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MERCURY IN SHALLOW SAVANNAH RIVER PLANT SOIL

Published: October 1988

E. I. du Pont de Nemours & Co.
Savannah River Laboratory
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PREPARED FOR THE U.S. DEPARTMENT OF ENERGY UNDER CONTRACT DE-AC09-76SR00001

DISCLAIMER

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MERCURY IN SHALLOW SAVANNAH RIVER PLANT SOIL

by

V. Price
J. R. Cook

Approved by:

J. C. Corey, Research Manager

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Executive Summary

Soil concentrations of adsorbed mercury at 999 sites at the Savannah River Plant (SRP) were determined by Microseeps Limited of Indianola, PA. The sites were in and around the 643-G Burial Ground, at the Savannah River Swamp adjacent to TNX Area, and at a background area. The Burial Ground was chosen as a test site because of a history of disposal of radioactive mercury there prior to 1968 (Horton, 1973). Extremely low traces of mercury have been detected in the water table beneath the Burial Ground (Oblath, 1985). Although the mercury concentrations at the majority of these sites are at background levels, several areas appear to be anomalously high. In particular, an area of large magnitude anomaly was found in the northwest part of the Burial Ground. Three other single point anomalies and several other areas of more subtle but consistently high values were also found. Several sites with anomalous mercury levels were found in an area of the Savannah River flood plain adjacent to TNX Area.

Introduction

Mercury occurs widely in nature and is associated with economically valuable mineral deposits. A trace element in many of the minerals of these ore deposits, mercury is also present in the metallic state due to oxidation of the host minerals. The relatively high volatility of mercury compared to the other heavy metals results in a uniquely high mobility and rapid migration in soils. Mercury is widely used as a pathfinder in geochemical exploration for base metal sulfides, gold, and silver. Pronounced local anomalies are often found directly above ore deposits; however, displacements of up to 2 km have been reported. The environmental fate of mercury vapor introduced into the atmosphere from natural sources such as active volcanoes and human activities such as ore refining and coal combustion has also stimulated investigation of the mercury cycle.

Fang (1978) and Landa (1978) investigated five Montana soils of differing characteristics to determine their efficiency and capacity to adsorb mercury vapor. Both the mineralogical makeup and organic matter content and type affected the adsorption capability of the soils. In both studies, dry soil samples were exposed to known concentrations of mercury vapor for measured lengths of time. Only a small fraction of the adsorbed mercury was in the oxidized mercuric form. The adsorbed mercury was not lost from the soils when maintained at air dryness and room temperature over a 16-day observation period. Soils maintained at one-third bar moisture-tension for the same period showed a maximum loss of 5% of the total adsorbed mercury. There was no loss of mercury after the soils were placed in a vacuum desiccator for 24 hr or heated in an oven at 110 °C for 2 hr. Major fractions (70-90%) of the adsorbed mercury were desorbed from the soils at temperatures between 150 and 200 °C. These data, coupled with the results of solvent extraction, suggest that 70 to 90% of the adsorbed mercury resides in the soils either in the form of organomercury complexes or as an inorganic complex.

The capacity of soils to retain mercury adsorbed as an organic or inorganic complex provides a sensitive mechanism for the accumulation of vaporous mercury flux in near-surface soils. The survey method used in this study was chosen because these mercury complexes can be decomposed by heat and because mercury will amalgamate to gold.

Sampling Areas

Soil concentrations of adsorbed mercury were measured at 999 sites at the 643-G Burial Ground, at the Savannah River Swamp adjacent to TNX Area, and at a background area. The background samples (953-975) were collected at 23 sites in Z Area, which is approximately 2.5 to 3 mi northeast of the 643-G Burial Ground. This area was chosen because its soil type is similar to the Burial Ground's. Naturally adsorbed mercury levels could be expected to be similar to the Burial Ground, assuming no naturally occurring localized mineralization or man-made effects.

Samples were collected in three areas in and around the Burial Ground. The location of the sample sites, of known and probably burials of mercury, and of ground-water monitoring wells with elevated mercury levels are shown in Figures 1 through 4. For purposes of mapping and discussion, the data are broken into three areas: A, B, and C. Area A comprises 125 sites (1-93 and 154-185) immediately south of the Burial Ground perimeter fence and a second traverse of 78 sites (471-548) immediately south of the main road (Figure 2).

Area B (Figure 3) is located at the west end of the Burial Ground. Four traverses in the south (250-312), with spacing of 100 ft by 50 ft, were sampled. Additional samples (313-470, 549-952) were collected in a 25-ft center grid to the north. A line of samples (186-221) was collected along the western fence of the Burial Ground.

Area C is located in the east part of the Burial Ground and consists of seven lines of sample sites (94-153 and 222-249) with 50-ft sample spacing and 100-ft separations, as shown in Figure 4.

An additional 24 sites (976-999) were located in a swamp area in the Savannah River flood plain adjacent to TNX Area (Figure 5).

Sample Collection

A 5-cm diameter soil core was collected by driving a sharpened pipe to an approximate depth of 30 cm at each site. Each core was placed on a clean paper plate and allowed to air dry until it could be field sieved to 40 mesh (0.5 mm). Samples were placed in labeled bags and analyzed within 48 hr of collection.

Sample Analysis

Mercury was desorbed from a 1-g portion of the 40-mesh fraction of each sample by heating the sample to 175 ^{o}C for 1 hr in a 8 mm by 60 mm fused silica tube. The inside bottom 25 mm of each silica tube was coated with a thin layer of gold that adsorbed the mercury released from the soil. Gold exhibits a maximum adsorptive capacity for mercury between 150 and 200 ^{o}C. Thus, the mercury was concentrated in a form from which it could later be quickly released for analysis.

The silica tubes were cooled, the soil was discarded, and each sample was analyzed using a Jerome Model 411 Gold Film Mercury Analyzer. The mercury was released from the gold film in each silica tube by rapid heating to 550 ^{o}C in

a resistance heater. A flow of nitrogen swept the contents of each tube into the Jerome analyzer where the mercury was adsorbed onto a calibrated gold film that changes resistance as a function of the amount of mercury adsorbed. The minimum detectable amount of mercury is 0.5 ng (0.5×10^{-9} g), which if released from 1 g of soil corresponds to a soil mercury content of 0.5 ppb. This level is approximately 10% of the normal background soil mercury level, which previous exploration surveys have found to be 5 ± 3 ppb.

Sensitivity of the Jerome Model 411 Gold Film Mercury Analyzer is reported to be 8 counts/ng and linear over its entire range. The instrument response and linearity were checked by injection of known amounts of air saturated with mercury vapor at 20 °C. Mean sensitivity over a range of 7.0 to 56.0 ng was found to be 8.24 counts/ng with a standard deviation of 0.4 counts/ng. As shown in Table 1, the sensitivity increases slightly but consistently over the range. Additionally, multiple runs were performed on two samples from sites 938 and 942 (Table 2). Standard deviations in both cases are less than 10% of the mean value.

The mercury content of a garden soil from Indianola, PA, was determined prior to this survey. A 1-lb sample of soil was air dried and sieved to 40 mesh. Seventy-five gold-plated silica tubes were each filled with 1 g of this sieved soil and analyzed for adsorbed mercury using the method described above. Mean adsorbed mercury content was found to be 5.43 ppb with a standard deviation of 0.88 ppb or 16%. This variation reflects the variability of the soil mercury content and the analytical variability.

