

INTEGRATED DRY NO_x/SO₂ EMISSIONS CONTROL SYSTEM

Final Report, Volume 2: Project Performance and Economics

Appendices

Clean Coal Technology Projects
Federal Energy Technology Center (FETC)

DOE Contract Number DE-FC22-91PC90550

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INTEGRATED DRY NO_x/SO₂ EMISSIONS CONTROL SYSTEM

FINAL REPORT, VOLUME 2: PROJECT PERFORMANCE AND ECONOMICS

Appendix A

DPSC LANCE PARAMETRIC DATA SUMMARY

PSCC Arapahoe Unit 4 DPSC Parametric Summary																		
Test	Date & Time	Urea Injection Parameters										Baseline			SNCR Performance			
		Load Mills	O2cr	Injection	DPSC	Urea	Total Inj	air Conc	N/NO	NO	SO2	dNO (ave-W/E)	SNCR	dNO	dN2O	dNO		
		MWt	QOS %wet	Location	Angle	gpm	gpm	psi	wt%	ppmc	ppmc	%	%	ppmc	%			
1152	11/7/96 0:24	60	C	6.7	DPSC	34	1.04	4	11.5	35.9	1.06	345	399	29	31.0	24	22.1	
												355	400		31.5	35	31.5	
												338	397		26.0	16	18.6	
1153	11/7/96 4:30	60	C	6.70	DPSC	34	2.00	4	11.5	35.9	2.03	345	399	40	30.0	25	24.5	
												345	399		38.8	38	28.7	
												355	400		40.2	54	38.0	
1154	11/7/96 23:47	60	C	6.70	DPSC	34	1.03	4	11.1	35.9	1.08	338	397	28	39.3	28	21.0	
												334	401		29.7	25	24.9	
												343	407		27.4	33	34.7	
1155	11/8/96 4:15	60	C	6.90	DPSC	34	2.05	4	11.1	35.9	2.15	340	399	41	39.2	37	28.3	
												340	399		28.0	16	17.2	
												334	401		39.2	37	28.3	
1156	11/8/96 4:15	60	C	6.80	DPSC	34	2.70	4	11.1	35.9	2.83	343	407	49	40.4	51	36.8	
												340	399		41.6	27	18.7	
												334	401		44.7	43	28.8	
1157	11/9/96 23:24	60	C	6.50	DPSC	45	0.95	4	12.0	35.9	0.96	343	407	30	50.5	61	35.0	
												340	399		47.5	30	18.9	
												347	405		32.9	26	23.0	
1158	11/10/96 2:00	60	C	6.50	DPSC	45	2.10	4	12.0	35.9	2.13	347	405	41	33.6	38	32.7	
												307	401		26.9	17	20.7	
												347	405		42.9	42	28.6	
1159	11/10/96 3:17	60	C	6.60	DPSC	45	3.00	4	12.0	35.9	3.04	347	405	47	46.3	58	36.7	
												347	405		38.1	27	24.5	
												307	401		46.8	52	31.9	
1160	11/10/96 4:40	60	C	6.60	DPSC	65	3.00	4	12.0	35.9	3.04	347	405	43	51.3	70	39.5	
												307	401		42.3	36	27.5	
												347	405		50.6	53	30.4	
1161	11/10/96 5:50	60	C	6.50	DPSC	65	2.10	4	12.0	35.9	2.13	347	405	35	48.1	47	28.0	
												307	401		50.9	64	36.1	
												347	405		35.1	33	30.4	
1162	11/10/96 7:25	60	C	6.40	DPSC	65	1.00	4	12.0	35.9	1.01	347	405	27	41.3	37	26.2	
												307	401		40.7	47	33.2	
												347	405		30.3	27	28.7	
1162	11/10/96 8:15	60	C	6.40	DPSC	65	0.00	4	12.0	35.9	0.00	347	405	27	32.2	22	20.0	
												307	401		27.9	28	28.6	
												347	405		26.7	18	22.3	
												347	405		7.2	3	11.8	
												307	401		-4.2	2	-13.8	
												307	401		-2.4	3	-35.0	
												322	406					
												362	410					
												315	400					

PSCC Arepahoë Unit 4

Test	Date & Time	Economizer Exit, dry (1-12): Base (dry)										Economizer Exit, dry (1-12): w/Urea (dry)										NH3 Slip		Comments
		O2					CO2					NO					CO					AHO	ppm	
		ppm	ppm	ppm	ppm	%	ppm	ppm	ppm	ppm	%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm		
1152	11/7/96 0:24	8.9	268	232	21	0.2	10.89	2.6	8.9	269	160	27	-5	11.1	18.5	19.6	Composite West							
		8.70	251	223	31	-4	10.25	2.7	9.90	250	150	36	-5	10.17	24.4	10.3	Composite East							
		8.00	287	244	8	-4	11.70	0.4	7.90	284	182	17	-5	11.80	12.3	28.8	Composite							
1153	11/7/96 4:30	8.9	268	232	21	0.2	10.89	2.6	9.00	265	161	28	-5	10.92	19.5	25.6	Composite West							
		8.9	268	232	21	0.2	10.89	2.6	8.90	276	142	31	-5	11.03	28.4	28.6	Composite East							
		9.70	251	223	31	-4	10.25	2.7	9.90	240	131	44	-5	10.22	30.1	22.5	Composite							
1154	11/7/96 23:47	8.00	287	244	8	-4	11.70	0.4	8.00	274	148	22	-5	11.70	20.6	10.4	Composite West							
		9.20	263	219	20	-2	10.73	-0.6	9.20	261	154	23	-4	10.67	15.6	13.6	Composite East							
		###	242	204	31	-2	9.77	0.9	10.6	239	144	27	-4	9.65	19.7	7.2	Composite							
1155	11/8/96 4:15	8.40	279	238	13	-2	11.38	-1.6	8.50	276	170	14	-4	11.30	9.8	38.9	Composite West							
		9.20	263	219	20	-2	10.73	-0.6	9.30	243	132	30	-4	10.48	23.5	54.8	Composite East							
		###	242	204	31	-2	9.77	0.9	###	217	117	37	-4	9.37	30.1	23.0	Composite							
1156	11/8/96 4:15	8.40	279	238	13	-2	11.38	-1.6	8.30	276	140	20	-4	11.37	17.1	42.5	Composite West							
		9.20	263	219	20	-2	10.73	-0.5	9.60	237	117	35	-4	10.40	28.7	58.1	Composite East							
		###	242	204	31	-2	9.77	0.9	###	199	99	42	-4	9.69	36.3	26.9	Composite							
1157	11/9/96 23:24	8.40	279	238	13	-2	11.38	-1.6	8.10	277	128	23	-4	11.64	20.2	4.6	Composite West							
		9.00	270	231	18	-2	10.72	0.3	8.00	268	155	25	-3	10.72	17.8	8.3	Composite East							
		9.90	251	214	21	-2	9.99	1.2	###	243	140	28	-4	9.70	24.3	0.9	Composite							
1158	11/10/96 2:00	7.70	296	227	16	-2	11.77	-0.5	7.70	298	168	18	-3	11.06	12.1	24.2	Composite West							
		9.00	270	231	18	-2	10.72	0.3	9.00	255	132	31	-4	10.72	28.6	33.1	Composite East							
		9.90	251	214	21	-2	9.99	1.2	9.70	226	117	47	-4	10.07	38.2	15.3	Composite							
1159	11/10/96 3:17	7.70	296	227	16	-2	11.77	-0.5	7.70	287	145	34	-3	11.67	19.6	39.0	Composite West							
		9.00	270	231	18	-2	10.72	0.3	9.00	235	123	34	-4	10.76	34.8	52.3	Composite East							
		9.90	251	214	21	-2	9.99	1.2	9.70	204	106	45	-4	9.94	45.4	25.6	Composite							
1160	11/10/96 4:40	7.70	296	227	16	-2	11.77	-0.5	7.90	272	129	26	-4	11.58	25.6	24.3	Composite West							
		9.00	270	231	18	-2	10.72	0.3	8.90	256	121	32	-4	10.79	31.6	28.0	Composite East							
		9.90	251	214	21	-2	9.99	1.2	9.70	239	107	39	-4	10.11	41.2	20.6	Composite							
1161	11/10/96 5:50	7.70	296	227	16	-2	11.77	-0.5	7.90	280	145	23	-3	11.51	23.4	10.8	Composite West							
		9.00	270	231	18	-2	10.72	0.3	8.70	272	139	31	-4	10.97	25.9	12.8	Composite East							
		9.90	251	214	21	-2	9.99	1.2	9.90	256	127	25	-4	9.91	30.1	8.8	Composite							
1162	11/10/96 7:25	7.70	296	227	16	-2	11.77	-0.5	7.80	294	157	20	-3	11.56	19.1	1.5	Composite West							
		9.00	270	231	18	-2	10.72	0.3	8.90	272	158	19	-3	10.82	15.3	1.5	Composite East							
		9.90	251	214	21	-2	9.99	1.2	###	256	153	22	-4	9.80	18.1	1.4	Composite							
1162	11/10/96 8:15	7.70	296	227	16	-2	11.77	-0.5	7.90	294	164	16	-3	11.47	12.8		Composite West							
		9.00	270	231	18	-2	10.72	0.3	8.80	275	218	18	-2	10.76	2.3		Composite East							
		9.90	251	214	21	-2	9.99	1.2	###	248	219	18	-2	9.67	2.4		Composite							
		7.70	296	227	16	-2	11.77	-0.5	7.90	291	229	13	-3	11.50	1.4		Composite							
		8.80	275	218	18	-2	10.76	2.3																
		###	248	219	18	-2	9.67	2.4																
		7.90	291	229	13	-3	11.50	1.4																

PSC Arapahoe Unit 4 DPSC Parametric Summary

Test	Date & Time	Urea Injection Parameters										Baseline		SNCR Performance			
		Load Mills MW	O2cr %wet	Injection Location	DPSC Angle	Urea gpm	Total gpm	Inj air psi	Conc wt%	N/NO	NO ppmc	SO2 ppmc	dNO(ave-W/E) %	SNCR %	dNO ppmc	econ %	dN2O %
1163	11/10/96 23:45	83	C	6.50	DPSC	65	2.00	4	11.1	35.9	1.93	346	408	38	38.9	36	26.7
												345	413		38.0	46	35.2
												343	411		38.9	28	21.2
1164	11/11/96 2:47	60	C	6.50	DPSC	90	2.08	4	11.1	35.9	2.11	346	408	36	38.6	33	24.5
												345	413		35.7	34	27.9
												343	411		36.8	27	21.7
1165	11/11/96 4:20	60	C	6.40	DPSC	34	2.00	4	11.1	35.9	2.02	346	408	39	40.2	41	29.2
												345	413		39.0	51	37.8
												343	411		38.5	28	21.1
1166	11/11/96 4:20	60	C	6.40	DPSC	34	0.00	4	11.1	35.9	0.00	346	408	3	-0.4	1	-54.5
												345	413		1.0	2	64.1
												343	411		4.1	4	28.3
1166	11/11/96 7:00	60	C	6.70	DPSC	65	1.33	4	12.2	35.9	1.34	348	415	33	33.2	28	24.2
												342	418		33.9	34	29.7
												329	384		32.9	20	18.7
1167	11/12/96 0:58	50	B&C	6.80	DPSC	90	0.80	4	12.0	36.9	0.98	343	412	32	29.0	25	24.7
												324	416		26.3	22	25.3
												369	412		38.1	22	15.7
1168	11/12/96 3:08	50	B&C	6.70	DPSC	65	0.80	4	12.0	35.9	0.98	343	412	31	32.0	25	22.9
												324	416		28.3	27	29.2
												369	412		34.5	23	17.7
1169	11/12/96 4:16	50	B&C	6.70	DPSC	45	0.80	4	12.0	35.9	0.98	343	412	30	34.0	31	26.4
												324	416		27.1	35	39.7
												369	412		33.5	25	20.0
1169	11/12/96 5:30	50	B&C	6.70	DPSC	45	0.00	4	12.0	35.9	0.00	334	410		-5.4	0	-1.7
												330	411		3.8	2	12.4
															-3.6	0	-3.2
1170	11/13/96 11:47	71	C	6.00	DPSC	45	2.40	4	12.1	35.9	2.00	356	425	34	33.2	34	28.6
												377	434		36.8	42	30.3
												365	427		31.2	28	23.2
1171	11/14/96 3:00	71	C	6.00	DPSC	45	1.20	4	12.1	35.9	1.00	356	425	25	26.5	22	23.8
												377	434		28.2	27	25.7
												365	427		22.3	16	19.4
1172	11/14/96 4:20	71	C	6.00	DPSC	45	3.47	4	12.1	35.9	2.89	356	425	41	41.5	40	27.4
												377	434		41.5	49	31.6
												365	427		41.4	32	21.2
1173	11/14/96 5:15	71	C	6.00	DPSC	65	3.43	4	12.1	35.9	2.86	356	425		38.0	32	25.2
1174	11/14/96 11:45	60	B&C	7.00	DPSC	45	1.70	4	12.1	35.9	1.97	363	425	48	48.7	53	29.9
												328	420		49.9	60	36.4
												380	423		46.7	40	22.5

PSCC Arapahoe Unit 4

Test	Date & Time	Economizer Exit, dry (1-12): Base (dry)						Economizer Exit, dry (1-12): w/Urea (dry)						NH3 Slip ppm	Comments		
		O2	SO2	NO	CO	N2O	CO2	N2O	O2	SO2	NO	CO	CO			CO2	N2O
		%dry	ppm	ppm	ppm	ppm	%	ppm	%dry	ppm	ppm	ppm	ppm	%	ppm		
1163	11/10/96 23:45	9.10	270	229	19	-2	10.46	0.5	9.00	276	141	32	-4	10.70	24.5	5.2	Composite West
		9.85	256	214	27	-2	9.95	1.9	###	247	131	33	-4	9.79	30.1	8.6	East
		8.35	289	241	14	-2	11.11	-0.3	7.85	296	153	24	-4	11.58	20.4	1.8	Composite
1164	11/11/96 2:47	9.10	270	229	19	-2	10.46	0.5	9.15	270	140	34	-4	10.58	22.1	4.6	West
		9.85	256	214	27	-2	9.95	1.9	9.90	252	137	37	-4	9.88	23.1	8.0	East
		8.35	289	241	14	-2	11.11	-0.3	8.20	289	154	21	-4	11.30	19.2	1.2	Composite
1165	11/11/96 4:20	9.10	270	229	19	-2	10.46	0.5	9.10	255	137	35	-4	10.73	27.4	25.0	West
		9.85	256	214	27	-2	9.95	1.9	9.90	236	130	44	-5	9.81	33.3	35.0	East
		8.35	289	241	14	-2	11.11	-0.3	8.20	286	150	24	-4	11.30	19.5	15.0	Composite
1165	11/11/96 4:20	9.10	270	229	19	-2	10.46	0.5	9.20	272	228	16	-3	10.44	1.0		West
		9.85	256	214	27	-2	9.95	1.9	9.90	258	211	24	0	9.73	3.2		East
		8.35	289	241	14	-2	11.11	-0.3	8.25	272	233	10	0	10.78	2.5		Composite
1166	11/11/96 7:00	9.20	272	228	16	-3	10.44	1.0	9.15	264	153	24	-1	10.26	19.4	3.0	West
		9.90	258	211	24	0	9.73	3.2	###	249	137	31	-2	9.48	24.0	1.3	East
		8.25	272	233	10	0	10.78	2.5	8.20	282	157	19	-1	10.86	16.9	4.7	Composite
1167	11/12/96 0:58	9.30	268	223	45	-2	10.25	6	9.70	259	153	46	-1	9.78	20.9	0.8	West
		###	255	198	69	-2	9.64	9	###	250	146	83	-2	9.54	21.9	1.3	East
		8.40	289	259	15	-1	10.96	3	8.40	284	160	21	-1	10.80	18.6	0.3	Composite
1168	11/12/96 3:08	9.30	268	223	45	-2	10.25	6	9.50	262	149	44	-3	9.95	21.7	1.4	West
		###	255	198	69	-2	9.64	9	###	258	142	69	-4	9.67	25.1	2.4	East
		8.40	289	259	16	-1	10.96	3	8.80	278	164	19	-3	10.64	18.3	0.4	Composite
1169	11/12/96 4:15	9.30	268	223	45	-2	10.25	6	9.40	267	148	51	-4	10.08	25.5	0.9	West
		###	255	198	69	-2	9.64	9	###	246	139	60	-4	9.32	29.0	1.1	East
		8.40	289	259	16	-1	10.96	3	8.90	276	165	21	-4	10.55	19.6	0.6	Composite
1189	11/12/96 5:30	9.10	271	221	50	0	10.40	5.7	9.50	265	225	40	-3	10.09	5.7		West
		###	249	200	61	0	9.52	8.2	9.90	260	198	76	-3	9.76	9.3		East
		8.20	291	258	17	1	11.04	3.0	8.80	286	259	15	-2	11	3.20		Composite
1170	11/13/96 11:47	8.30	300	251	20	3	11.53	1.6	8.50	298	165	29	2	11.36	25.0	11.5	West
		9.50	277	241	20	3	10.49	2.8	9.30	289	155	42	1	10.77	30.2	8.0	East
		7.35	324	277	8	3	12.21	-0.3	7.60	300	187	14	2	12.05	19.4	15.0	Composite
1171	11/14/96 3:00	8.30	300	251	20	3	11.53	1.6	8.40	302	183	27	1	11.51	17.3	1.4	West
		9.50	277	241	20	3	10.49	2.8	9.30	289	176	30	0	10.78	20.6	0.9	East
		7.35	324	277	8	3	12.21	-0.3	7.50	321	213	13	1	12.33	11.5	1.9	Composite
1172	11/14/96 4:20	8.30	300	251	20	3	11.53	1.6	8.20	300	148	26	0	11.80	30.4	23.4	West
		9.50	277	241	20	3	10.49	2.8	9.1	284	146	29	-1	11	35.6	23.2	East
		7.35	324	277	8	3	12.21	-0.3	7.30	312	163	21	0	12.41	24.1	23.6	Composite
1173	11/14/96 5:15	8.30	300	251	20	3	11.53	1.6	8.20	303	162	30	0	11.64	24.5	11.1	West
		9.40	274	234	33	3	10.54	1.4	9.60	252	118	36	1	10.30	34.9	23.9	East
1174	11/14/96 11:45	9.25	274	214	41	2	10.74	5.0	9.6	254	104	50	0	10.5	42.8	32.1	Composite
		9.00	282	253	16	3	10.75	-0.2	9.25	267	132	21	26	11	25.8	15.6	West

PSCC Arapahoe Unit 4 DPSC Parametric Summary

Test	Date & Time	Urea Injection Parameters										Baseline		SNCR Performance				
		Load MWt	Mills	O2cr	Injection	DPSC	Urea	Total	Inj air	Conc	N/N/O	NO	SO2	dNO	SNCR	dNO	dN2O	dNO
		MWe	OOS	%wet	Location	Angle	gpm	psi	wt%	ppmc	ppmc	%	%	%	ppmc	%	%	
1175	11/15/96 1:38	50	B&C	7.00	DPSC	90	1.70	4	11.9	35.9	1.97	363	425	40	43.2	36	22.8	
												328	420		37.7	42	33.7	
1176	11/15/96 3:00	50	B&C	7.00	DPSC	65	1.70	4	11.9	35.9	1.97	380	423	45	43.0	33	20.0	
												363	425		48.1	46	26.1	
												328	420		41.4	51	37.5	
1177	11/15/96 4:05	50	B&C	7.00	DPSC	35	1.70	4	11.9	35.9	1.97	380	423	49	48.2	35	19.4	
												363	425		51.7	51	27.1	
												328	420		46.6	61	39.8	
1178	11/15/96 5:14	50	B&C	6.90	DPSC	45	2.50	4	11.9	35.9	2.90	380	423	52	51.4	45	23.1	
												363	425		55.6	61	30.2	
												328	420		50.5	75	45.3	
												380	423		54.2	50	24.2	
1179	11/16/96 5:14	60	C	6.50	DPSC	45	1.90	4	11.9	35.9	2.00	334	428	43	41.4	40	29.2	
												351	431		48.7	53	31.2	
												346	431		36.9	27	21.0	
												325	426		27.7	40	44.1	
												333	424		23.6	31	39.7	
												320	415		60.1	69	36.0	
												347	429		54.6	53	27.9	
												336	413		52.3	58	33.0	
												328	424		49.2	49	30.7	
												319	418		45.9	37	25.0	
												312	388		37.9	26	21.9	
												354	428		38.0	25	19.5	
												373	476		35.2	21	18.6	
												418	520		33.7	23	19.8	
												235	309		24.2	21	27.3	
												###	467		57.1	69	37.7	
												336	413		52.9	58	32.5	
												310	386		32.9	28	27.2	
												333	424		23.4	30	38.6	
												347	429		54.0	52	27.6	

PSCC Arapahoe Unit 4

Test	Date & Time	Economizer Exit, dry [1-12]: Base (dry)					Economizer Exit, dry [1-12]: w/Urea (dry)					NH3 Slip		Comments							
		O2	SO2	NO	CO	NO2	CO2	N2O	%dry	ppm	ppm	O2	SO2		NO	CO	O	CO2	N2O	AHO	ppm
1175	11/15/96 1:36	9.40	274	234	33	3	10.54	1.4	9.40	266	133	24	1	10.30	24.4				12.9		Composite West
		9.25	274	214	41	2	10.74	5.0	9.8	254	127	55	1	9.83	30.7				11.5		Composite East
1176	11/15/96 3:00	9.00	282	253	16	3	10.75	-0.2	9.10	274	143	19	1	10.66	21.4				14.3		Composite West
		9.40	274	234	33	3	10.54	1.4	9.45	259	121	32	1	10.32	30.6				18.0		Composite East
1177	11/15/96 4:05	9.25	274	214	41	2	10.74	5.0	9.85	255	119	52	0	10.1	36.3				16.9		Composite West
		9.00	282	253	16	3	10.75	-0.2	9.10	267	130	23	0	10.74	23.2				19.1		Composite East
1178	11/15/96 5:14	9.40	274	234	33	3	10.54	1.4	9.30	259	114	42	-1	10.60	34.5				35.5		Composite West
		9.25	274	214	41	2	10.74	5.0	9.9	243	108	74	-1	10.4	42.2				43.4		Composite East
1179	11/16/96 5:14	9.00	282	253	16	3	10.75	-0.2	8.80	277	125	25	-1	11.00	30.4				27.6		Composite West
		9.40	274	234	33	3	10.54	1.4	9.60	234	103	36	-2	10.32	40.3				47.3		Composite East
1179	11/16/96 5:14	9.25	274	214	41	2	10.74	5.0	9.8	235	101	64	-2	10.2	51.4				52.9		Composite West
		9.00	282	253	16	3	10.75	-0.2	9.00	254	116	24	-2	10.58	33.0				41.6		Composite East
1179	11/16/96 5:14	8.60	295	230	20	2	10.93	0.3	9.40	263	126	34	1	10.47	26.3						Composite West
		9.55	274	223	20	2	10.32	1.4	9.60	223	112	47	0	10.04	34.5						Composite East
TRAVERSE		8.00	311	250	10	2	11.59	-1.5	8.40	290	153	21	0	11.16	17.3						1
		9.80	265	202	23	2	9.79	2.0	###	222	133	36	1	8.98	24.3						2
AT THE		###	233	183	22	2	8.88	2.9	###	215	130	24	0	8.18	18.6						3
		7.60	309	238	24	1	11.57	2.3	8.30	210	90	57	0	10.96	51.0						4
ECONOMIZER		###	262	212	24	2	9.52	3.2	9.00	266	105	40	0	10.35	38.7						5
		9.10	273	222	17	2	10.22	2.3	9.20	180	105	44	0	10.28	40.3						6
AND AT		8.70	290	224	22	2	10.81	2.0	8.90	223	112	41	0	10.46	35.2						7
		6.20	342	262	22	2	12.68	1.2	6.90	318	135	26	0	11.99	29.8						8
THE		6.2	317	255	15	2	12.46	1.3	6.80	318	152	20	-1	12.06	21.5						9
		6.30	333	275	9	2	12.61	0.0	6.60	330	167	20	0	12.40	20.0						10
APHO		7.00	325	255	10	2	11.96	0.4	7.70	313	157	22	-1	11.59	16.2						11
		8.70	289	232	9	2	10.58	0.5	8.60	263	155	25	0	10.76	16.1						12
3R		###	230	175	7	1	8.67	0.7	###	185	130	23	0	8.67	12.0						3R
		7.60	309	238	24	1	11.57	2.3	8.40	237	96	54	-1	10.96	50.3						5R
5R		9.10	273	222	17	2	10.22	2.3	8.70	233	108	42	-1	10.63	41.8						6R
		6.2	317	255	15	2	12.46	1.3	7.50	315	156	16	-1	11.58	22.0						2R
2R		###	233	183	22	2	8.88	2.9	###	225	136	30	-1	8.41	18.8						4R
		###	262	212	24	2	9.52	3.2	8.70	281	109	38	-2	10.65	38.9						

INTEGRATED DRY NO_x/SO₂ EMISSIONS CONTROL SYSTEM

FINAL REPORT, VOLUME 2: PROJECT PERFORMANCE AND ECONOMICS

Appendix B

AIR TOXICS SUMMARY SECTION

FOR

LOW NO_x COMBUSTION SYSTEM RETROFIT

IV. Summary of Air Toxics Monitoring Results

A total of 52 potential air toxics were measured at Arapahoe 4 after the combustion modifications were installed and optimized. Table 3 lists the air toxics that were sampled during this baseline air toxics test program. Sampling of the air toxics occurred from November 17, 1992 through November 19, 1992. The unit was operated at a base load of a nominal 100 MWe during the testing. No sampling occurred during sootblowing operations.

