Technical Report #23

Trace Metals in the Gulf of Maine Determined by Differential Pulse Anodic Stripping Voltammetry

by

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Abstract

The method of Differential Pulse Anodic Stripping Voltammetry is briefly explained along with its application to trace metal analysis of cadmium, lead, and copper in seawater. Data has been collected for the past few years at several locations in the Gulf of Maine. The results are displayed in a clear bar graph form. Because numerous measurements were taken at the same time, there is the potential of comparing and correlating trace metals with other parameters.

Introduction

Trace metals are an important factor in the marine environment. For many of these metals a small amount is necessary in the role as a nutrient, but larger amounts become toxic. Marine life reacts in different ways to this stress. While some forms can adjust in various ways, others cannot survive. The latter seems to be the case for *Gonyaulax tamerensis*, and thus trace metals are an important measurement in our study of the red tide.

The method of Differential Pulse Anodic Stripping Voltammetry (DPASV) was chosen for seawater trace metal analysis for many reasons. Probably the two most important reasons are: 1) this method can analyze only the "available" portion of the metals, i.e. the portion that marine life sees, and 2) the sample needs no pre-treatment, only to be frozen during storage. Very few chemicals are required and concentrations as low as tenths of ppb can be measured and reproduced.

The basic ideas behind DPASV are as follows: The trace metals positive of the deposition potential are reduced at the working electrode, which is simply a mercury drop. The trace metal actually forms an amalgam with the mercury. At the end of the deposition time, the magnetic stirrer stops and the cell quiets down. Following this, the stripping phase begins. The instrument scans from the deposition (initial) potential to the final potential. As each trace metal's characteristic half potential is reached, it is oxidized back into solution, thereby releasing electrons which are processed by the instrument and recorded as peaks on the trace.

Materials and Methods

New nalgene LPE bottles are used for samples. The bottles are acid washed in 6N Nitric acid, then 6 N Hydrochloric acid, and finally clean, i.e. trace metal free, seawater. Each step takes at least 24 hours. After washing, the bottle is rinsed with copious amounts of ultrapure water.

The samples are collected from the ocean either by hand or from a plastic bucket, keeping as far away as possible from boat bottoms, chains on docks, etc. The bottle is rinsed five times before the final filling, capped and frozen immediately. The trace metal analysis is done with a polarographic analyzer. The instrumental set-up consists of: PAR model 174 Polarographic Analyzer; PAR model 315A Automated Electroanalysis Controller; PAR model 303 Static Mercury Drop Electrode; a Moseley model 7000 AMR X-Y Recorder; a voltage regulator; and a magnetic stirrer regulated by the line frequency.

Instrumental parameters vary with the samples, but here are some typical settings:

Model 174 - rate = 2 mv/s, scan direction = +, range = 1.5 volts, initial potential = -0.00 v, modulation amplitude = 100 mv, operating mode = diff. pulse, current range = 5 uA, display direction = -.

Model 135 A - conditioning potential = - 0.00 V, deposition/initial potential = - 1.02 V, final potential = -0.08 V, equilibration = 15 seconds, and the deposition time usually ranges between 100 and 500 seconds with the maximum being 999 seconds.

One of the greatest advantages of trace metal analysis by ASV is the use of very few chemicals. These are: triple distilled mercury (or better), reagent grade nitric and hydrochloric acid, ultra pure water, ultra pure nitric acid, siliconizing fluid, carbon dioxide gas, saturated KCl, AgCl electrolyte for reference electrode, and 1000 ppm atomic absorbtion standards of cadmium, lead and copper.

A primary standard is made at least four times a year from 1000 ppm standards by diluting 2.5 ml of Cd and 25.0 ml each of Pb and Cu to 100 ml in a volumetric flask. The secondary standard is made once a week from the primary standard by diluting 0.50 ml to 50 ml in a volumetric flask. Spiking is done with a 10 or 20 µl micropipette.

The sample is thawed immediately prior to analysis. All three electrodes and purge tube are rinsed with 6 N nitric acid, then ultra pure water, dried with a Kimwipe, then about 50 drops of mercury are dispensed to help clear any air from the mercury column. A 10.0 ml sample is placed in a glass cell. The cells are soaked in 6 N nitric acid, then in clean un-acidified seawater, then in the sample itself before hand. Hopefully, by this point, the cell walls and sample have reached equilibrium, and trace metals will not be absorbed or released during the analysis. A teflon coated stirring bar which is soaked in nitric acid when not in use is rinsed with the ultra pure water and placed in the cell. The cell is then loaded and purged for about ten minutes with CO_2 to rid the sample of interfering oxygen. After purging is completed, deposition begins at a selected potential. This automatically continues for the selected amount of time, depending on the sample. This is followed by a 15 second equilibration and then a scan from -1.02 volts to -0.08 volts at a rate of 2 mV/s. During this stripping phase the trace metals are oxidized at their characteristic half potentials, slightly variable, appearing in order, Cd, Pb, and Cu. One mercury drop is used for each sample.

Concentrations are determined by the method of standard additions. Usually the spikes are 0.25 or 0.50 parts per billion (ppb) for Cd, and 2.5 or 5.00 ppb for Pb and Cu. Three standard additions are made. The final concentration is calculated using a linear regression program, plotting peak height against concentration of spikes, and shifting the calibration curve to pass through the origin. If the samples are from the same location and general time period, and if the shape of the traces is identical, then a standard curve is made in the morning and the rest of the samples for that day are calculated using that standard curve.

Results

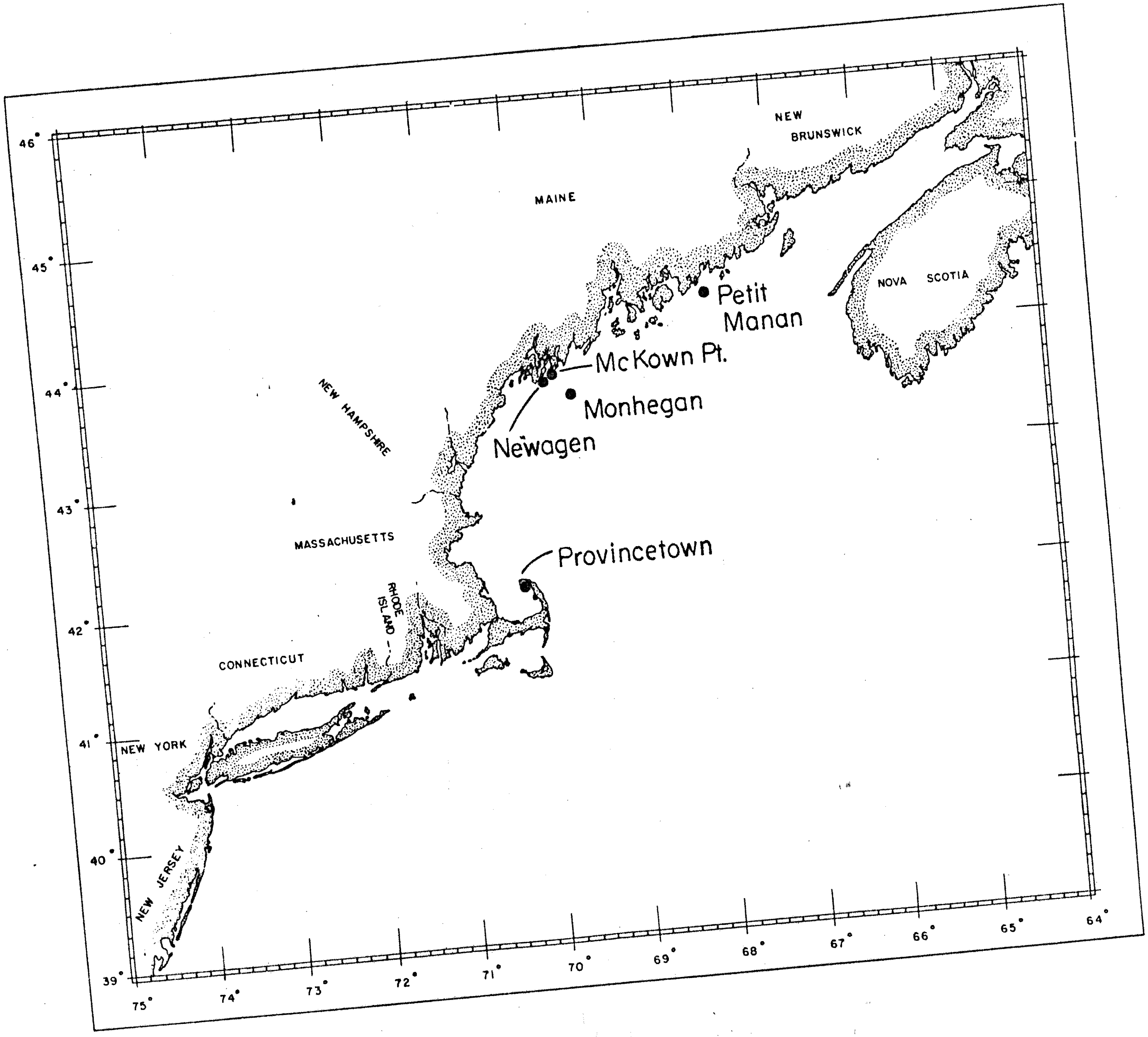
During the past three years, 1977-1979, several monitoring stations have been established. In 1977, Monhegan Island (about 15 miles SE of Boothbay Harbor, Maine) was the only station. In 1978, four more stations were added: Cape Newagen, near Boothbay Harbor; a station at the lab, in the harbor, called McKown Point; Petit Manan Point, east of Penobscot Bay; and Provincetown, Mass. In 1979, samples were taken at

Monhegan Island, Cape Newagen, Petit Manan Point, and Provincetown. Provincetown and Newagen samples are now taken year round, the others only in the summer. Sampling locations are shown on the chart.

The samples are taken in the manner described previously. For a while samples were acidified, but it has been decided that the samples are to be frozen. Only frozen data is reported here. The data is also in the form of bar graphs for the three metals, cadmium, lead, and copper, for all stations for 1977, 1978 and part of 1979. All the samples are analyzed after purging with carbon dioxide, which gives a pH of about 4.8. Therefore, the concentrations reported are the metals that are available for reduction in untreated seawater at a pH of 4.8.

Discussion

This data is presented merely to show what sort of concentrations have been found in the Gulf of Maine with the method of DPASV. Concurrent with these samples, chlorophyll, salinity, temperature, nutrients, cell counts, some paralytic shellfish poison and iron measurements have been taken. The weather conditions and sea state are also available. Therefore, there is the opportunity to compare trace metal concentrations with other parameters. This has been done on a very limited basis with no significant results so far. It seems that trace metal ion concentrations would be influenced by such things as run off, upwelling, changes in organics, etc., with many factors simultaneously affecting the trace metals. In the future, organic measurements could also be made to compliment the trace metal data. Perhaps factors influencing trace metals can be established and the influence of trace metals on the marine environment defined.