Analytical Results

The analytical results are presented in Table 3. The data displayed a nonlinear distribution of mercury concentrations that approximated a log-normal distribution (Figure 6). The log mean is .8224 and the log-standard deviation is .36 (Table 4). Table 5 shows the symbols used on the maps to illustrate mercury concentrations. Each successive change in symbol represents an incremental change of one log-standard deviation in mercury concentration.

The background data have an arithmetic mean of 7.6 ppb and a standard deviation of 3.1 ppb. The distribution is near normal, with a variation coefficient of 0.41. The range (min = 2 ppb, max = 14 ppb) is approximately the mean $\pm$ 2 standard deviations. The threshold for anomalous concentrations in geological sampling is not well defined; however, use of 2 standard deviations above the mean is common. Based on this definition, the range of the data further suggests that no anomalous concentrations exist in the background data set and that these parameters could reasonably be expected to represent the background levels in and around the Burial Ground prior to burial of mercury.

For the most part, the data in Area A (Figure 7) are at or near background values with the exception of two zones: the first at sites 22 and 23 and the second along the eastern half of the Burial Ground north of the main road. Both of these zones contain samples in excess of 23 ppb, which are anomalous based on the log normally distributed data of Burial Ground 643-G and on the log normally distributed data of the background area. Both of these zones are located immediately south of known or suspected mercury burial

sites. The observed anomalous concentrations are considerably diminished, if at all detectable, on the traverse south of the main road.

Anomalous zones (Figure 8) located in sections C-2 and D-2 of Area B contain several sites with mercury levels 3 to 4 log-standard deviations above the mean. These mercury levels are clearly not a part of the natural background. Other single point anomalies are noted in sections B-1, B-3, and F-1. Sections E-2, E-3, E-4, and E-5 show a consistently elevated level of adsorbed mercury in the 10 to 23 ppb range although the data are only 1 to 2 log-standard deviations above the mean. The four traverses in the southern part of Area B do not reveal any noticeable anomalous values and, in particular, do not suggest any source for the anomalous levels in section 7 just south of the Burial Ground fence.

No prominent anomalies are observed in Area C (Figure 9). Several consistently higher values are found in the northwest corner of this area, approximately in sections A-29, A-30, B-29, B-30, C-29, and C-30. Several higher sites are also noticeable along the southernmost traverse through sections G-29 to 35.

Samples collected from the Savannah River flood plain have concentrations of adsorbed mercury in the 4 to 200 ppb range. The higher concentrations may be related to contamination but may just as well be related to the organic nature of the flood-plain soil. Because only 27 samples were taken from this large area, the areal distribution pattern cannot be used to indicate a source for the observed mercury.

TABLE 1

Sensitivity of the Jerome Model 411 Mercury Vapor Analyzer

Mercury Injected (ng)	Average Instrument Response (counts)	Instrument Sensitivity (counts/ng)
7.0	53	7.6
14.0	114	8.1
28.0	234	8.4
42.0	356	8.5
56.0	482	8.6

TABLE 2

Precision of Mercury Determinations (ppb)

Site 938	Site 942
9.8	22.3
9.4	21.4
12.0	20.8
10.9	21.3
10.0	20.1
10.1	22.3
Mean = 10.4 ppb	Mean = 21.4 ppb
SD = 0.94 ppb	SD = 0.86 ppb

TABLE 3

Mercury Concentrations (ppb) in Soils of 643-G Burial Ground

Site	Conc.	Site	Conc.	Site	Conc.	Site	Conc.
1	11	41	0	81	6	121	19
2	8	42	2	82	8	122	9
3	4	43	0	83	6	123	5
4	5	44	3	84	5	124	4
5	3	45	4	85	10	125	4
6	4	46	3	86	13	126	7
7	2	47	8	87	5	127	4
8	2	48	4	88	5	128	5
9	4	49	0	89	3	129	4
10	3	50	4	90	16	130	6
11	3	51	1	91	17	131	9
12	2	52	1	92	28	132	13
13	1	53	2	93	22	133	3
14	2	54	2	94	10	134	16
15	2	55	5	95	19	135	7
16	2	56	7	96	20	136	7
17	2	57	7	97	21	137	21
18	2	58	8	98	3	138	28
19	1	59	4	99	9	139	5
20	0	60	3	100	26	140	4
21	1	61	4	101	18	141	5
22	26	62	5	102	13	142	8
23	37	63	7	103	7	143	8
24	4	64	6	104	10	144	17
25	2	65	11	105	9	145	8
26	1	66	16	106	2	146	9
27	4	67	9	107	8	147	4
28	0	68	30	108	21	148	4
29	3	69	23	109	1	149	0
30	1	70	8	110	5	150	3
31	0	71	9	111	5	151	6
32	0	72	5	112	8	152	4
33	2	73	2	113	12	153	21
34	10	74	3	114	5	154	26
35	4	75	7	115	3	155	16
36	0	76	16	116	9	156	40
37	1	77	20	117	8	157	20
38	0	78	36	118	5	158	27
39	2	79	9	119	9	159	10
40	2	80	6	120	3	160	5

Table 3 (cont.)

Site	Conc.	Site	Conc.	Site	Conc.	Site	Conc.
161	21	212	10	263	5	314	4
162	8	213	6	264	4	315	4
163	8	214	4	265	6	316	3
164	9	215	13	266	17	317	2
165	14	216	3	267	9	318	5
166	9	217	2	268	13	319	9
167	4	218	2	269	5	320	4
168	11	219	1	270	5	321	3
169	8	220	1	271	4	322	1
170	4	221	2	272	10	323	3
171	8	222	14	273	4	324	8
172	17	223	27	274	5	325	9
173	14	224	21	275	4	326	9
174	12	225	5	276	5	327	15
175	7	226	11	277	2	328	7
176	9	227	15	278	4	329	7
177	6	228	23	279	2	330	3
178	11	229	19	280	4	331	4
179	22	230	5	281	3	332	6
180	29	231	8	282	3	333	10
181	9	232	4	283	5	334	3
182	8	233	14	284	1	335	0
183	7	234	26	285	6	336	5
184	9	235	2	286	6	337	2
185	10	236	7	287	3	338	4
186	2	237	8	288	7	339	4
187	2	238	8	289	1	340	5
188	3	239	10	290	1	341	5
189	5	240	1	291	3	342	673
190	3	241	4	292	4	343	5
191	26	242	3	293	2	344	3
192	5	243	6	294	4	345	5
193	5	244	5	295	5	346	5
194	10	245	10	296	5	347	6
195	6	246	11	297	7	348	7
196	10	247	25	298	1	349	4
197	4	248	7	299	3	350	2
198	2	249	6	300	14	351	2
199	1	250	8	301	9	352	2
200	0	251	6	302	4	353	2
201	2	252	12	303	3	354	5
202	3	253	4	304	3	355	8
203	3	254	8	305	28	356	5
204	8	255	9	306	2	357	10
205	9	256	5	307	1	358	6
206	4	257	5	308	3	359	2
207	5	258	3	309	2	360	8
208	11	259	3	310	5	361	5
209	8	260	3	311	2	362	6
210	6	261	2	312	2	363	6
211	2	262	13	313	3	364	8

Table 3 (cont.)

