

Radionuclides and Inorganics in WIPP Exhaust Air

Introduction

Beginning in late 1998, studies have been conducted on the loadings and composition of aerosol samples collected from the WIPP exhaust shaft. The samples for this part of the WIPP EM program are collected at Station A, which is an aerosol sampling platform shared with the Environmental Evaluation Group (EEG) and Washington TRU solutions (WTS). Data from Station A not only provide a means for monitoring the effluent from the WIPP, but data from the station also could be of critical importance for reconstructing public or worker exposure if a release were to occur at the WIPP. This report summarizes analyses completed through the 3rd Quarter (Sept. 30th) 2002.

From a practical standpoint, the WIPP exhaust shaft is where radioactive or hazardous materials would most likely first be detected in the event of a release. Therefore, CEMRC has developed procedures and methods to provide information about the exhaust emissions on a short turn-around time schedule (i.e., weeks). This addresses a strategic need for the monitoring program because most of the other WIPP EM analyses require relatively long turn-around times; that is, it may take several months to complete the chemical and radiochemical analyses after the samples are collected. Therefore, the Station A studies provide quick-look monitoring results, which while less specific and less detailed than those from other studies, can be used to trigger more detailed investigations if necessary. This was dramatically demonstrated in January 2001 when a fire extinguisher discharged, and the CEMRC monitoring program identified elevated gross beta radioactivity from the extinguisher on Station A filters.

Methods

The aerosol samples at Station A are typically collected daily except for weekends (the weekend samples run from Friday to Monday so the coverage is continuous). If waste operations occur on the weekend then

samples are also collected on the weekends. The samples are collected from a shrouded probe, commonly referred to as a fixed air sampler (FAS), which has a transfer line running to each of three sampling legs; thus a total of three concurrent samples can be collected from the FAS, one each for CEMRC, EEG and WTS.

Detailed descriptions of the sampling and analytical methods have been included in the CEMRC Annual Reports for 1999 and 2000. Briefly, after the samples are returned to the laboratory, the individual filters are weighed to determine mass loadings, and they are counted for gross alpha/beta activities. Elemental and gamma-ray analysis are conducted on weekly composites of the filter, and quarterly composites are used for the determination of actinide activities.

As with all other WIPP EM activities, the Station A studies have come under more rigorous quality control in FY 2002.

Results and Discussion

Routine Monitoring

The Station A studies are unique among the WIPP EM activities in that quick-look data sets are posted for public inspection at the CEMRC website (<http://www.cemrc.org>) within a few weeks after the samples are collected. The strategic design for the WIPP EM was to compare pre- vs. post-disposal data. The first radioactive waste shipments were received at the WIPP on March 26, 1999, and this is considered the cut-off between the pre-disposal vs. operational phase.

Operational values of gross alpha activity concentration and density (Table 10) ranged from < MDC (≈ 0.1 mBq m⁻³) to 0.42 mBq m⁻³ and < MDC (≈ 0.7 Bq g⁻¹) to 9.6 Bq g⁻¹, respectively. Values of gross beta activity concentration and density ranged from < MDC (≈ 0.2 mBq m⁻³) to 58 mBq m⁻³ and < MDC (≈ 1.7 Bq g⁻¹) to 190 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 1999. (Table 10, Figs. 14 and 15).

The WIPP began receiving mixed waste on September 9, 2000, and therefore for the elemental constituents, samples collected prior to that date represent a baseline while the results for samples collected afterwards represent operational monitoring data. Numerous elemental constituents were quantified in weekly composites (Table 11). More than 85% of all of the 36 elements that can be routinely quantified with the ICP-MS used for the FAS sample analyses were observed in 75-100% of the weekly composites.

Many of the potentially toxic elements (e.g. Pb, Be, Cd, etc.) which are known or expected to be contained in WIPP mixed waste were already present in measurable amounts in the WIPP aerosol effluent prior to the receipt of mixed waste. The Station A studies show that the concentrations of the hazardous metals and other elements were highly variable even in the samples collected prior to receipt of the mixed waste.

Aside from the heavy metals, one non-radiogenic constituent of considerable interest is Na; this is because a variety of operations in the underground cause the generation of salt dusts. The Na concentration in the FAS samples showed strong temporal peaks, and these generally appeared when mining or other activities (e.g. panel excavation) were occurring in the repository (Fig.16).