MAINE
NEW BRUNSWICK
NOVA SCOTIA
Petit Manan
McKown Pt.
Monhegan
Newagen
NEW HAMPSHIRE
MASSACHUSETTS
Provincetown
RHODE ISLAND
CONNECTICUT
NEW YORK
NEW JERSEY
46°
45°
44°
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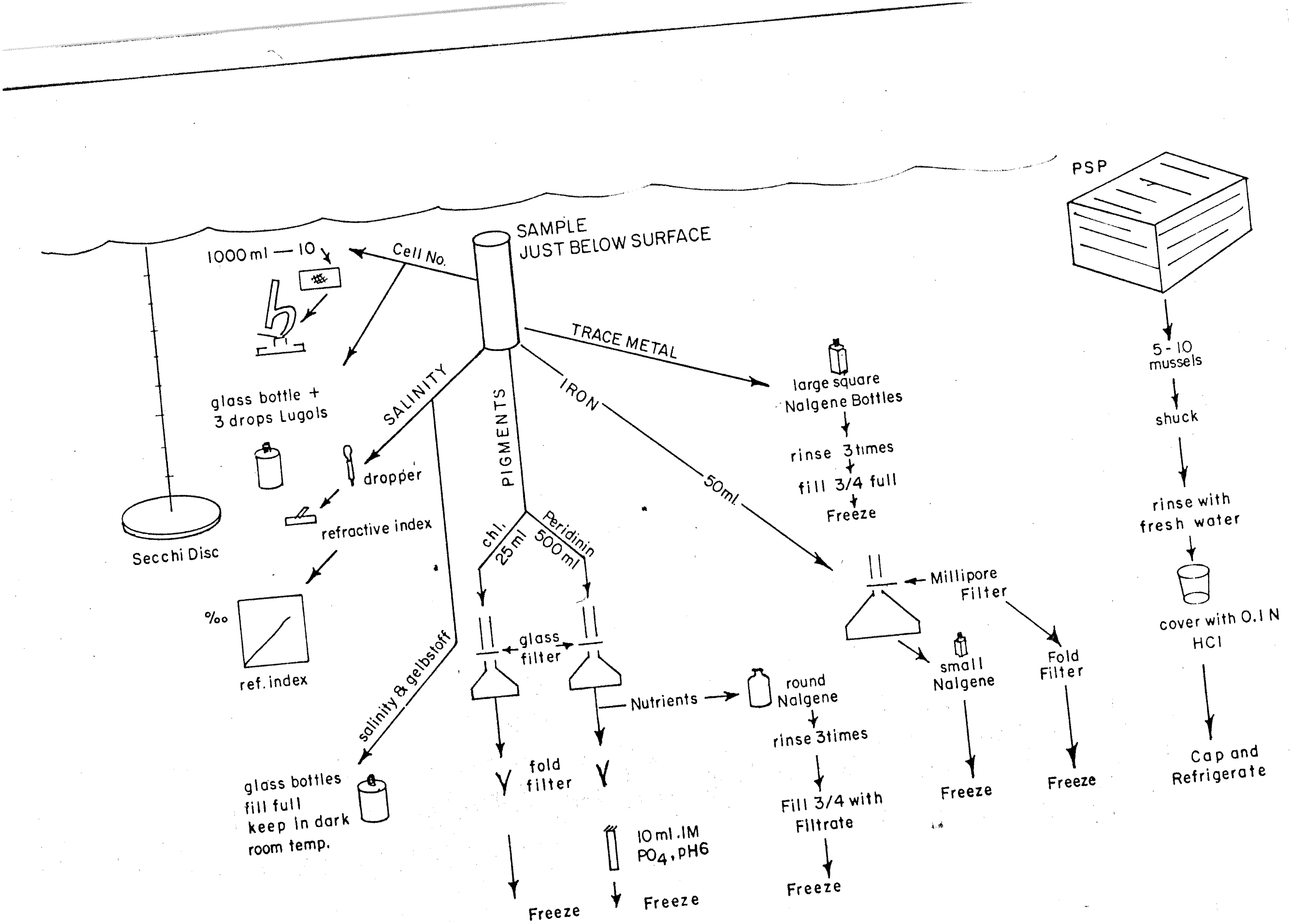
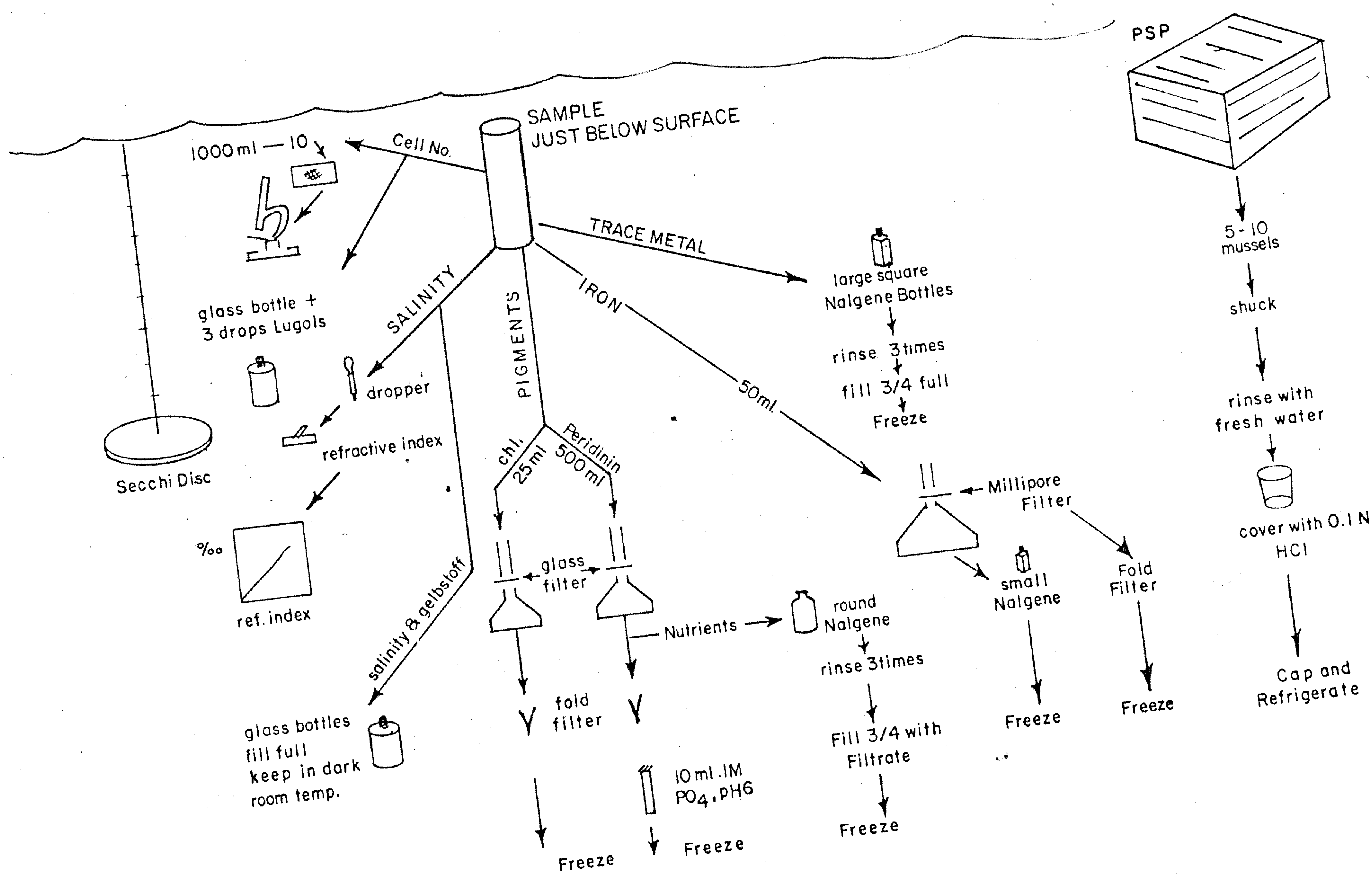

SAMPLE
JUST BELOW SURFACE
Cell No.
1000 ml — 10
glass bottle +
3 drops Lugols
SALINITY
dropper
refractive index
‰
ref. index
Secchi Disc
salinity & gelbstoff
glass bottles
fill full
keep in dark
room temp.
PIGMENTS
chl.
25 ml
Peridinin
500 ml
glass
filter
fold
filter
Freeze
10 ml .1M
PO4, pH6
Freeze
Nutrients
round
Nalgene
rinse 3times
Fill 3/4 with
Filtrate
Freeze
TRACE METAL
large square
Nalgene Bottles
rinse 3 times
fill 3/4 full
Freeze
IRON
50 ml.
Millipore
Filter
small
Nalgene
Freeze
Fold
Filter
Freeze
PSP
5 - 10
mussels
shuck
rinse with
fresh water
cover with 0.1 N
HCl
Cap and
Refrigerate


SAMPLE
JUST BELOW SURFACE
Cell No.
1000 ml — 10
glass bottle +
3 drops Lugols
SALINITY
dropper
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glass bottles
fill full
keep in dark
room temp.
PIGMENTS
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25 ml
Peridinin
500 ml
glass
filter
fold
filter
Freeze
10 ml .1M
PO4, pH6
Freeze
Nutrients
round
Nalgene
rinse 3 times
Fill 3/4 with
Filtrate
Freeze
TRACE METAL
large square
Nalgene Bottles
rinse 3 times
fill 3/4 full
Freeze
IRON
50 ml
Millipore
Filter
small
Nalgene
Freeze
Fold
Filter
Freeze
PSP
5 - 10
mussels
shuck
rinse with
fresh water
cover with 0.1 N
HCl
Cap and
Refrigerate

Argument on why total concentration, not available, are obtained from the ASV

During the past 2½ years, the results obtained from the method of ASV have been reported as representing the available portion of the trace metals, not the total concentration. While it is true that only the available, or reducible trace metals are actually analyzed by this method, the final concentration calculated could be the total concentration. It seems unlikely that total concentrations could be obtained from an instrument that can only analyze available and this is why I never questioned it.

First, let me explain a few terms. The "available" portion is that fraction of the total trace metals that is either in an ionic form or loosely bound. Trace metals in these forms can be used by marine organisms, thus, the term available. For the same reason they are also reducible by the method of ASV. On the other hand, trace metals that are either tightly bound chemically to organics or physically trapped inside a colloidal particle cannot be used by marine organisms and also cannot be chemically reduced by ASV. Thus, they are called the non-reducible fraction. For the sake of clarity trace metals are now called either reducible or non-reducible.

Basically, concentrations are determined as follows. A scan is run on the sample (untreated seawater, purged with CO_2, pH = 4.8) and the peak heights represent the reducible fraction of trace metals in the sample itself. Say, for example, Cd has a peak height of 2. Then a known amount, a spike, say 0.25 ppb of Cd^{+2}, is added and a scan is run. This second peak height represents both the sample and the spike, but again only the reducible fraction. Say Cd now has a peak height of 8. Subtracting the sample peak height from the spike gives the increase in peak height due to the spike. This increase which is 8-2 = 6, has always been called 0.25 ppb because that is what was added. On the basis of this, the sample's concentration of Cd is calculated, which is 0.25 x 2/6 = 0.083 ppb of Cd.

The problem with this stems from the fact that the peak increase of 6 does not really represent 0.25 ppb. When the spike is added some stays in the ionic form, and some form inorganic compounds, some of which are non-reducible. Thus, the peak height of 6 is due to the reducible fraction of the 0.25 ppb spike and really only represents say 0.20 ppb of Cd.

Now, assuming that equilibrium is reached rapidly and that the ratio of reducible to non-reducible trace metals is always the same, the following conclusions are reached. Say, for example, 20% of all Cd is non-reducible. That means that if the peak height were to represent total concentration then the sample peak height of Cd would now be 2 + 20% of 2 which is 2.4, and the spike would be 8 + 20% of 8 which is 9.6. Calculating the concentration as before: 9.6-2.4 = 7.2 (spike height alone) and 0.25ppb x $\frac{2.4}{7.2}$ = 0.083 ppb of Cd. The result is obviously total but yet it is the same as the first calculation. The reason for this is that the ratio of sample to spike is the same whether the peaks are reducible fractions or total concentrations.