Site	Conc.	Site	Conc.	Site	Conc.	Site	Conc.
365	7	416	9	467	246	518	8
366	1	417	6	468	7	519	1
367	3	418	12	469	86	520	1
368	0	419	10	470	436	521	2
369	3	420	11	471	2	522	3
370	2	421	11	472	2	523	5
371	4	422	6	473	2	524	2
372	4	423	6	474	0	525	1
373	10	424	5	475	4	526	4
374	3	425	10	476	2	527	3
375	4	426	12	477	2	528	1
376	4	427	7	478	3	529	2
377	2	428	24	479	2	530	5
378	3	429	27	480	1	531	11
379	2	430	9	481	0	532	18
380	1	431	6	482	1	533	8
381	2	432	6	483	2	534	13
382	5	433	4	484	2	535	5
383	1	434	5	485	1	536	3
384	22	435	6	486	1	537	9
385	5	436	7	487	1	538	11
386	9	437	6	488	1	539	5
387	8	438	4	489	0	540	6
388	13	439	12	490	1	541	3
389	12	440	7	491	3	542	6
390	9	441	10	492	1	543	4
391	11	442	1	493	5	544	5
392	14	443	6	494	5	545	3
393	3	444	18	495	12	546	4
394	2	445	2	496	0	547	6
395	5	446	9	497	0	548	3
396	4	447	3	498	1	549	124
397	6	448	3	499	0	550	9
398	8	449	5	500	0	551	11
399	15	450	3	501	2	552	19
400	11	451	3	502	2	553	12
401	3	452	4	503	1	554	22
402	13	453	11	504	3	555	10
403	12	454	4	505	15	556	5
404	5	455	5	506	11	557	8
405	75	456	7	507	2	558	34
406	5	457	7	508	1	559	16
407	7	458	2	509	1	560	16
408	17	459	5	510	2	561	14
409	10	460	2	511	6	562	18
410	137	461	10	512	3	563	16
411	12	462	9	513	9	564	24
412	10	463	57	514	5	565	11
413	8	464	13	515	6	566	12
414	9	465	6	516	6	567	7
415	5	466	12	517	13	568	105

Table 3 (cont.)

Site	Conc.	Site	Conc.	Site	Conc.	Site	Conc.
569	18	620	31	671	6	722	10
570	11	621	17	672	7	723	13
571	5	622	10	673	8	724	6
572	7	623	13	674	6	725	8
573	14	624	12	675	6	726	7
574	10	625	9	676	7	727	9
575	17	626	9	677	4	728	8
576	20	627	7	678	7	729	8
577	11	628	7	679	6	730	19
578	23	629	7	680	7	731	13
579	6	630	5	681	52	732	13
580	8	631	10	682	13	733	19
581	7	632	10	683	12	734	12
582	6	633	6	684	15	735	7
583	8	634	8	685	12	736	7
584	172	635	6	686	38	737	7
585	13	636	6	687	11	738	3
586	97	637	9	688	7	739	8
587	9	638	5	689	10	740	11
588	13	639	6	690	5	741	7
589	9	640	8	691	14	742	3
590	17	641	4	692	27	743	5
591	17	642	7	693	12	744	4
592	10	643	9	694	22	745	4
593	11	644	6	695	13	746	9
594	8	645	6	696	9	747	11
595	8	646	4	697	11	748	8
596	4	647	5	698	10	749	5
597	5	648	7	699	8	750	4
598	6	649	8	700	25	751	5
599	7	650	8	701	11	752	9
600	14	651	9	702	3	753	7
601	12	652	4	703	14	754	12
602	14	653	3	704	13	755	10
603	14	654	8	705	12	756	6
604	25	655	7	706	6	757	9
605	11	656	2	707	8	758	16
606	21	657	3	708	8	759	13
607	16	658	3	709	9	760	12
608	20	659	6	710	12	761	11
609	7	660	5	711	8	762	14
610	6	661	6	712	6	763	2
611	6	662	5	713	4	764	6
612	6	663	2	714	4	765	10
613	13	664	2	715	9	766	11
614	8	665	9	716	7	767	19
615	54	666	6	717	8	768	10
616	14	667	4	718	12	769	6
617	14	668	6	719	14	770	9
618	18	669	2	720	19	771	15
619	11	670	20	721	19	772	10

Table 3 (cont.)

Site	Conc.	Site	Conc.	Site	Conc.	Site	Conc.
773	5	824	11	875	13	926	5
774	10	825	10	876	8	927	5
775	13	826	18	877	4	928	4
776	7	827	11	878	6	929	2
777	9	828	29	879	3	930	5
778	13	829	4	880	4	931	6
779	13	830	8	881	5	932	3
780	7	831	14	882	5	933	5
781	13	832	6	883	13	934	6
782	10	833	7	884	16	935	5
783	12	834	8	885	12	936	2
784	14	835	10	886	8	937	4
785	12	836	7	887	3	938	10
786	7	837	10	888	3	939	3
787	9	838	7	889	4	940	13
788	6	839	2	890	3	941	21
789	28	840	7	891	3	942	22
790	17	841	11	892	7	943	3
791	8	842	7	893	5	944	3
792	7	843	16	894	13	945	4
793	5	844	10	895	11	946	7
794	10	845	9	896	18	947	4
795	14	846	8	897	4	948	5
796	6	847	13	898	11	949	4
797	5	848	13	899	5	950	7
798	14	849	8	900	6	951	3
799	15	850	10	901	18	952	15
800	4	851	5	902	7	953	6
801	15	852	10	903	5	954	11
802	13	853	9	904	25	955	14
803	6	854	9	905	2	956	8
804	12	855	12	906	8	957	8
805	8	856	11	907	7	958	6
806	9	857	8	908	4	959	8
807	19	858	7	909	12	960	7
808	8	859	7	910	7	961	7
809	9	860	11	911	10	962	4
810	5	861	3	912	7	963	2
811	12	862	6	913	16	964	2
812	11	863	1	914	5	965	6
813	3	864	9	915	6	966	10
814	10	865	5	916	3	967	6
815	18	866	8	917	1	968	12
816	5	867	5	918	7	969	10
817	5	868	9	919	5	970	9
818	8	869	5	920	5	971	6
819	16	870	4	921	5	972	11
820	5	871	3	922	9	973	4
821	11	872	2	923	5	974	6
822	9	873	11	924	2	975	11
823	10	874	13	925	7	976	30

Table 3 (cont.)

Site	Conc.
977	23
978	202
979	40
980	78
981	49
982	21
983	34
984	28
985	14
986	15
987	4
988	5
989	4
990	7
991	4
992	10
993	7
994	3
995	13
996	15
997	48
998	69
999	19

Note: The values in this table were truncated.

TABLE 4

Statistical Summary of Field Measurements and Analyses of Adsorbed Mercury Concentrations (ppb)

Sampling Locations	No. Sites	Maximum	Minimum*	Mean	Stdv	Mean#	Stdv#
Background Area Sites 953-975	23	14	2	7.6	3.1	.8338	.220
Swamp Area Sites 976-999	24	202	3	30.9	41.8	1.238	.473
Burial Ground 643-G							
Area A							
Fence line traverse Sites 1-93, 154-185	125	40	0	8.2	8.4	.7709	.402
Parking lot traverse Sites 471-548	78	18	0	3.6	3.5	.4407	.330
Areas B & C	749	673	0	10.2	29.0	.8151	.358
Sites 1-500	500	673	0	10.3	38.2	.7445	.399
Sites 501-952	452	172	1	10.1	12.7	.8857	.306
Combined Sites 1-999	999	673	0	-	-	.8224	.36

* Minimum values (<0.5 ppb) were rounded to zero (0).