Another non-radiogenic constituent of interest is Al. The Al concentrations in FAS samples exhibit a seasonal cycle, peaking in the spring (Fig. 17). As noted in the chapter of this report dealing with ambient aerosols, this phenomenon has also been observed in ambient aerosol samples collected above ground in the vicinity of the WIPP. Spring is typically the windiest time of the year and the increase in Al concentrations in the exhaust air likely is caused by an increase in dust (soil) entrained in the ambient air entering the mine air intake and circulated throughout the mine. Aluminum has been used as an indicator of mineral dust, and a relationship has been demonstrated between Al, and $^{239,240}\text{Pu}$ concentration in ambient aerosols (Arimoto et al., 2002) and soil (Kirchner et al., 2002)

where an ambient aerosol $^{239,240}\text{Pu}:\text{Al}$ ratio of approximately $0.025 \text{ nBq ng}^{-1}$ has been observed.

Assuming the $^{239,240}\text{Pu}:\text{Al}$ ratio of $0.025 \text{ nBq ng}^{-1}$ observed on the surface holds true for aerosols entering the WIPP underground, One can use this information to address the question – will we ever detect plutonium in the exhaust air samples? The concentration of $^{239,240}\text{Pu}$ in the WIPP underground air can be estimated using the Al concentration observed in the exhaust air by:

$$[\text{Pu}] = R * [\text{Al}] \quad \text{Equation (1)}$$

Where:

$[\text{Pu}] = ^{239,240}\text{Pu}$ concentration (nBq m^{-3})

$R = ^{239,240}\text{Pu}$ to Al ratio = $0.025 \text{ nBq ng}^{-1}$

$[\text{Al}] = \text{Exhaust air Al concentration } (\text{ng m}^{-3})$

If the average (450 ng m^{-3}) and maximum (1400 ng m^{-3}) Al concentrations measured during the operational monitoring period (Table 11) are inserted in equation 1, the $^{239,240}\text{Pu}$ concentration in WIPP underground air is estimated to range from approximately 11.3 to 35 nBq m^{-3} . This estimate is very close to the detection limit of the composite samples analyzed for $^{239,240}\text{Pu}$ by alpha spectroscopy (Table 12). To date, all quarterly composite samples analyzed by alpha spectroscopy have been below the MDC for $^{239,240}\text{Pu}$ with the MDC's for the individual quarterly samples ranging from 27 to 137 nBq m^{-3} (average = 75 nBq m^{-3}).

Since the MDCs for $^{239,240}\text{Pu}$ are only approximately a factor of 2-3 higher than the predicted concentrations, it appears very probable that $^{239,240}\text{Pu}$ could be detected in future composite samples with source being dust-loaded ambient air circulating through the underground as opposed to a release of Pu from WIPP operations. This is important to note because while it may not be possible to definitively prove that ambient aerosols are the source of Pu detected in an exhaust sample, it at least provides a defensible explanation of the source of Pu.

This is further supported by the ^7Be data. With the exception of ^7Be , no detectable gamma-emitting radionuclides were observed during this monitoring period (June 2001 –

September 2002). ^7Be 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). ^7Be was detected in approximately 52% of samples, ranging in activity concentration and density from 3 to 13 mBq m^{-3} and 12 to 332 Bq g^{-1} , respectively. For detectable results, mean values (\pm SE) of activity concentration and density were 6.7 (\pm 0.4) mBq m^{-3} and 85 (\pm 15) Bq g^{-1} , respectively. ^7Be values during this monitoring period were consistent with those reported in the CEMRC 1999, 2000 and 2001 Reports. The presence of ^7Be in the exhaust is also an indicator that the aerosols entering through the WIPP air intake eventually reach the exhaust system and are released as exhaust effluents. This finding supports the hypothesis

that aerosols containing radionuclides (e.g. $^{239,240}\text{Pu}$, ^{137}Cs) enter the underground via the ventilation system, circulate and are expelled in the exhaust where they may be detected in FAS samples even in the absence of a WIPP-related contamination event.

Isotopes of naturally occurring U and Th isotopes have been detected in all quarterly composites reported for this monitoring period. Concentrations and activity densities of U and Th isotopes for all quarters reported herein were consistent with that reported in the CEMRC 1999, 2000 and 2001 Reports.

As stated above, no detectable concentrations of ^{238}Pu , $^{239,240}\text{Pu}$, ^{241}Pu , or ^{241}Am (Table 12) were observed in any operational quarter reported herein. These results are consistent with those reported in the CEMRC 1999, 2000 and 2001 Reports.