Recommendations: The only way to determine the reducible fraction is to find out what a certain amount really looks like. Possible, one way to do this, would be to make up a solution of distilled water and a simple salt such as NaCl or KCl. There can be no trace metal or organic contamination from the reagents and there can be nothing that will irreversibly complex the trace metals. Reproducibility should be checked for varying temperature, salinity and pH. Having established these conditions, scans should be run for all situations (i.e. varying deposition time, sensitivity, etc.) and basically then, all the sample peaks could be compared to the scan having matching conditions.

Another possible way would be to run a scan on the sample and then by acid digestion or UV irridation (or whatever is necessary) break up the trace metal compounds and oxidize the organics. Then when the spike is added, the metal ions will stay reducible because there is nothing to complex with.

Primary Reference: P.L. Brezonik, P.A. Brauner, W. Strumm. Trace Metal Analysis by Anodic Stripping Voltammetry:Effect of Sorption by Natural and Model Organic Compounds. *Water Res.* 10: 605-612.

PETIT MANAN POINT 1979

Date	Cd ppb	Pb ppb	CU ppb
7-27-79	0.00	0.788	0.518
9-5	0.00	0.599	0.00
9-8	0.00	1.01	0.344
9-11	0.00	1.86	0.735
9-23	0.00	0.00	0.00
9-14	0.123	0.631	0.00
9-17	0.00	0.00	0.00
8-5	1.37	2.27	1.17
9-26	0.172	1.19	0.431
7-13	0.270	1.32	0.30
9-30	0.126	0.373	0.00
7-21	0.07	1.40	0.00
7-9	0.169	16.88	0.778
7-23	0.04	0.560	0.00
*7-25	0.114	1.54	0.00
8-8	0.311	1.12	0.767

*Samples were stored frozen

PETIT MANAN POINT (PMP) 1978

Date	Cd ppb	Pb ppb	Cu ppb
7-13-1978	0.00	0.683	1.12
7-14	0.00	0.583	0.00
7-16	0.00	1.94	0.528
7-17	0.487	1.73	5.15
7-19	0.00	0.769	0.530
7-21	0.00	0.412	0.788
7-23	0.083	0.293	0.00
7-24	0.00	1.29	0.00
7-26	0.00	0.458	0.00
7-28	0.00	0.490	0.00
7-30	0.250	1.13	0.911
8-1	0.00	0.275	0.00
8-3	0.00	0.412	0.00
8-5	0.084	0.458	0.00
8-4	0.042	0.234	0.381
8-9	0.021	0.469	0.00
8-11	0.042	0.557	0.00
8-13	0.104	0.352	0.00
8-15	0.00	0.586	0.381
8-17	0.063	0.205	0.190
8-19	0.104	0.446	0.457
8-21	0.250	1.40	0.480
8-23	0.133	1.23	2.90

PETIT MANAN POINT (PMP) 1979 - continued

Date	CD ppb	Pb ppb	Cu ppb
8-26-79	0.00	1.09	0.00
8-28	0.079	0.939	0.00
8-30	0.00	0.797	0.302
9-3	0.026	0.531	0.490
9-5	0.053	0.531	0.321
9-7	0.0	0.836	1.10
9-11	0.053	0.817	0.00
9-17	0.00	0.408	0.059
9-19	0.00	0.327	0.00
9-20	0.221	0.648	0.382
9-23	0.131	0.449	0.321
9-27	0.053	0.643	0.326

*All samples were acidified

PROVINCETOWN, MASS. (P) 1978 - 1979

Date	Cd ppb	Pb ppb	Cu ppb
3-15-78	0.330	0.940	1.30
3-22	0.190	0.970	1.80
3-29	0.180	0.450	1.50
4-5	0.00	2.16	1.84
4-12	0.379	0.304	0.853
4-17	0.300	3.07	1.37
4-26	0.808	4.13	4.21
5-3	0.00	2.83	0.909
5-10	0.563	1.46	0.00
5-17	0.00	-	1.81
5-24	0.442	3.75	2.80
5-31	0.309	8.26	2.36
6-7	0.00	2.45	0.814
6-14	0.137	1.84	1.62
6-21	0.942	8.41	0.967
6-28	0.518	1.78	0.00
7-5	0.452	0.749	1.12
7-12	0.250	5.50	0.946
7-19	0.230	1.40	2.50
8-3	3.29	1.86	0.533
8-9	0.480	6.60	3.53
8-16	0.120	3.30	0.372
8-23	0.650	3.60	2.57

PROVINCETOWN, MASS. (P) 1978-1979 - continued

Date	Cd ppb	Pb ppb	Cu ppb
8-31-1978	0.700	4.17	2.99
9-13	0.998	2.28	4.20
9-20	1.54	3.00	6.60
9-28	0.910	1.80	0.923
10-5	0.390	2.69	1.01
10-11	0.400	7.59	2.20
10-18	0.980	10.87	5.79
10-26	0.392	7.11	8.29
11-29	0.336	7.56	0.727
12-8	0.289	1.05	0.00
12-13	0.168	1.34	0.00
12-21	0.213	0.825	1.28
12-27	0.536	1.85	0.760
1-3-1979	0.00	2.83	0.326
1-10	0.285	13.33	0.00
1-17	0.321	1.73	0.00
1-24	0.357	2.05	0.00
1-31	0.178	2.46	0.00
2-8	0.393	0.725	0.00
2-2	0.035	0.797	0.00
3-7	2.14	2.19	0.00
3-22	0.00	2.56	1.15

PROVINCETOWN, MASS. (P) 1978 - 1979 - Continued

Date	Cd ppb	Pb ppb	Cu ppb
3-28-1979	0.194	3.19	1.10
4-4	0.194	0.799	0.00
4-25	0.535	1.86	2.83
5-3	0.392	2.03	2.00
5-10	0.214	1.48	3.83
5-16	0.225	1.51	1.87

*All samples were frozen

MCKOWN POINT (MP) 1978

Date	Cd ppb	Pb ppb	Cu ppb
7-3-1978	0.028	0.180	0.928
7-6	0.056	1.06	1.75
7-11	0.028	1.80	0.948
7-13	0.079	0.301	1.05
7-18	0.040	0.356	0.405
7-20	0.099	1.04	1.64
7-25	0.119	0.575	1.33
7-27	0.020	0.575	0.619
8-1	0.079	0.575	0.619
8-3	0.020	0.438	0.953
8-8	0.040	1.37	2.33
8-10	0.099	0.657	0.595
8-15	0.028	0.309	1.73
8-17	0.083	0.574	7.03
8-22	0.083	1.77	0.00
8-24	0.111	0.530	0.00
8-29	0.139	0.441	0.00
8-31	0.056	0.618	0.973
9-6	0.222	1.10	0.379
9-8	0.00	0.397	0.00
9-13	0.00	0.441	0.00
9-15	0.083	1.46	0.00
9-18	0.139	0.971	0.811

*Samples were stored acidified

MCKOWN POINT (MP) 1978

Date	Cd ppb	Pb ppb	Cu ppb
5-25-1978	–	–	0.289
5-30	–	–	0.00
6-1	1.45	2.51	1.14
6-6	2.88	1.27	0.610
6-8	–	–	1.06
6-13	0.643	1.54	6.10
6-15	0.964	2.29	0.970
6-20	1.13	2.32	1.09
6-27	1.75	0.449	0.638
6-29	–	–	0.435
9-21	0.125	0.877	0.580
9-22	–	–	0.435
9-25	0.00	0.065	0.203
9-28	0.00	1.01	0.493

*Samples were stored frozen

NEWAGEN (NW) 1979

Date	Cd ppb	PB ppb	Cu ppb
1-4-79	0.105	0.690	0.893
1-11	0.00	–	0.00
1-19	0.156	0.295	0.00
2-1	1.69	0.737	0.00
2-9	0.245	0.295	0.864
2-15	2.59	0.652	0.853
2-22	0.531	3.12	2.68
3-1	0.406	0.765	1.28
3-8	0.313	0.765	0.548
3-23	0.00	0.00	0.592
4-6	0.00	–	0.563
4-20	0.062	0.495	0.813
4-26	0.00	–	0.438
5-14	0.302	0.748	0.512
5-15	0.00	1.27	0.00
5-17	0.00	0.00	0.00
5-18	0.00	0.00	0.308
5-21	0.174	0.953	0.00
5-22	0.00	0.00	0.00
5-23	0.00	2.35	0.551
5-24	0.290	0.715	0.00
5-25	0.00	0.00	0.00
5-26	0.06	0.446	0.710

NEWAGEN (NW) 1979 - continued

Date	Cd ppb	PB ppb	Cu ppb
5-28-79	0.00	0.465	0.443
5-29	0.00	0.883	0.00
5-30	0.00	0.00	0.441
6-1	0.164	1.75	0.521
6-2	0.211	1.81	0.413
6-3	0.07	0.446	0.418
6-4	0.080	0.643	0.00
6-5	0.00	1.10	0.640
6-6	0.263	0.643	0.00
6-7	0.00	1.06	0.00
6-8	0.195	1.22	1.27
6-10	0.269	0.815	1.08
6-11	0.167	1.49	1.20
6-12	0.202	1.30	0.692
6-13	0.445	3.55	4.67
6-15	0.269	1.26	0.845
6-16	0.312	1.94	0.00
6-17	0.078	1.04	0.00
6-18	0.221	1.81	0.501
6-19	0.185	0.321	0.00
6-20	0.00	.963	0.00
6-21	0.185	0.723	0.580

NEWAGEN (NW) 1979 - continued

Date	Cd ppb	Pb ppb	Cu ppb
6-22-79	0.850	4.40	1.03
6-24	0.250	1.37	1.91
6-26	0.161	1.44	0.250
6-27	0.221	1.65	1.67
6-29	0.221	0.604	0.543
6-30	0.680	1.90	1.02
7-1	0.098	9.03	0.00
7-2	0.115	1.86	0.417
7-3	0.098	1.13	0.190
7-4	0.110	0.815	0.00
7-5	0.017	0.184	0.00
7-13	0.159	0.884	1.91
7-14	0.195	1.49	1.12
7-16	0.221	1.63	0.919
7-17	0.148	1.60	0.00
7-21	0.054	0.281	0.00
7-22	5.55	1.17	0.00
7-23	0.524	0.643	0.00
7-24	0.213	1.01	0.312
7-25	0.524	0.00	0.00
7-26	0.181	0.997	0.418
7-27	0.837	1.48	2.66
7-28	0.090	0.155	0.00

NEWAGEN (NW) 1979 - continued

Date	Cd ppb	PB ppb	Cu ppb
7-30-79	0.259	0.814	1.34
7-31	0.233	0.845	0.542
8-1	0.250	0.756	1.76
8-2	0.00	0.408	0.00
8-6	2.06	0.971	1.55
8-7	0.202	1.89	0.922
8-8	0.151	0.680	0.00
8-10	0.00	0.00	0.00
8-12	0.111	1.66	0.824
8-13	0.347	1.41	0.496
8-14	0.00	0.408	0.00
8-15	0.00	1.18	0.551
8-16	0.00	1.47	0.882
8-20	0.00	0.380	0.00
8-24	0.161	0.526	0.125
8-29	0.237	0.803	0.997

