation

Table 8. Summary Statistics for Elemental Constituents in Weekly FAS Composites

Analyte	[a]Baseline Volume Concentration 12 December 1998 – 9 September 2000 (ng m^{-3})				[b]Operational Volume Concentration 9 September 2000 – 1 July 2001 (ng m^{-3})			
	[c]FD (%)	[d]Mean	[e]SE	[f]Max	FD (%)	Mean	SE	Max
Ag	79	1.1E-01	2.2E-02	1.2E+00	48	5.9E-01	3.1E-01	5.5E+00
Al	99	7.2E+02	9.7E+01	7.8E+03	92	4.6E+02	4.3E+01	1.4E+03
As	70	1.3E+00	1.2E-01	4.7E+00	73	1.2E+00	1.6E-01	3.8E+00
Ba	100	7.6E+00	4.1E-01	2.0E+01	92	6.1E+00	5.6E-01	2.3E+01
Be	7	2.9E-01	1.4E-01	9.8E-01	0	[g]NA	NA	NA
Ca	100	4.1E+03	8.8E+02	7.0E+04	92	8.8E+03	3.1E+03	1.3E+05
Cd	82	9.4E-01	2.4E-01	1.5E+01	46	6.3E-01	1.4E-01	2.4E+00
Ce	99	7.4E-01	4.7E-02	2.1E+00	92	5.4E-01	6.5E-02	2.1E+00
Co	94	3.1E+00	4.5E-01	2.4E+01	88	9.4E+00	2.3E+00	8.5E+01
Cr	61	5.8E+01	1.3E+01	6.2E+02	75	5.2E+01	5.1E+00	1.7E+02
Cu	100	3.7E+01	2.0E+00	1.1E+02	88	4.6E+01	6.1E+00	2.7E+02
Dy	100	4.6E-02	3.4E-03	1.6E-01	33	4.9E-02	7.2E-03	1.2E-01
Er	96	2.8E-02	2.4E-03	1.5E-01	6	4.9E-02	6.5E-03	6.1E-02
Eu	93	1.5E-02	9.3E-04	3.7E-02	6	2.5E-02	2.4E-03	2.9E-02
Fe	100	8.0E+02	7.9E+01	5.8E+03	92	7.6E+02	1.1E+02	4.6E+03
Gd	99	7.2E-02	5.5E-03	2.8E-01	60	7.8E-02	9.8E-03	2.3E-01
Hg	30	1.6E-01	2.9E-02	5.7E-01	0	NA	NA	NA
K	99	1.3E+03	1.1E+02	5.4E+03	92	1.4E+03	2.2E+02	8.9E+03
La	100	4.5E-01	3.0E-02	1.3E+00	92	2.6E-01	2.5E-02	9.0E-01
Li	76	2.4E+00	2.7E-01	1.4E+01	90	2.2E+00	6.5E-01	2.7E+01
Mg	100	2.7E+03	6.4E+02	5.1E+04	92	4.1E+03	1.5E+03	6.1E+04
Mn	100	3.4E+01	3.5E+00	1.4E+02	92	3.5E+01	5.4E+00	2.2E+02
Mo	70	4.3E+00	1.3E+00	7.5E+01	81	4.4E+00	6.3E-01	2.3E+01
Na	99	6.7E+04	7.2E+03	2.9E+05	96	4.5E+04	6.4E+03	2.2E+05
Nd	100	3.1E-01	2.0E-02	9.2E-01	58	2.6E-01	3.0E-02	7.6E-01
Ni	91	1.8E+01	5.7E+00	4.2E+02	92	2.4E+01	4.1E+00	1.4E+02
Pb	100	7.0E+00	7.4E-01	4.6E+01	92	5.3E+00	5.0E-01	1.7E+01
Pr	100	8.9E-02	5.6E-03	2.7E-01	92	5.6E-02	5.9E-03	1.9E-01
Sb	100	3.1E+01	3.1E+00	2.2E+02	92	1.7E+01	1.2E+00	4.9E+01
Se	28	5.5E-01	4.7E-02	1.1E+00	10	7.7E-01	1.5E-01	1.3E+00
Sm	100	4.7E-01	2.0E-02	1.2E+00	67	4.7E-01	1.8E-02	6.8E-01
Sr	100	6.8E+01	1.8E+01	1.4E+03	92	1.8E+02	7.3E+01	3.1E+03
Th	94	1.1E-01	9.7E-03	4.8E-01	73	6.3E-02	9.3E-03	2.6E-01
Ti	99	4.4E+01	3.3E+00	2.1E+02	81	3.1E+01	4.6E+00	1.8E+02