Table 10. 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 2002								
Alpha	1378	50	9.4E-05	2.1E-06	4.2E-04	1.2E+00	4.6E-02	9.6E+00
Beta	1378	96	1.0E-03	5.2E-05	5.8E-02	1.1E+01	4.4E-01	1.9E+02

^aN = number of samples^bMDC = minimum detectable concentration^cMean = arithmetic mean^dSE = standard error^eMax = maximum

Table 11. Summary Statistics for Elemental Constituents in Weekly FAS Composites

Analyte	^a Baseline Aerosol Concentration December 1998 – September 2000 (ng m ⁻³)				^b Operational Aerosol Concentration September 2000 – September 2002 (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	51	4.0E-01	1.4E-01	5.5E+00
Al	99	7.2E+02	9.7E+01	7.8E+03	100	4.5E+02	2.5E+01	1.4E+03
As	70	1.3E+00	1.2E-01	4.7E+00	76	1.1E+00	1.3E-01	9.1E+00
Ba	100	7.6E+00	4.1E-01	2.0E+01	100	6.3E+00	5.8E-01	5.2E+01
Be	7	2.9E-01	1.4E-01	9.8E-01	3	4.2E-01	1.1E-01	6.2E-01
Ca	100	4.1E+03	8.8E+02	7.0E+04	100	5.9E+03	1.4E+03	1.3E+05
Cd	82	9.4E-01	2.4E-01	1.5E+01	36	6.5E-01	1.6E-01	5.6E+00
Ce	99	7.4E-01	4.7E-02	2.1E+00	100	5.8E-01	4.2E-02	2.2E+00
Co	94	3.1E+00	4.5E-01	2.4E+01	98	7.2E+00	1.1E+00	8.5E+01
Cr	61	5.8E+01	1.3E+01	6.2E+02	93	8.5E+01	6.6E+00	4.3E+02
Cu	100	3.7E+01	2.0E+00	1.1E+02	79	4.9E+01	6.3E+00	3.3E+02
Dy	100	4.6E-02	3.4E-03	1.6E-01	44	6.8E-02	1.1E-02	4.9E-01
Er	96	2.8E-02	2.4E-03	1.5E-01	24	6.2E-02	1.3E-02	3.4E-01
Eu	93	1.5E-02	9.3E-04	3.7E-02	14	7.5E-02	3.3E-02	4.8E-01
Fe	100	8.0E+02	7.9E+01	5.8E+03	100	8.0E+02	5.6E+01	4.6E+03
Gd	99	7.2E-02	5.5E-03	2.8E-01	78	9.4E-02	9.4E-03	5.4E-01
Hg	30	1.6E-01	2.9E-02	5.7E-01	13	1.3E+00	2.6E-01	3.6E+00
K	99	1.3E+03	1.1E+02	5.4E+03	96	1.2E+03	1.1E+02	8.9E+03
La	100	4.5E-01	3.0E-02	1.3E+00	97	3.0E-01	1.8E-02	1.1E+00
Li	76	2.4E+00	2.7E-01	1.4E+01	70	1.7E+00	4.0E-01	2.7E+01
Mg	100	2.7E+03	6.4E+02	5.1E+04	100	2.1E+03	6.5E+02	6.1E+04
Mn	100	3.4E+01	3.5E+00	1.4E+02	100	3.1E+01	2.7E+00	2.2E+02
Mo	70	4.3E+00	1.3E+00	7.5E+01	96	8.6E+00	5.5E-01	2.6E+01
Na	99	6.7E+04	7.2E+03	2.9E+05	100	3.7E+04	3.5E+03	2.2E+05
Nd	100	3.1E-01	2.0E-02	9.2E-01	75	2.7E-01	1.9E-02	9.4E-01
Ni	91	1.8E+01	5.7E+00	4.2E+02	100	4.6E+01	4.1E+00	2.7E+02
Pb	100	7.0E+00	7.4E-01	4.6E+01	100	6.3E+00	8.0E-01	7.9E+01
Pr	100	8.9E-02	5.6E-03	2.7E-01	97	7.2E-02	6.5E-03	5.1E-01
Sb	100	3.1E+01	3.1E+00	2.2E+02	100	1.1E+01	7.6E-01	4.9E+01
Se	28	5.5E-01	4.7E-02	1.1E+00	19	6.0E-01	6.5E-02	1.3E+00
Sm	100	4.7E-01	2.0E-02	1.2E+00	47	4.8E-01	2.0E-02	7.9E-01
Sr	100	6.8E+01	1.8E+01	1.4E+03	100	1.0E+02	3.2E+01	3.1E+03
Th	94	1.1E-01	9.7E-03	4.8E-01	88	8.0E-02	9.1E-03	6.9E-01
Ti	99	4.4E+01	3.3E+00	2.1E+02	71	2.5E+01	3.0E+00	1.8E+02
U	91	4.7E-02	4.5E-03	2.4E-01	88	4.1E-02	5.2E-03	4.1E-01
Zn	98	2.7E+02	8.0E+01	4.7E+03	100	1.2E+02	1.5E+01	1.2E+03