*samples were stored frozen

NEWAGEN (NW) 1978

Date	Cd ppb	Pb ppb	Cu ppb
4-12-78	0.146	0.371	1.56
4-21	0.188	2.95	2.44
4-28	0.156	2.67	1.90
5-18	0.312	1.48	1.08
5-25	0.187	0.758	0.563
6-2	–	–	0.00
6-5	0.341	0.863	1.12
6-6	0.971	2.32	0.983
6-7	0.299	0.842	0.269
6-8	0.185	2.89	1.28
6-9	0.124	0.290	0.537
6-12	0.249	0.232	0.314
6-13	0.473	1.25	0.314
6-14	0.00	5.13	7.69
6-15	0.523	0.377	0.00
6-16	0.069	0.769	0.964
6-19	0.998	2.15	0.313
6-21	0.270	1.51	0.563
6-22	0.149	0.261	0.671
6-23	0.00	0.272	3.13

* samples were stored frozen

NEWAGEN (NW) 1978 - continued

6-26-78	0.208	-	1.00
6-27	0.156	1.58	3.13
6-28	0.443	0.365	0.00
6-29	0.469	1.14	1.88
9-21	0.00	0.00	0.432
9-22	0.156	0.324	0.864
9-25	0.00	0.088	0.00
9-26	0.00	0.501	0.00
9-27	0.037	0.115	0.00
9-28	0.00	-	0.540
9-29	-		0.446
10-5	0.156	0.383	0.00
10-12	0.067	0.413'	1.08
10-19	0.281	0.709	0.609
11-17	0.055	0.230	0.00
11-22	0.129	0.402	0.529
11-30	0.314	2.19	4.01
12-7	0.222	1.96	0.982
12-14	0.00'	0.097	0.00
12-21	-	0.369	0.00
12-28	0.185	0.245	0.502

* samples were stored frozen

NEWAGEN (NW) 1978

Date	Cd ppb	Pb ppb	Cu ppb
6-30-78	0.00	0.482	1.40
7-3	0.00	0.593	0.00
7-5	0.099	0.223	0.425
7-6	0.133	0.408	0.00
7-7	0.00	0.354	0.00
7-10	0.079	0.248	0.00
7-11	0.027	0.248	1.60
7-12	0.106	0.00	0.456
7-13	0.079	0.036	0.608
7-14	0.158	0.354	0.380
7-17	0.079	0.177	0.951
7-18	0.083	0.317	0.00
7-19	0.028	0.202	0.574
7-20	0.00	0.260	0.00
7-21	0.028	0.433	0.00
7-24	0.00	0.189	0.00
7-25	0.106	0.472	0.00
7-26	0.035	0.472	0.00
7-27	0.035	0.142	0.00
7-28	0.142	0.425	1.49
7-31	0.142	0.236	0.416
8-1	0.079	0.374	0.719

NEWAGEN (NW) 1978 - continued

Date	Cd pbb	Pb ppb	Cu ppb
8-2-78	0.063	0.214	0.569
8-3	0.032	0.294	0.180
8-4	0.063	0.828	0.00
8-7	0.032	0.267	0.00
8-8	0.079	0.267	0.00
8-9	0.079	0.427	0.360
8-10	0.00	0.240	1.05
8-11	0.00	0.150	0.323
8-14	0.00	0.275	0.00
8-15	0.093	0.175	1.37
8-16	0.037	0.250	0.223
8-17	0.00	0.200	0.00
8-18	0.056	1.03	0.049
8-19	0.148	0.702	2.81
8-22	0.092	0.376	1.48
8-23	0.184	1.28	1.43
8-24	0.092	0.482	0.00
8-25	0.062	0.535	0.00
8-28	0.092	0.641	0.00
8-29	0.123	0.535	0.00
8-31	0.107	0.639	1.13
9-1	0.053	0.545	0.614
9-5	0.018	0.331	0.593

NEWAGEN (NW) 1978 - continued

Date	Cd ppb	Pb ppb	Cu ppb
9-6-78	0.071	0.284	0.00
9-7	0.036	0.426	0.00
9-8	0.142	0.521	0.00
9-11	0.339	1.16	0.553
9-13	0.053	0.260	0.00
9-14	0.125	0.710	0.00
9-15	0.079	0.339	2.04
9-18	0.019	0.498	1.50
9-19	0.039	0.279	0.074
9-20	0.079	0.737	0.056

* samples were acidified

MONHEGAN 1977

Date	Cd ppb	Pb ppb	Cu ppb
6-16-77	0.19	0.32	3.23
6-17	0.22	2.25	3.45
6-18	0.24	0.17	1.04
6-20	0.11	0.13	0.88
6-22	0.09	0.72	3.15
6-23	0.00	0.25	1.60
6-24	0.08	0.24	1.40
6-26	0.00	0.12	2.10
6-27	0.00	0.27	1.90
6-28	0.27	0.32	1.88
6-29	0.22	0.35	1.70
6-30	0.36	0.26	1.90
7-1	0.12	0.23	2.40
7-2	0.24	0.17	0.97
7-3	0.83	0.65	1.15
7-4	0.85	0.56	0.98
7-5	0.36	0.00	2.22
7-6	0.08	0.00	1.62
7-7	0.28	0.33	1.50
7-8	0.38	0.26	1.60
7-9	0.48	1.37	1.20
7-10	0.38	2.94	3.47
7-11	0.22	2.94	3.47

MONHEGAN 1977 - continued

Date	Cd ppb	Pb ppb	Cu ppb
7-12-77	0.74	0.63	2.64
7-13	0.86	0.31	4.15
7-15	0.14	0.13	1.40
7-16	0.15	0.27	1.43
7-17	0.09	0.24	2.60
7-18	0.47	1.30	2.60
7-19	0.00	0.00	1.30
7-20	0.07	0.51	0.50
7-21	0.22	0.28	1.42
7-22	0.00	0.00	1.21
7-26	0.21	0.23	0.64
7-27	0.07	0.51	0.50
7-28	0.00	0.26	0.60
7-29	0.14	0.10	1.28
7-30	0.08	0.20	2.70
7-31	0.00	0.24	1.47
8-1	0.09	0.18	0.91
8-2	0.00	0.80	0.95
8-3	0.01	0.13	1.06
8-4	0.00	0.15	2.07
8-5	0.81	0.21	-
8-7	0.10	0.32	1.57
8-8	0.64	0.76	-

MONHEGAN 1977 - continued

Date	Cd ppb	Pb ppb	Cu ppb
8-9-77	0.45	0.27	1.45
8-10	0.00	0.39	1.58
8-11	0.58	0.51	1.28
8-14	0.42	0.34	1.35
8-18	0.06	0.22	0.78
8-21	0.00	0.17	4.23
8-22	0.42	1.36	3.80
8-23	0.00	0.00	1.13
8-24	0.00	0.12	1.30
8-25	0.00	0.28	1.90
8-26	0.08	0.07	1.37
8-27	0.08	0.38	1.74
8-28	0.14	1.01	1.43
8-29	0.12	0.01	0.83
8-30	0.19	0.28	0.70
8-31	0.00	0.22	1.60
9-2	0.00	0.41	3.70
9-4	0.18	0.28	1.66
9-5	0.12	0.35	1.93
9-6	0.00	0.70	5.90
9-8	0.01	0.23	0.00
9-9	0.03	0.16	1.37
9-10	0.07	0.17	1.60

MONHEGAN 1977 - continued

Date	Cd ppb	Pb ppb	Cu ppb
9-11	0.08	0.37	0.83
9-15	0.03	0.28	1.00
9-16	0.13	0.14	0.80

*samples stored frozen

MONHEGAN 1978

Date	Cd ppb	Pb ppb	Cu ppb
6-7-78	0.56	0.99	1.19
7-9	0.00	4.40	1.08
7-10	–	–	0.00
7-11	–	–	0.00
7-12	0.092	6.53	9.15
7-13	0.00	0.216	1.18
7-14	0.00	2.16	2.57
7-15	0.354	3.78	4.56
7-16	0.062	0.698	0.579
7-17	0.00	2.10	0.616
7-18	0.333	3.04	2.81
7-19	0.354	–	1.25
7-20	0.00	0.00	1.48
7-21	0.284	1.36	2.36
7-22	0.35	2.16	3.82
7-23	0.208	1.74	1.94
7-24	0.00	0.413	0.415
7-25	0.289	1.26	0.609
7-26	0.00	12.96	2.74
7-27	0.186	0.782	0.00
7-28	0.084	0.00	0.783
7-29	0.145	0.271	0.00
7-30	0.236	12.37	1.33

MONHEGAN 1978 - continued

Date	Cd ppb	Pb ppb	Cu ppb
7-31	0.00	0.094	0.00
8-1	0.00	0.095	0.00
8-2	0.37	11.41	2.13
8-3	0.118	1.57	0.354
8-4	0.167	1.47	0.00
8-5	0.057	0.569	0.00
8-6	0.00	0.262	0.00
8-7	0.157	0.523	3.33
8-8	0.054	8.29	1.39
8-9	5.30	8.52	7.41
8-10	0.00	0.248	0.909
8-11	0.112	0.428	1.18
8-12	0.114	4.16	1.32
8-13	0.207	1.29	1.06
8-14	0.112	0.500	0.00
8-15	0.108	1.43	3.26
8-16	0.00	0.00	0.00
8-17	0.00	0.188	0.00
8-18	0.567	1.75	3.83
8-20	0.00	–	0.00
8-21	0.057	0.133	0.00
8-23	0.00	7.42	0.00
8-24	0.029	1.19	0.00

MONHEGAN 1978 - continued

Date	Cd ppb	Pb ppb	Cu ppb
8-25	0.00	0.00	0.00
8-26	0.00	0.00	1.06
8-27	0.00	0.723	2.34
8-28	0.00	5.41	1.97
8-29	0.204	1.82	0.00
8-30	0.00	0.928	0.00
8-31	0.00	-	0.579
9-2	0.292	0.928	1.65
9-3	0.00	0.00	0.00
9-4	-	-	0.773
9-5	0.00	0.467	0.870
9-6	0.091	17.70	2.31
9-7	0.115	0.339	1.06
9-8	0.208	0.467	1.06
9-10	0.066	0.399	0.319
9-11	0.00	3.67	3.49
9-12	0.00	0.469	0.354
9-13	0.098	1.12	4.18
9-14	0.00	0.262	0.00
9-15	0.00	0.928	0.00
9-16	0.233	1.04	0.056
9-17	0.00	9.91	2.98
9-18	0.029	0.334	0.00

MONHEGAN 1978 - continued

Date	Cd ppb	Pb ppb	Cu ppb
9-19	0.305	4.90	1.79
9-20	0.104	0.785	0.731
9-21	0.00	5.46	1.35
9-22	0.00	0.631	0.00
9-23	0.00	0.334	0.112
9-24	0.058	0.631	0.00
9-25	0.058	0.483	0.503
9-26	0.00	0.334	0.00
9-27	0.07	0.942	0.262
9-28	0.00	0.557	0.00