Log Units

TABLE 5

Statistical Distribution Symbols for Areal Maps

Symbol	Hg Conc. (ppb)	No. Sites	Percentile Range*	Standard Dev. from Log Mean
★	>120.8	7	>99.3	>2.082
◆	52.7 to 120.8	8	98.5-99.3	1.722-2.082
●	23.0 to 52.7	35	95.0-98.5	1.362-1.722
•	10.0 to 23.0	214	73.6-95.0	1.002-1.362
○	4.4 to 10.0	434	30.1-73.6	0.642-1.002
o	1.9 to 4.4	240	6.1-30.1	0.282-0.642
□	<1.9	61	<6.1	<0.2820

Note: Log Mean = .8224; Log standard deviation = .36.

* Percentile assumes accumulation from the smallest to the largest.

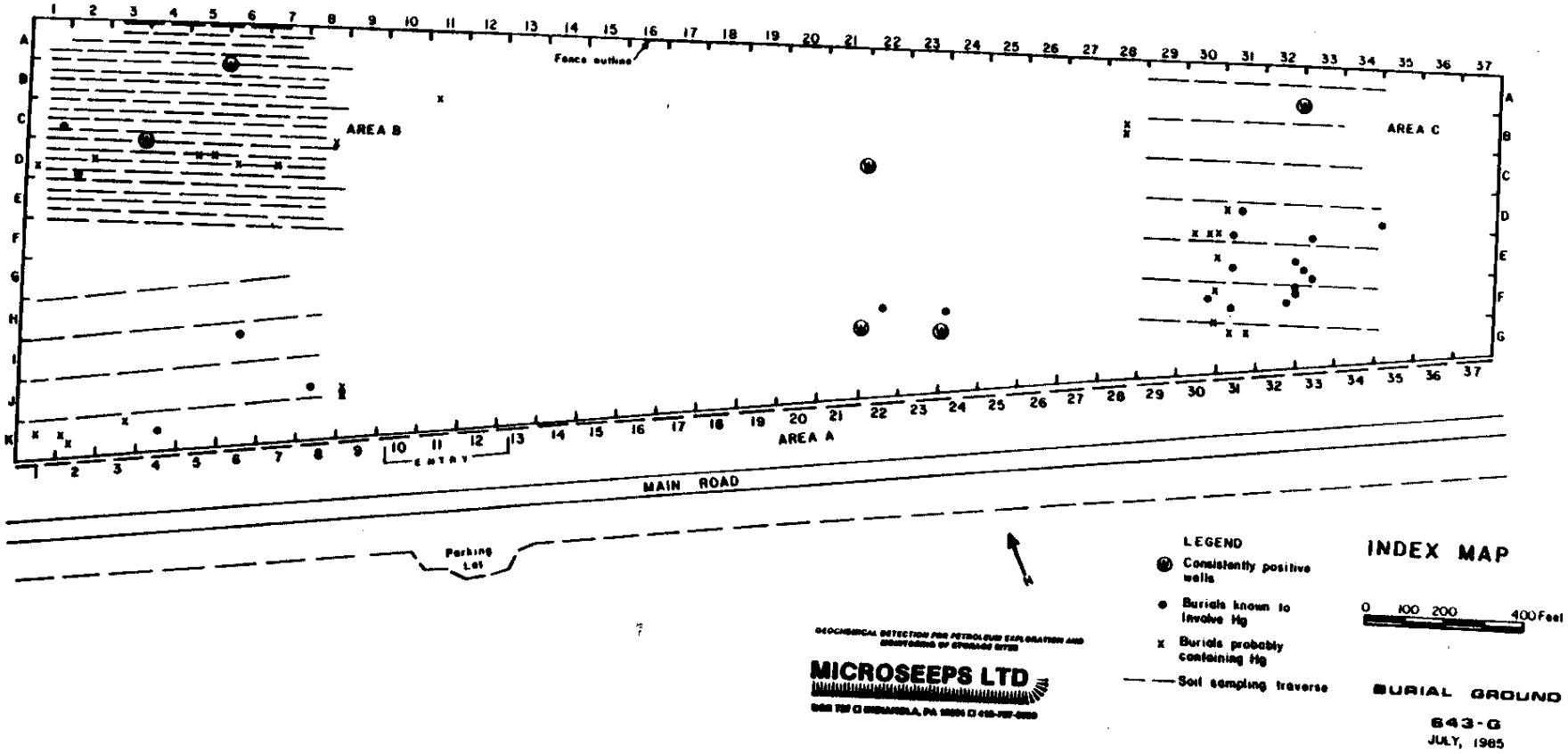
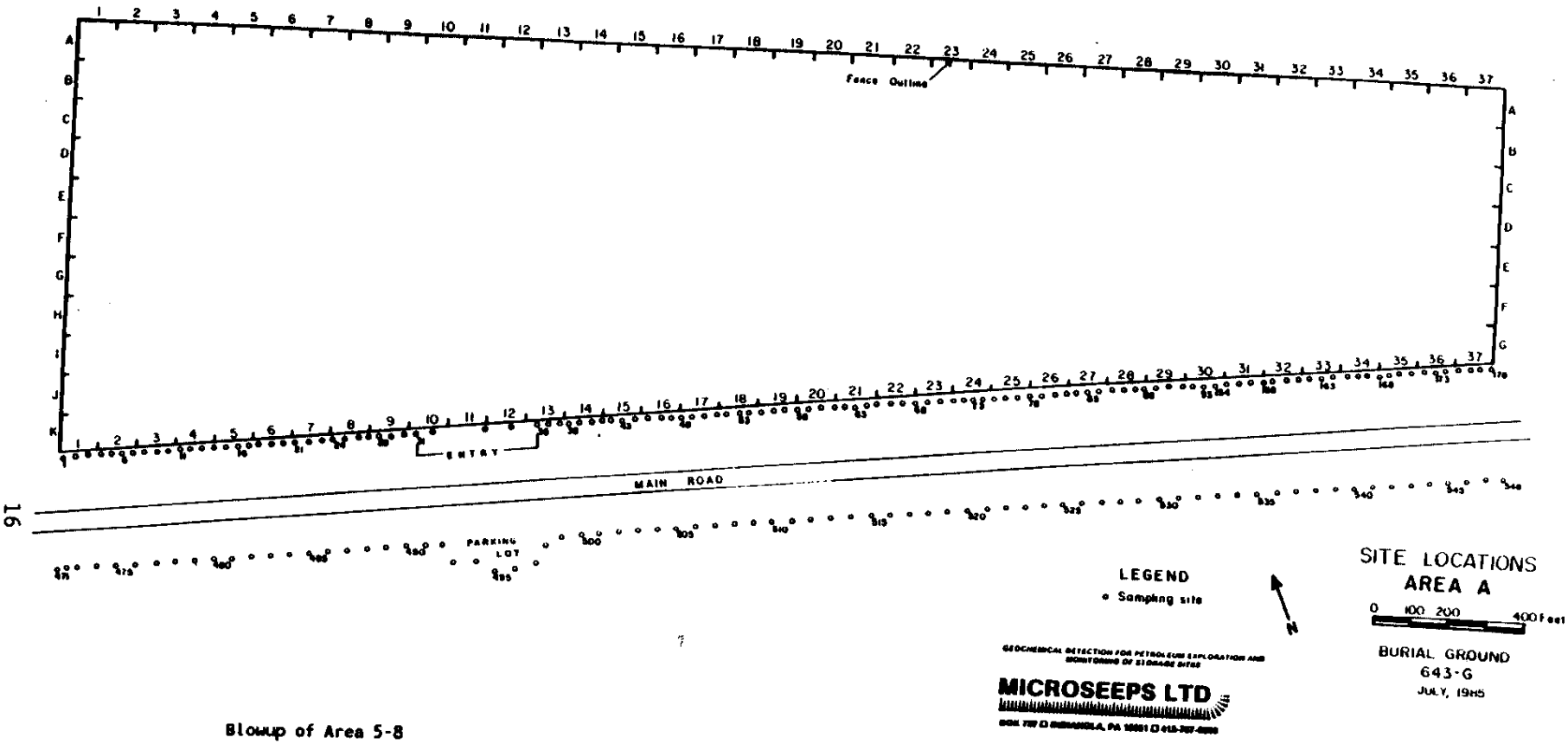