^aA total of 102 weekly composites were analyzed during this interval^bA total of 90 weekly composites were analyzed during this interval^cFD = frequency of detection^dMean = arithmetic mean^eSE = standard error^fMax = maximum

Table 12. Results of Actinide Analyses for Quarterly FAS Composite Samples

Radionuclide	Activity Concentration (Bq m ⁻³)			Activity Density (Bq g ⁻¹)		
	^a C	^b SD	^c MDC	C	SD	MDC
Pre-Operational Baseline						
²⁴¹ Am	<MDC	^d NA	4.0E-08	<MDC	NA	4.3E-04
²³⁸ Pu	<MDC	NA	3.3E-08	<MDC	NA	3.5E-04
^{239,240} Pu	<MDC	NA	2.7E-08	<MDC	NA	2.9E-04
(e) ²⁴¹ Pu	^f NR	NR	NR	NR	NR	NR
²²⁸ Th	8.1E-07	5.6E-08	5.8E-08	8.7E-03	6.0E-04	6.2E-04
²³⁰ Th	7.5E-07	5.3E-08	6.5E-08	8.1E-03	5.7E-04	7.0E-04
²³² Th	5.2E-07	4.0E-08	3.8E-08	5.6E-03	4.3E-04	4.0E-04
²³⁴ U	9.5E-07	5.3E-08	1.3E-08	1.0E-02	5.7E-04	1.3E-04
²³⁵ U	4.4E-08	1.6E-08	3.7E-08	4.8E-04	1.7E-04	3.9E-04
²³⁸ U	9.1E-07	5.2E-08	1.6E-08	9.8E-03	5.6E-04	1.8E-04
Operational Monitoring Second Quarter 1999 – Second Quarter 2001						
²⁴¹ Am	<MDC	NA	6.9E-08	<MDC	NA	4.0E-04
²³⁸ Pu	<MDC	NA	1.1E-07	<MDC	NA	7.3E-04
^{239,240} Pu	<MDC	NA	8.9E-08	<MDC	NA	4.9E-04
²⁴¹ Pu	<MDC	NA	2.2E-05	<MDC	NA	7.9E-02
²²⁸ Th	8.2E-07	3.9E-07	1.7E-07	5.8E-03	4.6E-03	1.0E-03
²³⁰ Th	5.7E-07	3.3E-07	1.4E-07	3.5E-03	2.0E-03	8.3E-04
²³² Th	3.9E-07	2.0E-07	8.0E-08	2.6E-03	2.1E-03	4.9E-04
²³⁴ U	8.2E-07	3.5E-07	8.3E-08	5.2E-03	2.7E-03	5.7E-04
²³⁵ U	1.1E-07	6.7E-08	9.4E-08	7.0E-04	5.8E-04	5.7E-04
²³⁸ U	6.6E-07	3.2E-07	9.0E-08	4.1E-03	2.1E-03	6.1E-04
Operational Monitoring Third Quarter 2001						
²⁴¹ Am	<MDC	NA	8.8E-08	<MDC	NA	1.3E-03
²³⁸ Pu	<MDC	NA	1.2E-07	<MDC	NA	1.8E-03
^{239,240} Pu	<MDC	NA	1.1E-07	<MDC	NA	1.6E-03
²⁴¹ Pu	<MDC	NA	3.2E-05	<MDC	NA	4.7E-01
²²⁸ Th	5.2E-07	9.4E-08	2.0E-07	7.6E-03	1.4E-03	3.0E-03
²³⁰ Th	4.3E-07	7.9E-08	1.6E-07	6.2E-03	1.2E-03	2.4E-03
²³² Th	3.4E-07	6.0E-08	1.1E-07	4.9E-03	8.6E-04	1.6E-03
²³⁴ U	8.5E-07	8.2E-08	8.1E-08	1.2E-02	1.2E-03	1.2E-03
²³⁵ U	<MDC	NA	1.1E-07	<MDC	NA	1.5E-03
²³⁸ U	5.4E-07	6.8E-08	1.1E-07	7.8E-03	9.8E-04	1.6E-03
Operational Monitoring Fourth Quarter 2001						
²⁴¹ Am	<MDC	NA	4.7E-08	<MDC	1.2E-04	4.8E-04
²³⁸ Pu	<MDC	NA	6.1E-08	<MDC	1.6E-04	6.2E-04
^{239,240} Pu	<MDC	NA	5.5E-08	<MDC	1.5E-04	5.6E-04
²⁴¹ Pu	<MDC	NA	2.1E-05	<MDC	5.3E-02	2.1E-01
²²⁸ Th	3.9E-07	5.0E-08	9.7E-08	3.9E-03	5.1E-04	9.9E-04
²³⁰ Th	2.2E-07	4.6E-08	1.0E-07	2.2E-03	4.7E-04	1.0E-03
²³² Th	1.7E-07	2.7E-08	4.8E-08	1.7E-03	2.8E-04	4.9E-04
²³⁴ U	2.8E-07	4.6E-08	7.2E-08	2.9E-03	4.7E-04	7.4E-04
²³⁵ U	<MDC	NA	1.0E-07	<MDC	3.3E-04	1.1E-03
²³⁸ U	1.9E-07	4.1E-08	9.7E-08	1.9E-03	4.2E-04	9.9E-04