* samples were stored frozen

MONHEGAN 1978 - continued

Date	Cd ppb	Pb ppb	Cu ppb
6-7-78	0.18	2.01	1.24
6-8	0.170	0.659	0.00
6-9	0.056	0.375	0.00
6-10	0.094	0.468	0.166
6-11	0.227	0.312	0.166
6-12	0.113	0.219	0.00
6-13	0.209	0.570	0.00
6-14	0.139	0.482	0.00
6-15	0.278	0.833	0.628
6-16	0.348	0.833	1.35
6-17	0.17	0.37	1.26
6-18	0.54	2.39	0.84
6-19	0.03	0.98	2.26
6-20	0.07	1.20	2.69
6-21	0.15	0.67	0.64
6-22	0.10	0.26	0.55
6-23	0.12	0.83	4.16
6-24	0.09	0.09	3.14
6-25	0.16	0.37	8.86
6-26-78	0.10	0.31	2.47
6-27	0.05	0.40	1.34
6-28	0.11	0.31	1.65
6-29	0.21	0.45	2.35

MONHEGAN 1978 - continued

Date	Cd ppb	Pb ppb	Cu ppb
7-1	0.035	0.219	0.00
7-2	0.104	0.702	1.44
7-3	0.313	0.307	0.00
7-4	0.278	4.34	3.59
7-5	0.00	0.439	0.00
7-6	0.00	0.00	0.00
7-7	0.035	0.351	0.00
7-8	0.243	0.351	0.00
7-9	0.00	0.594	0.798
7-10	0.209	0.219	0.00
7-11	0.062	0.378	0.00
7-12	0.00	2.59	2.52
7-13	0.062	0.258	0.00
7-14	0.00	2.18	2.90
7-15	0.094	0.420	0.00
7-16	0.219	0.798	0.00
7-17	0.125	0.462	0.00
7-18	0.031	0.168	0.00
7-19	0.00	0.714	0.00
7-20	0.062	0.294	0.00
7-21	0.156	0.294	0.00
7-22	0.00	1.34	1.70

MONHEGAN 1978 - continued

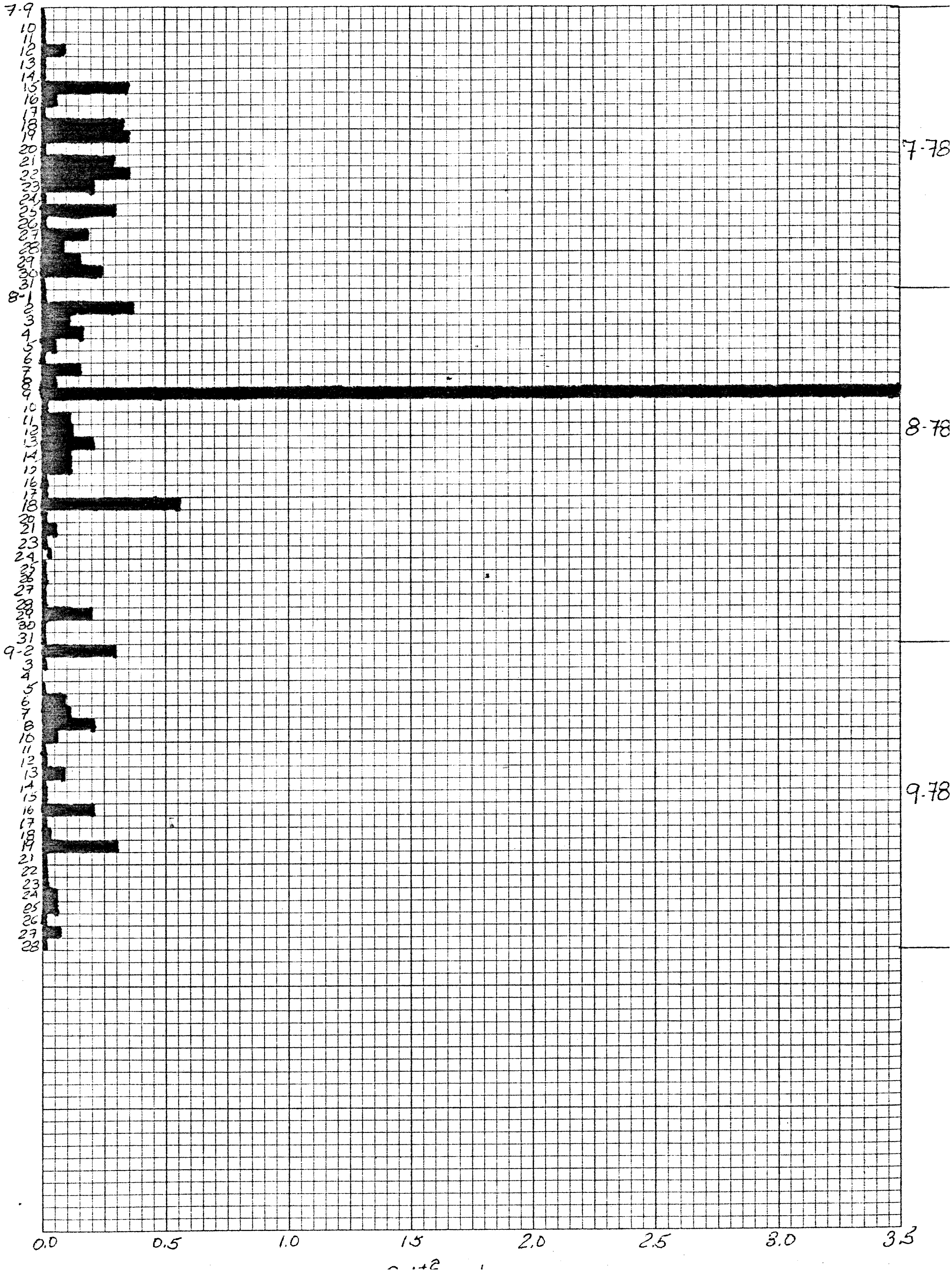
Date	Cd ppb	Pb ppb	Cu ppb
7-23-78	0.095	0.389	0.00
7-24	0.00	0.871	4.95
7-25	0.719	0.420	0.00
7-26	0.000	0.380	1.20
7-27	0.187	0.210	0.00
7-28	0.164	0.119	0.00
7-29	0.218	0.697	1.04
7-30	0.00	0.551	1.10
7-31	0.146	0.648	0.031
8-1	0.146	0.072	0.086
8-3	0.128	0.151	0.00
8-4	0.110	0.001	0.00
8-5	0.055	0.117	0.00
8-6	0.073	0.606	0.00
8-7	0.073	0.049	0.00
8-8	0.00	0.459	0.404
8-9	0.30	0.993	1.40
8-10	0.128	0.072	0.024
8-11	0.146	0.114	0.00
8-12	0.421	0.151	0.024
8-13	0.677	0.140	0.078
8-14	0.091	0.095	0.00
8-15	0.151	0.882	0.263

MONHEGAN 1978 - continued

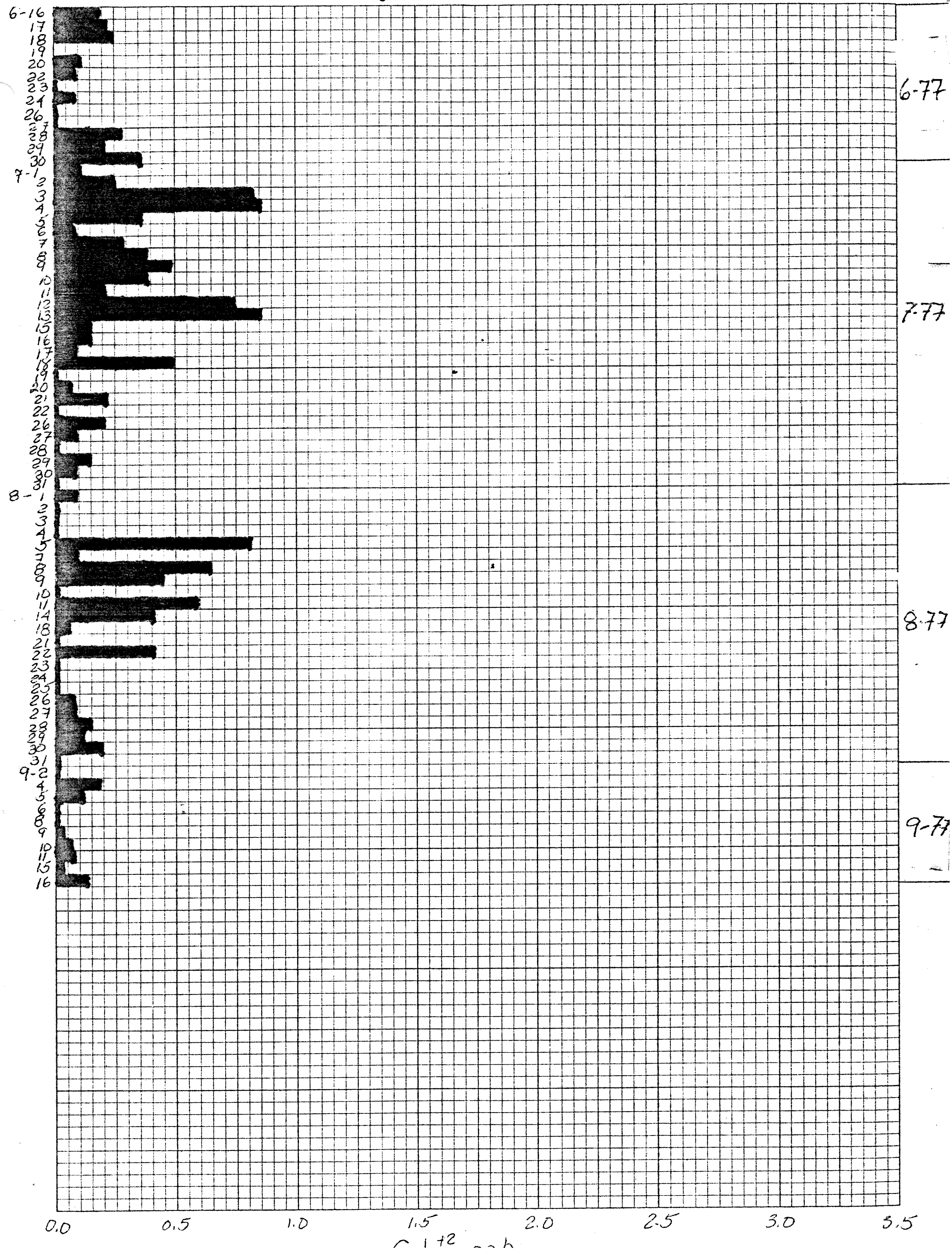
Date	Cd ppb	Pb ppb	Cu ppb
8-16-78	0.133	1.15	0.00
8-17	0.114	0.389	0.00
8-20	0.056	0.593	0.00
8-21	0.114	1.38	0.00
8-22	0.122	0.652	0.00
8-23	0.151	0.652	0.00
8-24	0.114	0.586	0.00
8-25	0.189	1.24	0.00
8-26	0.151	0.849	0.00
9-2	0.208	1.84	0.919
9-3	0.151	0.718	0.00
9-4	0.133	0.882	0.00
9-5	0.151	0.816	0.00
9-6	0.167	0.960	0.589
9-8	0.130	1.07	0.00
9-9	0.074	0.621	0.00
9-10	0.056	0.480	0.00
9-11	0.130	0.536	0.00
9-12	0.149	0.621	0.00
9-13	0.111	0.762	1.28
9-14	0.111	0.621	0.00
9-15	0.130	0.932	0.00