FIGURE 1. Index Map, SRP Burial Ground 643-G



Blowup of Area 5-8

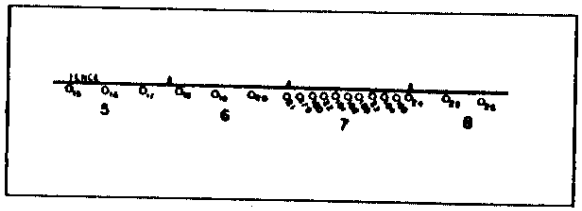


FIGURE 2. Site Locations, Area A, SRP Burial Ground 643-G

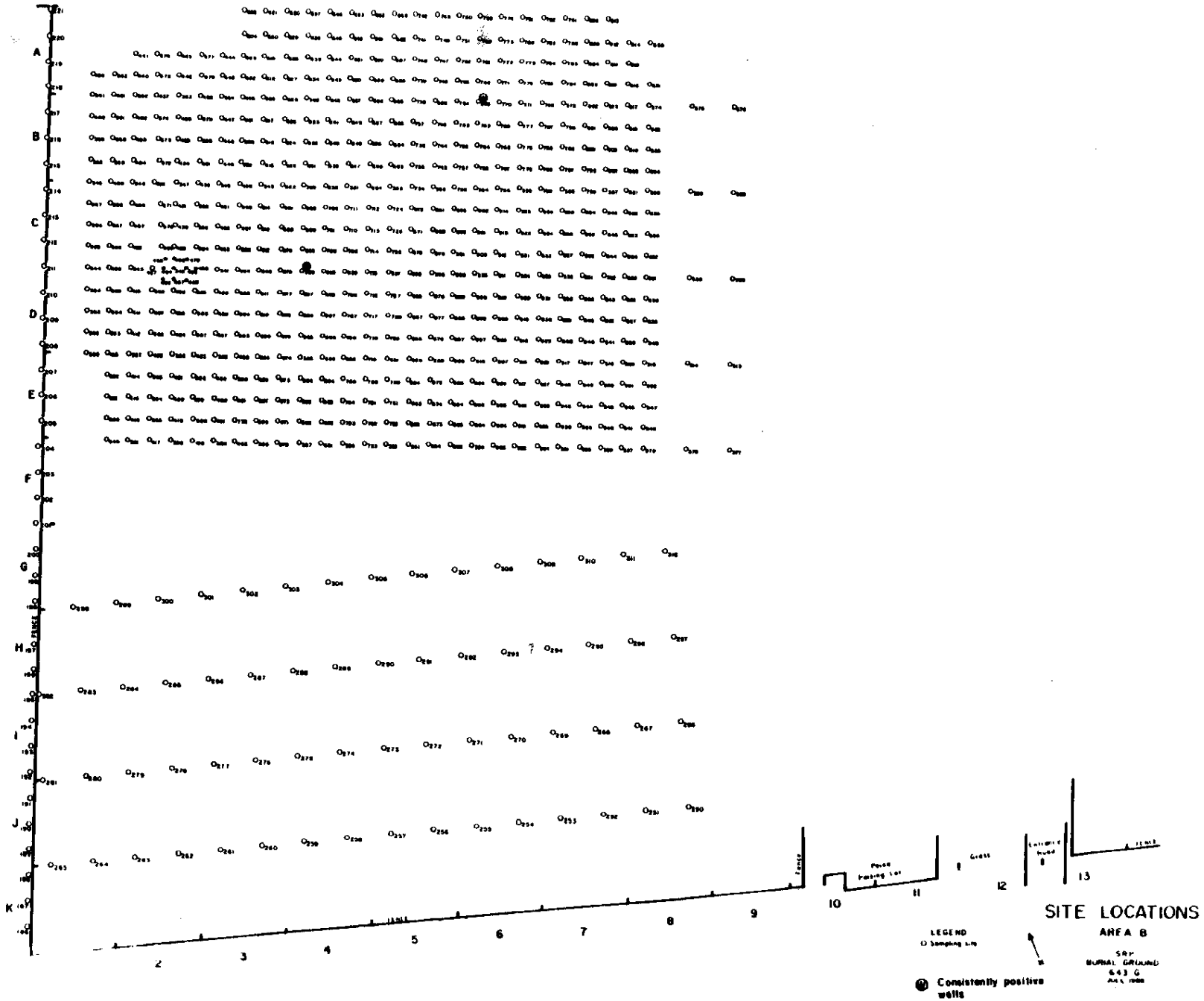


FIGURE 3. Site Locations, Area B, SRP Burial Ground 643-G