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Table 12. 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 2002						
²⁴¹ Am	<MDC	NA	6.0E-08	<MDC	NA	2.7E-04
²³⁸ Pu	<MDC	NA	7.3E-08	<MDC	NA	3.3E-04
^{239,240} Pu	<MDC	NA	7.5E-08	<MDC	NA	3.5E-04
²⁴¹ Pu	<MDC	NA	1.9E-05	<MDC	NA	8.7E-02
²²⁸ Th	4.3E-07	5.8E-08	1.0E-07	2.0E-03	2.7E-04	4.7E-04
²³⁰ Th	5.3E-07	7.5E-08	1.4E-07	2.4E-03	3.4E-04	6.6E-04
²³² Th	3.5E-07	4.7E-08	5.8E-08	1.6E-03	2.2E-04	2.6E-04
²³⁴ U	6.7E-07	5.9E-08	6.4E-08	3.1E-03	2.7E-04	3.0E-04
²³⁵ U	<MDC	NA	6.1E-08	<MDC	NA	2.8E-04
²³⁸ U	6.7E-07	5.8E-08	4.4E-08	3.1E-03	2.7E-04	2.0E-04
Operational Monitoring Second Quarter 2002						
²⁴¹ Am	<MDC	NA	5.13E-08	<MDC	NA	4.6E-04
²³⁸ Pu	<MDC	NA	7.22E-08	<MDC	NA	6.5E-04
^{239,240} Pu	<MDC	NA	5.87E-08	<MDC	NA	5.3E-04
²⁴¹ Pu	<MDC	NA	1.58E-05	<MDC	NA	1.4E-01
²²⁸ Th	4.39E-07	5.86E-08	1.09E-07	3.9E-03	5.3E-04	9.8E-04
²³⁰ Th	3.88E-07	6.03E-08	1.14E-07	3.5E-03	5.4E-04	1.0E-03
²³² Th	3.86E-07	4.81E-08	6.42E-08	3.5E-03	4.3E-04	5.8E-04
²³⁴ U	3.74E-07	4.73E-08	7.44E-08	3.4E-03	4.2E-04	6.7E-04
²³⁵ U	<MDC	NA	6.16E-08	<MDC	NA	5.5E-04
²³⁸ U	4.51E-07	5.06E-08	5.35E-08	4.0E-03	4.5E-04	4.8E-04
Operational Monitoring Third Quarter 2002						
²⁴¹ Am	<MDC	NA	6.08E-08	<MDC	NA	3.5E-04
²³⁸ Pu	<MDC	NA	3.45E-08	<MDC	NA	2.0E-04
^{239,240} Pu	<MDC	NA	4.95E-08	<MDC	NA	2.9E-04
²⁴¹ Pu	<MDC	NA	1.84E-05	<MDC	NA	1.1E-01
²²⁸ Th	3.71E-07	5.77E-08	1.22E-07	2.2E-03	3.4E-04	7.1E-04
²³⁰ Th	3.59E-07	6.07E-08	1.21E-07	2.1E-03	3.5E-04	7.0E-04
²³² Th	2.40E-07	3.98E-08	7.18E-08	1.4E-03	2.3E-04	4.2E-04
²³⁴ U	3.37E-07	4.48E-08	6.57E-08	2.0E-03	2.6E-04	3.8E-04
²³⁵ U	<MDC	NA	6.60E-08	<MDC	NA	3.8E-04
²³⁸ U	3.30E-07	4.38E-08	6.36E-08	1.9E-03	2.5E-04	3.7E-04

^aC = concentration^bSD = 1 standard deviation^cMDC = minimum detectable concentration^dNA = not applicable^e²⁴¹Pu = ²⁴¹Pu analyses were not performed on the samples until January 2001^fNR = data not reported