Table 4 lists the average operating conditions of the unit during the sampling period. The recently optimized combustion modifications were operated at approximately 25% overfire air during the sampling period. Figure 2 shows a simplified diagram of the unit and shows the five different sample locations. Gaseous samples were obtained at the inlet and the outlet of the FFDC. Solid samples were obtained of unpulverized coal, bottom ash, and flyash. This report lists the results of the air toxics testing. For details on the methods used for sampling, analysis, and quality assurance see the *Environmental Monitoring Plan (EMP) Addendum for Air Toxics Monitoring*, dated July 1993.

Table 4

Average Operating Conditions and Continuous Emissions Data	
Unit load	103.5 MW Gross
Steam flow	847 Mlb/hr
Stack oxygen	5.49% (wet)
Stack carbon monoxide	49 ppm (dry)
Stack nitrogen oxide	292 ppm (dry, 3% O ₂)
Stack sulfur dioxide	393 ppm (dry, 3% O ₂)

Public Service Company of Colorado contracted with Carnot, Inc of Tustin, California to complete the air toxics work at the Arapahoe 4 station. Fossil

**TABLE 3
PSCC ARAPAHOE UNIT 4
TARGET COMPOUND LIST**

TRACE METALS			
Arsenic Cadmium Copper Mercury Selenium	Barium Chromium Lead Molybdenum Phosphorus	Beryllium Cobalt Manganese Nickel Vanadium	
ACID-FORMING ANIONS OR PRECURSORS ¹			
Chloride	Fluoride Sulfate	Phosphate	
VOLATILE ORGANIC COMPOUNDS			
Benzene	Toluene	Formaldehyde	
SEMI-VOLATILE ORGANIC COMPOUNDS			
Polycyclic Aromatic Hydrocarbons			
Acenaphthene Benzo(a)anthracene Benzo(g,h,i)perylene Dibenzo(a,h)anthracene Indeno(1,2,3-cd)pyrene Pyrene	Acenaphthylene Benzo(a)pyrene Benzo(k)fluoranthene Fluoranthene Naphthalene 2-Methylnaphthalene 7,12-Dimethylbenz(a)anthracene	Anthracene Benzo(b)fluoranthene Chrysene Fluorene Phenanthrene 3-Methylcholanthrene	
RADIONUCLIDES			
Ra ²²⁶ Ra ²²⁸	Th ²³² Th ²³⁰ Th ²³¹	U ²³⁸ U ²³⁵ U ²³⁴	Po ²¹⁰ Pb ²¹⁰
NITROGEN COMPOUNDS			
Cyanide			

¹ Elemental precursors of these anions measured in the fuel (Cl, F, S, P)

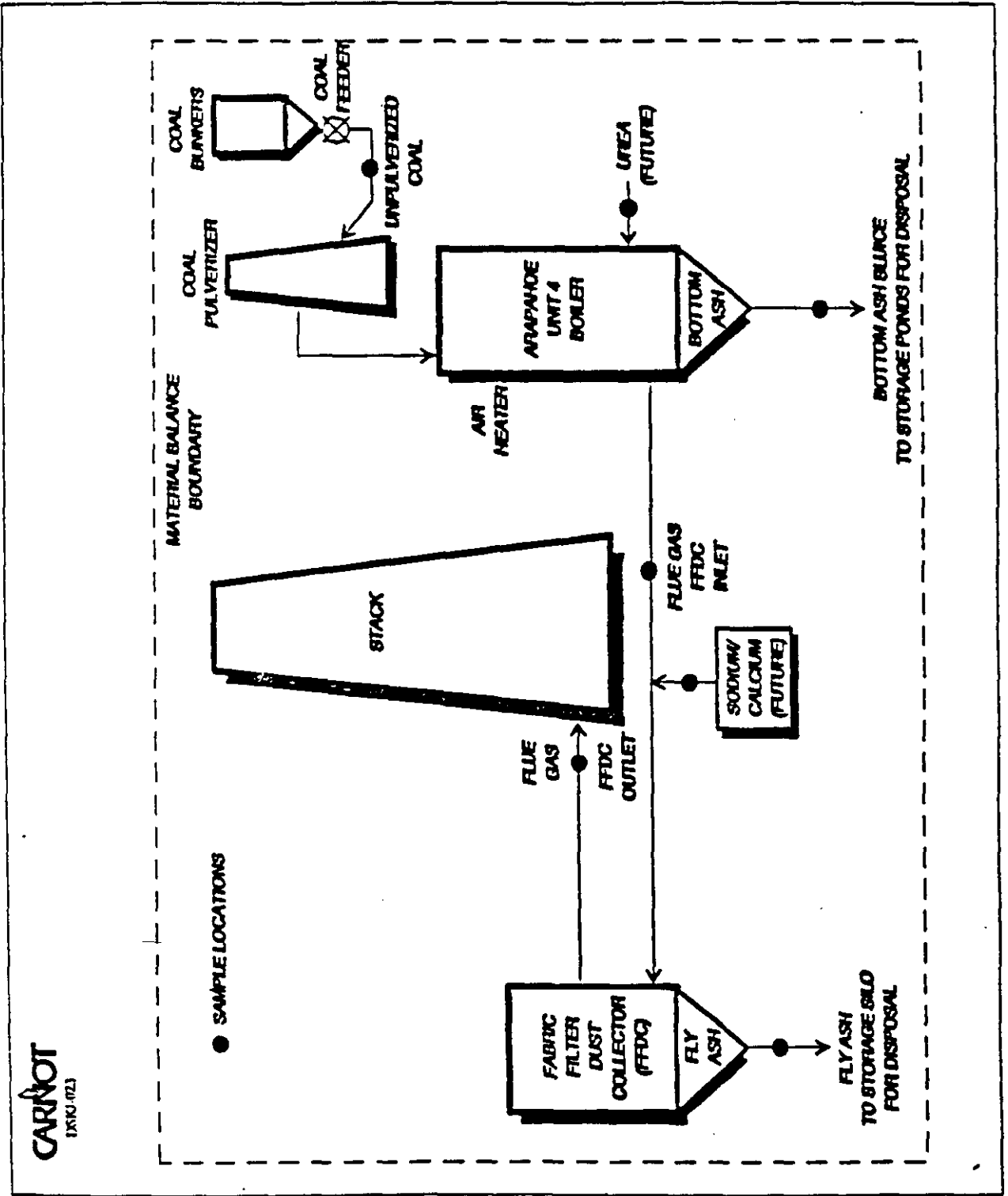


Figure 2. Sample Locations at PSCC Arapahoe Unit 4

Energy Research Corp of Laguna Hills, California provided some assistance at the site and with data collection. Table 5 lists the laboratories used to analyze the collected samples.

Table 5

Laboratories for Air Toxics Analyses		
Analysis	Laboratory	Location
Solid particulate	Carnot, Inc	Tustin, Ca.
Chloride (supplemental)	Carnot, Inc	Tustin, Ca.
Acid-forming anions	Curtis and Tompkins	Berkeley, Ca.
Trace metals	Curtis and Tompkins	Berkeley, Ca.
Volatile organic compounds	Atmosphere Assessment Associates	Chatsworth, Ca.
Semi-volatile organic compounds	Zenon Environmental Laboratories	Burlington, Ontario
Radionuclides	Accu-lab Research	Golden, Co.
Fuel analysis	Commercial Testing and Engineering	Denver, Co.
Neutron activation analysis	Massachusetts Institute of Technology	Cambridge, Ma.

A. Uncertainty Analysis

In the tables that follow, a value for uncertainty expressed as a percentage is provided for all data. The calculation method used is based upon ANSI/ASME PTC 19.1-1985, "Measurement of Uncertainty." The uncertainty is based on a 95% confidence interval for the mass emissions for the target species but is expressed as a percentage so that it may be applied to other units. A very important part of the method is assigning an estimated bias error for the major variables. The value presented represents only an approximation of the uncertainty as not all bias errors may be estimated. The uncertainty is also not a measure of long-term-trace-species emissions for this boiler, but only the uncertainty for the specific test period. It was assumed that the samples are a normal population distribution. Bias that were estimated as listed below:

- 1) For all non-detect data, a bias of one-half of the detection limit was used. No bias was assumed for analytical results reported above the detection limit.
- 2) A bias of 10% was assumed for the flue gas flow rate on both the inlet and outlet fabric filter ducts. Bias was estimated by comparing the calculated and measured flue gas flow rate.
- 3) A bias of 19% was assumed for the inlet particulate collection rate and 10% was assumed for the outlet particulate collection rate. The bias was estimated by examining the isokinetic sample rate for different flue gas flow rates.
- 4) A bias of 5% was assumed for the coal flow based on the difference of the calculated and measured coal flow rate.
- 5) A bias of 21% was calculated for the fly ash mass flow rate based upon the assumed biases for particulate collection and inlet flue gas flow rate.
- 6) A bias of 22% was calculated for the bottom ash mass flow based upon the assumed biases for particulate collection, inlet flue gas flow rate, and coal flow rate.
- 7) It was assumed that all other measurements were accurate and had a bias of 0%. While this scenario is not likely, insufficient data was available to make any reasonable assumptions.

B. Treatment of Non-Detectable Measurements

Many of the target species for which a measurement was attempted were not found using the specified sampling and analytical techniques. If a measurement was not possible, the value that could have been measured, i.e.

the detection limit, if the trace emissions were present are reported. The "non-detects" are shown as less than the detection limit. The difficulty occurs when averaging various samples of which some or all of the measurements are below the detection limit. The following summarizes the two cases:

1) All values below detection limit

The arithmetic average of the detection limit is shown with a "<" sign to indicate that the trace species is less than the reported average detection limit. For example, if a species was not found and the method provided a detection limit of 0.45, the values is reported as <0.45.

2) Some, but not all, values below detection limit

The value of all measurements above the detection limit are averaged with one-half of the detection limit. For example, if three measurements of 10, 8, and <6 are found, the average would be $(10+8+6/2)/3$ or 7. Note that no "<" sign is used in these reported averages even though some of the values are below the detection limit. If the average calculated with this method is less than the greatest detection limit; the largest detection limit is reported and a "<" symbol is used. For example, if values of 6, <4, and <2 were reported, the average would be reported as <4 and not $(6+4/2+2/2)/3$ or 3.

C. Treatment of Blank Values

Three different types of blanks were used as part of the air toxics test program quality assurance (QA) program. The QA program included field blanks, reagent blanks, and laboratory preparation blanks.

Field blanks are samples obtained by assembling a complete sample train at the test site using the same procedures as when obtaining the actual sample. The sample train is then leak checked and disassembled to recover and

analyze the sample. Field blanks are not used to "correct" the data generally but they are used to provide an indication of the quality of the sample.

Reagent blanks consist of samples of the reagent and/or filters that are collected at the site. Analysis of these samples show if any of the results were caused by existing levels of the trace species in the material used to collect or recover the sample. If measurable values of the trace species are found, the data is usually corrected by subtracting the value measured in the reagent.

Laboratory reagent blanks consist of samples of the chemicals used during the measurement analysis. If measurable values of the trace species are found, the data is usually corrected by subtracting the value measured in the reagent. Any measurable values in the laboratory reagent may be caused by initial trace species in the chemicals or to the analytical procedures.

In the tables that follow the value of the field blank is shown for reference, but none of the data has been changed due to these measurements. If a measurement has a value near the field blank measurement, there may be some question as to the accuracy of the data and the reported value may NOT be source related. A separate column lists a blank correction percentage for all trace species that were corrected due to either a reagent or laboratory reagent blank. This is an average percentage calculated as follows:

$$\text{Blank Correct} = \frac{\text{SUM}(\text{blank value}/\text{sample value} * 100)}{\text{number of samples}}$$

For example, if three samples contained 10, 5, and 4 mg/kg of a trace species and the reagent blank was 2 mg/kg, the blank correction would be $(2/10 + 2/5 + 2/4) * 100/3$ or 37%. Thus on average, the actual value measured was 37% higher than the value reported in the table. If the blank correction is reported as 0%, no blank correction was calculated and the reported value was the measured value. Note that in most cases a high blank correction value

does not mean that the data is inaccurate. If a sample was contaminated with a trace species due to a filter, and the filter was analyzed and the data corrected, it is likely that the data is meaningful.

D. Gaseous Species Monitoring

Table 6 lists the results of the gaseous air toxics monitoring at the inlet and outlet of the fabric-filter. Three replicate tests were completed for each air toxic species. Individual tests were averaged to determine the estimated air toxics emission. The uncertainty of the average as explained in section IV.A is also reported.

In general, trace metal emissions were very low at the FFDC outlet as the FFDC is very efficient for metals removal. The overall average removal rate of the trace metals for the fabric-filter measured during this test was 97.1%. Mercury and chromium are the metals of most interest due to their potential health impact. Mercury is the most difficult of the trace metals to remove as it may be present as a vapor rather than a solid particulate. The calculated removal rate for mercury of 78.2% assumes that the outlet mercury emissions existed at the detection limit. Additional methods are available to determine the speciation of these metals. The species of mercury are very important in the removal process as it is currently believed that ionic-mercury is much easier to remove than the other species. Chromium, especially hexavalent-chromium, is also gaining interest due to its potential toxicity. Additional baseline-testing is planned at a later date to determine speciation of these two important trace-metal emissions.

Outlet emissions of the semi-volatile organic compounds (polycyclic aromatic hydrocarbons, or PAH) were very low or non-existent. Of the 19 compounds measured, only naphthalene and 2-Methylnaphthalene were measured at average values above the detection limit at the outlet. For both of the PAH compounds, the field blank levels are actually higher than the reported outlet

Table 6 - Gaseous Air Toxics Emissions

	Fabric Filter Inlet							Fabric Filter Outlet						
	Test 1	Test 2	Test 3	Average	Uncert	Field Blank	Blank ¹ Correct	Test 1	Test 2	Test 3	Average	Uncert	Field Blank	Blank ¹ Correct
	µg/Nm ³	µg/Nm ³	µg/Nm ³	µg/Nm ³	%	µg/Nm ³	%	µg/Nm ³	µg/Nm ³	µg/Nm ³	µg/Nm ³	%	µg/Nm ³	%
Trace Metals														
Arsenic	33.5	19.4	37.0	30.0	81	1.28	0.0	0.47	1.8	0.65	0.97	183	0.82	0.0
Barium	237	88.4	588	305	210	3.39	2.5R	2.2	0.56	1.6	1.5	145	1.09	70.8R
Beryllium	6.7	14.4	14.1	11.7	95	<0.04	0.0	<0.03	<0.03	<0.03	<0.03	33	<0.03	0.0
Cadmium	2.5	2.7	3.7	3.0	60	0.15	0.0	0.28	0.14	<0.08	0.15	197	<0.08	0.0
Chromium	36.7	84.8	73.6	65.0	99	0.53	0.9R	0.72	0.70	1.1	0.85	72	0.19	31.8R
Cobalt	21.6	50.4	44.4	38.8	100	<0.38	0.0	<0.28	<0.28	<0.26	<0.27	33	<0.27	0.0
Copper	249	197	214	220	37	2.41	0.3R	1.6	1.6	1.0	1.4	63	<0.98	25.2R
Lead	147	36.3	65.0	82.9	174	0.15	2.7R	0.61	0.56	0.52	0.56	22	0.05	58.9R
Manganese	149	310	300	253	92	0.53	0.1R	1.3	1.9	0.65	1.3	119	0.22	16.4R
Mercury	2.4	1.5	1.3	1.7	91	0.32	9.4R	<0.28	<0.45	<0.39	<0.37	67	<0.38	0.0
Molybdenum	7.8	15.5	18.5	14.0	101	0.30	30.7R	0.22	0.22	0.21	0.22	17	0.22	94.0R
Nickel	19.4	50.4	48.1	39.3	112	1.13	0.0	19.5	2.5	1.3	1.9	400	<0.55	0.0
Scelenium	23.5	34.1	29.6	29.1	51	<0.08	0.0	0.42	0.73	0.26	0.47	127	<0.05	0.0
Phosphorus	17900	19000	18900	18600	23	<1.88	0.0	8.1	8.7	9.2	8.6	20	<1.36	0.0
Vanadium	100	213	215	176	95	0.23	0.1R	0.36	0.17	0.39	0.31	98	0.16	36.7R

NOTE < indicates that the quantity measured was less than the detection limit thus the detection limit is shown
¹ R (Reagent Blank Correction) or L (Laboratory Blank Correction) indicate the type of blank correction.

Table 6 - Gaseous Air Toxics Emissions Continued

	Fabric Filter Inlet						Fabric Filter Outlet						
	Test 1	Test 2	Test 3	Average	Uncert	Blank ¹ Correct	Test 1	Test 2	Test 3	Average	Uncert	Field Blank	Blank ¹ Correct
Semi-Volatile Organic Compounds	µg/Nm ³	µg/Nm ³	µg/Nm ³	µg/Nm ³	%	%	µg/Nm ³	µg/Nm ³	µg/Nm ³	µg/Nm ³	%	µg/Nm ³	%
Naphthalene	0.31	0.24	0.40	0.31	70	54L	0.42	0.25	0.34	0.34	63	.55	48L
Acenaphthylene	<0.012	<0.011	<0.033	<0.019	170	0	<0.011	<0.009	<0.008	<0.009	47	<.027	0
Acenaphthene	<0.014	<0.012	<0.012	<0.013	42	0	<0.014	<0.009	<0.015	<0.013	65	<.022	0
Fluorene	0.015	0.013	0.015	0.014	29	0	0.014	0.011	<0.013	<0.013	44	<.013	0
Phenanthrene	<0.142	<0.140	<0.183	<0.155	53	0	<0.134	<0.111	<0.141	<0.129	44	<.116	0
Anthracene	<0.019	<0.010	<0.019	<0.016	93	0	0.012	<0.014	<0.006	<0.014	74	<.013	0
Fluoranthene	<0.030	<0.033	<0.030	<0.031	38	0	<0.029	<0.024	<0.023	<0.025	43	<.025	0
Pyrene	<0.031	<0.034	<0.030	<0.032	39	0	<0.029	<0.024	<0.023	<0.025	43	<.025	0
Benz(a)anthracene ²	<0.019	<0.021	<0.040	<0.026	118	0	<0.018	<0.016	<0.014	<0.016	45	<.016	0
Chrysene ²	<0.019	<0.020	<0.037	<0.025	105	0	<0.018	<0.015	<0.014	<0.016	47	<.016	0
Benzo(b)fluoranthene ²	<0.011	<0.024	<0.030	<0.022	119	0	<0.007	<0.008	<0.014	<0.010	105	<.013	0
Benzo(k)fluoranthene ²	<0.021	<0.096	<0.069	<0.062	156	0	<0.013	<0.011	<0.018	<0.014	71	<.010	0
Benzo(a)pyrene ²	<0.056	<0.077	<0.011	<0.048	179	0	<0.011	<0.026	<0.008	<0.015	162	<.010	0
Indeno(1,2,3-cd)pyrene ²	<0.030	<0.029	<0.029	<0.029	36	0	<0.033	<0.047	<0.039	<0.040	55	<.028	0
Dibenzo(a,h)anthracene ²	<0.037	<0.037	<0.037	<0.037	36	0	<0.039	<0.056	<0.045	<0.047	56	<.034	0
Benzo(g,h,i)perylene ²	<0.037	<0.029	<0.029	<0.032	51	0	<0.030	<0.038	<0.034	<0.034	45	<.027	0
2-Methylnaphthalene	0.041	0.026	0.015	0.027	119	0	0.063	0.020	0.022	0.035	175	.2	0
7,12-Dimethylbenz(a)anthracene	<0.025	<0.004	<0.047	<0.025	218	0	<0.007	<0.006	<0.003	<0.005	109	<.007	0
3-Methylcholanthrene	<0.149	<0.007	<0.146	<0.101	204	0	<0.007	<0.006	<0.006	<0.006	43	<.006	0

NOTE < indicates that the quantity measured was less than the detection limit thus the detection limit is shown

¹ R (Reagent Blank Correction) or L (Laboratory Blank Correction) indicate the type of blank correction.