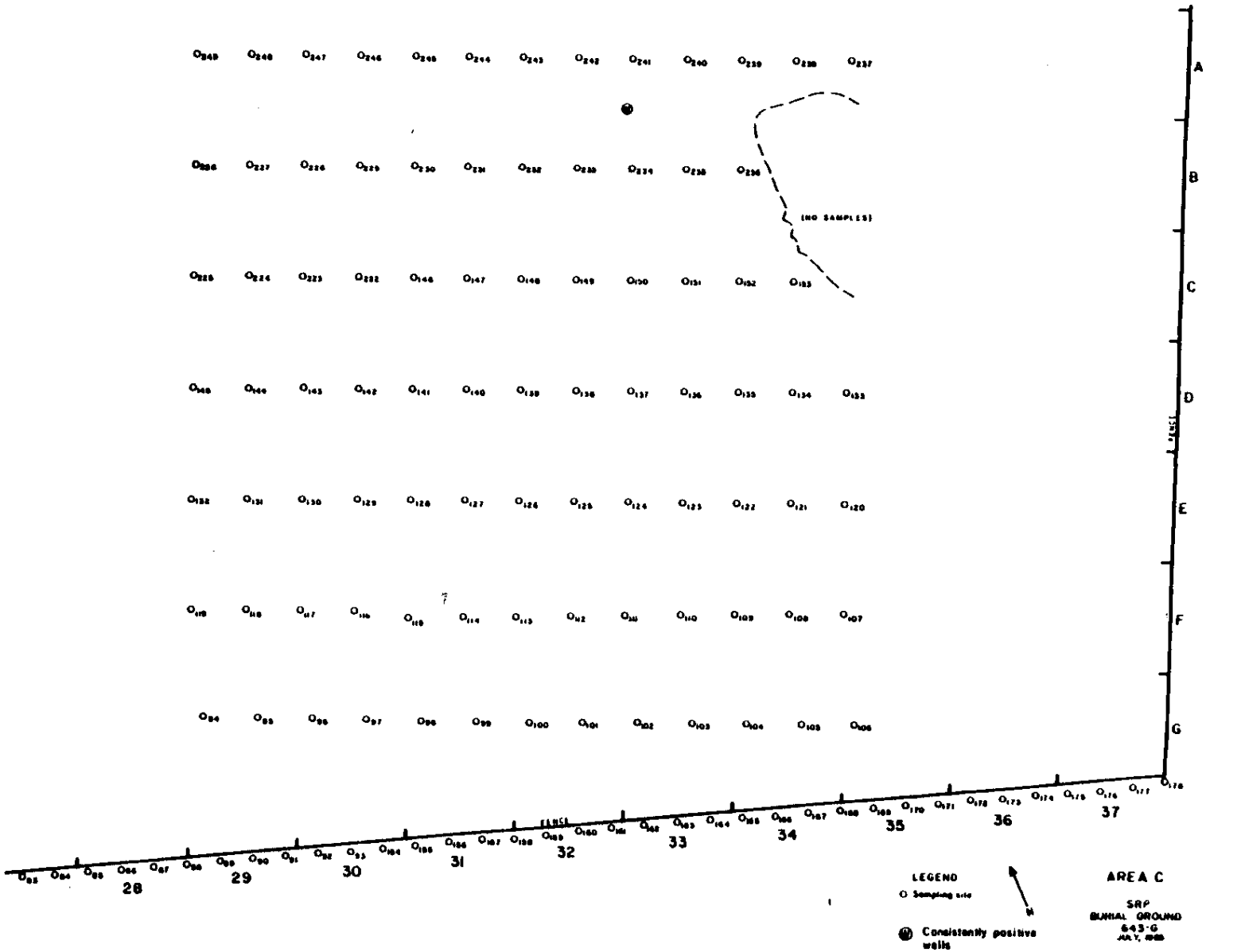


FIGURE 4. Site Locations, Area C, SRP Burial Ground 643-G

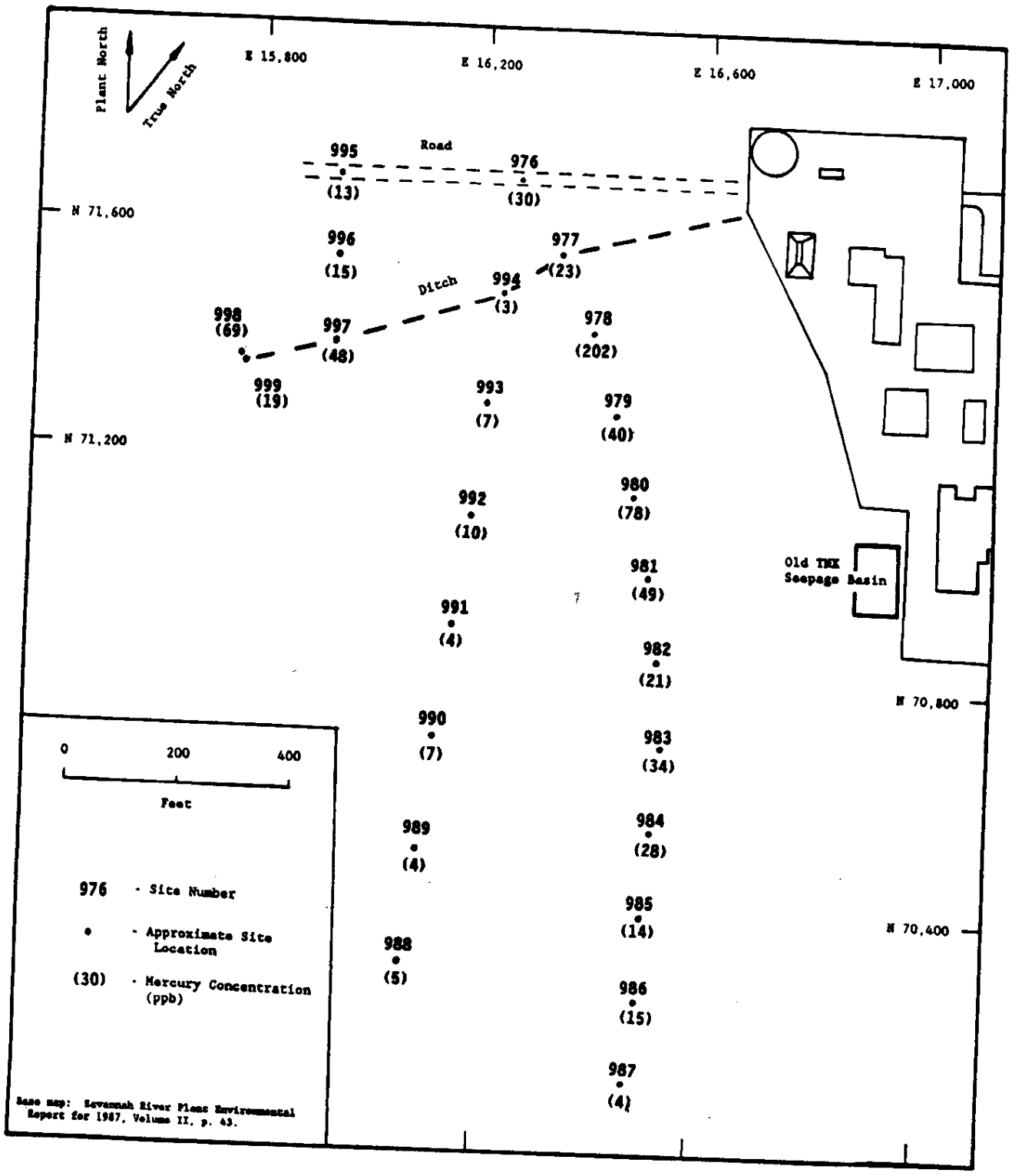


FIGURE 5. Site Locations and Adsorbed Mercury Concentrations, Swamp Area Adjacent to TNX Area