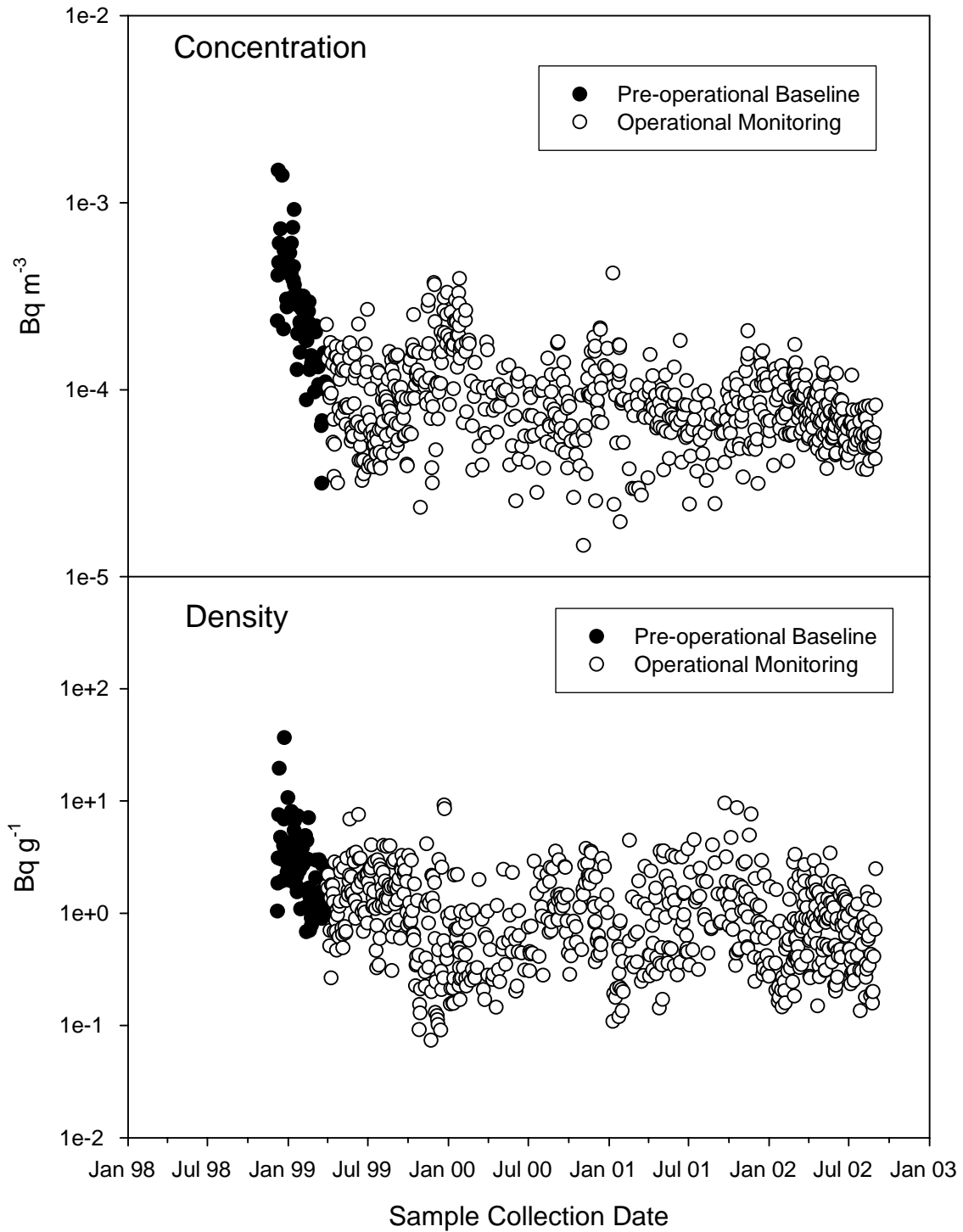


Figure 14. Alpha Emitting Radioactivity (>MDC) in FAS Samples Collected during December 1998 - September 2002