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Table 8. Summary Statistics for Elemental Constituents in Weekly FAS Composites (Cont.)

Analyte	[a]Baseline Volume Concentration 12 December 1998 – 9 September 2000 (ng m^{-3})				[b]Operational Volume Concentration 9 September 2000 – 1 July 2001 (ng m^{-3})			
	[c]FD (%)	[d]Mean	[e]SE	[f]Max	FD (%)	Mean	SE	Max
U	91	4.7E-02	4.5E-03	2.4E-01	88	3.4E-02	3.9E-03	1.5E-01
Zn	98	2.7E+02	8.0E+01	4.7E+03	92	1.3E+02	1.9E+01	5.4E+02

[a]A total of 88 weekly composites were analyzed during this interval
[b]A total of 59 weekly composites were analyzed during this interval
[c]FD = frequency of detection
[d]Mean = arithmetic mean
[e]SE = standard error
[f]Max = maximum
[g]NA = not applicable

Table 9. Results of Actinide Analyses for Quarterly FAS Composite Samples

Radionuclide	Activity Concentration (Bq m^{-3})			Activity Density (Bq g^{-1})		
	[a]C	[b]SE	[c]MDC	C	SD	MDC
Pre-Operational Baseline						
^{238}Pu	< MDC	[d]NA	2.4E-08	< MDC	NA	3.0E-04
$^{239, 240}$Pu	< MDC	NA	2.4E-08	< MDC	NA	2.9E-04
^{241}Am	< MDC	NA	5.5E-08	< MDC	NA	6.9E-04
^{228}Th	7.6E-07	5.2E-08	9.7E-08	8.1E-03	5.6E-04	1.2E-03
^{230}Th	7.0E-07	4.9E-08	6.8E-08	7.5E-03	5.3E-04	8.3E-04
^{232}Th	4.9E-07	3.7E-08	3.6E-08	5.2E-03	4.0E-04	4.3E-04
^{234}U	8.9E-07	4.9E-08	3.0E-08	9.5E-03	5.3E-04	3.8E-04
^{235}U	4.1E-08	1.5E-08	2.7E-08	4.4E-04	1.6E-04	3.2E-04
^{238}U	8.5E-07	4.9E-08	2.4E-08	9.1E-03	5.2E-04	3.0E-04
[d]Operational Monitoring April 1999 – June 2000						
^{238}Pu	<MDC	NA	1.1E-07	<MDC	NA	7.1E-04
$^{239, 240}$Pu	<MDC	NA	6.5E-08	<MDC	NA	2.3E-04
^{241}Am	<MDC	NA	5.4E-08	<MDC	NA	1.9E-04
^{228}Th	9.7E-07	1.8E-07	1.8E-07	7.3E-03	2.4E-03	1.1E-03
^{230}Th	5.9E-07	1.7E-07	1.4E-07	3.8E-03	1.0E-03	8.6E-04
^{232}Th	4.2E-07	1.0E-07	8.4E-08	3.0E-03	1.1E-03	5.3E-04
^{234}U	8.7E-07	1.9E-07	8.4E-08	5.8E-03	1.4E-03	6.0E-04
^{235}U	8.1E-08	5.1E-08	9.7E-08	3.6E-04	4.8E-05	6.1E-04
^{238}U	7.1E-07	1.7E-07	9.1E-08	4.6E-03	1.1E-03	6.9E-04
Operational Monitoring Third Quarter 2000						
^{238}Pu	<MDC	NA	8.6E-08	<MDC	NA	7.6E-04
$^{239, 240}$Pu	<MDC	NA	6.1E-08	<MDC	NA	5.4E-04
^{241}Am	<MDC	NA	7.0E-08	<MDC	NA	6.2E-04
^{228}Th	3.5E-07	5.9E-08	1.2E-07	3.1E-03	5.2E-04	1.1E-03
^{230}Th	2.3E-07	4.7E-08	1.0E-07	2.0E-03	4.2E-04	9.3E-04
^{232}Th	1.5E-07	3.1E-08	5.4E-08	1.4E-03	2.8E-04	4.8E-04
^{234}U	4.6E-07	5.0E-08	8.5E-08	4.0E-03	4.4E-04	7.5E-04
^{235}U	1.5E-07	3.6E-08	7.1E-08	1.4E-03	3.2E-04	6.3E-04
^{238}U	3.2E-07	4.3E-08	7.8E-08	2.9E-03	3.8E-04	6.9E-04
Operational Monitoring Fourth Quarter 2000						
^{238}Pu	<MDC	NA	1.4E-07	<MDC	NA	1.2E-03
$^{239, 240}$Pu	<MDC	NA	1.0E-07	<MDC	NA	8.4E-04
^{241}Am	<MDC	NA	7.1E-08	<MDC	NA	5.8E-04
^{228}Th	[e]NR	NR	NR	NR	NR	NR
^{230}Th	NR	NR	NR	NR	NR	NR
^{232}Th	NR	NR	NR	NR	NR	NR
^{234}U	NR	NR	NR	NR	NR	NR
^{235}U	NR	NR	NR	NR	NR	NR
^{238}U	NR	NR	NR	NR	NR	NR