* samples were acidified

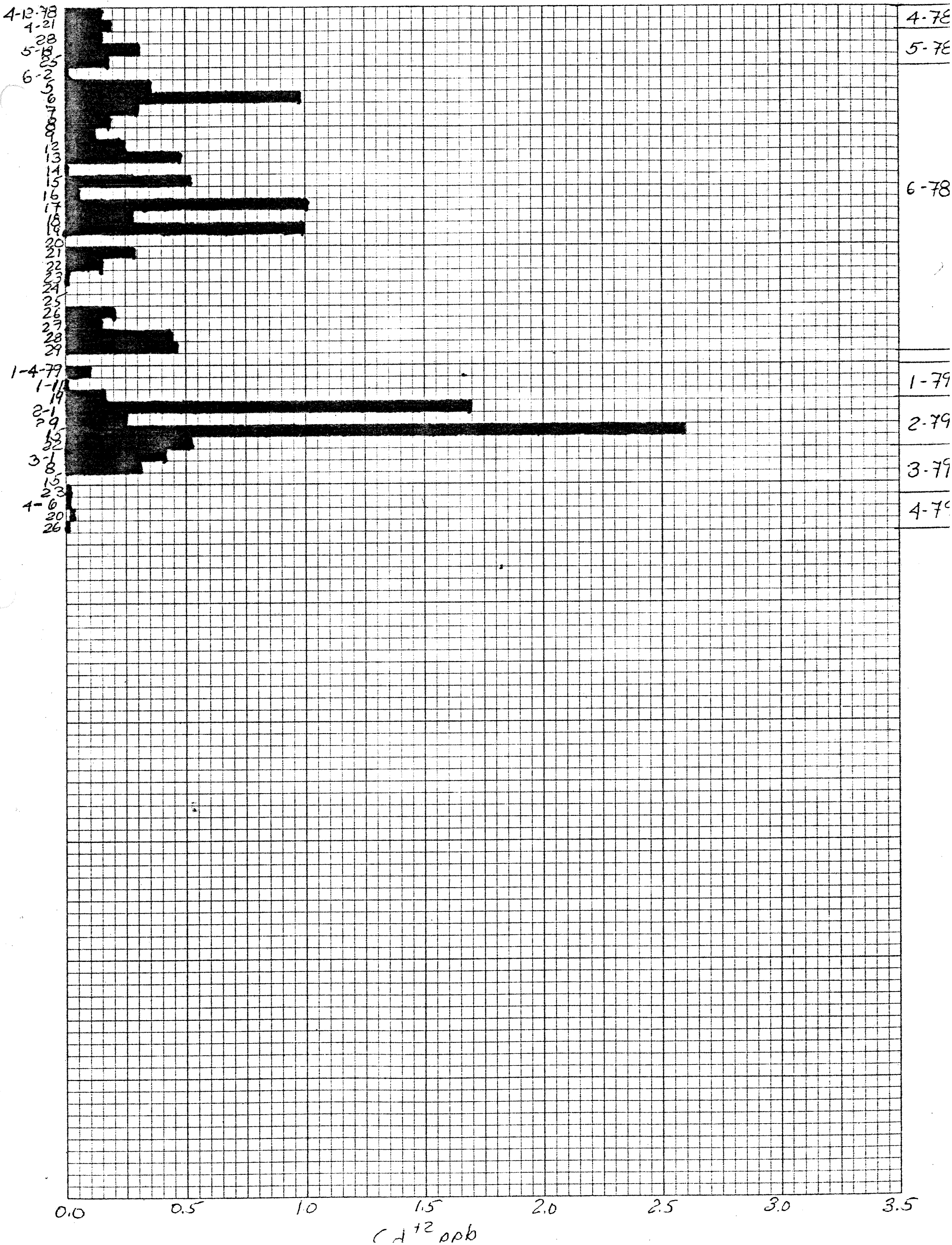
Monhegan 1978



Monhegan 1977



Newagen


4-12-78
4-21
28
5-18
25
6-2
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1-4-79
1-11
19
2-1
9
15
22
3-1
8
15
23
4-6
20
26
4-78
5-78
6-78
1-79
2-79
3-79
4-79
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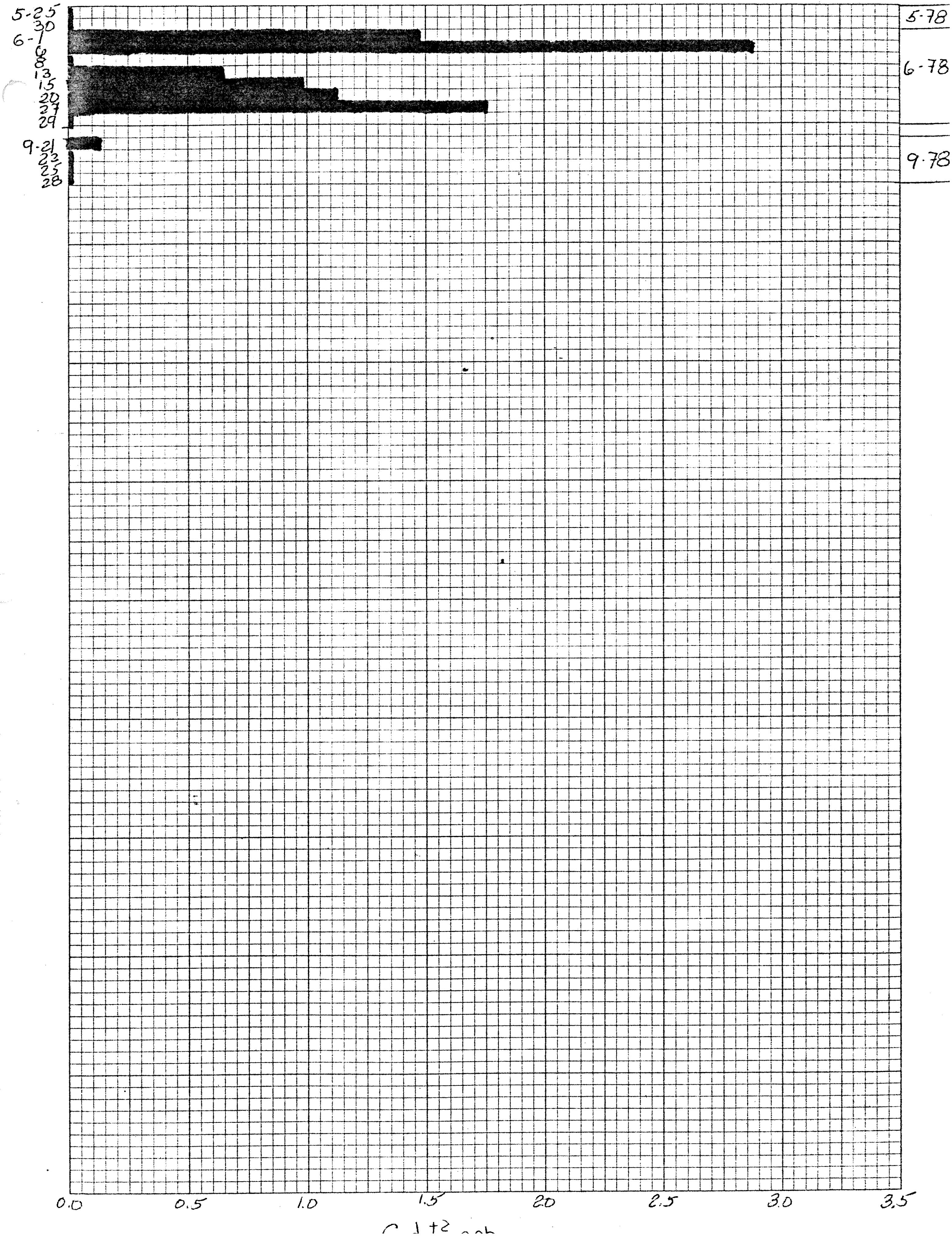
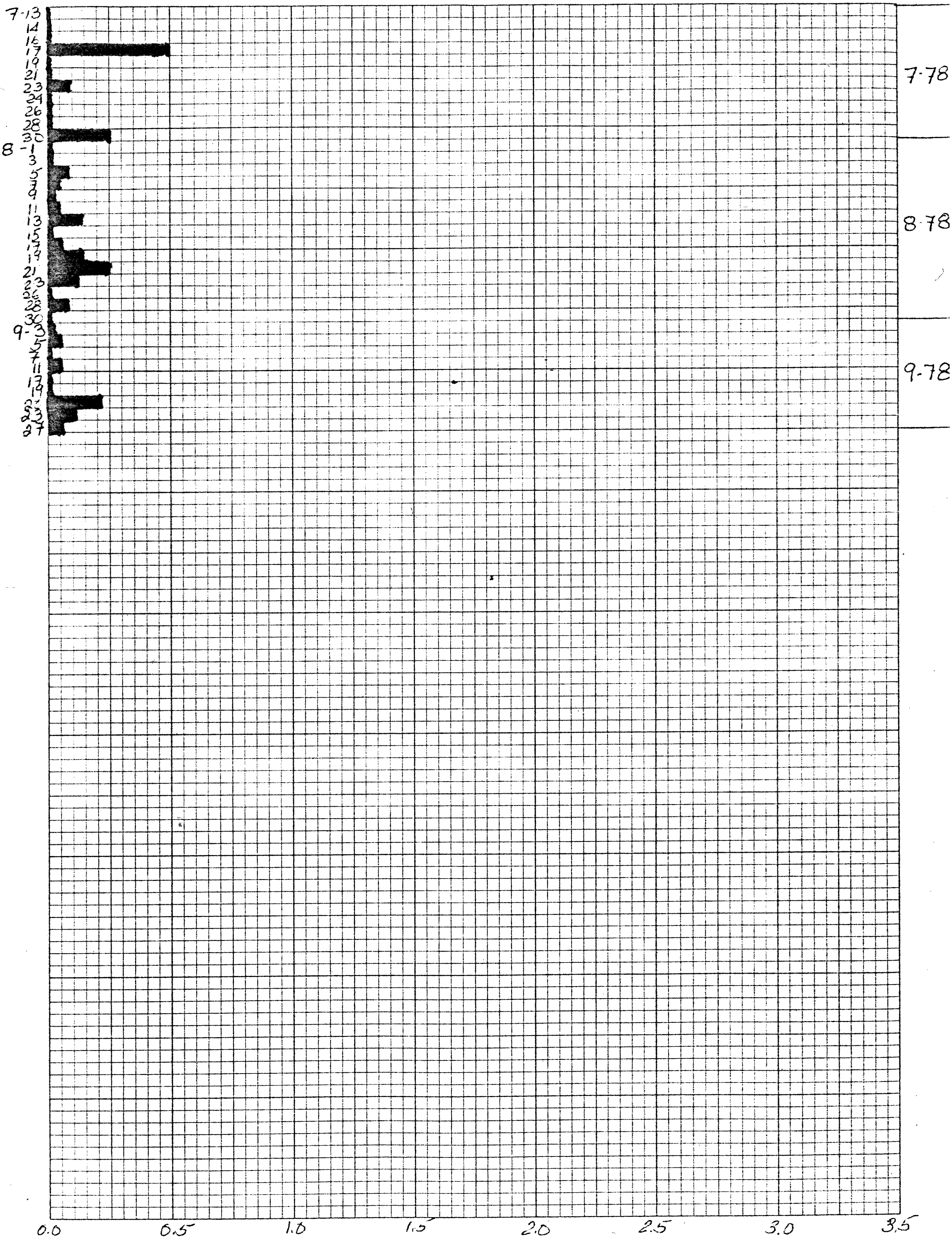
0.5
1.0
1.5
2.0
2.5
3.0
3.5
Cd+2 ppb