² Carcinogenic PAH compounds

Table 6 - Gaseous Air Toxics Emissions Continued

	Fabric Filter Inlet							Fabric Filter Outlet						
	Test 1	Test 2	Test 3	Average	Uncert	Field Blank	Blank Correct	Test 1	Test 2	Test 3	Average	Uncert	Field Blank	Blank Correct
Acid-Forming Anions	ppm	ppm	ppm	ppm	%	ppm	%	ppm	ppm	ppm	ppm	%	ppm	%
Chlorine (Total)	0.64	0.69	0.62	0.65	30	N/A	0	0.67	0.60	0.27	0.51	121	N/A	0
(Gaseous)	0.61	0.49	0.60	0.57				0.65	0.57	0.26	0.49			
(Solid)	0.03	0.20	<0.04	0.08				<0.03	0.03	<0.03	0.02			
Fluorine (Total)	8.5	6.7	6.7	7.3	42	N/A	0	9.5	7.6	2.6	6.6	137	N/A	0
(Gaseous)	7.7	5.8	6.3	6.6				9.5	7.5	2.5	6.5			
(Solid)	0.77	0.87	0.44	0.70				0.06	0.06	0.06	0.06			
Phosphate (Total)	0.35	0.64	0.18	0.39	149	N/A	0	<0.58	<0.47	<0.15	<0.40	142	N/A	0
(Gaseous)	<0.62	0.58	0.13	0.34				<0.54	<0.43	<0.11	<0.36			
(Solid)	0.04	0.06	0.06	0.05				<0.04	<0.04	<0.04	<0.04			
Sulfate (Total)	350	320	300	320	30	N/A	29.02 ¹	290	300	300	300	15	N/A	84.01 ¹
(Gaseous)	340	310	290	320				290	300	300	300			
(Solid)	5.3	4.2	3.4	4.3				0.03	0.03	0.02	0.02			
Radionuclides (solids)	Inlet Not Measured													
Uranium-233,234								<0.06	<0.06	0.05	<0.06	28	N/A	0
Uranium-235								<0.06	<0.06	0.05	<0.06	28	N/A	0
Uranium-238								<0.06	<0.06	<0.05	<0.06	33	N/A	0
Radium-226								0.11	0.11	0.11	0.11	15	N/A	0
Radium-228								0.80	0.96	0.76	0.84	34	N/A	0
Lead-210								<0.75	<0.73	0.22	<0.75	104	N/A	0
Polonium-210								0.06	<0.06	<0.05	<0.06	28	N/A	0
Thorium-228								<0.23	<0.34	<0.16	<0.24	96	N/A	0
Thorium-230								<0.17	<0.06	<0.16	<0.13	128	N/A	0
Thorium-232								<0.06	<0.11	<0.11	<0.09	88	N/A	0

NOTE < indicates that the quantity measured was less than the detection limit thus the detection limit is shown
¹ Majority of blank correction is due to sulfate in filter

Table 6 - Gaseous Air Toxics Emissions Continued

	Fabric Filter Inlet							Fabric Filter Outlet						
	Test 1	Test 2	Test 3	Average	Uncert	Field Blank	Blank Correct	Test 1	Test 2	Test 3	Average	Uncert	Field Blank	Blank Correct
Volatile Organic Compounds	ppb	ppb	ppb	ppb	%	ppb	%	ppb	ppb	ppb	ppb	%	ppb	%
Benzene	0.60	<0.26	0.46	0.40	152	0.04	0	0.69	0.88	1.34	0.97	85	.04	0
Toluene	3.8	1.4	1.4	2.2	154	0.29	0	43.8	23.1	30.7	32.5	80	.29	0
Formaldehyde	13.0	13.9	17.0	14.6	38	35.2	0	10.8	24.9	12.6	16.1	119	15.7	0
Nitrogen Compounds	ppb	ppb	ppb	ppb	%	ppb	%	ppb	ppb	ppb	ppb	%	ppb	%
Cyanide (as HCN)	<8	<8	9	<8	30	N/A	0	7	<4	<8	<8	76	N/A	0

NOTE < indicates that the quantity measured was less than the detection limit thus the detection limit is shown

emissions. It is believed that both these compounds may be an artifact of resin degradation and are not source related. This would explain similar emission levels in both the sample and the field blank. None of the carcinogenic PAH compounds were detected at either the inlet or the outlet of the FFDC. As all of the PAH compounds were measured near or below the detection limit or are not believed to be source related, it is impossible to determine if the FFDC removes any of the compounds.

An EPA Method 5 sampling train was used to sample anions. The sample train collected a solid sample in a particulate filter and a gaseous sample within a series of impinger baths. Table 6 shows three values for each anion: (1) total, (2) solid fraction, and (3) gaseous fraction. The results show that the majority of all anions exists in the gas phase. The fabric filter was effective in removal of the solid phase anions but removed only a small fraction of the gas phase anions. Gaseous phosphate at the inlet was only 0.34 ppm which represent only 3% of the total phosphorus measured with the multi-metals train. It would be expected that the two values would agree for both measurements, so the difference is likely caused by the two measurement methods. It is believed that the multi-metals train accurately measures phosphorus and that the data presented in the anion tables obtained with ion chromatography are not accurate. Gaseous sulfur emissions were approximately 320 ppm. This represents 90% of the sulfur present in the fuel. The total sulfate level at the outlet represents 83% of the coal sulfur. While the data indicates that some gaseous sulfur is removed across the fabric-filter, no removal is expected and the small difference is within the uncertainty of the data. The continuous emissions monitor averaged 334 ppm over the test period and thus agrees with the outlet sulfate emissions within the range of uncertainty of the data.

From the solids sample collected at the fabric-filter outlet by the EPA Method 5 sampling train, 11 types of radionuclide emissions were measured. Of the 11 potential radionuclides, only Radium-226 and Radium-228 had average values

above the detection limit. No reagent blank corrections were made for the data as correcting in some cases would have reduced the data to below zero. The reagent blank for Radium-226 was 0.1 versus a reported value of 0.11 pCi/Nm³ and for Radium-228 was 1.5 versus a reported value of 0.84 pCi/Nm³. Thus, although values are reported for these two radionuclides, they are not believed to be source related and the reported values are likely due to the fiberglass filter used for particulate collection.

Three volatile-organic compounds (VOC) were measured during the testing: benzene, toluene, and formaldehyde. The data indicate that both benzene and toluene actually increased across the fabric-filter. It is suspected that the both VOCs at the inlet were actually higher than shown, but as VOC's such as toluene and benzene may be absorbed directly on particulates, a representative sample may have not obtained in the high-particulate/high-carbon inlet test location. An additional test is planned to determine VOC emissions and confirm these data. While the formaldehyde emissions are very low, the field blanks contained 35 ppb of formaldehyde at the inlet and 16 ppb of formaldehyde at the outlet. The field blank measurements were at or even higher than the gaseous sample. The sample vials for both the field blank and measurement samples were NOT stored in an air-tight nitrogen-purged desiccator. It is possible that the samples may have been contaminated with formaldehyde in the air that may have penetrated the sample seal. Future testing will use the air-tight sealing system with a nitrogen purge to eliminate this possible contamination point.

Finally, the emissions of nitrogen-based cyanide at both the inlet and outlet were below the detection limit.

Table 7 - Coal Air Toxics Analysis

	Base Test Method						Neutron Activation Analysis					
	Test 1	Test 2	Test 3	Average	Uncert	Blank ⁴ Correct	Test 1	Test 2	Test 3	Average	Uncert	Blank Correct
	mg/Kg	mg/Kg	mg/Kg	mg/Kg	%	%	mg/Kg	mg/Kg	mg/Kg	mg/Kg	%	mg/Kg
Trace Metals												
Arsenic ²	<0.5	<0.5	<0.5	<0.5	29	0.0	0.55	0.40	0.49	0.48	40	0
Barium ²	0.6 ¹	28	21	25	182	6.9L	350	525	383	419	55	0
Beryllium	0.21	0.24	0.23	0.22	18	1.3L						
Cadmium	0.09	<0.05	<0.05	<0.05	117	0.0	0.13	0.09	0.11	0.11	50	0
Chromium	0.8	1.3	1.1	1.1	58	7.1L	3.00	3.50	2.05	2.85	64	0
Cobalt	0.8	1.0	1.0	0.9	31	0.0	0.74	0.75	0.70	0.73	11	0
Copper	2.7	2.8	2.7	2.7	7	1.5L						
Lead	2.1	2.5	1.6	2.1	55	12.0L						
Manganese	3.4	5.9	3.4	4.2	85	13.0L						
Mercury ²	<0.1	0.1	<0.1	<0.1	24	0.0	0.025	0.026	0.013	0.021	84	0
Molybdenum	<0.1	<0.1	0.2	0.1	217	0.0	0.89	1.20	0.95	1.01	41	0
Nickel	0.4	0.8	0.5	0.6	87	11.0L						
Selenium ²	<0.05	<0.05	<0.05	<0.05	29	0.0	0.75	0.77	0.93	0.82	31	0
Phosphorus	510	350	370	410	53	0.0						
Vanadium	2.6	3.5	2.8	3.0	40	3.3L						
Acid-Forming Anions												
Chloride as Cl ⁻²	600	<100 ¹	600	600	8	0	19	22	26	22	39	0
Fluorine as F ⁻	79	89	85	84	16	0						
Phosphate ³	1564	1073	1135	1300	53	0						
Sulfate	14100	13200	12300	13200	18	0						

NOTE < indicates that the quantity measured was less than the detection limit thus the detection limit is shown.

All values are reported on an as-received basis for the coal.

¹ Results from this sample inconsistent with other data and was not included in the average.

² Neutron activation analysis results was used for these trace species rather than the base method.

³ Phosphate values are reported but are not believed accurate. Ion-chromatography many not be appropriate technique for measurement.

⁴ R (Reagent Blank Correction) or L (Laboratory Blank Correction) indicate the type of blank correction.

Table 7 - Coal Air Toxics Analysis Continued

	Base Test Method						Neutron Activation Analysis					
	Test 1	Test 2	Test 3	Average	Uncert	Blank Correct	Test 1	Test 2	Test 3	Average	Uncert	Blank Correct
Radionuclides	pCi/g	pCi/g	pCi/g	pCi/g	%	%	Not Applicable					
Uranium-233,-234	0.16	0.13	0.11	0.13	47	0						
Uranium-235	<0.01	<0.01	0.02	0.01	217	0						
Uranium-238	0.12	0.05	0.11	0.09	101	0						
Radium-226	0.29	0.31	0.24	0.28	32	0						
Radium-228	0.35	0.20	0.16	0.24	105	0						
Lead-210 ¹	0.37	<0.69	0.77	0.50	122	0						
Polonium-210	0.10	<0.10	0.20	0.12	163	0						
Thorium-228	0.09	0.08	0.12	0.10	54	0						
Thorium-230	0.12	0.17	0.30	0.20	118	0						
Thorium-232	0.12	0.04	0.15	0.10	137	0						

NOTE < indicates that the quantity measured was less than the detection limit thus the detection limit is shown

All values are reported on a dry basis for the coal.

¹ The highest non-detect was not used for the average, detection limits varied by sample.

E. Solids Sampling

Coal Analysis

Table 7 presents the results of the analysis of the unpulverized coal samples. The fuel was analyzed for trace metals, acid-forming anions, and radionuclides.

Trace-metal analysis was completed using the base-test method described in the EMP. Instrumental neutron activation analysis (INAA) was also used to analyze the samples for certain elements and compounds. This second test was added to lower the detection limit of these materials and to confirm the validity of the base-test method. Generally, the results of the two test methods agreed. However, the values for barium, molybdenum, and selenium were much higher when using INAA analysis and provided a much lower detection limit for arsenic, mercury, and chloride.

The order of magnitude increase of barium from the INAA test cannot be explained. Both methods provided consistent results, although test 1 data from the base-test method were unreasonably low and was not included in the average value. INAA analysis provided a molybdenum measurement that was an order of magnitude higher than the base-test method. Both analytical test methods provided consistent results. Selenium measurements were also an order of magnitude higher when analyzed using INAA. The cause for this large variation may be due to volatilization of the selenium when using the base test method. Potential problems with these three elements will be further discussed in section IV.F.

Table 7 also shows the results from the testing of the coal for acid-forming anions. The INAA analysis method was used to provide another means of verifying the chloride measurement and reduce its detection limit. The base-test method reported two measurements: 600 mg/kg and one below the detection limit of 100 mg/kg. Additional testing of these samples by another

laboratory using the same method reported results below the detection limit for all three samples. Data obtained using the INAA method are consistent and are believed to be more accurate.

Radionuclides in the input coal stream were very low and the measured values were very close to their detection limits.

Ash Analysis

Table 8 shows the results of the solid sample ash analysis. It shows the results for the 15 metals analyzed for both the bottom ash and flyash. Each of the daily samples is actually a composite of three separate samples obtained throughout the day. In general, metals concentrations are higher in the ash than the coal because the reduction of the coal to ash results in a more than 90% reduction in material and concentrates the metals.

There are large uncertainties (greater than 100%) for mercury, outlet arsenic and outlet nickel. The high uncertainties are related to large variation of the samples. For mercury, all measured values were near the detection limit and the high uncertainty reflects the increased inaccuracies for measurements near the detection limit. The high uncertainty for outlet arsenic and nickel were caused by a single measurement substantially higher than the remaining values. In order to investigate the problem, a split of the same three samples was reanalyzed with the same analytical procedures and laboratory and substantially different results were obtained as shown below:

	Original Average	Reanalyzed Average
Arsenic	<2.5	3.8
Nickel	3.9	13.3

The reason for the large variation is unknown. Each of the samples in both tests had good agreement between replicates which indicates no major

Table 8 - Ash Air Toxics Analysis

	Bottom Ash/Sluice Water ¹						Fly Ash					
	Test 1	Test 2	Test 3	Average	Uncert	Blank Correct	Test 1	Test 2	Test 3	Average	Uncert	Blank Correct
Trace Metals	mg/Kg	mg/Kg	mg/Kg	mg/Kg	%	%	mg/Kg	mg/Kg	mg/Kg	mg/Kg	%	%
Arsenic	1.3	1.3	1.5	1.3	30	0	2.7	7.0	1.6	3.8	189	0
Barium	860	740	880	830	32	0	1800	1600	1500	1630	32	0
Beryllium	1.0	0.8	1.0	0.9	38	0	1.8	1.6	1.5	1.6	32	0
Cadmium	<0.25	<0.25	<0.25	<0.25	37	0	<0.25	<0.25	0.3	<0.25	43	0
Chromium	2.7	2.4	2.5	2.5	27	0	8.5	7.3	7.0	7.6	34	0
Cobalt	2.2	1.8	2.3	2.1	39	0	5.6	4.4	4.5	4.8	40	0
Copper	10	7.6	8.2	8.6	44	0	25	27	18	23	55	0
Lead	11	8.7	7.7	9.1	51	0	28	24	20	24	47	0
Manganese	40	33	34	36	36	0	66	70	69	68	22	0
Mercury	<0.1	0.29	<0.1	0.13	266	0	0.25	0.15	<0.1	0.15	167	0
Molybdenum	0.7	0.4	<0.7	<0.7	62	0	3.8	3.8	3.4	3.7	26	0
Nickel	2.2	<1.6	<1.6	<1.6	63	0	5.9	3.0	2.8	3.9	113	0
Selenium	<2.5	<2.5	<2.5	<2.5	37	0	4.2	3.9	3.8	4.0	25	0
Phosphorus	1910	1600	1810	1770	32	0	3900	3300	2900	3370	43	0
Vanadium	12	9.4	11	10.9	38	0	32	25	21	26	57	0
Acid-Forming Anions	mg/Kg	mg/Kg	mg/Kg	mg/Kg			mg/Kg	mg/Kg	mg/Kg	mg/Kg		
Chloride as Cl ⁻	47	41	51	47	36	0	13	8	13	11	64	0
Fluoride as F ⁻	<28	<25	<31	<28	46	0	20	18	34	24	93	0
Phosphate ²	<189	<165	<206	<187	46	0	<20	<20	<20	<20	36	0
Sulfate	189	759	617	522	143	0	1000	1100	840	980	39	0

NOTE < indicates that the quantity measured was less than the detection limit thus the detection limit is shown

¹ Samples were obtained wet and the reported values include the dry fraction and the water fraction. The water fraction was corrected for inlet sluice water concentrations when appropriate.

² Phosphate values are reported but are not believed accurate. Ion-chromatography many not be appropriate technique for measurement.

Table 8 - Ash Air Toxics Analysis Continued

	Bottom Ash/Sluice Water ¹						Fly Ash					
	Test 1	Test 2	Test 3	Average	Uncert	Blank Correct	Test 1	Test 2	Test 3	Average	Uncert	Blank Correct
Radionuclides	pCi/g	pCi/g	pCi/g	pCi/g	%	%	pCi/g	pCi/g	pCi/g	pCi/g	%	%
Uranium-233,-234	2.1	2.4	2.1	2.2	30	0	2.6	2.3	2.0	2.3	39	0
Uranium-235	0.1	0.1	0.1	0.1	23	0	0.2	0.1	<0.1	0.1	165	0
Uranium-238	2.0	2.3	2.3	2.2	30	0	2.6	2.4	2.2	2.4	30	0
Radium-226	2.2	3.1	2.9	2.7	49	0	3.2	2.7	2.5	2.8	38	0
Radium-228	1.8	2.0	2.1	2.0	30	0	2.0	1.6	1.7	1.8	36	0
Lead-210	0.7	0.9	0.6	0.7	57	0	0.8	1.1	1.3	1.1	62	0
Polonium-210	0.6	0.2	0.3	0.4	143	0	1.4	1.2	1.8	1.5	56	0
Thorium-228	3.2	2.9	3.2	3.1	27	0	2.8	2.5	2.2	2.5	37	0
Thorium-230	3.2	2.8	3.0	3.0	28	0	3.2	2.2	2.1	2.5	64	0
Thorium-232	3.4	3.3	3.0	3.2	28	0	2.7	2.7	2.4	2.6	27	0

NOTE: < indicates that the quantity measured was less than the detection limit thus the detection limit is shown

¹ Samples were obtained wet and the reported values include the dry fraction and the water fraction.

analytical problems and it is believed both analyzed samples were representative of the total sample. An unknown bias must be affecting these results. Thus even though the data has a high estimated uncertainty, the true uncertainty is higher due to this unknown analytical bias. As the arsenic value for the reanalyzed sample was more consistent with the mass balance data, this value is reported throughout the report.

Table 8 also lists the results for the four acid-forming anions. As discussed previously in section IV.D, the ICP method used to analyze the phosphate is not believed to be accurate. A mass balance for phosphate was not completed but the data obtained from the testing is shown in the table. The chloride values in the flyash account for only 3% of the total chloride. This confirms that chloride emissions are gaseous and are not collected with the particulate. An additional test for chloride was conducted using a mercuric nitrate titration of the flyash sample to confirm the low fly ash quantities. This single test provided a measurement of 5.2 mg/kg, slightly lower, but in the same range as provided by the base-test method. Bottom ash sulfate uncertainty was high at 143%. The uncertainty was due to the large variation in the samples, but as the total bottom ash sulfate is less than 0.1% of the total sulfates in the coal, the high uncertainty is insignificant.

The final analysis performed on the ash streams was for radionuclides. Generally, the values were an order of magnitude greater than reported in the fuel stream due to their concentration by the ashing of the coal. The distribution between the bottom ash and flyash appears to be approximately equal. Radionuclide concentrations were low and are not expected to be a concern at these low values.

F. Mass Balance

The mass balance is a very important quality check on toxics-emissions data. Using different sample and analytical techniques to measure toxics in both

gaseous and solid forms at very low absolute quantities makes the measurement for air toxics difficult, at best. A mass balance provides a quick means for determining if the various analysis methods agree. While it would be comforting to have mass balances of 100% for all toxics, it would be extremely unusual due to the different methods used and the low absolute quantities.

Table 9 contains an overall and an intermediate mass balance for the measured toxics. Note that a balance is only possible on those compounds that are dependant upon the inlet fuel levels. Balances for the semi-volatile and volatile organic compounds are not possible as these relate to combustion parameters. The overall balance was obtained by dividing the sum of the gaseous, bottom ash, and flyash outputs by the fuel input. In an effort to supply additional information, an intermediate balance was also completed. This balance was performed at the fabric-filter inlet and is obtained by dividing the sum of the toxics at the fabric-filter inlet and the bottom ash by the input-fuel toxics. This is a mass balance at the inlet of the FFDC. The units selected for the mass balance calculations are lb/10¹² Btu for the metals and anions and μ Curies/10¹² Btu for radionuclides. These units allow comparison of the data to other generating units of varying size.