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Table 9. Results of Actinide Analyses for Quarterly FAS Composite Samples (Cont.)

Radionuclide	Activity Concentration (Bq m^{-3})			Activity Density (Bq g^{-1})		
	[a]C	[b]SD	[c]MDC	C	SD	MDC
Operational Monitoring First Quarter 2001						
^{238}Pu	<MDC	NA	1.2E-07	<MDC	NA	4.4E-04
$^{239, 240}$Pu	<MDC	NA	1.4E-07	<MDC	NA	4.9E-04
^{241}Pu	<MDC	NA	2.2E-05	<MDC	NA	7.9E-02
^{241}Am	<MDC	NA	8.4E-08	<MDC	NA	3.0E-04
^{228}Th	5.6E-07	7.9E-08	1.7E-07	2.0E-03	2.8E-04	5.9E-04
^{230}Th	5.5E-07	8.0E-08	1.6E-07	2.0E-03	2.9E-04	5.8E-04
^{232}Th	3.2E-07	5.0E-08	8.5E-08	1.1E-03	1.8E-04	3.1E-04
^{234}U	8.9E-07	9.3E-08	8.3E-08	3.2E-03	3.3E-04	3.0E-04
^{235}U	<MDC	NA	1.2E-07	<MDC	NA	4.3E-04
^{238}U	6.3E-07	8.1E-08	1.3E-07	2.2E-03	2.9E-04	4.7E-04
Operational Monitoring Second Quarter 2001						
^{238}Pu	<MDC	NA	1.0E-07	<MDC	NA	6.3E-04
$^{239, 240}$Pu	<MDC	NA	1.0E-07	<MDC	NA	6.2E-04
^{241}Pu	NR	NR	NR	NR	NR	NR
^{241}Am	<MDC	NA	8.0E-08	<MDC	NA	5.0E-04
^{228}Th	8.3E-07	8.5E-08	1.5E-07	5.1E-03	5.3E-04	9.2E-04
^{230}Th	8.5E-07	8.9E-08	1.3E-07	5.3E-03	5.5E-04	8.3E-04
^{232}Th	5.4E-07	6.2E-08	7.5E-08	3.3E-03	3.9E-04	4.7E-04
^{234}U	8.3E-07	7.1E-08	7.7E-08	5.2E-03	4.4E-04	4.8E-04
^{235}U	<MDC	NA	7.1E-08	<MDC	NA	4.4E-04
^{238}U	7.1E-07	6.5E-08	5.1E-08	4.4E-03	4.0E-04	3.1E-04