Mckown Pt. 1978

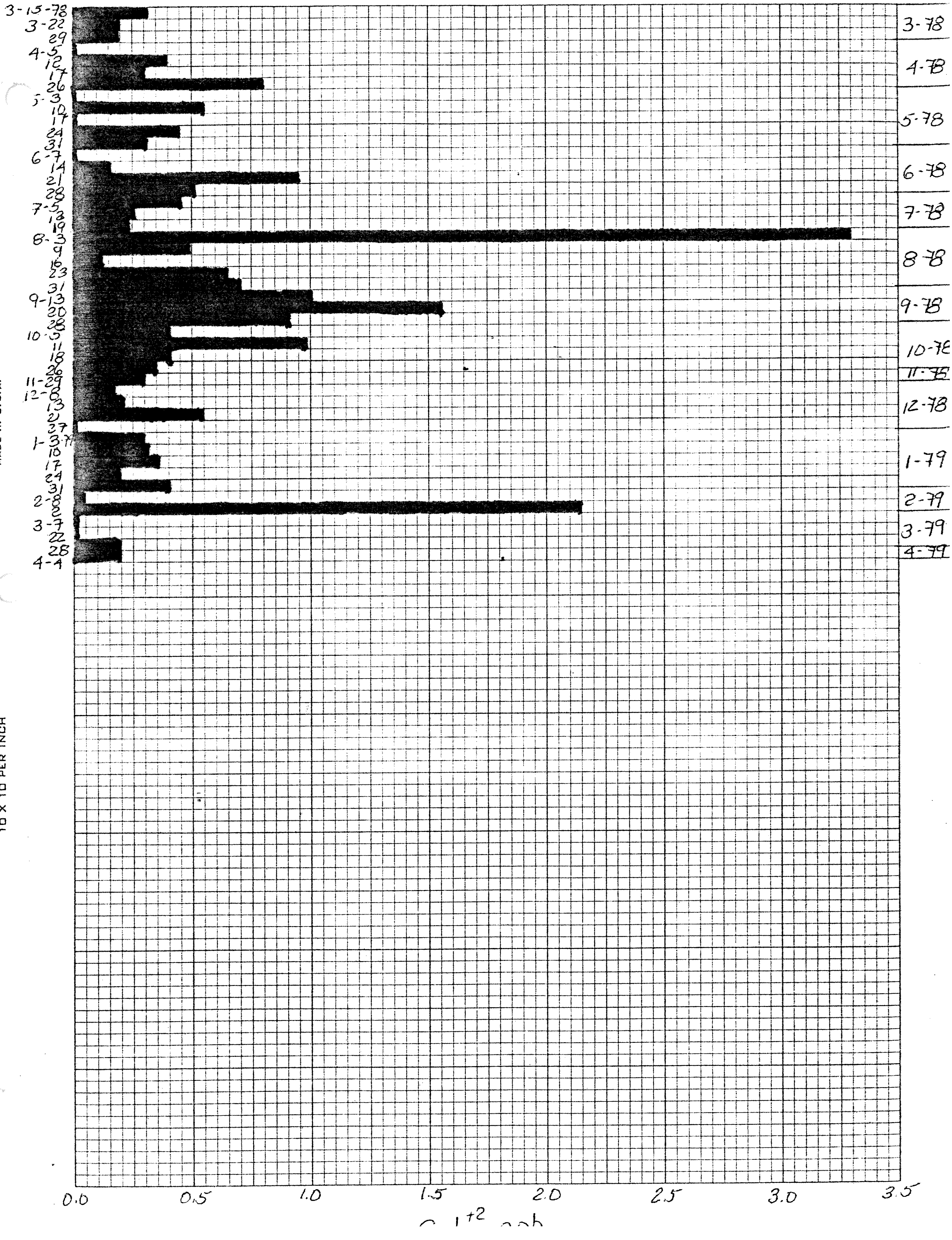


Petit Manan Pt. 1978

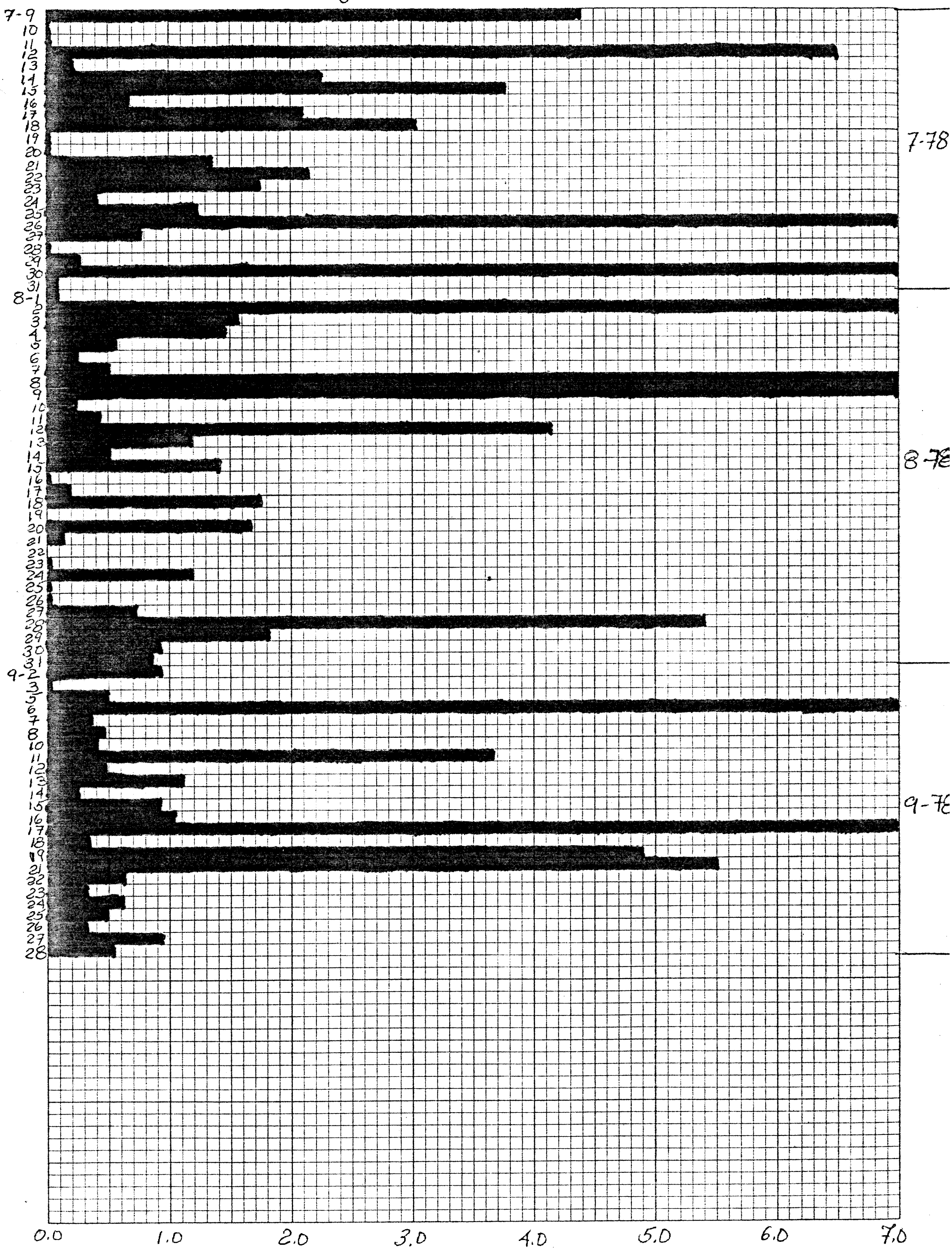


Cd µg/ppb

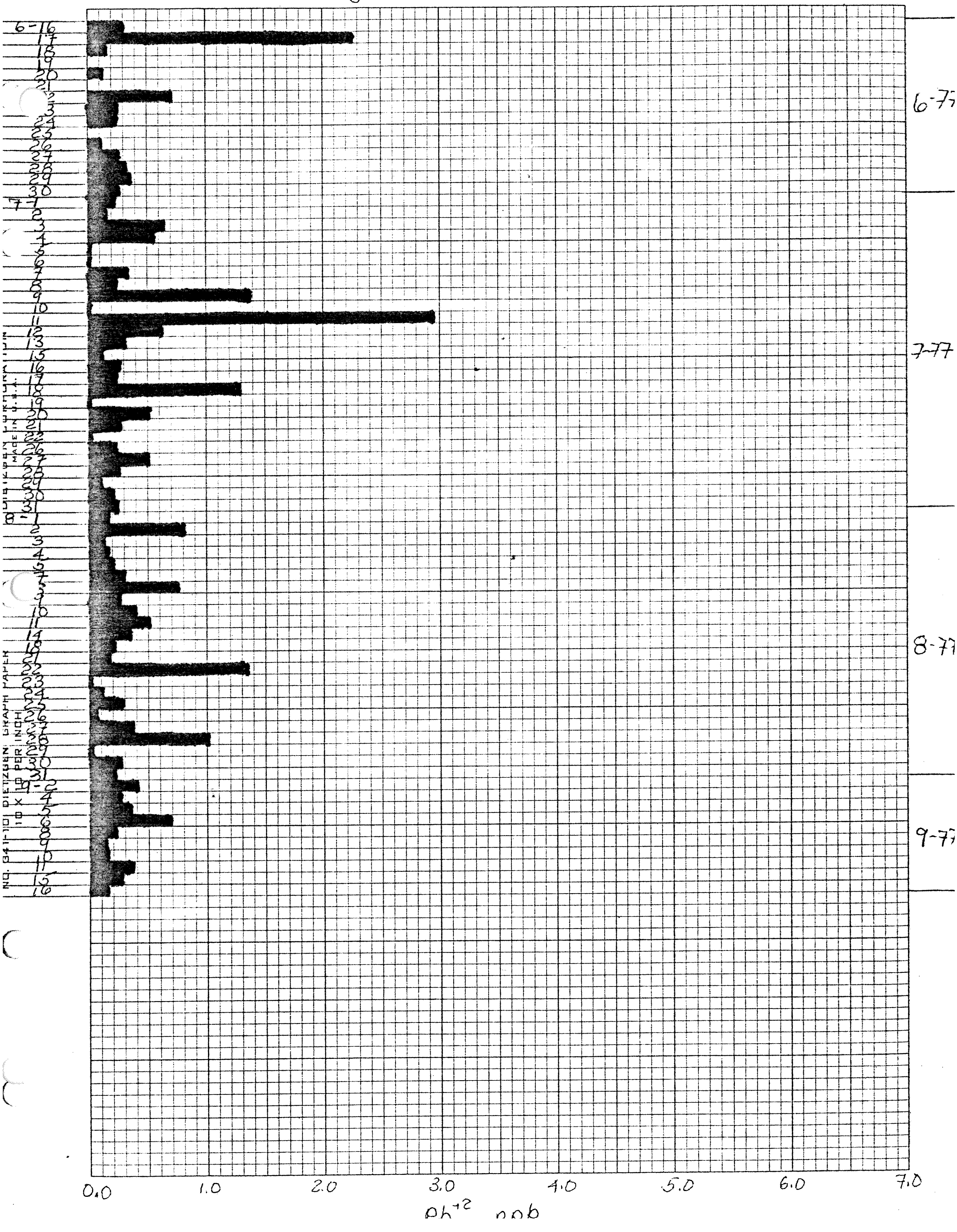
Provincetown 1978 + 1979