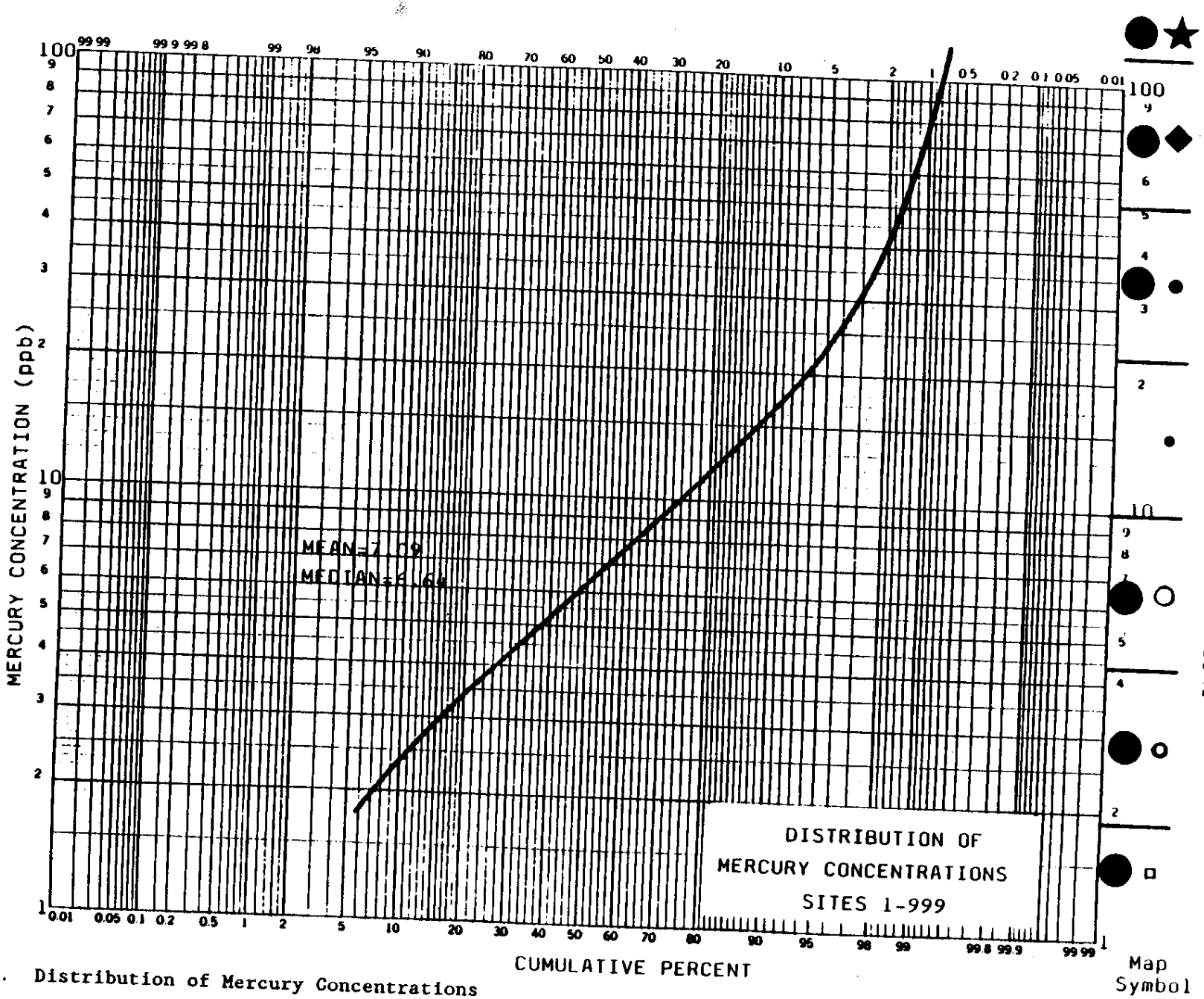


FIGURE 6. Distribution of Mercury Concentrations

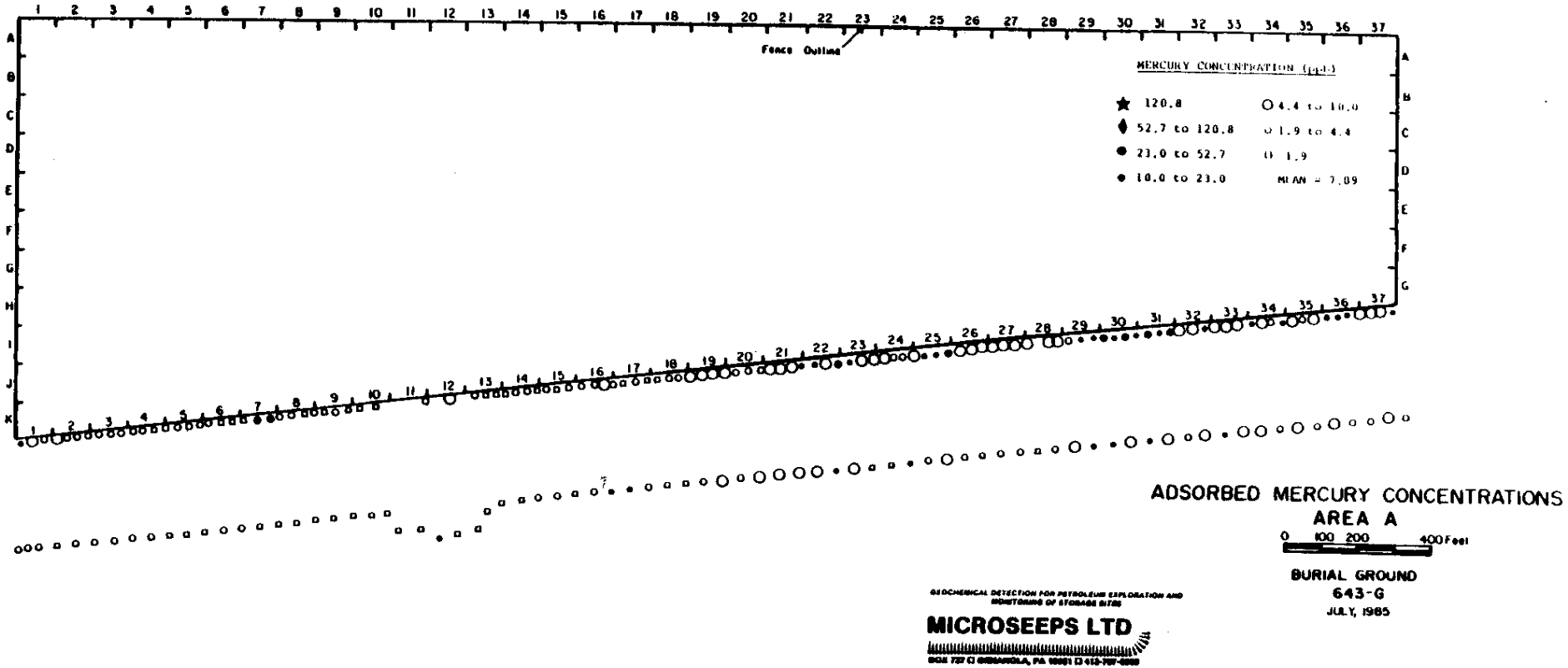


FIGURE 7. Adsorbed Mercury Concentrations, Area A, SRP Burial Ground 643-G

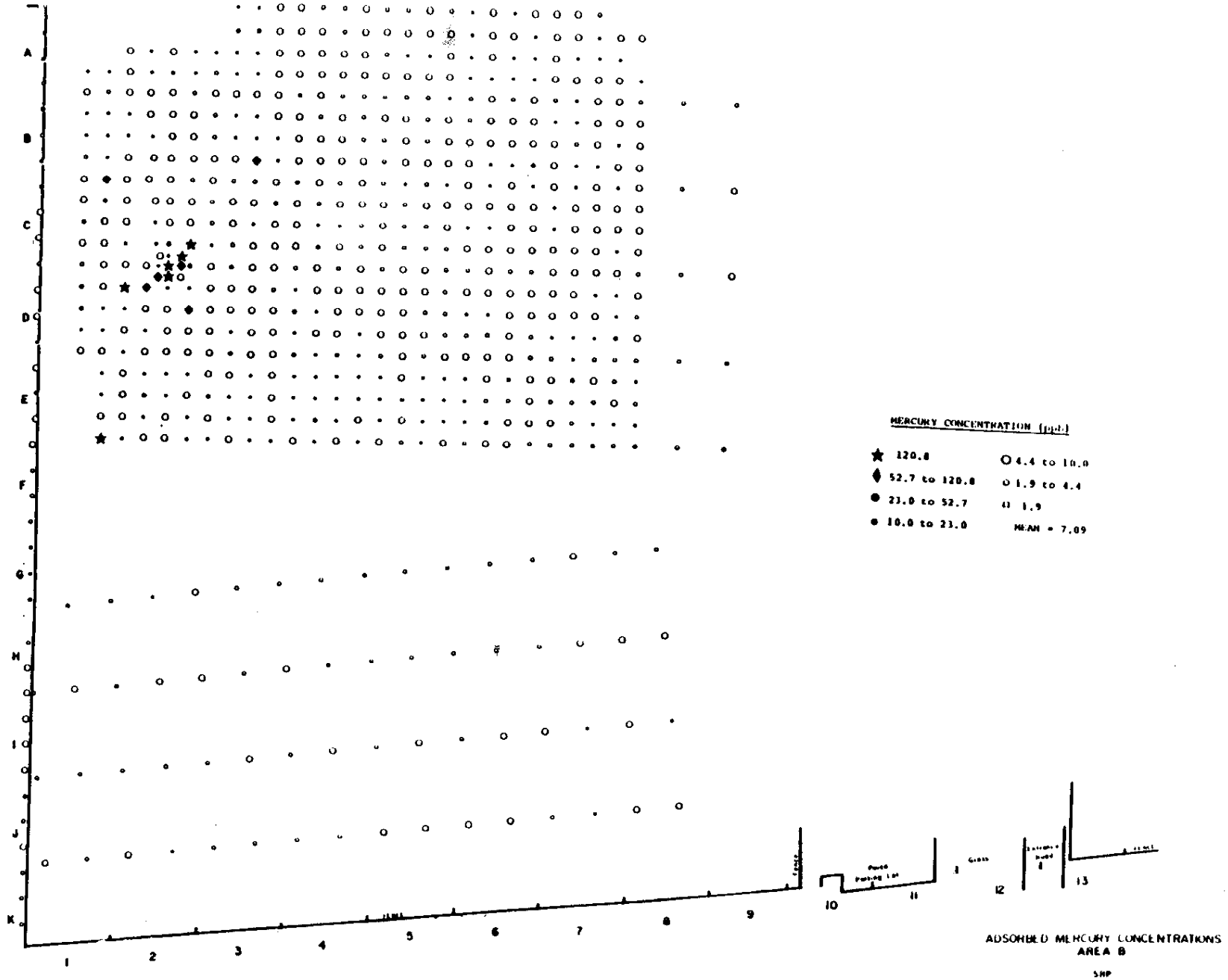