[a]C = concentration
[b]SE = standard error
[c]MDC = minimum detectable concentration
[d]NA = not applicable
[e]NR = data not reported ; analyses for U and Th isotopes were not reported for the fourth quarter of 2000 because of concern associated with digestate preservation; ^{241}Pu results were not reported for the second quarter of 2001 because of difficulties in preparing the alpha spectrometry source for liquid scintillation counting.

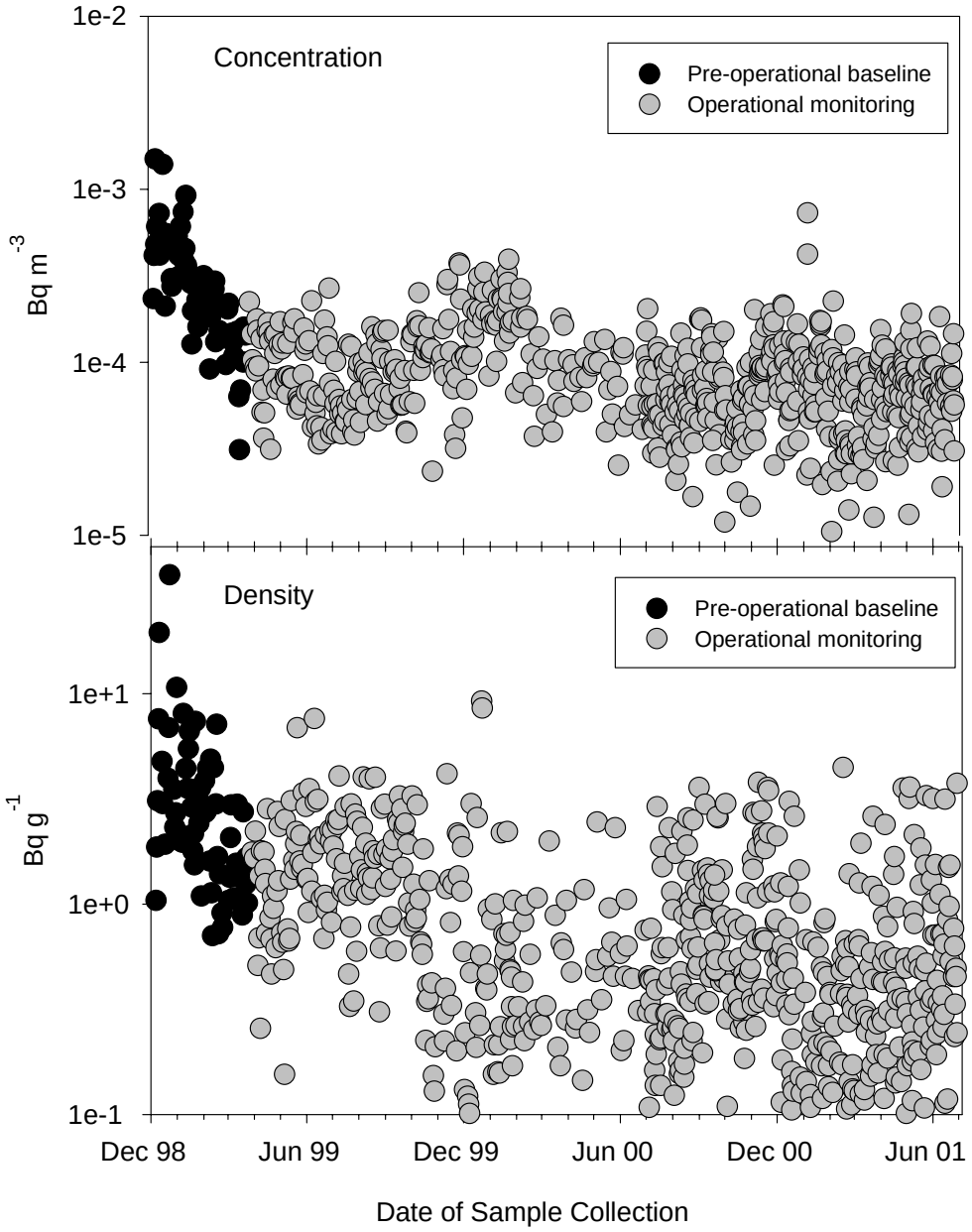

Figure 17. Alpha Emitting Radioactivity in FAS Samples Collected during December 1998 - July 2001