In general, the measured air toxic quantities at the outlet are lower than those measured at the inlet, so the mass balance is less than 100%. Most of the species are in the range of 50-90% closure except for barium, cobalt, lead, manganese, molybdenum, selenium, and chloride which are discussed below:

Barium

The fuel level of barium was determine using INAA analysis as ICP analysis appeared to be severely biased low as previously discussed. ICP analysis was used for the flue gas and ash samples. Thus the poor mass balance closure may be due to an undefined bias with the different analytical techniques. However, the calculated mass balance using the original ICP data also had

Table 9 - Mass Balance Results

	Fuel In Input	Gas FF In Intermediate	Bottom Ash Output	Fly Ash Output	Gas FF Out Output	Overall Mass Balance	Intermediate Mass Balance	FTDC Removal
Trace Metals	lb/10 ¹² Btu	lb/10 ¹² Btu	lb/10 ¹² Btu	lb/10 ¹² Btu	lb/10 ¹² Btu	%	%	%
Arsenic	43	23.1	3.1	22.7	0.75	62	61	96.7
Barium	37,600	234	1920	9790	1.1	31	6	99.5
Beryllium	20.0	9.0	2.2	9.8	<0.02	60	56	>99.8
Cadmium ¹	<4.5	2.3	<.58	<1.5	0.12	N/A	N/A	94.8
Chromium	97.4	50.0	5.9	45.5	0.66	53	57	98.7
Cobalt	83.6	29.9	4.9	29.0	<0.21	41	42	>99.3
Copper	241	169	20.0	140	1.1	67	78	99.4
Lead	185	64	21.2	144	0.44	89	46	99.3
Manganese	379	195	82.5	410	1.0	130	73	99.5
Mercury	1.9	1.3	0.30	0 ⁿ	<0.29	78	85	>78.3
Molybdenum	9.0	10.7	<1.6	22.0	0.17	265	138	98.4
Nickel	53.5	30.2	<3.7	23.3	1.5	53	63	95.1
Selenium	73.2	22.4	<5.8	23.8	0.36	41	38	98.4
Phosphorus	36,700	14,300	4,100	20,200	6.7	66	50	99.95
Vanadium	266	135	25.2	156	0.24	68	60	99.8
Acid-Forming Anions	lb/10 ¹² Btu	lb/10 ¹² Btu	lb/10 ¹² Btu	lb/10 ¹² Btu	lb/10 ¹² Btu	%	%	%
Chloride as Cl ⁻	2,000	790	89	68	630	40	45	20.3
Fluoride as F ⁻	7,600	4,800	<54	144	4,300	60	64	10.4
Phosphate ²	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Sulfate	1,180,000	1,060,000	985	5,880	983,000	84	90	7.3
Radionuclides	μCi/10 ¹² Btu	Not Measured	μCi/10 ¹² Btu	μCi/10 ¹² Btu	μCi/10 ¹² Btu	%	N/A	N/A
Uranium-233,-234	4,800		2,300	6,300	<20	178		
Uranium-235	360		100	320	<20	122		
Uranium-238	3,400		2,300	6,500	<20	262		
Radium-225	10,000		2,900	7,600	39	104		
Radium-228	8,000		2,100	4,800	290	84		
Lead-210	18,000		700	2,900	<260	22		
Polonium-210	4,200		390	4,000	<20	104		
Thorium-228	3,500		3,300	6,800	<85	291		
Thorium-230	7,100		3,200	6,800	<46	141		
Thorium-232	3,700		3,400	7,100	<20	281		

NOTE < indicates that the quantity measured was less than the detection limit thus the detection limit is shown

¹ Mass balance not possible as inlet was below the detection limit.

² Mass balance for phosphate not valid, use phosphorus mass balance results

closure problems but showed a very low coal based barium content. Due to these and other possible unknown biases, a low confidence exists with the barium data.

Cobalt

The low overall closure for both the overall and intermediate mass balance indicate that the fuel cobalt value reported may be higher than the actual concentration. Duplicate analysis using INAA showed an average 65 lb/10¹² Btu which would slightly improve the mass balance. However, in order to minimize the unknown analytical bias between the ICP and INAA analytical methods, the ICP analysis was used.

Lead

The overall mass balance appears reasonable but the intermediate mass balance is low at 46%. The most likely reason is a low bias on the sample obtained at the fabric filter inlet. As lead would be expected to be found in the particulate, similar values between the fly ash and fabric filter inlet would be expected. However, the fabric filter inlet value is one-third lower than the fly ash sample.

Manganese

Both mass balances appear reasonable at 130 and 73% but there is a significant variation between the intermediate and overall mass balance. The reason for the low intermediate balance appears to be a low bias on the fabric filter inlet sample similar to the lead value discussed above.

Molybdenum

The high overall mass balance of 265% is believed to be caused by a low bias on the fuel input measurement and is related to the high uncertainty (217%) in fuel measurement. The samples were also analyzed using INAA as shown in Table 7. Using the specified ICP method, the value was 9 lb/10¹² Btu while INAA analysis found 91 lb/10¹² Btu. The wide variation between the two

methods is not known. The correct fuel value for molybdenum is likely between the two extremes.

Selenium

Both balances were significantly low which indicates either a high fuel bias or a low outlet bias. As the base ICP method reported a non-detectable fuel value, the samples were reanalyzed using INAA. The INAA analysis reported a significantly higher value and an unknown bias must exist with the two different measurement methods. As all outlets were determined using ICP, the mass balance is based on two different analytical techniques that have a bias as shown by the widely different values obtain from the fuel. Selenium is a very difficult metal to measure and further research in the following test programs will be completed to increase the confidence of the selenium measurement.

Chloride

INAA analysis was used for the fuel measurement while different methods were used for the gaseous measurements in the inlet and outlet ducts. The different analytical techniques may have contributed to the low closure, but it is believed that a high biased fuel value is the most likely cause for the poor closure.

Table 9 does not show the mass balance for phosphate. In order to determine a mass balance, the inlet phosphate is determined by assuming that all phosphorus in the coal to phosphate. The preliminary mass balance showed very poor closure as only very low quantities of phosphate were found in the inlet and outlet multi-metals train. It is believed that ICP is not an accurate method for measuring phosphate. Thus the data is not presented and the phosphorus mass balance should be used.

The overall mass balance for radionuclides varied from 22% to 291% with an average balance of 159%. While this is a wide variation, the radionuclide

emissions were very low. Radionuclides were also near the detection limit in the testing of the inlet fuel. Small variations can cause a large variation in the mass balance. No known sampling or analytical problems were reported that would account for the varying closure. All duplicates, blanks, spikes, and other quality assurance checks were within acceptable ranges.

Table 9 also shows the percent removal for the metal and anions measured. The FFDC was very effective for metals removal with an overall 97.1% removal. The FFDC does appear to provide slight removal of the anions, however, the removals are within the uncertainty of the data and may not be significant.

Generally, the test program used the analytical methods specified in the EMP. However, some of the methods were changed in order to improve detection limits or confirm data that was measured using the analytical methods specified in the EMP. Table 10 lists the air toxics that were analyzed with a different method than specified in the EMP.

The EMP addendum for air toxics includes details on the method used to determine the total mass flow of the air toxics. In addition to the measured concentration of the toxic in the sample, mass flows of the solid and gas are required. Table 11 lists the mass flow rates of the flue gas and solids used to determine the mass flow of the toxics. Note that there are three different flue gas flow rates listed for metals, particulate matter and anions, and PAHs. The actual flue gas flow rate was used for each test as they were conducted at different times. The flue gas flow rate used for the VOC, formaldehyde and cyanide tests were from the concurrent major test that was being conducted. Coal flow was measured using the existing plant equipment. Flyash and stack ash flow was calculated using the measured particulate loading and flue gas flows. Bottom ash was calculated based on coal input and flyash flow.

Table 10

	EMP Specified Method	Method Used
FFDC Inlet		
Benzene	EPA TO-14 w/GC-PID	EPA TO-14 w/GC-MS
Toluene	EPA TO-14 w/GC-PID	EPA TO-14 w/GC-MS
Cadmium	EPA SW 846-7421 (GFAA)	EPA SW 846-6010 (ICP)
Chromium	EPA SW 846-7421 (GFAA)	EPA SW 846-6010 (ICP)
FFDC Outlet		
Benzene	EPA TO-14 w/GC-PID	EPA TO-14 w/GC-MS
Toluene	EPA TO-14 w/GC-PID	EPA TO-14 w/GC-MS
Cadmium	EPA SW 846-7421 (GFAA)	EPA SW 846-6010 (ICP)
Chromium	EPA SW 846-7421 (GFAA)	EPA SW 846-6010 (ICP)
Fuel		
Arsenic	EPA SW 846-7060(GFAA)	INAA
Barium	EPA SW 846-6010(ICP)	INAA
Chlorine	ASTM D-4208(ISE)	INAA
Mercury	EPA SW 846-7470(CVAA)	INAA
Selenium	EPA SW 846-7740(GFAA)	INAA
Cadmium	EPA SW 846-7131(ICP)	EPA SW846-6010(ICP-AES)
Chromium	EPA SW 846-7191(GFAA)	EPA SW846-6010(ICP-AES)
Lead	EPA SW 846-7421(GFAA)	EPA SW846-7420(GFAA)
Manganese	EPA SW 846-6010(ICP)	EPA SW846-6010(ICP-AES)
Bottom Ash		
Fluoride	EPA 300.0(IC)	EPA 340.2(ISE)
Lead	EPA SW 846-7421 (GFAA)	EPA SW 846-6010 (ICP)
Cadmium	EPA SW 846-7131(ICP)	EPA SW846-6010(ICP-AES)
Chromium	EPA SW 846-7191(GFAA)	EPA SW846-6010(ICP-AES)
Flyash		
Fluoride	EPA 300.0(IC)	EPA 340.2(ISE)
Lead	EPA SW 846-7421 (GFAA)	EPA SW 846-6010 (ICP)
Cadmium	EPA SW 846-7131(ICP)	EPA SW846-6010(ICP-AES)
Chromium	EPA SW 846-7191(GFAA)	EPA SW846-6010(ICP-AES)

Table 11

STREAM MASS FLOW DATA			
	Test 1	Test 2	Test 3
Flue gas flow, metals inlet (DSCFM)	247,200	252,100	261,800
Flue gas flow, metals outlet (DSCFM)	245,700	253,100	264,900
Flue gas flow, PM/Anions inlet (DSCFM)	245,800	250,200	255,900
Flue gas flow, PM/Anions outlet (DSCFM)	244,300	251,200	258,900
Flue gas flow, PAH inlet (DSCFM)	245,000	245,300	243,500
Flue gas flow, PAH outlet (DSCFM)	248,200	247,100	244,800
Coal flow (lb/hr)	86,800	88,900	88,800
Total ash flow (lb/hr) ¹	7,670	7,850	7,840
Bottom ash flow (lb/hr)	1,450	1,490	1,480
Flyash flow (lb/hr) ²	6,610	6,840	6,790
Stack ash flow (lb/hr) ²	0.56	4.1	1.9

¹Total carbon-free ash flow calculated using coal flow and average ash content of fuel over the test period.

²Mass flow of ash calculated from measurement of ash concentration multiplied by calculated flow of flue gas.

INTEGRATED DRY NO_x/SO₂ EMISSIONS CONTROL SYSTEM

FINAL REPORT, VOLUME 2: PROJECT PERFORMANCE AND ECONOMICS

Appendix C

AIR TOXICS SUMMARY SECTION

FOR

LOW NO_x COMBUSTION SYSTEM SNCR RETROFIT

IV. Summary of Air Toxics Monitoring Results

The current test period includes two groups of air toxics tests. The first group includes sampling for 26 potential air toxics with the SNCR system in operation. The second group includes some baseline tests conducted without the SNCR system in operation. The baseline tests included sampling for dioxins and furans, mercury speciation, chromium speciation, and the repeating of VOC tests to confirm the original baseline data.

This report presents data for all testing completed during this test period except for the dioxin and furan data. Due to contamination of the dioxin and furan samples, these data are not accurate. These tests will be repeated and reported in a later environmental monitoring report. Table 4 lists the potential air toxics measured during this test period, March 8, 9, and 15, 1993. Table 5 compares the air toxics measured during this test period with those measured in the original test period.

Trace Metals	Arsenic Cadmium Copper Mercury ¹ Selenium Calcium ⁴	Barium Chromium ² Lead Molybdenum Phosphate Sodium ⁴	Beryllium Cobalt Manganese Nickel Vanadium
Acid-Forming Anions or Precursors	Chloride Fluoride	Sulfate	Phosphate
Volatile Organic Compounds³ (VOC)	Benzene	Toluene	Formaldehyde
Semi-Volatile Organic Compounds	Polychlorinated Dibenzo-p-dioxins (PCDD) Polychlorinated Dibenzofurans (PCDF)		
Nitrogen Compounds	Cyanide	Ammonia	

1. The multi-metals train was analyzed for total-Hg. The Frontier Geoscience sampling train was analyzed for Hg, Hg⁺², methyl-Hg, and total-Hg.
2. Total-Cr, as determined from the multi-metals train. Both Cr⁺⁶ and total-Cr were analyzed in the EPA recirculation train.
3. Elemental precursors of these anions were measured in the fuel (Cl, F, S, and P).
4. Calcium and sodium were added to the trace metal list to provide baseline levels for comparison with the calcium and sodium injection tests planned for a later date.

Table 4: Target Compounds

Generally, the test program used the analytical methods specified in the *EMP*. Some of the methods were changed, however, to improve detection limits or confirm data that were measured using the analytical methods specified in the *EMP*. For more information on the test methods, see *Environmental Monitoring Plan for Air Toxics Monitoring*, dated July 1993. Table 6 lists the air toxics that were analyzed with a method different from that specified in the *EMP*.

Target Compounds		Baseline (11/92)	Baseline (3/93)	SNCR (3/93)
Trace Metals		X		X
Acid-Forming Anions		X		X
Volatile Organic Compounds	Benzene/toluene	X	X	
	Formaldehyde	X		
Semi-Volatile Organic Compounds	PAH	X		
	PCDD/PCDF ¹		X ²	
Solid Particulate		X	X	X
Radionuclides		X		
Trace Metals Speciation	Total/hexavalent chromium		X	
	Mercury		X	
Nitrogen Compounds		X		X
HHV, Ultimate/ Proximate Analysis		X		X
Loss-On-Ignition		X		X

1. Polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF).
2. Due to anomalous contamination of native 2,3,7,8, PCDD/PCDF isomers in the method blanks, samples, archived resin, the results of these tests are invalid and not reported in this report. These tests will be repeated during subsequent tests.

Table 5: Target Compound Comparison

Species		EMP Specified Method	Method Used
FFDC Inlet	Benzene	EPA TO-14 w/GC-PID	EPA TO-14 w/GC-MS
	Toluene	EPA TO-14 w/GC-PID	EPA TO-14 w/GC-MS
	Arsenic	EPA SW 846-7060 (GFAA)	EPA SW 846-6010 (ICP)
	Chromium	EPA SW 846-7191 (GFAA)	EPA SW 846-6010 (ICP)
	Lead	EPA SW 846-7421 (GFAA)	EPA SW 846-6010 (ICP)
	Selenium	EPA SW 846-7740 (GFAA)	EPA SW 846-6010 (ICP)
	Total Cr	AA	GFAA
FFDC Outlet	Benzene	EPA TO-14 w/GC-PID	EPA TO-14 w/GC-MS
	Toluene	EPA TO-14 w/GC-PID	EPA TO-14 w/GC-MS
	Arsenic	EPA SW 846-7060 (GFAA)	EPA SW 846-6010 (ICP)
	Chromium	EPA SW 846-7191 (GFAA)	EPA SW 846-6010 (ICP)
	Selenium	EPA SW 846-7740 (GFAA)	EPA SW 846-6010 (ICP)
Fuel	Arsenic	EPA SW 846-7060 (GFAA)	INAA
	Barium	EPA SW 846-6010 (ICP)	INAA
	Chlorine	ASTM D-4208 & ISP	INAA
	Mercury	EPA SW 846-7470 (CVAA)	INAA
	Selenium	EPA SW 846-7740 (GFAA)	INAA
	Cadmium	EPA SW 846-7131 (ICP)	EPA SW 846-6010 (ICP-AES)
	Chromium	EPA SW 846-7191 (GFAA)	EPA SW 846-6010 (ICP-AES)
	Lead	EPA SW 846-7421 (GFAA)	EPA SW 846-7420 (GFAA)
Manganese	EPA SW 846-6010 (ICP)	EPA SW 8-3-6010 (ICP-AES)	
Bottom Ash	Fluoride	EPA 300.0(IC)	EPA 340.2 (ISE)
	Lead	EPA SW 846-7421 (GFAA)	EPA SW 846-6010 (ICP)
	Chromium	EPA SW 846-7191 (GFAA)	EPA SW846-6010 (ICP-AES)
Flyash	Fluoride	EPA 300.0 (IC)	EPA 340.2 (ISE)
	Lead	EPA SW 846-7421 (GFAA)	EPA SW 846-6010 (ICP)
	Cadmium	EPA SW 846-7131 (ICP)	EPA SW 846-6010 (ICP-AES)
	Chromium	EPA SW 846-7191 (GFAA)	EPA SW 846-6010 (ICP-AES)

Table 6: Test Methods Different from EMP

In addition to the measured concentration of the air toxic in the sample, mass flows of the solid and gas are required. The *EMP* addendum for air toxics

includes details on the method used to determine the total mass flow of the air toxics. Table 7 lists the mass flow rates for the flue gas and the solids used to determine the mass flow of the toxics. The actual flue-gas flowrate is used for each of the trace metal, particulate matter, and anion tests. The flue-gas flowrates for the VOC and cyanide tests were from the major test conducted concurrently. The existing plant equipment was used to measure the coal flow. The measured particulate loading and flue-gas flowrate was used to calculate the flowrate of the fly ash and the stack ash. The coal input and the fly-ash flowrates were used to calculate the bottom ash flowrate.

Table 8 lists the average operating conditions of Arapahoe 4 during the SNCR testing. Figure 5 shows a simplified diagram of the unit and shows the five different sample locations. Gaseous samples were obtained at the inlet and the outlet of the FFDC. Solid samples of unpulverized coal, bottom ash, and fly ash were also obtained. This section lists the results of the air toxics testing. For details on the methods used for sampling, analysis, and quality assurance, see the *Environmental Monitoring Plan Addendum for Air Toxics Monitoring*, dated July 1993.

Stream	Test	Location	Test 1	Test 2	Test 3	
Flue Gas Flow Rate (DSCFM)	Trace Metals	Inlet	251,900	253,700	255,600	
		Outlet	253,500	257,300	261,800	
	VOC	Inlet	241,900	254,800	254,800	
		Outlet	253,400	253,400	257,000	
	Particulate Matter	Inlet	245,800	258,400	255,900	
		Outlet	247,500	262,000	262,100	
	Anions	Inlet	245,800	258,400	255,900	
		Outlet	247,500	262,000	262,100	
	Cyanide	Inlet	265,700	265,700	265,700	
		Outlet	273,400	273,400	273,400	
	NH ₃	Inlet	249,200	N/A	260,725	
		Outlet	250,506	N/A	261,944	
	Chromium Speciation	Inlet	241,900	241,900	254,800	
		Outlet	N/A	N/A	N/A	
	Mercury Speciation	Inlet	227,200	227,200	227,200	
		Outlet	244,700	244,700	244,700	
	Coal Flow (lb/h)			89,000	96,100	93,700
	Fly Ash Flow (lb/h)			6,170	6,890	7,210
Bottom Ash Flow (lb/h)			2,080	2,040	1,540	
Total Ash Flow (lb/h)			8,250	8,930	8,750	
Stack Ash Flow (lb/h)			2.5	0.8	0.6	

Table 7: Stream Mass Flow Data

		Baseline	SNCR
Unit load		103.4 MW gross	103.5 MW gross
Steam flow		851,000 lb/h	847,000 lb/h
FFDC outlet	Oxygen	6.08% (wet)	5.49% (wet)
	Carbon monoxide	37 ppmd	58 ppmd
	Nitrogen oxide	277 ppm (dry, 3% O ₂)	189 ppm (dry, 3% O ₂)
	Sulfur dioxide	473 ppm (dry, 3% O ₂)	401 ppm (dry, 3% O ₂)

Table 8: Average Operating Conditions and Continuous Emissions Data

Public Service Company of Colorado (PSCC) contracted with Carnot, Inc of Tustin, California to complete the air toxics work at the Arapahoe 4 station. Fossil Energy Research Corp of Laguna Hills, California provided some assistance at the site and with data collection. Table 9 lists the laboratories used to analyze the collected samples.

Analysis	Laboratory	Location
Solid particulate	Carnot, Inc	Tustin, CA
Chloride (supplemental)	Carnot, Inc	Tustin, CA
Acid-forming anions	Curtis and Tompkins	Berkeley, CA
Trace metals	Curtis and Tompkins	Berkeley, CA
Chromium speciation	Research Triangle Institute	RTP, NC
Volatile organic compounds	Atmosphere Assessment Associates	Chatsworth, CA
Semi-volatile organic compounds	Zenon Environmental Laboratories	Burlington, Ontario, Canada
Cyanide	Associated Laboratories	Orange, CA
Ammonia	FERCo	Laguna Hills, CA
LOI for ash	Commercial Testing and Engineering	Denver, CO
Fuel analysis	Commercial Testing and Engineering	Denver, CO
Fuel analyses	A.J. Edmonds	Long Beach, CA
Instrumental neutron activation analysis	Massachusetts Institute of Technology	Cambridge, MA

Table 9: Laboratories for Analyses

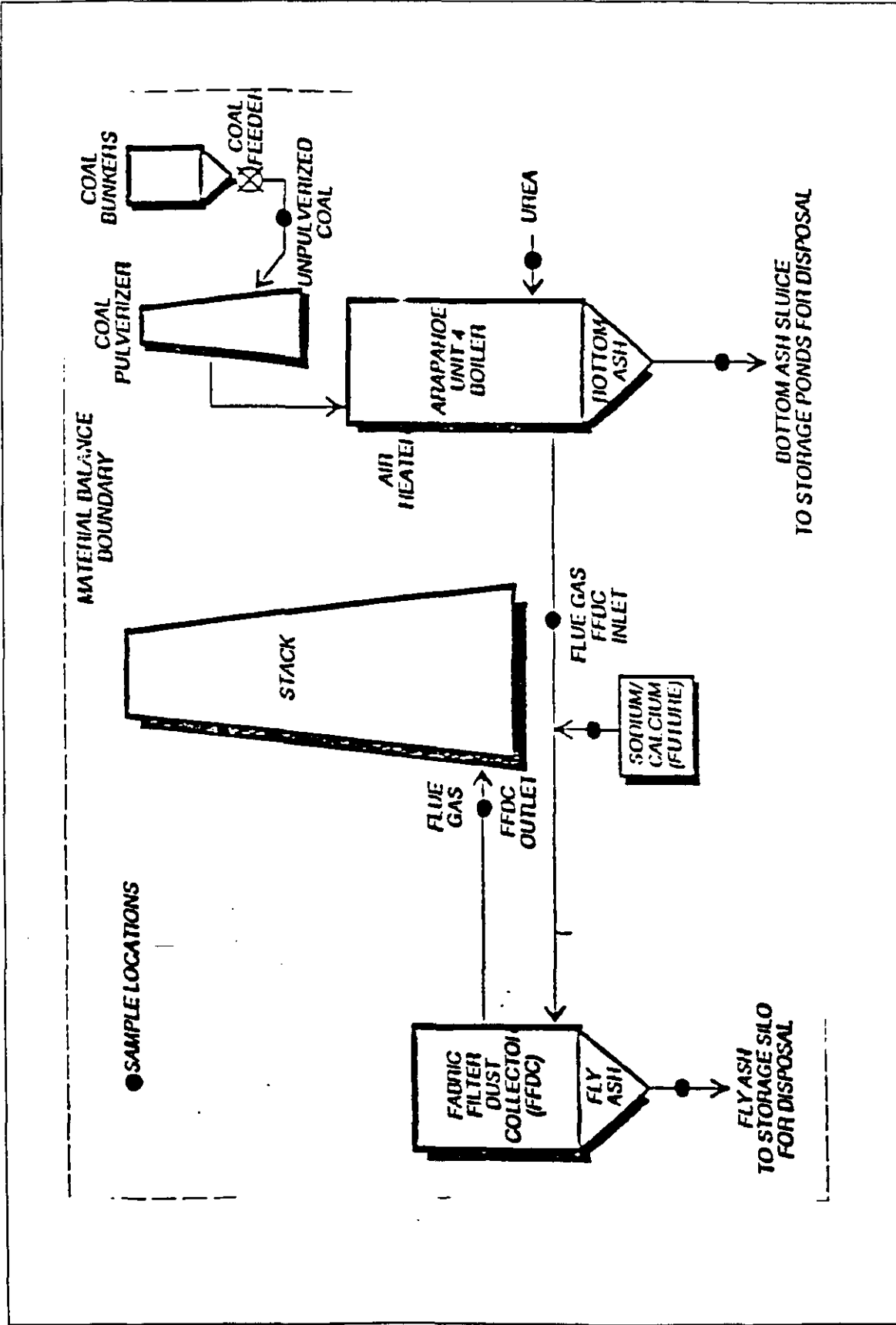


Figure 5: Sampling Locations

A. Uncertainty Analysis

In the tables that follow, a value for uncertainty expressed as a percentage is provided for all data. The calculation method used is based upon ANSI/ASME PTC 19.1-1985, "Measurement of Uncertainty." The uncertainty is based on a 95% confidence interval for the mass emissions for the target species but is expressed as a percentage so that it may be applied to other units. An important part of the method is assigning an estimated bias error for the major variables. The value presented only approximates the uncertainty as not all bias errors can be estimated. The uncertainty is also not a measure of long-term-trace-species emissions for this boiler, but only the uncertainty for the specific test period. It was assumed that the samples are a normal population distribution. Table 10 summarizes the bias values used to determine uncertainties.