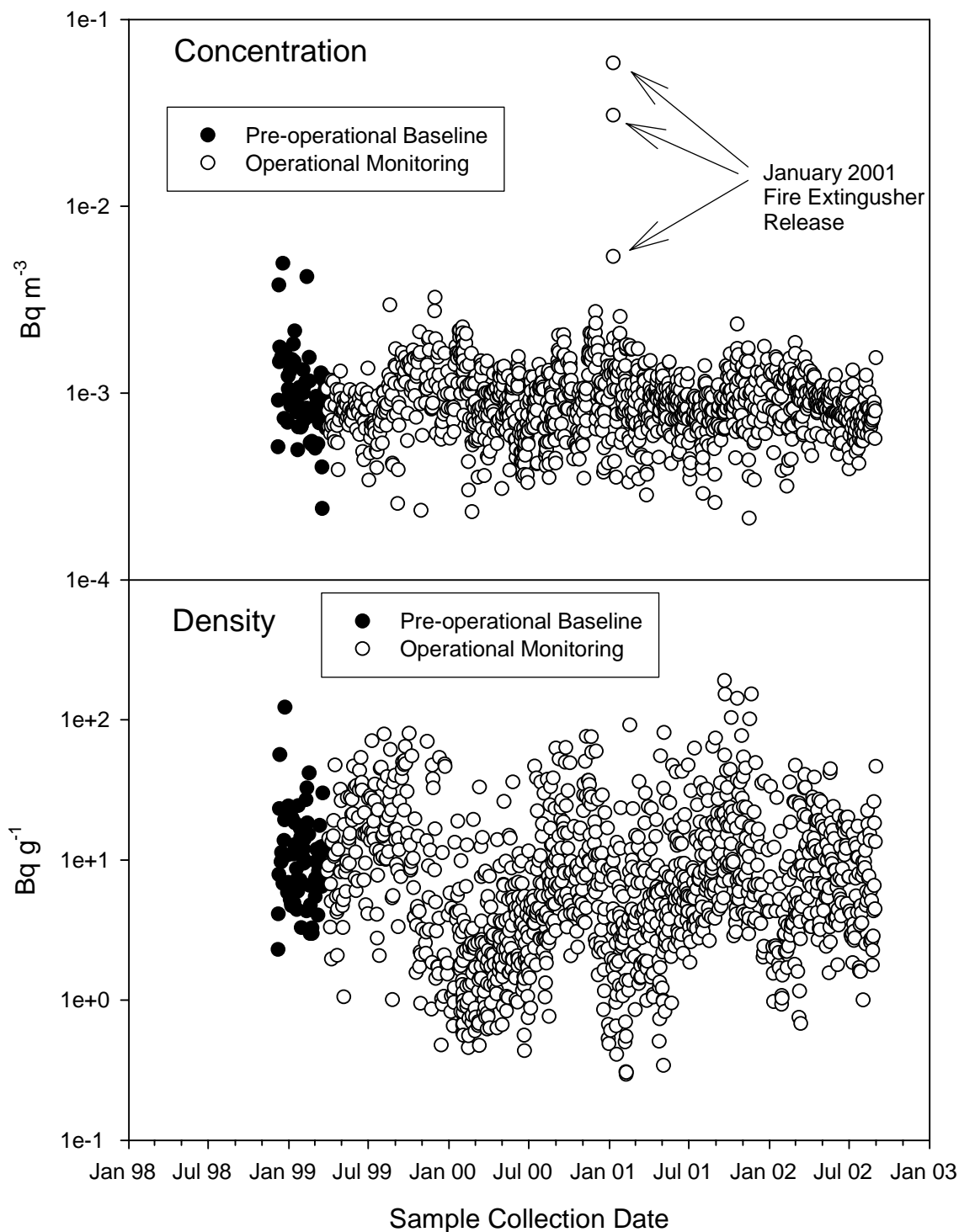


Figure 15. Beta Emitting Radioactivity (>MDC) in FAS Samples Collected during December 1998 - September 2002