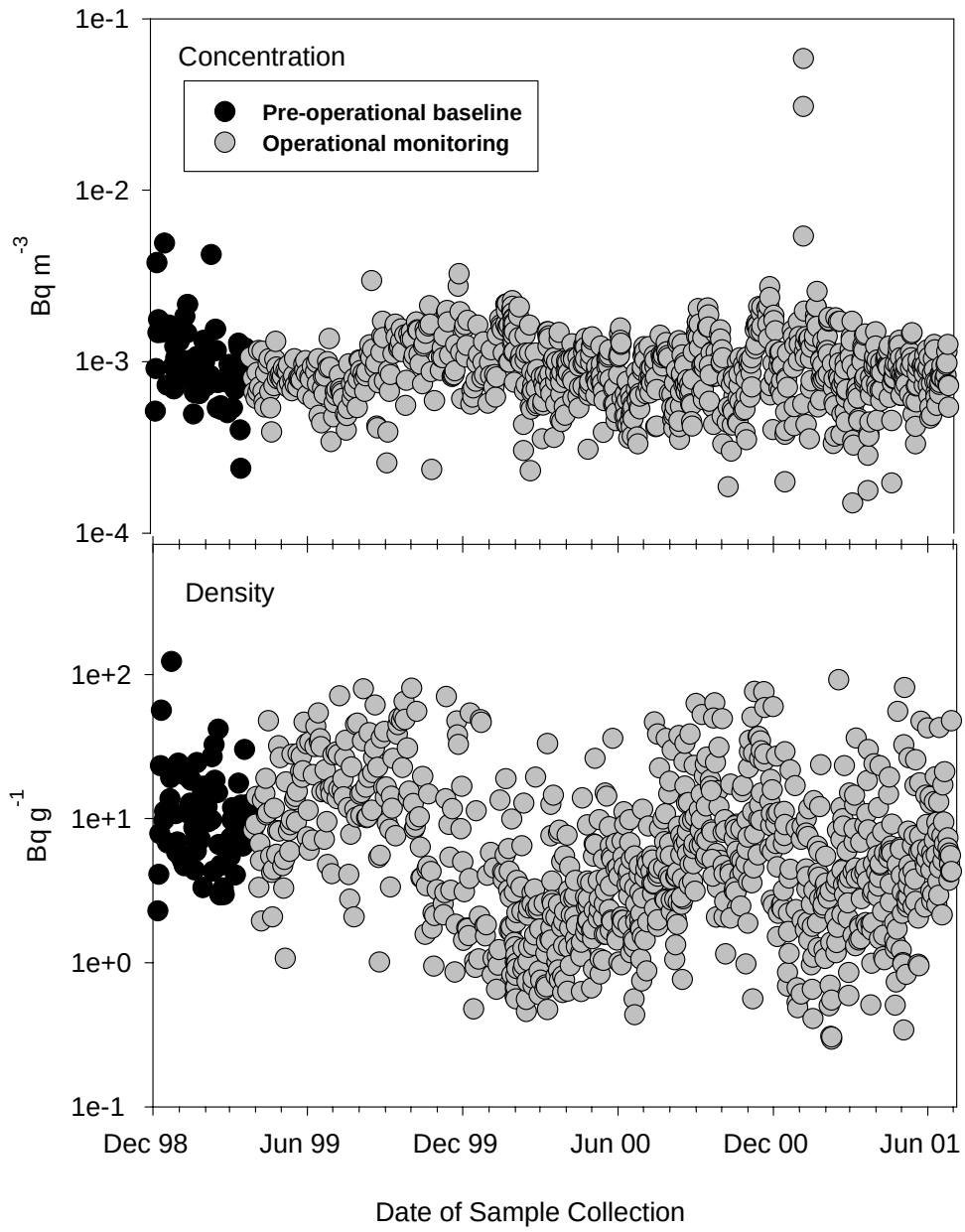

Figure 18. Beta Emitting Radioactivity in FAS Samples Collected during December 1998 - July 2001