Test Series	Location	Particle Collection ¹	Flowrate ²	Fuel Flowrate ³	Fly Ash Flowrate ⁴	Bottom Ash Flow Rate ⁵
Baseline	Inlet	-18%	+7%	N/A	N/A	N/A
	Outlet	-7%	+7%	N/A	N/A	N/A
SNCR	Inlet	-14%	+7%	+5%	+16%	+16%
	Outlet	-7%	+7%	N/A	N/A	N/A

1. Bias equals difference between pitot and heat rate flowrates.
2. Bias equals difference between outlet pitot and heat rate flow rates.
3. Bias equals difference between fuel flow and heat rate flowrates rounded to nearest 5%.
4. Bias is a combination of the inlet particle collection bias and the inlet flow rate bias using root sum squares.
5. Bias is a combination of the inlet particle collection bias, the inlet flow rate bias, and the fuel flow rate bias using root sum squares.

Table 10: Summary of Bias Values Used for Uncertainty Calculations

B. Treatment of Non-Detectable Measurements

Many of the target species for which a measurement was attempted were not found using the specified sampling and analytical techniques. If a measurement was not possible, the value that could have been measured,

i.e. the detection limit, if the trace emissions were present are reported. The "non-detects" are shown as less than the detection limit. The difficulty occurs when averaging various samples of which some or all of the measurements are below the detection limit. The following summarizes the two cases:

- 1. All values below detection limit:** The arithmetic average of the detection limit is shown with a "<" sign to indicate that the trace species is less than the reported average detection limit. For example, if a species was not found and the method provided a detection limit of 0.45, the value is reported as <0.45.
- 2. Some, but not all, values below detection limit:** The value of all measurements above the detection limit are averaged with one-half of the detection limit. For example, if three measurements of 10, 8, and <6 are found, the average would be $(10+8+6/2)/3$ or 7. Note that no "<" sign is used in these reported averages even though some of the values are below the detection limit. If the average calculated with this method is less than the greatest detection limit, the largest detection limit is reported and a "<" symbol is used. For example, if values of 6, <4, and <2 were reported, the average would be reported as <4 and not $(6+4/2+2/2)/3$ or 3.

C. Treatment of Blank Values

The quality assurance (QA) program for the air toxics test program used three different types of blanks: field blanks, reagent blanks, and laboratory preparation blanks.

Field blanks are samples obtained by assembling a complete sample train at the test site using the same procedures as when obtaining the actual sample. The sample train is then leak checked and disassembled to recover and analyze the sample. Generally, field blanks are not used to "correct" the data, but to indicate the quality of the sample.

Reagent blanks consist of samples of the reagent and/or filters that are collected at the site. Analysis of these samples show if any of the results were caused by existing levels of the trace species in the material used to collect or recover the sample. If measurable values of the trace species are found, the data is usually corrected by subtracting the value measured in the reagent.

Laboratory reagent blanks consist of samples of the chemicals used during the measurement analysis. If measurable values of the trace species are found, the data is usually corrected by subtracting the value measured in the reagent. Any measurable values in the laboratory reagent may be caused by initial trace species in the chemicals or to the analytical procedures.

In the tables that follow the value of the field blank is shown for reference, but none of the data have been changed due to these measurements. If a measurement has a value near the field blank measurement, there may be

some question as to the accuracy of the data and the reported value may NOT be source related. A separate column lists a blank correction percentage for all trace species that were corrected due to either a reagent or laboratory reagent blank. This is an average percentage calculated as follows:

$$\%blank\ correct = \frac{\sum \left(\frac{blank\ value}{sample\ value} \right)}{number\ of\ samples} \times 100$$

For example, if three samples contained 10, 5, and 4 mg/kg of a trace species and the reagent blank was 2 mg/kg, the blank correction would be $(2/10 + 2/5 + 2/4) * 100/3$ or 37%. Thus on average, the actual value measured was 37% higher than the value reported in the table. If the blank correction is reported as 0%, no blank correction was calculated and the reported value is the measured value. Note that in most cases a high blank correction value does not mean that the data is inaccurate. If a sample was contaminated with a trace species due to a filter, and the filter was analyzed and the data corrected, it is likely that the data is meaningful.

D. Gaseous Species Monitoring

Trace Metals

Table 11 lists the gaseous trace metal emissions for the SNCR test program. Three replicate tests were completed for each air toxics species. Individual tests were averaged to determine the estimated air toxics emission. The uncertainty of the average, as described in Section IV.A, is also reported.

Species	FFDC Inlet							FFDC Outlet						
	Test 1	Test 2	Test 3	Avg.	Uncert	Field Blank	Blank Correct 1	Test 1	Test 2	Test 3	Avg.	Uncert	Field Blank	Blank Correct 1
	$\mu\text{g}/\text{Nm}^3$							$\mu\text{g}/\text{Nm}^3$						
Trace Metals														
Arsenic	22.6	18.1	7.7	16.2	119	0.10	4.2R	0.23	0.20	0.13	0.19	64	0.08	70.8R
Barium	268	167	266	241	68	9.2	1.6R	2.8	0.03	1.1	1.3	268	12.6	73.4R
Beryllium	9.4	8.0	10.7	9.4	39	<0.04	0.0	<0.03	<0.03	<0.03	<0.03	32	<0.03	0.0
Cadmium	2.6	2.0	3.0	2.5	52	<0.11	0.0	<0.08	<0.09	<0.08	<0.08	32	<0.08	0.0
Chromium	57.6	55.1	78.7	63.7	53	2.3	1.1L	0.42	0.26	0.43	0.37	64	1.5	58.1L
Cobalt	35.2	25.9	37.9	33.0	50	<0.37	0.0	<0.28	<0.29	<0.27	<0.28	32	<0.28	0.0
Copper	228	203	341	258	73	1.1	0.0	2.0	1.4	1.6	1.7	46	8.5	0.0
Lead	18.8	65.0	87.2	57.0	153	0.62	6.3R	0.48	0.50	0.51	0.50	12	0.59	30.0R
Manganese	101	87.1	144	111	69	1.2	0.6R	0.28	2.7	0.30	1.1	317	0.95	46.4R
Mercury	4.3	1.7	1.1	2.4	177	<0.42	0.0	0.79	0.56	<0.40	0.52	143	<0.14	0.0
Molybdenum	15.9	15.6	12.8	14.8	33	5.5	28.6R	0.56	0.23	0.22	0.34	144	3.7	92.6R
Nickel	33.7	29.1	47.6	36.8	67	0.73	2.1R	0.56	0.58	0.54	0.56	13	<0.56	33.3R
Selenium	22.8	17.1	<10.0	15.0	152	<11.0	0.0	<0.08	<0.08	<0.08	<0.08	32	<0.08	0.0
Phosphorus	12,000	9,600	13,500	11,700	45	<2.2	0.0	5.9	10.5	<1.6	5.7	210	1.7	0.0
Vanadium	152	124	176	151	46	0.81	0.0	0.37	0.29	0.40	0.35	41	0.22	0.0
Calcium	1,900	550	890	1,100	156	143	4.9R	36.6	23.4	45.8	35.3	80	56	49.8R
Sodium	7,200	1,600	1,300	3,400	246	4,005	48.5R	390	205	7,455	450	154	3,651	79.9R

NOTE: "<" indicates that the quantity measured was less than the detection limit thus the detection limit is shown

- "R" indicates reagent blank correction. "L" indicates laboratory blank correction.
- For barium test 2-out; lead tests 1-out, 2-out, and 3-out; molybdenum 2-out and 3-out; and Nickel tests 1-out, 2-out, and 3-out; subtracting the reagent blank level lowered the results below the detection limit, so the detection limit was used.

Table 11: SNCR Gaseous Air Toxics Emissions (Trace Metals)

All 17 metals were detected at the FFDC inlet. All quality assurance checks were completed and, except for calcium and sodium, the data are believed to represent the unit's emissions for all species. The inlet level for calcium represents only 0.5% and the inlet level for sodium represents only 6.8% of their fuel-input levels, indicating a severely low bias. The multi-metals train was used to sample sodium and calcium even though EPA Method 29 is not intended to measure them. The source of error is not known, but neither the calcium nor the sodium data are believed to represent the unit's emissions.

Arsenic, lead, mercury, and selenium have uncertainties greater than 100%. Wide variations between the triplicate samples caused these high uncertainties. The specific causes of these uncertainties have not been determined, but the general observations that follow may account for them.

- GFAA and ICP-AES are generally used to analyze samples for arsenic, lead, and selenium. In the original baseline tests, GFAA was used for arsenic and lead, and ICP-AES with hydride generation was used for selenium. After comparing the results, GFAA appears to give more consistent results and will be used in subsequent test programs.
- The substantially higher results of the first mercury sample caused its high uncertainty. This value, $4.3 \mu\text{g}/\text{Nm}^3$, is substantially higher than the fuel input value and is suspect. No sampling or analytical abnormality, however, could be found to justify the exclusion of this data point.

In general, trace metal emissions were very low at the FFDC outlet as the FFDC is very efficient removing trace metals. Beryllium, cadmium, cobalt, and selenium were not measurable at their detection limits. As at the FFDC inlet, the calcium and sodium data are suspect and not believed to be accurate. Barium, manganese, mercury, molybdenum, and phosphorus had uncertainties above 100%. Variation between the triplicate samples

was the major cause of the high uncertainties. At these low levels, small differences between the sample values cause large uncertainties. Also, small reagent blank levels cause larger blank correction percentages and higher uncertainties.

Anions

Table 12 lists the gaseous anion emissions. Chloride levels at both the inlet and outlet were below 1 ppm. 94% of the total inlet and more than 98% of the total outlet chloride were determined to be gas-phase chloride or HCl. Outlet levels accounted for 51% of the chlorine in the fuel.

Inlet and outlet levels of fluoride were between 7 and 9 ppm. Gas-phase fluoride (HF) accounted for 89% of the inlet and 99% of the outlet levels. Of the fluorine in the fuel, 65% was detected at the FFDC outlet.

Phosphate was detected only in its solid phase and only at the FFDC inlet (0.03 ppm). The nondetected gas fraction accounts for 69% of the total phosphate level at the inlet (0.09 ppm = 320 lb/10¹² Btu) and accounts for only 11% of the phosphorous detected in the fuel. The severe bias of the ion-chromatography method used to detect the phosphate accounts for this disparity and caused the exclusion of phosphate from the mass balance.

— The FFDC inlet level for sulfate (290 ppm) accounts for 86% of the fuel input. The solid fraction (3.5 ppm) detected at the inlet consisted of sulfuric acid mist and solid sulfate. The outlet sulfur level (338 ppm, 100% gaseous) is consistent with that measured by the CEM.

Species	FFDC Inlet							FFDC Outlet							
	Test 1	Test 2	Test 3	Avg.	Uncert.	Field Blank	Blank Correct	Test 1	Test 2	Test 3	Avg.	Uncert.	Field Blank	Blank Correct	
	ppm							ppm							%
Acid Forming Anions															
Chlorine (Cl ⁻)	Total	0.78	0.84	0.79	0.80	241	N/A	0.52	0.53	0.63	0.55	29	N/A	N/A	
	Gaseous ¹	0.75	0.76	0.74	0.75			0.51	0.52	0.62	0.55				
	Solid ²	0.03	0.07	0.05	0.05			<0.02	<0.03	<0.02	<0.03				
Fluorine (F ⁻)	Total	8.2	9.0	8.4	8.6	19	N/A	7.1	6.6	7.3	7.0	15	N/A	N/A	
	Gaseous ¹	7.3	7.9	7.6	7.6			7.1	6.5	7.2	6.9				
	Solid ²	0.95	1.1	0.81	0.81			0.06	0.06	0.06	0.06				
Phosphate (PO ₄ ⁻³)	Total	0.09	0.12	0.08	0.09	55	N/A	<0.13	<0.15	<0.12	<0.13	44	N/A	N/A	
	Gaseous ¹	<0.13	<0.16	<0.10	<0.13			<0.09	<0.10	<0.09	<0.09				
	Solid ²	0.04	0.04	0.03	0.03			<0.03	<0.05	<0.03	<0.04				
Sulfate (SO ₄ ⁻²)	Total	300	298	271	290	19	N/A	417	302	296	338	158	N/A	N/A	
	Gaseous ¹	296	294	267	286			417	302	296	338				
	Solid ²	3.5	3.7	3.4	3.5			0.09	0.01	0.01	0.04				
Nitrogen Compounds															
Ammonia	ppm							ppm							%
	14.0	N/A	18.0	16.0	N/A	N/A	N/A	5.6	N/A	9.2	7.4	N/A	N/A	N/A	
Cyanide (HCN)	ppb							ppb							%
	<13	<10	<13	<12	47	N/A	0	<10	<9	<8	<9	37	N/A	0	

* < indicates that the quantity measured was less than the detection limit thus the detection limit is shown.

1. Solid fraction consists of filter and front-half rinse.
2. Gaseous fraction consists of bicarbonate/carbonate and 3% peroxide rinses.

Table 12: SNCR Gaseous Air Toxics Emissions (Anions and Nitrogen Compounds)

The trace metal and anion results from this test program were compared qualitatively with data from the Cyprus Yampa Valley Coal Corp. and the United States Geological Society (USGS). Generally, the test data compared well with the USGS data.

Nitrogen Compounds

Table 12 also lists the results from the testing for nitrogen compounds. All tests showed cyanide below the detection limit. As expected, unreacted urea increased NH_3 emissions; they averaged 16 ppm at the FFDC inlet and 7.4 ppm at the FFDC outlet.

FFDC Removal Efficiency

Table 13 shows the FFDC's removal efficiency for trace metals. The FFDC averaged 96.9% removal efficiency for trace metals and 99.98% for total particulates. The removal rate for mercury was the lowest, 77.9%. A significant amount of the mercury occurs as vapor instead of as particulates in the FFDC, so the removal rate for mercury was actually higher than anticipated. It is theorized that mercury vapor deposited onto the carbon in the fly ash and that the high carbon content of the fly ash caused the higher than expected removal rate for mercury. During the SNCR testing, the loss-on-ignition (LOI) for the fly ash averaged 9.52%.

Species	Inlet	Outlet	FFDC Removal
Trace Metals	lb/10 ¹² Btu	lb/10 ¹² Btu	%
Arsenic	12.8	0.15	98.8
Barium	192	1.1	99.5
Beryllium	7.5	<0.02	>99.7
Cadmium	2.0	<0.07	>96.6
Chromium	50.8	0.30	99.4
Cobalt	26.3	<0.23	>99.1
Copper	206	1.3	99.3
Lead	45.6	0.40	99.1
Manganese	88.3	0.89	99.0
Mercury	1.9	0.41	77.9
Molybdenum	11.7	0.27	97.7
Nickel	29.4	0.45	98.5
Selenium	11.9	<0.06	>99.5
Phosphorus	9,300	4.6	99.95
Vanadium	120	0.29	99.8
Calcium	880	29	96.8
Sodium	2,700	370	86.3
Average	--	--	96.9
Total Particulate	6.09 lb/MMBtu	0.0012 lb/MMBtu	99.98%
Acid-Forming Anions	lb/10 ¹² Btu	lb/10 ¹² Btu	%
Chloride as Cl ⁻	65	<32	>50.5
Fluoride as F ⁻	648	40	93.9
Phosphate	100	<130	--
Sulfate	12,100	130	98.9

NOTE: "<" indicates that the quantity measured was less than the detection limit thus the detection limit is shown.

">" indicates that the percentage removed is based on a detection limit and the removal rate is the expected minimum removal rate.

Table 13: FFDC Removal Efficiency

Baseline VOC Emissions

The baseline tests for benzene and toluene were repeated during this test period because of the inconsistent results obtained in the original baseline test period. Table 14 lists the baseline VOC emissions. This testing indicated that the benzene and toluene levels increased across the FFDC.

While higher values were measured for both benzene and toluene during this report's test period, it still appears that a sampling problem is causing a low bias for the FFDC inlet values. Because of the high particulate loading at the FFDC inlet, it is believed the inlet-sample-filter collected particulates, and that the particulates absorbed benzene and toluene; causing a low bias. The FFDC inlet values are considered suspect, but because of the minimal particulate loading at the FFDC outlet, these values are considered accurate.

Baseline Results for Mercury Speciation

Table 15 lists the baseline mercury speciation results. At the FFDC inlet, it is likely that carbon and/or other particulate matter impacted the filter plug used to prevent solid matter from entering the sample train and removed vapor-phase mercury from it. Therefore, the results for Hg^{+2} , methyl-Hg, and Hg are semi-quantitative and represent the lower boundaries in their emission levels.

The total-Hg level in the filter plug was $1.9 \mu\text{g}/\text{Nm}^3$. This level compares well with the total-Hg level from the multi-metals tests conducted during the SNCR testing ($2.4 \mu\text{g}/\text{Nm}^3$) but, recall that this result is believed to be biased high because of one high value. Due to possible sampling problems, Test 3 appears to be severely biased low and was not included in the average.

Species	FFDC Inlet						FFDC Outlet							
	Test 1	Test 2	Test 3	Avg.	Uncert.	Field Blank	Blank Correct	Test 1	Test 2	Test 3	Avg.	Uncert.	Field Blank	Blank Correct
VOC	ppb						ppb						%	
Benzene	2.92	3.96	4.61	3.83	57	0.14	0	2.76	2.53	1.80	2.36	52	0.14	0
Toluene	19.1	33.4	12.5	21.6	123	12.8	0	43.8	54.1	18.7	38.9	115	12.8	0

Note: "<" indicates that the quantity measured was less than the detection limit thus the detection limit is shown.

Table 14: Baseline VOC Emissions

Mercury	FFDC Inlet						FFDC Outlet							
	Test 1	Test 2	Test 3	Avg. ⁴	Uncert.	Field Blank	Blank Correct	Test 1	Test 2	Test 3	Avg.	Uncert.	Field Blank	Blank Correct
Hg ⁺²	0.44	0.39	0.03	0.41	83	N/A	N/A	<0.02	0.03	0.05	0.03	166	N/A	N/A
Methyl-Hg	0.08	0.08	0.04	0.08	7	N/A	N/A	<0.01	0.01	0.08	0.03	317	N/A	N/A
Hg	0.32	0.53	0.05	0.42	306	N/A	N/A	<0.01	<0.01	<0.01	<0.01	30	N/A	N/A
Total-Hg - filter plug + Probe ²	0.99	0.94	0.09	0.97	36	N/A	N/A	<0.005	<0.005	<0.005	<0.005	30	N/A	N/A
Total-Hg ³	1.8	1.9	0.22	1.9	34	N/A	N/A	<0.05	0.05	0.14	0.07	207	N/A	N/A

"<" indicates that the quantity measured was less than the detection limit thus the detection limit is shown

"R" indicates reagent blank correction. "I." indicates laboratory blank correction.

1. Results corrected for field blank levels, but correction data is not available.

2. Total-Hg calculated using PISCES data handling conventions.

3. High particulate loading on the filter plug was analyzed for total-Hg only.

4. Test-3 was not included in the average, sampling problems appear to have severely biased the results low.

Table 15: Summary of Baseline Mercury Speciation Emissions

Only Hg^{+2} and methyl-Hg were detected at the FFDC outlet. No mercury species were detected in Test 1. Total-Hg emissions at the FFDC outlet averaged $0.07 \mu\text{g}/\text{Nm}^3$. In contrast, during the SNCR testing, the multi-metals tests for total-Hg averaged $0.52 \mu\text{g}/\text{Nm}^3$. Although there is no explanation for the order-of-magnitude difference between the two mercury values, it should be noted that both values are very near their detection limits.

Frontier Geoscience analyzed coal and fly ash samples taken during testing on March 15, 1993 and performed a mass balance, shown in Table 16. Overall, the mercury speciation results agree with the fuel and ash levels. Note that the use of total-Hg level from the mercury speciation testing increases the FFDC's removal rate for mercury to 96.3% from the 77.9% of the multi-metals train.