FIGURE 8. Adsorbed Mercury Concentrations, Area B, SRP Burial Ground 643-G

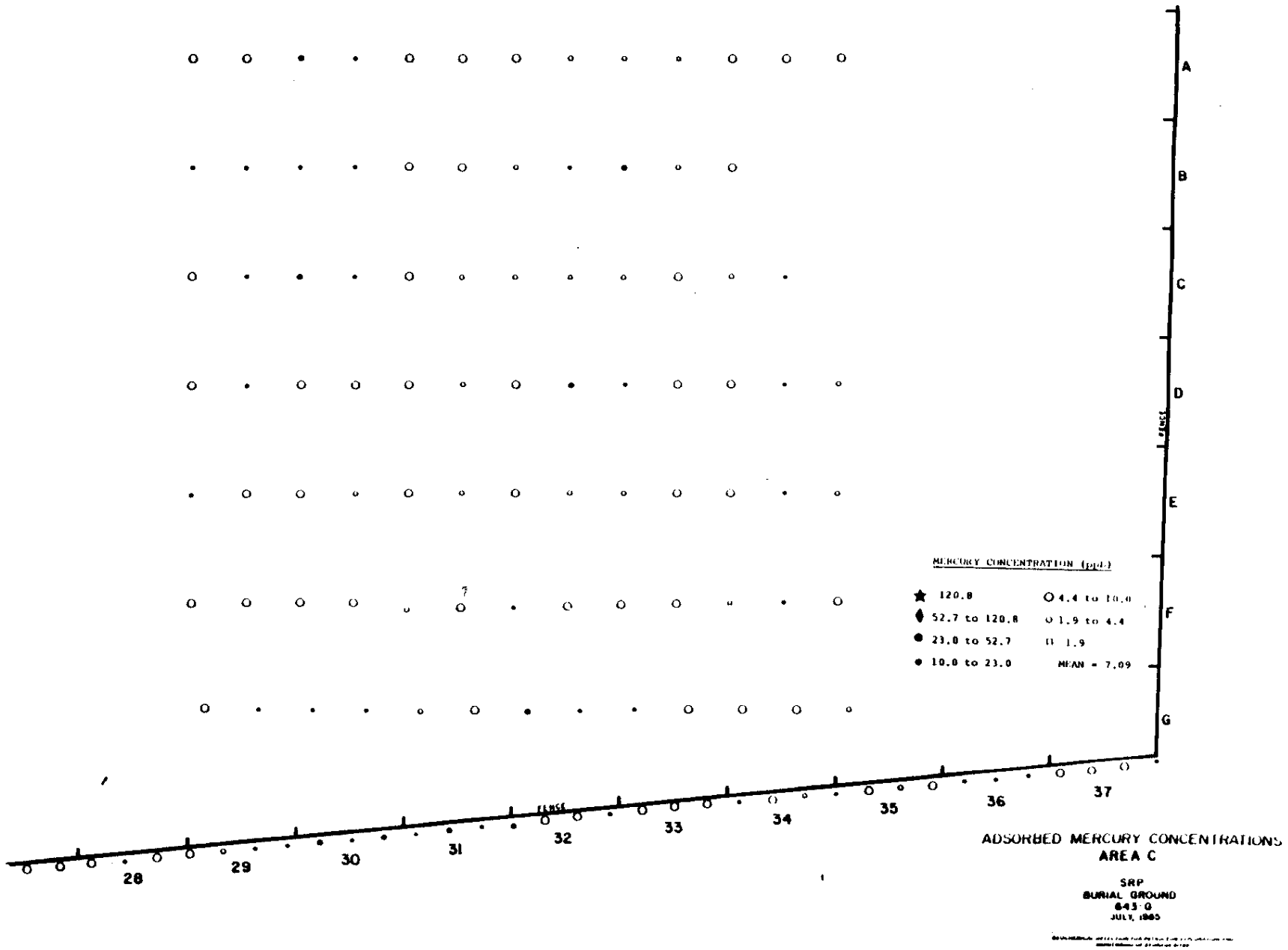


FIGURE 9. Adsorbed Mercury Concentrations, Area C, SRP Burial Ground 643-G

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