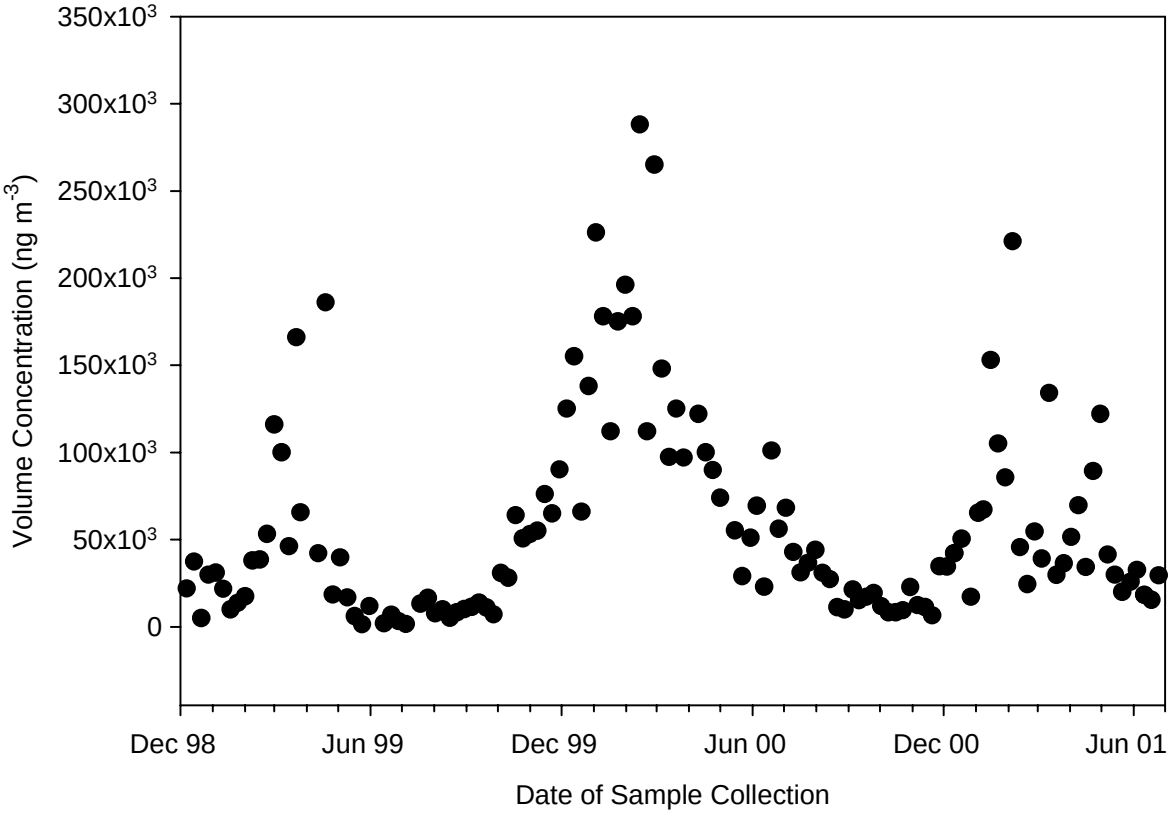

Figure 19. Sodium Released as Aerosols in the Exhaust from the WIPP