Baseline Results for Total and Hexavalent Chromium

An EPA recirculation train was used to measure total-Cr and Cr^{+6} levels at baseline conditions. Since there is significantly more chromium at the FFDC inlet, testing was conducted there to obtain more accurate speciation results than could be obtained at the FFDC outlet. Table 17 lists the baseline total-Cr and Cr^{+6} results. The recirculation train detected an average total-Cr level of $93.3 \mu\text{g}/\text{Nm}^3$ compared to an average of $63.7 \mu\text{g}/\text{Nm}^3$ for the multi-metals train performed during the SNCR tests.

Species	Inputs		Intermediate		Outputs			Mass Balance		
	Fuel		FFDC Inlet		Bottom Ash	Fly Ash	Outlet	Boiler/FFDC	Boiler	FFDC
Total-Hg ¹ (lb/10 ¹² Btu)	1.7		1.4		0.24	1.3	0.06	98%	102%	96%
FFDC Removal Efficiency										
96%										

1. All total-Hg results from Frontier Geoscience laboratory except bottom ash values.
2. Bottom ash results from Curtis & Tompkins analysis of ash samples collected during baseline testing in November 1992.
3. Boiler/FFDC mass balance calculated as: (outlet + fly ash + bottom ash) / fuel.
4. Boiler mass balance calculated as: (inlet + bottom ash) / fuel.
5. FFDC mass balance calculated as: (outlet + fly ash) / inlet.

Table 16: Frontier Geoscience Mercury Speciation Mass Balance

Element	Test 1	Test 2	Test 3	Avg.	Field Blank	Uncert.
Total-Cr ($\mu\text{g}/\text{Nm}^3$)	121	90.1	69.2	93.3	40.9	70%
Cr ⁶⁺ ($\mu\text{g}/\text{Nm}^3$)	5.74	2.52	7.25	5.17	2.56	11%
Cr ⁶⁺ /Total-Cr	4.8%	2.8%	5.2%	4.3%	--	--
Estimated Cr ⁶⁺ Outlet Emissions ⁴ ($\mu\text{g}/\text{Nm}^3$)				0.02	--	--

1. Total-Cr = (Total-Cr) * (filtrant + HNO₃ fraction) + (Cr⁶⁺) * (NaOH fraction).
2. Total-Cr and Cr⁶⁺ reagent blank levels were not detected.
3. Field blank levels were **not** subtracted from laboratory results, average sample volume used for $\mu\text{g}/\text{Nm}^3$ calculations.
4. Cr⁶⁺ outlet emissions = total-Cr (outlet) * Cr⁶⁺/Total-Cr. %.
5. O₂, CO₂, and flue-gas flowrate from corresponding isokinetic test.

Table 17: Total and Hexavalent Chromium Emissions from EPA Recirculation Method

This difference is within the range of uncertainties but it may have been affected by two other factors:

- The recirculation train uses a single-point sample at the FFDC inlet. In contrast, the multi-metals train uses a traverse of the inlet duct. The multi-metals train may obtain a more representative sample.
- The field blank levels were very high for both total-Cr (44% of sample) and Cr⁶⁺ (50% of sample). While no sampling or recovery problems could be determined, one may have existed that caused the chromium results from the recirculation train to be biased high.

Only 4.3% of the total-Cr was measured as the potentially more toxic Cr⁶⁺. Assuming that the FFDC collects all chromium species equally, it is estimated that the total Cr⁶⁺ emission at the stack is only 0.02 $\mu\text{g}/\text{Nm}^3$.

E. Solids Stream Monitoring

Coal Analysis

Table 18 lists the analysis of the coal for trace metals and acid forming anions. In addition to the standard analytical method described in the *EMP* (ICP-AES), instrumental neutron activation analysis (INAA) was used to detect arsenic, barium, mercury, selenium, and chlorine to achieve better accuracy. The resolution of the standard method was too low to detect arsenic, mercury, selenium, and chlorine, but not barium. INAA and the standard method (ICP-AES), however, produced grossly disparate results for barium. After careful examination, the ICP-AES results for barium were judged inconsistent with the coal matrix and the INAA results were used.

An elemental analysis was performed for chlorine (as Cl^-), fluorine (as F^-), phosphorous (as PO_4^{2-}), and sulfur (as SO_4^{2-}). Low uncertainties for these values indicate good agreement between the replicates. The results measured for Cl^- , however, were higher than expected and not consistent with the gaseous data. INAA was also used to measure Cl^- and it reported much lower values for it. The INAA data are believed to be more representative of the coal.

Trace Metals	Base Test Method						INAA					
	Test 1	Test 2	Test 3	Average	Uncert	Blank Correct	Test 1	Test 2	Test 3	Average	Uncert	Blank Correct
	mg/kg						%					
Arsenic ¹	<3	<3	<3	<3	31	0	0.75	0.47	0.70	0.64	58	0
Barium ¹	27	15	38	27	108	0	350	335	333	339	9	0
Beryllium	0.30	0.58	0.77	0.55	107	0						
Cadmium	<0.05	<0.06	0.06	<0.06	29	0	0.12	0.10	0.13	0.12	34	0
Chromium	1.2	2.1	1.0	1.4	102	0	3.4	2.4	2.5	2.7	50	0
Cobalt	1.1	1.4	1.4	1.3	35	0	0.97	1.00	0.79	0.92	33	0
Copper	3.8	4.0	3.3	3.7	20	0						
Lead	1.7	2.3	2.7	2.2	57	0						
Manganese	4.2	6.7	4.8	5.2	63	0						
Mercury ¹	<0.1	<0.1	<0.1	<0.1	31	0	0.011	NP	0.027	0.019	524	0
Molybdenum	<0.4	0.4	0.7	0.5	87	0	1.6	1.4	1.5	1.5	11	0
Nickel	1.0	1.0	1.0	1.0	10	0						
Selenium ¹	<3	<3	<3	<3	31	0	1.1	0.91	2.4	1.5	135	0
Phosphorus	320	310	320	317	9	0						
Vanadium	3.5	5.3	4.2	4.3	53	0						
Calcium	1,870	2,770	1,770	2,140	65	40						
Sodium	270	400	680	450	116	6						
Acid Forming Anions	mg/kg						%					
Chloride (Cl ⁻ (2))	236	239	238	238	10	0	16	17	16	16	11	0
Fluorine (F ⁻)	79	89	85	84	14	0						
Phosphate (PO ₄ ³⁻)	981	951	981	971	9	0						
Sulfate (SO ₄ ²⁻)	13,200	13,200	12,900	13,100	11	0						

• "<" indicates that the quantity measured was less than the detection limit thus the detection limit is shown.

• "NP" indicates not performed.

• All values are reported on an as-received basis for the coal.

1. INAA results were used for these trace species rather than the base method.

Table 18: SNCR Coal Air Toxics Analysis for Trace Metals and Acid Forming Anions

Fly Ash

Table 19 lists the analysis of the fly ash for trace metals and anions. Except for cadmium and chloride, all trace metal and anion species were reported above their detection limits and, except for arsenic and mercury, with relatively good precision (uncertainty below 100%). A single low value for arsenic increased the uncertainty for arsenic and biased its average low. The results for mercury are very near its detection limit, so the higher uncertainty reflects a lack of confidence in these values.

As discussed in Section IV.B, ion-chromatography fails to measure the entire amount of oxidized phosphorous compared with the elemental phosphorous measured by ICP-AES, so phosphate results are not included in Table 19. Also, a laboratory problem occurred with the measurement of chloride in the fly ash. A laboratory interference caused the detection limit to increase from the expected limit of 5 to 50 mg/kg. All chloride fly ash values were below this limit. As chloride emissions are gaseous, only low levels, if any, of chloride would be expected in the fly ash.

Bottom Ash

Bottom ash is sluiced from the boiler to an on-site pond. The sluice water was sampled before it contacted the bottom ash and analyzed for trace metals. The mixture of the sluice water and bottom ash was sampled, analyzed, and corrected for any toxics found in the sluice water alone. Table 19 also lists these results.

Trace Metals ¹	Bottom Ash/Sluice Water						Fly Ash ¹					
	Test 1	Test 2	Test 3	Avg.	Uncert.	Blank Correct	Test 1	Test 2	Test 3	Avg.	Uncert.	Blank Correct
	mg/kg						mg/kg					
Arsenic	8.8	3.8	9.7	7.5	88	0	11	11	3.7	9	124	0
Barium	879	999	1,499	1,126	65	0	1,200	880	690	923	73	0
Beryllium	1.4	1.6	1.8	1.6	39	0	2.4	2.8	2.4	2.5	24	0
Cadmium	<0.5	<0.5	<0.5	<0.5	56	0	<1	<1	<1	<1	37	0
Chromium	9	9	10	9.6	39	0	15	16	12	14	33	0
Cobalt	5	6	7	6	43	0	13	12	12	12	21	0
Copper	14	15	19	16	43	0	40	38	36	38	21	0
Lead	17	2.7	12	11	77	0	31	34	24	30	38	0
Manganese	38	55	64	52	52	0	61	68	62	64	21	0
Mercury	<0.1	<0.1	<0.1	<0.1	56	0	0.3	0.2	0.1	0.2	126	0
Molybdenum	<1.0	<1.0	<1.0	<1.0	56	0	3	3	5	4	82	0
Nickel	5	6	7	6	43	0	15	10	13	13	54	0
Selenium ⁵	<10	<43	<12	<22	220	0	<8.8	2.6	4.3	3.8	81	0
Phosphorus	1,600	1,900	2,500	2,000	47	0	4,200	4,400	4,000	4,200	21	0
Vanadium	21	24	27	24	39	0	66	54	54	58	30	0
Calcium	14,500	13,500	25,500	17,900	78	0	30,000	31,000	30,000	30,333	23	0
Sodium	3,020	2,720	3,810	3,190	44	0	4,100	5,600	4,700	4,800	35	0
Acid-Forming Anions ^{2,3}	mg/kg						mg/kg					
Chloride as Cl ⁻	90	18	70	59	163	0	<50	<50	<50	<50	37	0
Fluoride as F ⁻	<3	<3	<3	<3	56	0	23	40	34	32	70	0
Sulfate	251	932	1,214	808	163	0	1,500	1,500	1,500	1,500	23	0

* "<" indicates that the quantity measured was less than the detection limit thus the detection limit is shown.

1. Bottom ash (solid fraction) results calculated by subtracting the sluice water blank from the bottom ash/sluice rinse fraction.

2. Phosphate not included since IC does not measure all oxidized phosphorous.

3. Bottom ash solid fraction not analyzed for anions, anion concentration found in liquid fraction and corrected to total weight of sample.

4. No metals or anions detected in the laboratory blank.

5. Highest nondetect not used for flyash average, detection limits varied by sample.

Table 19: SNCR Air Toxics Analysis of Ash

Cadmium, mercury, molybdenum, selenium, and fluoride were reported below their detection limits. Of the species reported above their detection limits, only lead, chloride, and sulfate exhibited relatively poor precision. The lead and chloride uncertainties can be attributed to the low levels reported for one replicate. Since the sulfate levels in the bottom ash are less than 0.1% of the total input of sulfur, the uncertainty for sulfate is insignificant.

F. Mass Balance Results

Mass balances are an important quality check on toxics-emission data. The use of different sample and analytical techniques to measure toxics in both gaseous and solid forms is, at best, difficult. Mass balances provide a quick means for determining how well various analytical methods agree. The low absolute quantities of the measured materials, however, make a 100% mass balance very unlikely.

There are three major sources of potential error in the mass balance: operating conditions, analytical difficulties, and sample collection and handling. Since Arapahoe 4 operated at or near steady-state conditions and the daily tests show that the same coal was fired throughout the tests, operating conditions are not likely to contribute any significant sources of error. Analytical difficulties usually only affect the results for individual replicates or species, so they are considered with each species. Normally, analytical difficulties outweigh sampling problems. On a utility coal-fired unit, however, obtaining representative samples from process streams flowing at thousands of pounds per hour adds a major source of potential error. It should also be noted that uncertainties only represent consistency, not accuracy.

Table 20 shows the mass balance results for the SNCR testing. Only compounds dependent on the fuel inputs can be balanced. The boiler/FFDC mass balance uses the coal as its input; it uses the bottom ash, fly ash, and FFDC outlet as its outlets; and represents the overall mass balance. The boiler mass balance uses the coal for its input; it uses the FFDC inlet and the bottom ash as its outlets; and it represents an intermediate mass balance.

A comparison of the intermediate and overall mass balances in Table 20 shows that, in general, the intermediate balances are significantly lower than the overall balances. On average, the aggregate of the intermediate balance is 44% lower than the aggregate of the overall balance. A low bias for the bottom ash is the most likely reason for the low bias of the intermediate balance. Since obtaining a bottom ash sample from a utility coal-fired unit is very difficult, only a small grab sample from one part of the boiler is obtained. This sampling technique does not meet any of the general requirements for obtaining a representative sample and introduces an unknown bias. The bottom ash data, however, affect the overall mass balance least, so the overall mass balance is considered more accurate than the intermediate mass balance.

The mass balances for the majority of the trace metals and anions range from 68 to 119%. The mass balances for barium, beryllium, molybdenum, and selenium, however, were significantly lower; they ranged from 26 to 57%.

Species	Inputs	Intermediate	Outputs			Mass Balance	
	Fuel	FFDC Inlet	Bottom Ash	Fly Ash	FFDC Outlet	Boiler/ FFDC ¹	Boiler ¹
Trace Metals	lb/10 ¹² Btu					%	
Arsenic ²	56	12.8	15	51	0.15	119	50
Barium ²	29,700	192	2,210	5,550	1.1	26	8
Beryllium	48	7.5	3.2	15	<0.02	39	22
Cadmium	<5.3	2.0	<1.0	<6	<0.07	N/A	N/A
Chromium	125	50.8	19	87	0.30	85	56
Cobalt	114	26.3	12	75	<0.23	77	34
Copper	324	206	32	231	1.3	81	73
Lead	195	45.6	22	180	0.44	103	35
Manganese	458	88.3	103	388	0.89	107	42
Mercury	1.7	1.9	<0.2	1.2	0.41	108	124
Molybdenum	44	11.7	<2.0	23	0.27	57	31
Nickel	88	29.4	12	77	0.45	102	47
Selenium	127	11.9	<43	23	<0.06	52	44
Phosphorus	27,700	9,300	4,000	25,500	4.6	107	48
Vanadium	379	120	48	351	0.29	105	44
Average Metals						83	47
Calcium	187,000	880	34,900	185,000	28.6	117	19
Sodium	39,000	2,700	6,300	29,300	367	91	23
Acid-Forming Anions	lb/10 ¹² Btu					%	
Chloride as Cl ⁻	1,400	1,650	122	<300	719	81	80
Fluoride as F ⁻	7,400	5,780	<6.1	198	4,810	68	78
Phosphate ²	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Sulfate	1,150,000	988,000	1,520	9,130	759,000	103	86

Note: "<" indicates that the quantity measured was less than the detection limit thus the detection limit is shown

1. Boiler/FFDC mass balance calculated using (inlet + bottom ash)/fuel.
2. Fuel concentrations from INAA.

Table 20: SNCR Mass Balance Results

Barium

As the results from ICP analysis appeared to be severely biased low (as previously described), INAA was used to determine the level of barium in the coal. ICP analysis was used for the flue gas and ash samples. The use of different analytical techniques may have introduced an unidentified bias and caused the poor mass balance closure. The mass balance calculated by using the original ICP data also had closure problems, but it showed a very low barium content for the fuel. Due to these and other possible unknown biases, the confidence in the barium data is low.

Beryllium

The fuel results for beryllium appear to be biased high. A triplicate sample from previous fuel testing showed a beryllium content of 20 lb/MMBtu compared with 48 lb/MMBtu for the current testing. Using the 20 lb/MMBtu value to calculate the mass balance results in a 91% mass balance. In addition, a comparison of the results for beryllium from this test period with the USGS data indicates that this test period's value is biased high.

Molybdenum

The results for molybdenum were very low, less than five times its detection limit. The fuel results from this test period appear to show a high bias while the fuel data from the previous test period appeared to show a low bias for molybdenum. The molybdenum value from this test period is within the range of the USGS data. Considering the low levels detected, a mass balance of 57% for molybdenum is reasonable.

Selenium

The mass balance for selenium was low, indicating either a high fuel bias or a low outlet bias. As with beryllium, INAA was used to analyze the coal samples while ICP was used to analyze the FFDC-outlet samples; the use of two techniques may have introduced an unknown bias. Also, it should be noted that selenium is a very difficult element to measure.

Comparison of Baseline and SNCR Test Results

Table 21 compares the fuel-input, FFDC-inlet, and FFDC-outlet results for the baseline and SNCR testing. Within the variability and accuracy of the sampling and analytical procedures, the injection of urea into the boiler did not change the emission levels of most trace metals and anions, except for ammonia. The results for benzene and toluene measured at the FFDC inlet during the SNCR test period are an order of magnitude higher than the last test period. Because of the difficulty of sampling in a duct with a high particulate loading, both sets of these values are believed to be biased low. The high particulate loading appears to have had a greater effect on the results from the last test period.

Species	Fuel Input		FFDC Inlet		FFDC Outlet	
	Baseline	SNCR	Baseline	SNCR	Baseline	SNCR
	lb/10 ¹² Btu		lb/10 ¹² Btu		lb/10 ¹² Btu	
Arsenic	43	56	23.1	12.8	0.75	0.15
Barium	37,600	29,700	234	192	1.1	1.1
Beryllium	20.0	48	9.0	7.5	<0.02	<0.02
Cadmium	<4.5	<5.3	2.3	2.0	0.12	<0.07
Chromium	97.4	125	50.0	50.8	0.66	0.30
Cobalt	83.6	114	29.9	26.3	<0.21	<0.23
Copper	241	324	169	206	1.1	1.3
Lead	185	195	64	45.6	0.44	0.40
Manganese	379	458	195	88.3	1.0	0.89
Mercury	1.9	1.7	1.3	1.9	<0.29	0.41
Molybdenum	9.0	44	10.7	11.7	0.17	0.27
Nickel	53.5	88	30.2	29.4	1.5	0.45
Selenium	73.2	127	22.4	11.9	0.36	<0.06
Phosphorous	36,700	27,700	14,300	9,300	6.7	4.6
Vanadium	266	379	135	120	0.24	0.29
Chloride	2,000	1,400	795	1,010	626	719
Fluoride	7,600	7,400	4,800	5,800	4,300	4,800
Phosphate	113,000	85,000	1,282	319	<1,313	<450
Sulfate	1.18 (10 ⁵)	1.15 (10 ⁵)	10.6 (10 ⁵)	9.88 (10 ⁵)	9.83 (10 ⁵)	11.7 (10 ⁵)
Cyanide	N/A	N/A	<8	<12	<7	<9
Ammonia	N/A	N/A	<100	12,000	N/A	7,000
Benzene	N/A	N/A	1.1	10.5	2.6	6.7
Toluene	N/A	N/A	7.0	69.9	105	129

Table 21: Summary of Emissions from Baseline and SNCR Testing

INTEGRATED DRY NO_x/SO₂ EMISSIONS CONTROL SYSTEM

FINAL REPORT, VOLUME 2: PROJECT PERFORMANCE AND ECONOMICS

Appendix D

AIR TOXICS SUMMARY SECTION

FOR

SODIUM-BASED DRY SORBENT INJECTION SYSTEM RETROFIT

IV. Summary of Air Toxics Monitoring Results

Table 3 lists the 21 potential air toxics measured at Arapahoe Unit 4 during the sodium-based DSI test period. Sampling of the air toxics occurred on October 14 and 15, 1993. No sampling occurred during sootblowing operations.

Trace Metals	Arsenic	Lead
	Cadmium	Molybdenum
	Copper	Phosphorous
	Mercury	Beryllium
	Selenium	Cobalt
	Calcium	Manganese
	Barium	Nickel
	Chromium	Vanadium
	Calcium	Sodium
Anions ¹	Chloride	Sulfate
	Fluoride	

1. Elemental precursors of these anions measured in the fuel (Cl, F, S).

Table 3: Target Compounds for Sodium-Based DSI System

This report presents the air toxics data for the sodium-based DSI system.

Three other series of air toxics

measurements were completed as part of the project. Baseline air toxics were measured from November 17, 1992 through November 19, 1992. Results from this testing are contained in the Environmental Monitoring Report for the Low NO_x Combustion System Retrofit Test Period, report dated February 1994. Air toxics were also measured during the Selective Non-Catalytic Test period from March 8, 1993 through March 11, 1993. Results from this testing are contained in the Environmental Monitoring Report dated November 1994. Air toxics were also measured during the calcium injection testing period on October 19, 20, 1993. Results from this testing is contained in the Environmental Monitoring Report dated April 1997. Table 4 compares the target air toxics measured during each of the four test series.

Target Compounds		Test Period					
		Low-NOx Combustion	SNCR		Calcium-Based DSI		Sodium- Based DSI
			Baseline ³	SNCR	Baseline	Calcium	
Trace Metals		X		X		X	X
Acid-Forming Anions		X		X		X	X
Volatile Organic Compounds	Benzene/toluene	X	X				
	Formaldehyde	X					
Semi-Volatile Organic Compounds	PAH	X					
	PCDD/PCDF ¹		X ²		X		
Solid Particulate		X		X		X	X
Radio Nuclides		X					
Trace Metals Speciation	Total/hexavalent chromium		X				
	Mercury		X				
Nitrogen Compounds		X		X			
HHV, Ultimate/ Proximate Analysis		X	X	X	X	X	X
Loss-On- Ignition		X		X		X	X

1. Polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF).

2. Due to anomalous contamination of native 2,3,7,8-PCDD/PCDF isomers in the method blanks, samples, archived resin, the results of these tests are invalid and were repeated during the calcium-based DSI test period.

3. Some baseline tests were repeated in the SNCR test period.

Table 4: Target Compounds-Test Period Comparison

PSCC contracted with Carnot, Inc. of Tustin, California to complete the air toxics work at Arapahoe Unit 4. Fossil Energy Research Corp. of Laguna Hills, California provided some assistance at the site and with data collection. Table 5 lists the laboratories used to analyze the collected samples.