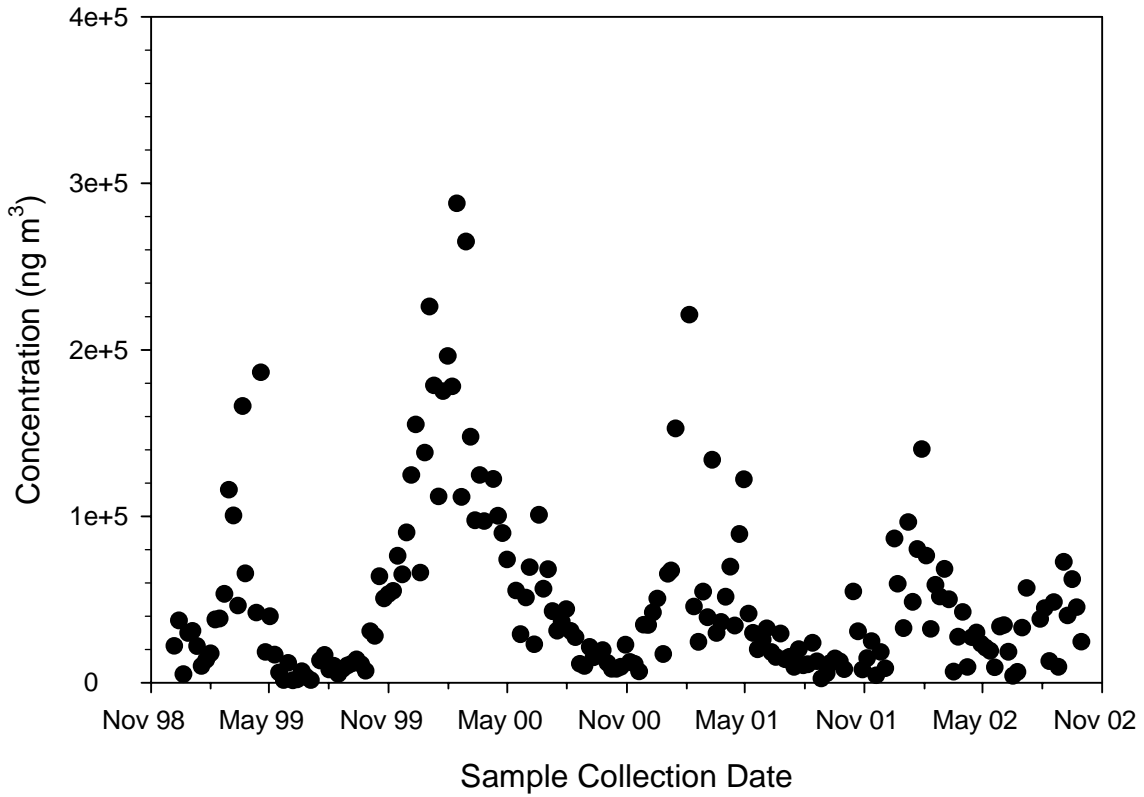


Figure 16. Sodium Released as Aerosols in the Exhaust from the WIPP

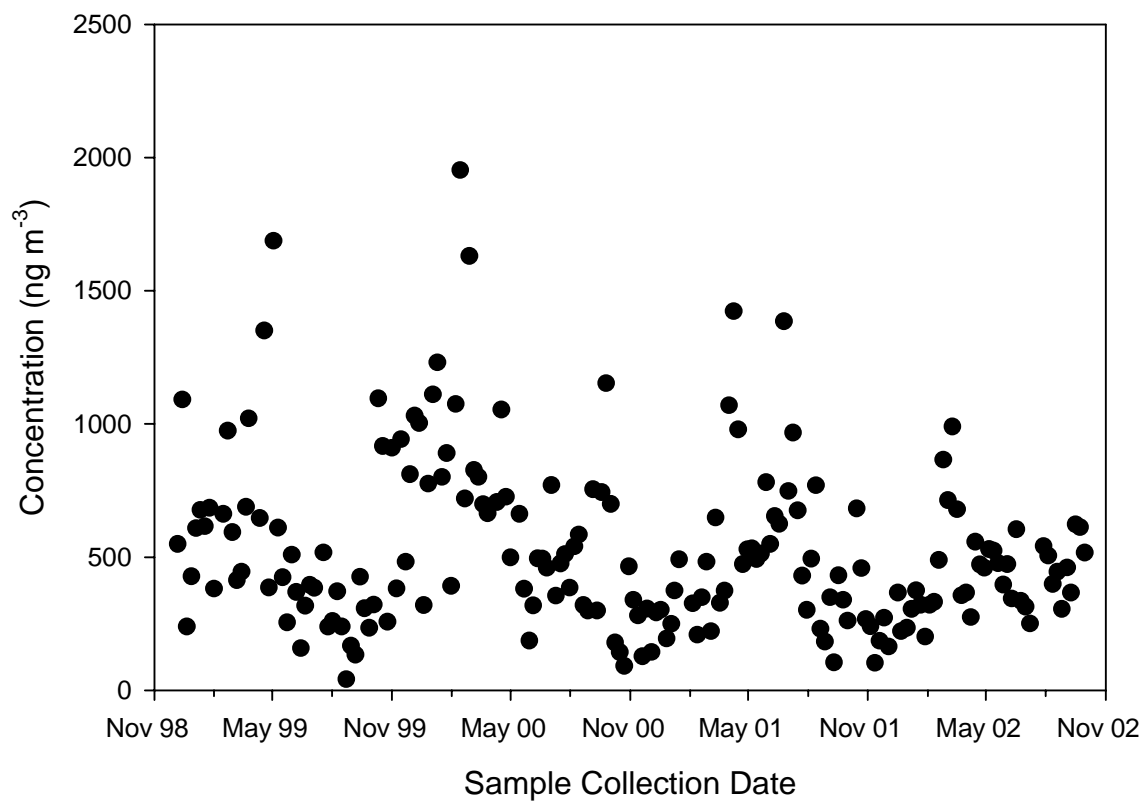


Figure 17. Aluminum Released as Aerosols in the Exhaust from the WIPP