Analysis	Laboratory	Location
Solid particulate	Carnot, Inc	Tustin, CA
Chloride and sulfate (as necessary for confirmation)	Carnot, Inc	Tustin, CA
Acid-forming anions	Curtis and Tompkins	Berkeley, CA
Trace metals	Curtis and Tompkins	Berkeley, CA
Semi-volatile organic compounds	Zenon Environmental Laboratories	Burlington, Ontario, Canada
LOI for ash	Commercial Testing and Engineering	Denver, CO
Trace metals and anions analysis of fuel and ash	Curtis and Tompkins	Berkeley, CA
Coal preparation and ultimate analysis, including anions	Commercial Testing and Engineering	Denver, CO
Neutron activation analysis	Massachusetts Institute of Technology	Cambridge, MA
Coal preparation	A. J. Edmonds	Long Beach, CA
Ash preparation and anion analysis	Commercial Testing and Engineering	Denver, CO
Ash preparation	Carnot	Tustin, CA

Table 5: Laboratories for Air Toxics Analyses

The *Environmental Monitoring Plan (EMP) Addendum for Air Toxics Monitoring*, dated July 1993 includes details on the method used to determine the total mass flow of the air toxics. In addition to the measured concentration of the air toxics in the sample, mass flows of the solid and gas are required. Table 6 lists the mass flow rates for the flue gas and the solids used to determine the mass flow of the toxics. The actual flue gas flow rate is used for each of the trace metal, particulate matter, and anion tests. The existing plant equipment was used to measure the coal flow. The measured particulate loading and flue gas flow rate was used to calculate the flow rate of the fly ash and the stack ash. The coal input and the fly ash flow rates were used to calculate the bottom ash flow rate.

Table 7 lists the average operating conditions of Arapahoe Unit 4 during this test period.

Figure 1 shows a simplified diagram of the unit and shows the five different sample locations. Gaseous samples were obtained at the inlet and the outlet of the FFDC. Solid samples of unpulverized coal, bottom ash, and fly ash were also obtained.

Table 8 shows the test methods used that differed from those planned in the EMP.

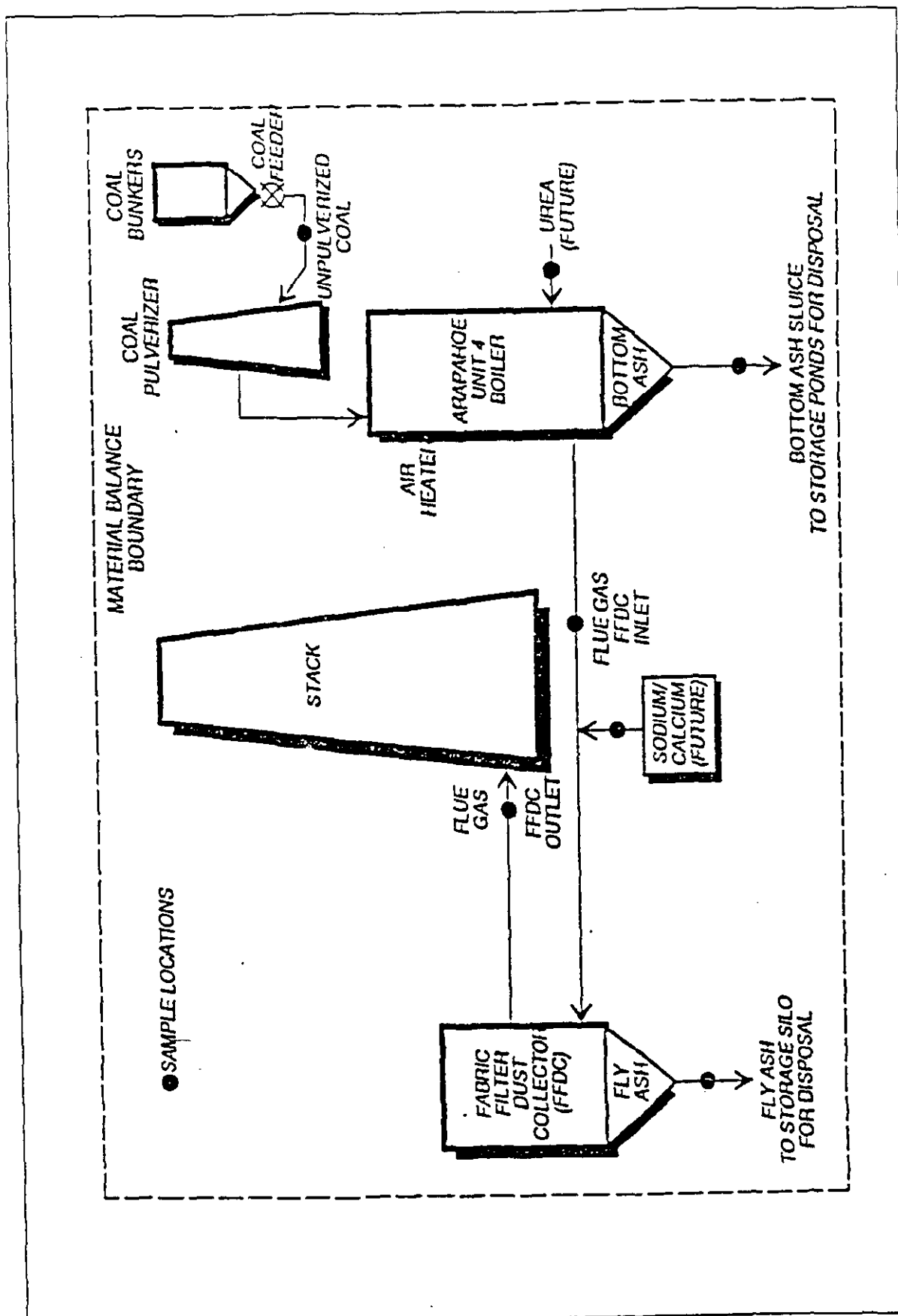


Figure 1: Sampling Locations

	Species	EMP Specified Method	Method Used
FFDC Inlet	Arsenic	EPA SW 846-7060 (GFAA)	EPA SW 846-6010 (ICP)
	Cadmium	EPA SW 846-7131 (ICP)	EPA SW 846-6010 (ICP)
	Chromium	EPA SW 846-7191 (GFAA)	EPA SW 846-6010 (ICP)
FFDC Outlet	Arsenic	EPA SW 846-7060 (GFAA)	EPA SW 846-6010 (ICP)
	Cadmium	EPA SW 846-7131 (ICP)	EPA SW 846-6010 (ICP)
	Chromium	EPA SW 846-7191 (GFAA)	EPA SW 846-6010 (ICP)
Fuel	Arsenic	EPA SW 846-7060 (GFAA)	INAA
	Barium	EPA SW 846-6010 (ICP)	EPA SW 846-6010 (ICP with EPA3050 digestion)
	Chlorine	ASTM D-4208 & ISP	INAA
	Sulfate	EPA SW 846-300-IC	ASTM D4239 & LECO SC-132
	Cadmium	EPA SW 846-7131 (ICP)	INAA
	Mercury	EPA SW 846-7470 (CVAA)	INAA
	Selenium	EPA SW 846-7740 (GFAA)	INAA
	Chromium	EPA SW 846-7191 (GFAA)	EPA SW846-6010 (ICP-AES)
	Lead	EPA SW 846-7421 (GFAA)	EPA SW846-7420 (GFAA)
	Calcium	EPA SW 846-6010 (ICP)	EPA SW 846-6010 (ICP with EPA3050 digestion)
	Sodium	EPA SW 846-6010 (ICP)	EPA SW 846-6010 (ICP with EPA3050 digestion)
	Manganese	EPA SW 846-6010 (ICP)	INAA
	Vanadium	EPA SW 846-6010 (ICP)	INAA
Flyash/ Bottom Ash	Barium	EPA SW 846-6010 (ICP)	EPA SW 846-7060 ICP-AES
	Beryllium	EPA SW 846-6010 (ICP)	EPA SW 846-7060 ICP-AES
	Cadmium	EPA SW 846-6010 (ICP)	EPA SW 846-7060 ICP-AES
	Chromium	EPA SW 846-6010 (ICP)	EPA SW 846-7060 ICP-AES
	Cobalt	EPA SW 846-6010 (ICP)	EPA SW 846-7060 ICP-AES
	Copper	EPA SW 846-6010 (ICP)	EPA SW 846-7060 ICP-AES
	Manganese	EPA SW 846-6010 (ICP)	EPA SW 846-7060 ICP-AES
	Mercury	EPA SW 846-7470 CVAA	EPA SW 846-7471 ICP-AES
	Molybdenum	EPA SW 846-6010 (ICP)	EPA SW 846-7060 ICP-AES
	Nickel	EPA SW 846-6010 (ICP)	EPA SW 846-7060 ICP-AES
	Phosphorus	EPA SW 846-6010 (ICP)	EPA SW 846-7060 ICP-AES
	Vanadium	EPA SW 846-6010 (ICP)	EPA SW 846-7060
	Calcium	EPA SW 846-6010 (ICP)	EPA SW 846-7060 (ICP with EPA3050 digestion)
	Sodium	EPA SW 846-6010 (ICP)	EPA SW 846-7471 (ICP with EPA3050 digestion)
	Fluoride	EPA 300.0(IC)	EPA 340.2 (ISE)
	Sulfate	EPA 300.0(IC)	ASTM D4239 & LECO SC-132

Table 8: Test Methods Different from EMP

A. Uncertainty Analysis

In the tables that follow, a value for uncertainty expressed as a percentage is provided for all data. The calculation method used is based upon ANSI/ASME PTC 19.1-1985, "Measurement of Uncertainty." The uncertainty is based on a 95% confidence interval for the mass emissions for the target species but is expressed as a percentage so that it may be applied to other units. A very important part of the method is assigning an estimated bias error for the major variables. The value presented represents only an approximation of the uncertainty as not all bias errors may be estimated. The uncertainty is also not a measure of long-term trace species emissions for this boiler, but only the uncertainty for the specific test period. It was assumed that the samples are a normal population distribution. No bias values were assumed for analytical results unless the result is less than the detection limit. If so, then one-half of the detection limit was used as an estimated bias. Table 9 summarizes the bias values used to determine uncertainties for other measured variables.

Location	Particle Collection ¹	Flowrate ²	Fuel Flowrate ³	Fly Ash Flowrate ⁴	Bottom Ash Flow Rate ⁴
Inlet	15%	0%	0%	15%	15%
Outlet	0%	0%	N/A	N/A	N/A

1. Bias equals difference between particulate pitot flue gas flow measurement and heat rate flowrates.
2. No Bias estimate as measured inlet, measured outlet, and calculated flow agreed within 5%.
3. No Bias estimate as calculated flue gas flow based on coal feed agreed with measured outlet flow.
4. Bias equal to the inlet particulate collection bias.

Table 9: Summary of Bias Values Used for Uncertainty Calculations

B. Treatment of Non-Detectable Measurements

Many of the target species for which a measurement was attempted were not found using the specified sampling and analytical techniques. If a measurement was not possible, the value that could have been measured, i.e. the detection limit, if the trace emissions were present are reported. The "non-detects" are shown as

less than the detection limit. The difficulty occurs when averaging various samples of which some or all of the measurements are below the detection limit. The following summarizes the two cases:

1. **All values below detection limit:** The arithmetic average of the detection limit is shown with a "<" sign to indicate that the trace species is less than the reported average detection limit. For example, if a species was not found and the method provided a detection limit of 0.45, the value is reported as <0.45.
2. **Some, but not all, values below detection limit:** The value of all measurements above the detection limit are averaged with one-half of the detection limit. For example, if three measurements of 10, 8, and <6 are found, the average would be $(10+8+6/2)/3$ or 7. Note that no "<" sign is used in these reported averages even though some of the values are below the detection limit. If the average calculated with this method is less than the greatest detection limit; the largest detection limit is reported and a "<" symbol is used. For example, if values of 6, <4, and <2 were reported, the average would be reported as <4 and not $(6+4/2+2/2)/3$ or 3.

C. Treatment of Blank Values

Three different types of blanks were used as part of the air toxics testing quality assurance (QA) program. The QA program included field blanks, reagent blanks, and laboratory preparation blanks.

Field blanks are samples obtained by assembling a complete sample train at the test site using the same procedures as when obtaining the actual sample. The sample train is then leak checked and disassembled to recover and analyze the sample. Field blanks are not used to "correct" the data generally but they are used to provide an indication of the quality of the sample.

Reagent blanks consist of samples of the reagent and/or filters that are collected at the site. Analysis of these samples show if any of the results were caused by existing levels of the trace species in the material used to collect or recover the sample. If measurable values of the trace species are found, the data is usually corrected by subtracting the value measured in the reagent.

Laboratory reagent blanks consist of samples of the chemicals used during the measurement analysis. If measurable values of the trace species are found, the data is usually corrected by subtracting the value measured in the reagent. Any measurable values in the laboratory reagent may be caused by initial trace species in the chemicals or in the analytical procedures.

In the tables that follow the value of the field blank is shown for reference, but none of the data has been changed due to these measurements. If a measurement has a value near the field blank measurement, there may be some question as to the accuracy of the data and the reported value may NOT be source related. A separate column lists a blank correction percentage for all trace species that were corrected due to either a reagent or laboratory reagent blank. This is an average percentage calculated as follows:

$$\% \text{ blank correct} = \frac{\sum \left(\frac{\text{blank value}}{\text{sample value}} \right)}{\text{number of samples}} * 100$$

For example, if three samples contained 10, 5, and 4 mg/kg of a trace species and the reagent blank was 2 mg/kg, the blank correction would be:

$$\text{blank correction} = \left(\frac{2}{10} + \frac{2}{5} + \frac{2}{4} \right) * \frac{100}{3} = 37\%$$

Thus on average, the actual value measured was 37% higher than the value reported in the table. If the blank correction is reported as 0%, no blank

correction was calculated and the reported value was the measured value. Note that in most cases a high blank correction value does not mean that the data is inaccurate. If a sample was contaminated with a trace species due to a filter, and the filter was analyzed and the data corrected, it is likely that the data is meaningful.

D. Gaseous Species Monitoring

This section reports the trace metal, acid-forming anion, and FFDC removal efficiency from the air toxics testing of the sodium-based DSI system.

Trace Metal and Anion Emissions

Table 10 lists the gaseous trace metal emissions and Table 11 lists the gaseous anion emissions for this test period. Although calcium and sodium are neither trace metals nor air toxics, Table 10 also lists them.

Previous air toxics test series have reported a wide unexplained variation of barium, calcium, and sodium in various solid streams between different test methods. Curtis and Tompkins, the laboratory completing the analysis, investigated and discovered a problem with the ASTM D3683 ashing/acid digestion method of sample preparation. Coal samples were prepared according to ASTM D3683 and also EPA method 3050. The EPA method does not require ashing or digestion using HF acid. A comparison of the data with the two different digestion methods compared to INAA is shown in Table 12 and suggests that ASTM D3683 may have a significant low bias.

EPA method 29, multi-metals method, also uses HF acid for digestion of solid matter collected in the sample train. Due to the potential negative bias that may be caused with HF acid, all data collected for barium, calcium, and sodium from the solid samples using Method 29 are believed invalid and are presented for

Trace Metals	FFDC Inlet						FFDC Outlet							
	Test 1	Test 2	Test 3	Avg.	Uncert.	Field Blank ³	Blank Correct ¹	Test 1	Test 2	Test 3	Avg.	Uncert.	Field Blank ³	Blank Correct ¹
	$\mu\text{g}/\text{Nm}^3$						$\mu\text{g}/\text{Nm}^3$	%	$\mu\text{g}/\text{Nm}^3$					
Arsenic	47	33	37	39	47	<4.7	6L	1.4	0.21	0.20	0.60	286	0.29	45L
Barium	439	98	193	243	180	0.19	IR	2.6	4.6	2.5	3.2	92	0.59	35R
Beryllium	17	11	6.4	12	115	<0.037	0.0	<0.029	<0.028	<0.031	<0.029	30	<0.029	0.0
Cadmium ⁴	6.8	3.5	3.7	4.6	99	<0.095	0.0	<0.074	<0.072	0.11	<0.074	84	<0.075	0.0
Chromium ⁶	381	85	55	173	258	0.19	IR	0.15	0.26	0.16	0.19	81	0.15	81R
Cobalt	88	39	38	55	131	<0.37	0.0	<0.29	<0.28	<0.31	<0.29	30	<0.29	0.0
Copper	323	211	412	315	81	0.37	0.2R	0.71	1.0	0.53	0.75	79	0.48	33R
Lead ⁶	103	94	110	102	26	0.058	9R	0.045	1.0	0.28	0.45	283	0.045	94R
Manganese	323	46	67	145	263	0.19	0.4R	0.51	0.37	0.23	0.37	94	0.19	38R
Mercury	1.2	1.9	1.7	1.6	65	<0.12	0.0	0.66	0.72	0.16	0.51	150	<0.087	0.0
Molybdenum ⁶	77	24	22	41	191	2.4	18R	0.29	0.28	0.31	0.29	8.6	0.29	0.9R 44R
Nickel ⁶	129	53	56	79	136	0.37	IR	0.29	0.28	0.31	0.29	8.6	2.7	0.0
Selenium	<94	<54	<105	<84	87	<0.95	0.0	0.63	0.41	0.31	0.45	92	<0.07	0.0
Phosphorus	15,900	11,800	16,900	14,900	48	<1.9	0.0	<1.5	3.1	2.1	2.0	150	<1.5	0.0
Vanadium	352	201	135	229	122	0.19	0.0	0.15	0.15	0.18	0.16	32	<0.15	0.0
Calcium ⁵	502	50	187	246	234	9.5	20R	31	67	28	42	128	26	39R
Sodium ⁵	4,280	1,319	1,156	2,252	195	9.5	8R	63	252	112	142	171	75	48R
Iron ²	55,500	47,000	18,300	40,200	--	--	--	--	--	--	--	--	--	--

- ♦ "<" indicates that the quantity measured was less than the detection limit thus the detection limit is shown
1. "R" indicates reagent blank correction. "L" indicates laboratory blank correction.
 2. Iron presented for information only.
 3. Calculated using average sample volume from metals tests and subtracting reagent or lab blank levels, as indicated.
 4. The average calculated by dividing the non-detect in half was less than the highest non-detect, so the highest non-detect was used for the average.
 5. Included even though neither trace metals nor air toxics.
 6. For the outlet values for Cr Test-1,2; Pb Test-1; Mb Test-1,2,3; and Ni Test-1,3; subtracting reagent blank value lowered result below the detection limit, so the detection limit was used and reported as a detect.

Table 10: Gaseous Air Toxics Emissions (Trace Metals)

Acid Forming Anions		FFDC Inlet							FFDC Outlet						
		Test 1	Test 2	Test 3	Avg.	Uncert.	Field Blank	Blank Correct	Test 1	Test 2	Test 3	Avg.	Uncert.	Field Blank	Blank Correct
		ppm							%						
Chlorine (Cl ⁻)	Total	0.65	0.65	0.79	0.70	30	N/A	--	0.44	0.78	0.72	0.65	69	N/A	--
	Gaseous	0.63	0.62	0.76	0.67			NC ¹	0.43	0.76	0.71	0.63			6,2R ¹
	Solid	0.027	0.033	0.034	0.031			30 ²	0.015	0.018	0.013	0.016			NC ²
Fluorine (F ⁻)	Total	11	12	12	12	25	N/A	--	2.6	1.3	1.2	1.7	114	N/A	--
	Gaseous	10	11	12	11			0	2.6	1.3	1.1	1.7			0
	Solid	0.57	0.65	0.67	0.63			0	0.036	0.039	0.044	0.040			0
Sulfate (SO ₄ ⁻²)	Total	352	338	331	340	21	N/A	--	110	96	22	109	31	N/A	--
	Gaseous	350	335	328	338			0.01R	110	96	22	109			NC ¹
	Solid	2.1	3.2	2.7	2.7			7R ²	0.024	0.024	0.032	0.026			6,2R ²

♦ "<" indicates that the quantity measured was less than the detection limit thus the detection limit is shown.

♦ Solid fraction consists of filter and front-half rinse.

♦ Gaseous fraction consists of bicarbonate/carbonate and 3% peroxide rinses.

1. Blank correction to 3% peroxide results.

2. Blank correction to filter results.

Table 11: Gaseous Air Toxics Emissions (Anions)

	D3683 mg/Kg	E3050 mg/Kg	INAA mg/Kg
Barium	5,976	24,390	33,122
	6,670	17,447	28,925
Calcium	122,740	213,404	NP
	78,917	204,879	NP
Sodium	14,843	64,322	105,096
	31,849	27,423	46,099

Table 12: Comparison of Alternate Digestion Methods with INAA

information only. Table 13 compares the inlet fuel levels to the values measured at the FFDC inlet determined from the Method 29 test using HF digestion. Note the very large discrepancy in the inlet values. It is believed that the fuel values are more accurate and that the FFDC inlet values for the three elements presented are invalid. They are shown in this table only to note the large variation that was believed due to the HF digestion technique. Note that the inlet values are based on a large amount of particulate matter that is present at the FFDC inlet. Due to the very low particulate at the FFDC outlet, the possible interference with HF digestion is not believed to significantly affect the outlet data. While fly ash and coal samples could be reanalyzed after the discovery of the possible interference, it was not possible to re-analyze the Method 29 train.

	Fuel lb/10 ¹² Btu	FFDC Inlet lb/10 ¹² Btu	Percent Difference
barium	24,400	189	12,810%
calcium	213,000	192	110,838%
sodium	64,300	1,751	3,572%

Table 13: Comparison of fuel vs FFDC Inlet Measurements

In addition to the high uncertainty for barium, calcium, and sodium discussed above, high uncertainty of greater than 100% occurred for beryllium, chromium, cobalt, manganese, molybdenum, nickel, and vanadium. All these high uncertainties were caused by very high readings for Test 1. A review of the data logs and sample methods did not reveal any sampling errors that could explain the differences. The measured inlet values for chromium, cobalt, molybdenum and nickel, when combined with the bottom ash analysis, resulted in values that were larger than the fuel input rates indicating that a problem with sampling may have occurred. One possible explanation for the high readings in a single run is that during sample recovery some of the acid reagent used for clean-up contacted the stainless steel fittings of the sample train and contaminated the samples. It is also possible that rust or other material not associated with the combustion product was collected in the sample train and contaminated the sample.

At the FFDC outlet, only air toxics arsenic, lead, mercury, and phosphorous had uncertainty values above 100%. Possible sources of these high uncertainties are:

- Arsenic. It has been difficult to obtain good agreement among the results generated by ICP-hydrate analysis.

- Lead. 7
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- Mercur
limits.

At the FFD

The removal efficiency of sodium injection and the FFDC for chloride was only 6%. Outlet levels for chloride accounted for 54% of the chloride input of the coal. This is significantly lower removal than the other three air toxics tests which were over 50% especially since sodium injection is believed to efficiently capture gaseous chloride. An investigation of the sample procedure could find no reasons for the lower than expected removal, but the outlet chloride levels are lower than in the first two test programs. This suggests a possible measurement problem with the inlet chloride levels. The removal efficiency of sodium injection and the FFDC for fluoride was 85%. The flue gas levels of fluoride decreased from 12 ppm at the FFDC inlet to 1.7 ppm at the FFDC outlet. Outlet fluoride levels accounted for only 12% of the fuel input. These removals compare well with other testing that obtained approximately 90% fluoride removal. This indicates that sodium injection did not improve fluoride emission reduction across the FFDC. The removal efficiency of sodium injection and the FFDC for sulfate was 68%. Outlet sulfate levels accounted for only 32% of the sulfur input of the coal.

Species		Inlet	Outlet	FFDC Removal
Trace Metals		lb/10 ¹² Btu	lb/10 ¹² Btu	%
Arsenic		30	0.47	98.4
Barium ²		189	2.53	NV
Beryllium		9.0	<0.02	>99.7
Cadmium		3.6	<0.06	>98.4
Chromium		135	0.15	99.9
Cobalt		43	<0.23	>99.5
Copper		245	0.59	99.8
Lead		80	0.36	99.6
Manganese		113	0.29	99.7
Mercury		1.2	0.41	67.5
Molybdenum		32	0.23	99.3
Nickel		62	0.23	99.6
Selenium		<66	0.36	99.5
Phosphorus		11,600	1.5	99.99
Vanadium		178	0.13	99.9
Calcium ^{1,2}		192	33	NV
Sodium ^{1,2}		1,750	112	NV
Average		--	--	>97.2
Total Particulates		5.92 lb/MMBtu	0.0019 lb/MMBtu	99.97%
Acid-Forming Anions		lb/10 ¹² Btu	lb/10 ¹² Btu	%
Chloride (Cl)	Solid	39	19	50.0
	Gas	825	791	4.1
	Total	864	811	6.1
Fluoride (F)	Solid	418	27	93.7
	Gas	7,250	1,110	84.6
	Total	7,670	1,140	85.1
Sulfate	Solid	8,910	89	99.0
	Gas	1.13(10 ⁶)	3.69(10) ⁵	67.5
	Total	1.14(10 ⁶)	3.69(10) ⁵	67.7

◆ * < * indicates that the quantity measured was less than the detection limit thus the detection limit is shown.

1. Included even though neither are trace metals nor air toxics.
2. Values for these FFDC inlet metals are reported but believed invalid due to possible interferences (see text).

Table 14: FFDC Removal Efficiency

E. Solids Stream Monitoring

Sorbent Analysis

Table 15 lists the analysis results for the sodium-based sorbent.

Coal Analysis

During the previous air toxics test series it was believed that non-representative sampling may have contributed to some of the variation that was seen. For the current program, an independent sample consultant was used to assist in reviewing and modifying the coal sampling procedure. Rather than obtain coal samples from the coal hopper, the feeders were stopped for a short time and coal samples were retrieved directly from the feeder.

As discussed in the gaseous trace metal sections, coal samples were analyzed using different methods for many of the trace metal data points. On average, there were three sets of data with some having as many as six sets. For example, one point had results from:

- Curtis & Tompkins analysis using conventional digestion.
- Curtis & Tompkins analysis using EPA 3050 digestion.

Element	Sodium-Based Sorbent (mg/kg)
Arsenic	< 11
Barium	16
Beryllium	< 0.42
Cadmium	< 1.1
Chromium	< 2.1
Cobalt	< 4.2
Copper	1.1
Lead	7.9
Manganese ¹	9.6
Mercury	< 0.1
Molybdenum	< 4.2
Nickel	< 4.2
Selenium	< 11
Phosphorous	91
Vanadium	2.7
Chloride ¹	1,075
Fluoride	13
Sulfate	< 130

◆ No blank corrections used.

1. Chloride result average of EPA 300.0 and EPA 325.2 analysis results.

Table 15: Air Toxics Analysis of Sodium-Based Sorbent

- Standard Laboratory's analysis.
- Curtis & Tompkins triplicate analysis using conventional digestion.
- Curtis & Tompkins triplicate analysis using EPA 3050 digestion.
- INAA.

Except for a few cases, the results from these different sources did not agree. Ideally, if the data for one element from one set was consistent with expected levels and other process streams, then the data for elements within the same data set processed by the same lab and method would also be consistent.

Unfortunately, a common bias for a data set could not be found other than methods that depend upon HF acid digestion concerns. Therefore, the use of a particular data set depended on its agreement with levels determined in other input and output streams from the same test program.

Table 16 lists the analysis of the coal for trace metals and acid-forming anions for the INAA and base method analysis. Although neither calcium nor sodium are trace metals or air toxics, Table 16 also includes them. All trace metals were detected in each replicate. Of the 15 trace metals, phosphorous and barium were the predominant metals and were consistent within expected levels. All elements had uncertainties under 100% except for cadmium.

Trace Metals	Base Test Method						INAA					
	Test 1	Test 2	Test 3	Average	Uncert.	Blank Correct	Test 1	Test 2	Test 3	Avg.	Uncert.	Blank Correct
	mg/kg						%					
Arsenic ¹	NP	NP	NP	NP	NP	0	0.69	0.67	0.66	0.67	5.9	0
Barium ³	271	266	263	267	3.1	0	348	357	382	362	13.4	0
Beryllium	0.30	0.48	0.34	0.37	63	0	0.05	0.32	0.031	0.038	239	0
Cadmium ^{1,2}	<0.14	<0.16	<0.13	<0.14	26	0	2.7	3.1	3.1	3.0	19	0
Chromium ¹	1.9	2.5	1.8	2.1	45	0	0.9	0.90	1.0	0.9	15	0
Cobalt	1.1	1.8	1.1	1.3	80	0	32	20	25	26	59	0
Copper	8.0	6.1	4.5	6.2	72	0	0.05	0.062	0.037	0.050	62	0
Lead ³	4.1	3.9	3.7	3.9	11	0	1.2	1.0	1.1	1.1	25	0
Manganese ^{1,3}	17	14	22	18	5	0	0.58	0.47	0.49	0.51	30	0
Mercury ¹	NP	NP	NP	NP	NP	0	9.9	8.2	7.4	8.5	38	0
Molybdenum	0.51	0.52	0.44	0.49	23	0	1,031	1,282	1,136	1,149	28	0
Nickel ³	2.4	2.2	1.1	1.9	94	0						
Selenium ¹	NP	NP	NP	NP	NP	0						
Phosphorus	434	659	500	531	54	0						
Vanadium ¹	5.3	6.9	5.0	5.7	44	0						
Calcium ³	2,350	2,290	2,360	2,330	3.4	0						
Sodium ³	678	769	663	703	20	0						
Acid-Forming Anions	mg/kg	mg/kg	mg/kg	mg/kg	%	%	mg/kg	mg/kg	mg/kg	mg/kg	%	%
Chloride (Cl) ¹	NP	NP	NP	NP	NP	0	15	21	8.4	15	105	0
Fluorine (F)	100	90	110	100	25	0						
Sulfate	12,600	3,200	12,600	12,800	7.0	0						

- ◆ * < indicates that the quantity measured was less than the detection limit thus the detection limit is shown.
 - ◆ "NP" indicates not performed.
 - ◆ All values are reported on an as-received basis for the coal.
1. INAA results were used for these trace species rather than the base method.
 2. Since the result for Cd Test-2 (INAA) was inconsistent with expected levels, it was not used in the average.
 3. Analysis performed after an EPA 3050 digestion (acid only).

Table 16: Air Toxics Analysis of Coal

Fly Ash

Table 17 lists the analysis of the bottom and fly ash for trace metals and anions. Although sodium and calcium are neither trace metals nor air toxics, Table 17 also lists them. Except for cadmium, all trace metals were measured above their detection limits. Of the 15 trace metals, phosphorous and barium were the predominant elements. However, the barium levels were not consistent with the input levels and indicate a low bias for the barium levels in the fly ash. The trace metal levels for the replicates exhibit good agreement, thus uncertainties are relatively good at significantly less than 100%.

With the increase in the FFDC's removal efficiency for anions, the fly ash levels of chloride, fluoride, and sulfate are higher than those from the low-NO_x combustion and SNCR test periods. The fluoride result for Test 1 was significantly lower than the two replicate tests. A review of the sample and analysis methods did not find any reason for the large variation but this sample point was not included in the average.

Trace Metals	Fly Ash						Bottom Ash/Sluice Water 2						
	Test 1	Test 2	Test 3	Avg.	Uncert.	Blank Correct	Test 1	Test 2	Test 3	Avg.	Uncert.	Blank Correct	
	mg/kg						mg/kg						%
Arsenic	5.3	5.3	5.0	5.2	23	0	1.4	1.6	<1.2	1.2	89	0	
Barium	680	610	670	653	23	0	640	530	630	680	39	0	
Beryllium	3.2	3.8	3.6	3.5	25	0	4.1	4.2	4.0	4.1	44	0	
Cadmium	<1.1	<1.0	<1.2	<1.1	40	0	<1.0	<1.3	<1.2	<1.2	48	0	
Chromium	23	25	28	25	27	0	30	29	29	29	44	0	
Cobalt	14	15	15	15	24	0	16	16	14	15	37	0	
Copper	37	41	41	40	23	0	43	45	40	43	36	0	
Lead	16	20	17	18	29	0	18	15	12	15	45	0	
Manganese	140	140	150	143	24	0	250	290	320	287	37	0	
Mercury	0.12	0.15	0.15	0.14	32	0	<0.020	<0.020	<0.019	<0.020	53	0	
Molybdenum	5.1	5.1	5.2	5.1	26	0	<3.9	<5.0	<4.7	<4.5	47	0	
Nickel	14	14	19	16	41	0	24	22	20	22	38	0	
Selenium	3.2	5.4	5.1	4.6	70	0	<1.2	<1.2	<1.2	<1.2	52	0	
Phosphorus	3,300	3,600	3,900	3,600	25	0	4,400	4,300	4,000	4,230	45	0	
Vanadium	49	55	57	54	25	0	58	61	58	59	44	0	
Calcium 3	20,000	19,000	19,000	19,300	23	0	17,300	15,300	17,200	16,600	36	0	
Sodium 3	53,000	63,000	61,000	59,000	26	0	1,530	1,280	1,990	1,600	48	0	
Acid-Forming Anions	mg/kg						mg/kg						%
Chloride as Cl ⁻	140	270	270	227	86	0	209	161	170	180	38	0	
Fluoride as F ⁽⁻⁾	76	980	1,100	1,040	36	0	4.5	3.8	1.9	3.4	79	0	
Sulfate	46,400	63,200	66,500	58,700	41	0	1,100	1,260	1,170	1,180	36	0	

♦ * < * indicates that the quantity measured was less than the detection limit thus the detection limit is shown.

2. For trace metals, excluding calcium and sodium: results are from bottom ash solid fraction only. For anions, calcium, and sodium: solid and liquid fractions were analyzed separately and combined proportionally by weight after sluice water blank subtractions.

3. Included even though neither are trace metals nor air toxics.

Table 17: Air Toxics Analysis of Ash

Bottom Ash

As with the coal and fly ash analyses, phosphorous and barium were the predominant elements in the bottom ash. The average results for cadmium, mercury, molybdenum, and selenium are reported below their detection limits. Uncertainty levels below 100% indicate good agreement between the replicates.

F. Mass Balance Results

Mass balances are an important quality check on toxics emissions data. Using different sample and analytical techniques to measure toxics in both gaseous and solid forms, at best, is difficult. Mass balances provide a quick means for determining how well various analytical methods agree. The low absolute quantities of the measured materials, however, makes the occurrence of a 100% mass balance very unlikely.

There are three major sources of potential error in the mass balance: operating conditions, analytical difficulties, and sample collection and handling. Since Arapahoe Unit 4 operated at or near steady-state conditions and the daily tests show that the same coal was fired throughout the tests, operating conditions are not likely to contribute any significant sources of error. Analytical difficulties usually only affect the results for individual replicates or species, so they are considered with each species. Normally, analytical difficulties outweigh sampling problems, but in this program the difficulty of obtaining representative samples from process streams flowing at thousands of pounds per hour adds unusual sources of potential error. It should also be noted that uncertainties only represent consistency, not accuracy.

Table 18 shows the mass balance results for the sodium-based DSI test period. Only compounds dependent on the fuel inputs can be balanced. Since semi-volatile organic compounds depend on combustion parameters, they cannot be balanced. The boiler/FFDC mass balance uses the coal as its input and the bottom ash, fly ash, and FFDC outlet as its outlets. The boiler mass balance uses the coal for its input and the FFDC inlet and the bottom ash as its outlets.

Species	Inputs		Intermediate	Outputs			Mass Balance	
	Fuel	DSI ² (Sodium)	FFDC Inlet	Bottom Ash	Fly Ash	FFDC Outlet	Boiler/ FFDC ¹	Boiler ¹
Trace Metals	lb/10 ¹² Btu		lb/10 ¹² Btu	lb/10 ¹² Btu			%	
Arsenic ³	62	<30	30	4.5	45	0.47	80	57
Barium	24,400	43	NV	2,310	5,590	2.5	32	--
Beryllium	34	<1.1	9.0	16	30	<0.023	131	73
Cadmium ³	3.5	<3.0	3.6	<4.5	<9.3	<0.058	--	104
Chromium ³	272	<5.6	135	113	216	0.15	119	91
Cobalt	122	<11	43	59	125	<0.23	138	83
Copper	568	3.0	245	164	339	0.59	88	72
Lead	358	21	80	57	151	0.36	55	38
Manganese ³	2,340	26	113	1,120	1,220	0.29	99	53
Mercury ³	4.6	<0.27	1.2	<0.076	1.2	0.41	37	29
Molybdenum	45	<11	32	<18	44	0.23	110	110
Nickel	175	<11	62	84	133	0.23	117	83
Selenium ³	47	<30	<66	<4.6	39	0.36	93	80
Phosphorus	48,500	245	11,600	16,300	30,700	1.5	96	57
Vanadium ³	779	7.3	178	227	458	0.13	87	52
Average Metals							92	70
Calcium	213,000	NP	NV	64,000	166,000	33	108	--
Sodium ³	64,300	784,000	NV	6,240	503,000	112	60	--
Acid-Forming Anions	lb/10 ¹² Btu		lb/10 ¹² Btu	lb/10 ¹² Btu			%	
Chloride (Cl) ³	1,370	2,890	864	689	1,910	811	80	113
Fluoride (F)	9,140	35	7,670	13	8,900	1,140	110	84
Sulfate	1.17(10 ⁶)	<350	1.14(10 ⁶)	4,560	498,000	369,000	75	98
Average Anions							88	99

◆ "<" indicates that the quantity measured was less than the detection limit thus the detection limit is shown.

◆ "NP" indicates not performed, "NV" indicates not valid.

1. Boiler/FFDC mass balance calculated using: (outlet + fly ash + bottom ash)/(fuel + sorbent). Boiler mass balance calculated using (inlet + bottom ash)/fuel.

2. Sodium sorbent flow rate as: (weight% of Na) * (Na flow rate) * (10⁶).

3. Fuel concentrations from INAA.

Table 18: Mass Balance Results

For the overall boiler/FFDC mass balance, closure results for most species are in the range of 70 to 130% which is believed reasonable considering the many variables in determining these values. The closure for barium, cobalt, lead, mercury, and sodium were outside the expected range.

The fuel input for barium is consistent with expected values based on coal mine analysis but the closure was only 32%. It is most likely that the fly ash and bottom ash values are biased low. Appropriate digestion procedures for the barium sample were investigated and sufficient problems were discovered to invalidate the FFDC inlet values. More investigation is required to determine the appropriate barium digestion techniques.

Cobalt closure was also slightly poorer than expected with a value of 138%, meaning that more output cobalt was found than was contained in the fuel. The most likely reason was a low biased fuel measurement. Alternative analysis with INAA provided an even lower fuel input. Note that the coal cobalt measurement had a high uncertainty of 80% suggesting that fuel variation may be one source of the poor closure.

Lead also had a very low closure with only 38% of the measured fuel levels found in the output. Uncertainties for the lead measurements in all streams were not excessive. It is possible that measurement technics may have problems with the low lead levels found.

Mercury emissions are very low but the closure was not very good with the outputs only accounting for 37% of the inlet mercury. Mercury is a very difficult species to obtain valid measurements. The coal value obtained during the sodium test program was substantially higher than that obtained in the remaining three air toxics test periods. Uncertainties were high for all mercury measurements and these may be responsible for the low closure.

A mass balance was also attempted with sodium although this is not an air toxic. The boiler/FFDC closure was only 60%. As the inlet sodium values are reasonably measurable and accurate, the fly ash levels are suspect. While most air toxics are evenly distributed as they are associated with the coal, sodium is injected separately in the duct and is not well distributed. Improvements were made to the fly ash sampling technique during the current program, but the most likely cause of the low fly ash sodium levels is obtaining a non-representative sample.

G. Summary of Test Results

Table 19 summarizes the fuel input, FFDC inlet, and FFDC outlet results for each of the test periods. Coal from the Yampa mine in Colorado was fired at Arapahoe Unit 4 for low-NO_x combustion, SNCR, and sodium-based DSI test periods. For the calcium-based DSI test period, coal from the Edna mine in Colorado was fired at Arapahoe Unit 4. It is not clear whether the slightly higher values for many trace metals in the coal tested during the sodium- and calcium-based DSI test periods is due to more representative techniques or the coal.

The increase of the trace metal levels in the FFDC inlet are consistent with the fuel input levels. However, if the FFDC inlet is considered as a point of uncontrolled emissions, the emissions levels are consistently in the same range.

Both sodium and calcium injection before the FFDC significantly reduced the FFDC outlet levels of phosphorous, chloride, fluoride, and sulfate. The lower levels of arsenic, mercury, and selenium suggest that calcium injection removes these elements more effectively than sodium injection. This is likely due to the humidification and subsequent cooling of the flue gas and the volatility of these metals.

Parameter	Fuel Input				FFDC Inlet				FFDC Outlet			
	Low-NO _x Combustion	SNCR	DSI (Sodium)	DSI (Calcium)	Low-NO _x Combustion	SNCR	DSI (Sodium)	DSI (Calcium)	Low-NO _x Combustion	SNCR	DSI (Sodium)	DSI (Calcium)
	lb/10 ¹² Btu				lb/10 ¹² Btu				lb/10 ¹² Btu			
Arsenic	43	56	62	47	23	13	30	20	0.75	0.15	0.47	0.093
Barium	37,600	29,700	24,400	17,400	234	192	189	431	1.1	1.1	2.5	0.94
Beryllium	20	48	34	32	9.0	7.5	9.0	9.5	<0.021	<0.023	<0.023	<0.022
Cadmium	<4.5	<5.3	3.5	5.4	2.3	2.0	3.6	3.9	0.12	<0.066	<0.058	0.15
Chromium	97	125	272	224	50	51	135	63	0.66	0.30	0.15	0.26
Cobalt	84	114	122	93	30	26	43	53	<0.21	<0.23	<0.23	<0.22
Copper	241	324	568	396	169	206	245	310	1.1	1.3	0.59	0.42
Lead	185	195	358	310	64	46	80	55	0.44	0.40	0.36	0.38
Manganese	379	458	2,340	1,450	195	88	113	108	1.0	0.89	0.29	0.59
Mercury	1.9	1.7	4.6	2.7	1.3	1.9	1.2	3.4	<0.29	0.41	0.41	0.21
Molybdenum	9.0	44	45	38	10	12	32	26	0.17	0.27	0.23	0.22
Nickel	53.5	88	175	141	30	29	62	19	1.5	0.45	0.23	0.22
Selenium	73	127	47	115	22	12	<66	57	0.36	<0.064	0.36	<0.057
Phosphorous	36,700	27,700	48,500	35,200	14,300	9,300	11,600	12,800	6.7	4.6	1.5	<1.1
Vanadium	266	379	779	565	135	120	178	194	0.24	0.29	0.13	<0.11
Calcium	NP	185,000	213,000	205,000	NP	880	192	1,240	NP	29	33	106
Sodium	NP	29,300	64,300	27,400	NP	2,700	1,750	2,580	NP	367	112	13
Chloride	2,000	1,400	1,370	1,720	795	1,010	864	825	626	719	811	371
Fluoride	7,600	7,400	9,140	6,650	4,780	5,780	7,670	6,700	4,290	4,810	1140	167
Sulfate	1.18(10 ⁵)	1.15(10 ⁵)	1.17(10 ⁵)	1.59(10 ⁵)	10.6(10 ⁵)	9.88(10 ⁵)	1.14(10 ⁵)	1.58(10 ⁵)	9.83(10 ⁵)	1.17(10 ⁵)	3.69(10 ⁵)	9.9(10 ⁵)
Cyanide	N/A	N/A	N/A	N/A	<8	<12	NP	NP	<7	<9	NP	NP
Ammonia	N/A	N/A	N/A	N/A	<100	12,000	NP	NP	N/A	7,000	NP	NP

NP indicates test not performed.

Table 19: Summary of Fuel Input, FFDC Inlet, and FFDC Outlet Levels

Table 20 compares the trace metal levels in the output streams as a percentage of the fuel input. A larger distribution of the trace metals in the bottom ash improved the mass balances for the sodium- and calcium-based DSI test periods. The bottom ash levels for the SNCR test period appear negatively biased by 15% of fuel input. For the low-NO_x combustion test period, the bottom ash levels appear negatively biased by 20% of fuel input and the fly ash levels appear negatively biased by 15% of fuel input. The use of the same collection methods for all four test periods suggests that the closer adherence to ASTM preparation methods during the sodium- and calcium-based DSI test periods improved the trace metal results. Also, the use of more representative sampling techniques for fly ash during these test periods appears to have reduced the occurrence of poor trace metal results seen during the low-NO_x combustion test period.

Test Period	Output Stream (% of Fuel Input ¹)			Total (% Closure)
	Bottom Ash	Fly Ash	FFDC Outlet	
Low-NO _x Combustion ²	9	53	2	64
SNCR	14	67	2	83
DSI (Sodium)	28	63	1	92
DSI (Calcium)	31	68	:	100

1. Fuel input for sodium- and calcium-based DSI test periods include the sorbent injection streams.

2. The fuel result for molybdenum appears to be severely biased low. The percentages for the low-NO_x combustion test period are based on an average of the molybdenum levels in the fuels from the SNCR and sodium-based DSI test periods.

Table 20: Distribution of Trace Metals Across Output Streams