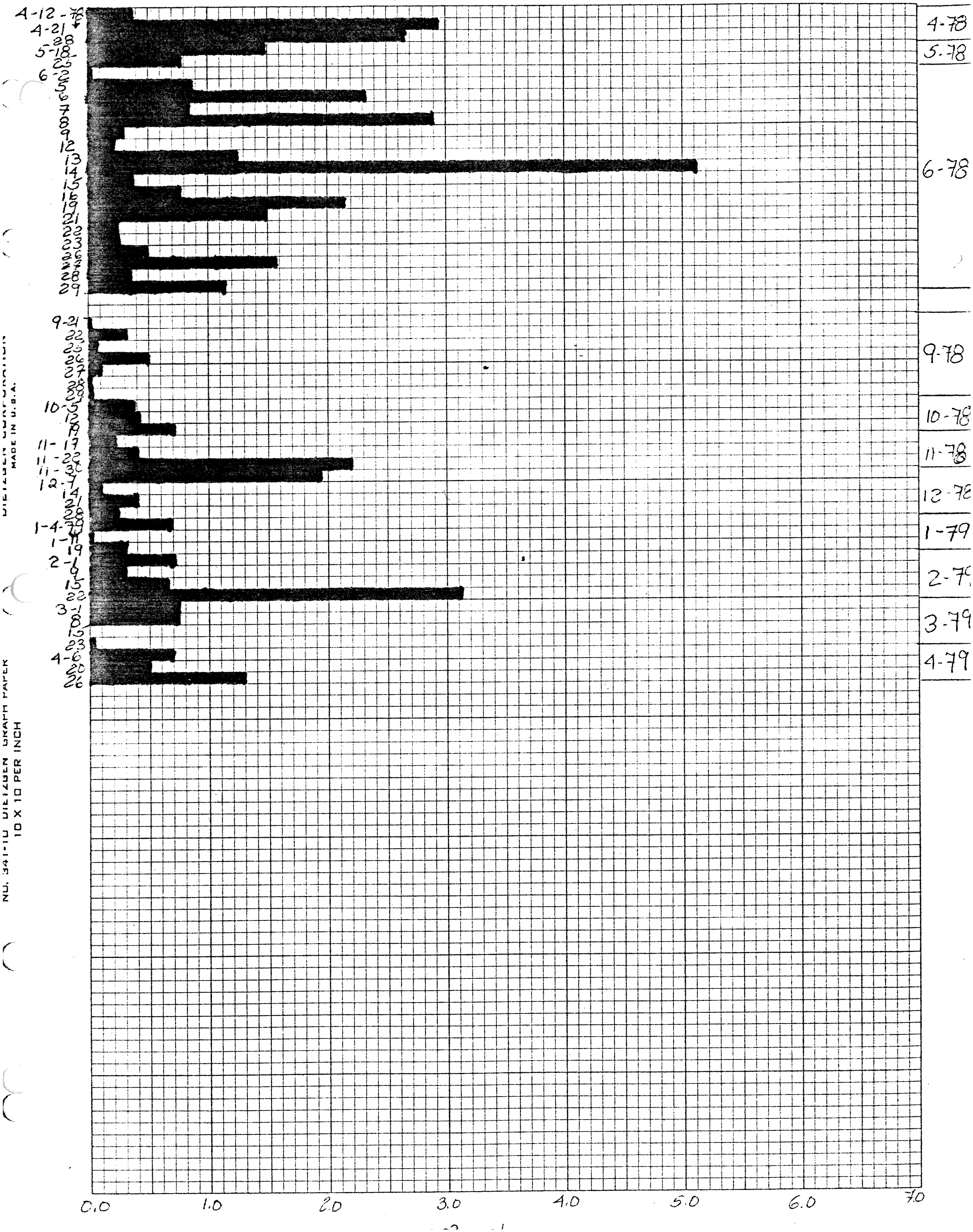
Monhegan 1978



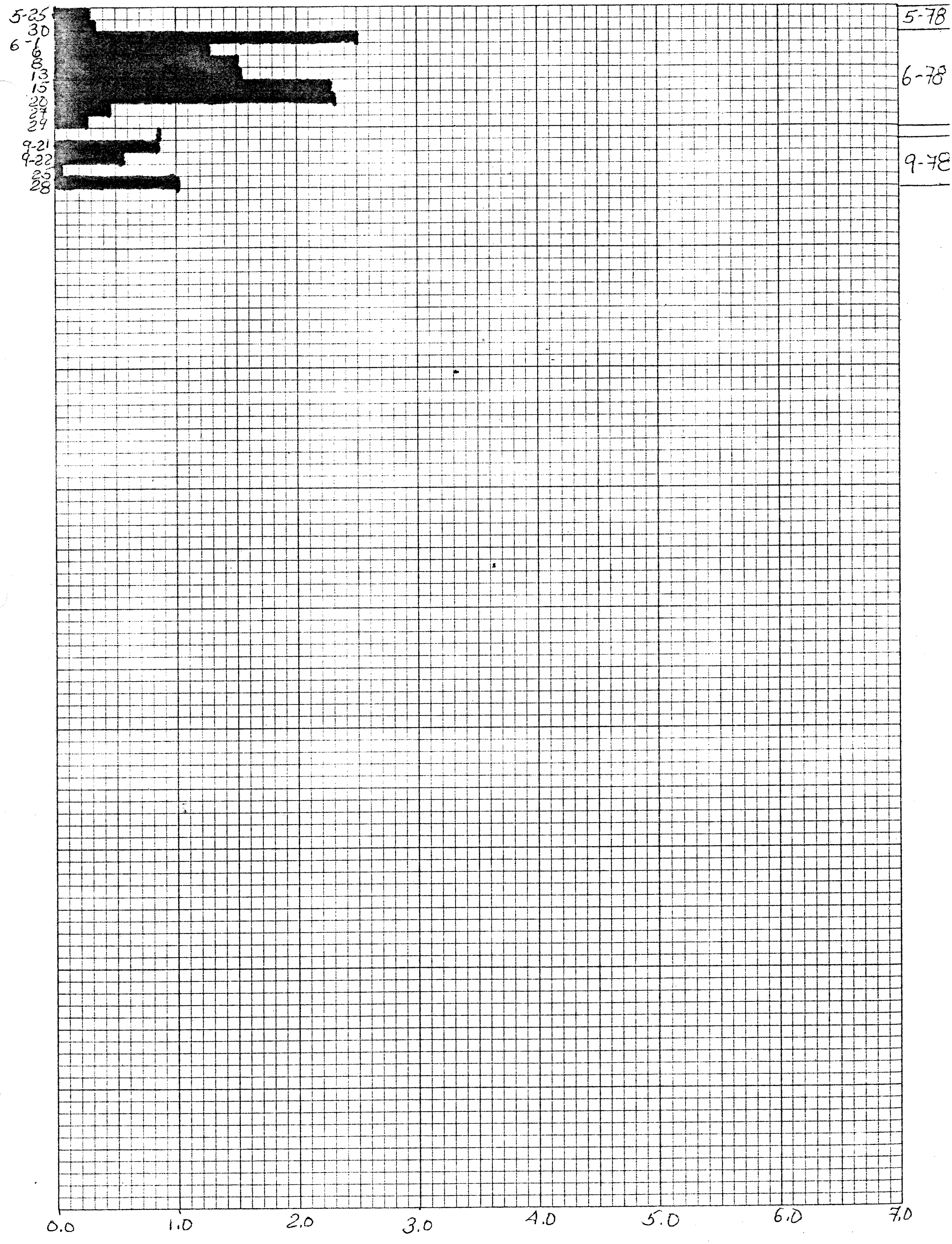
Monhegan 14++



Newagen 1978-1979

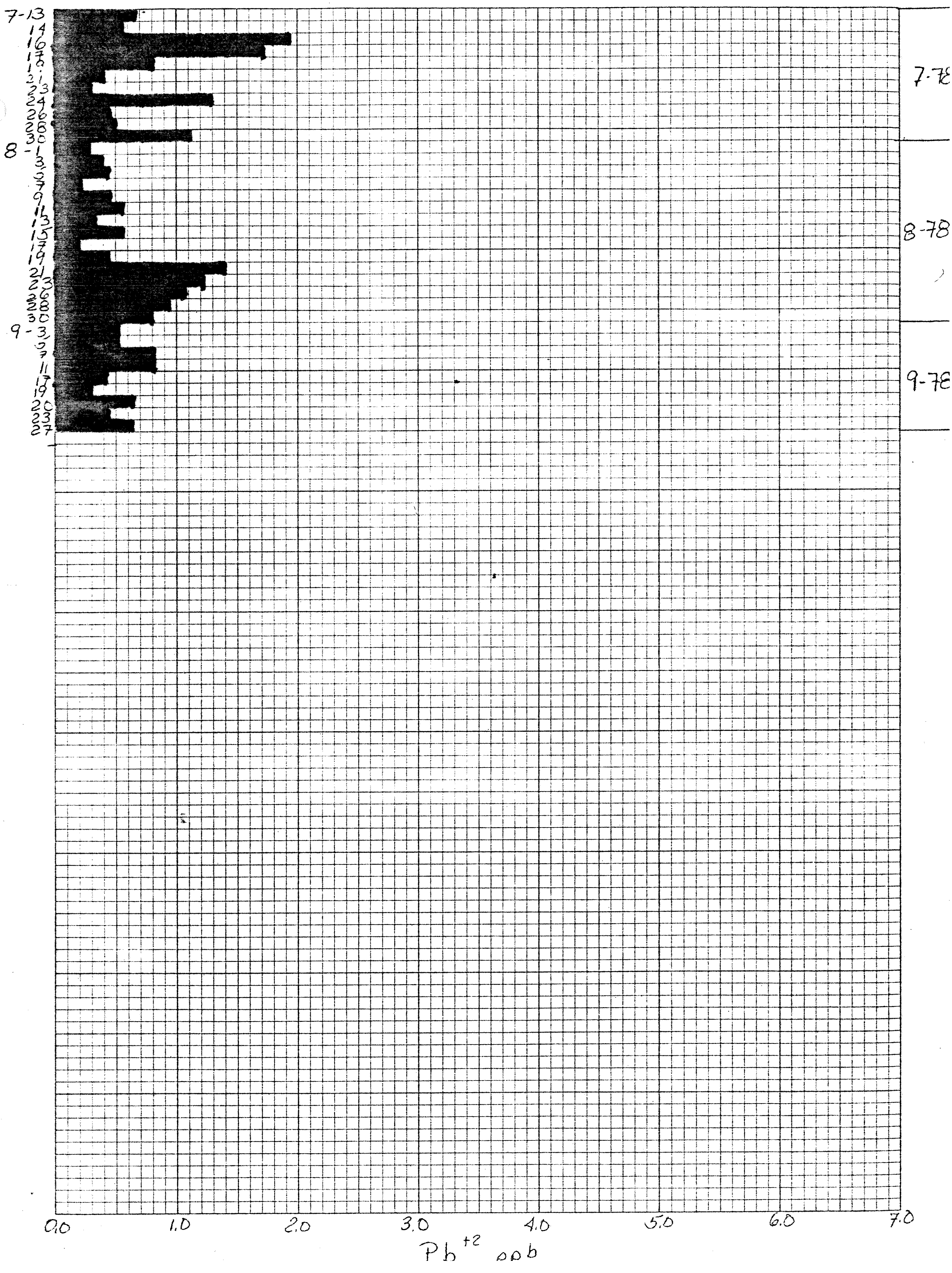


Mckown Pt. 1978

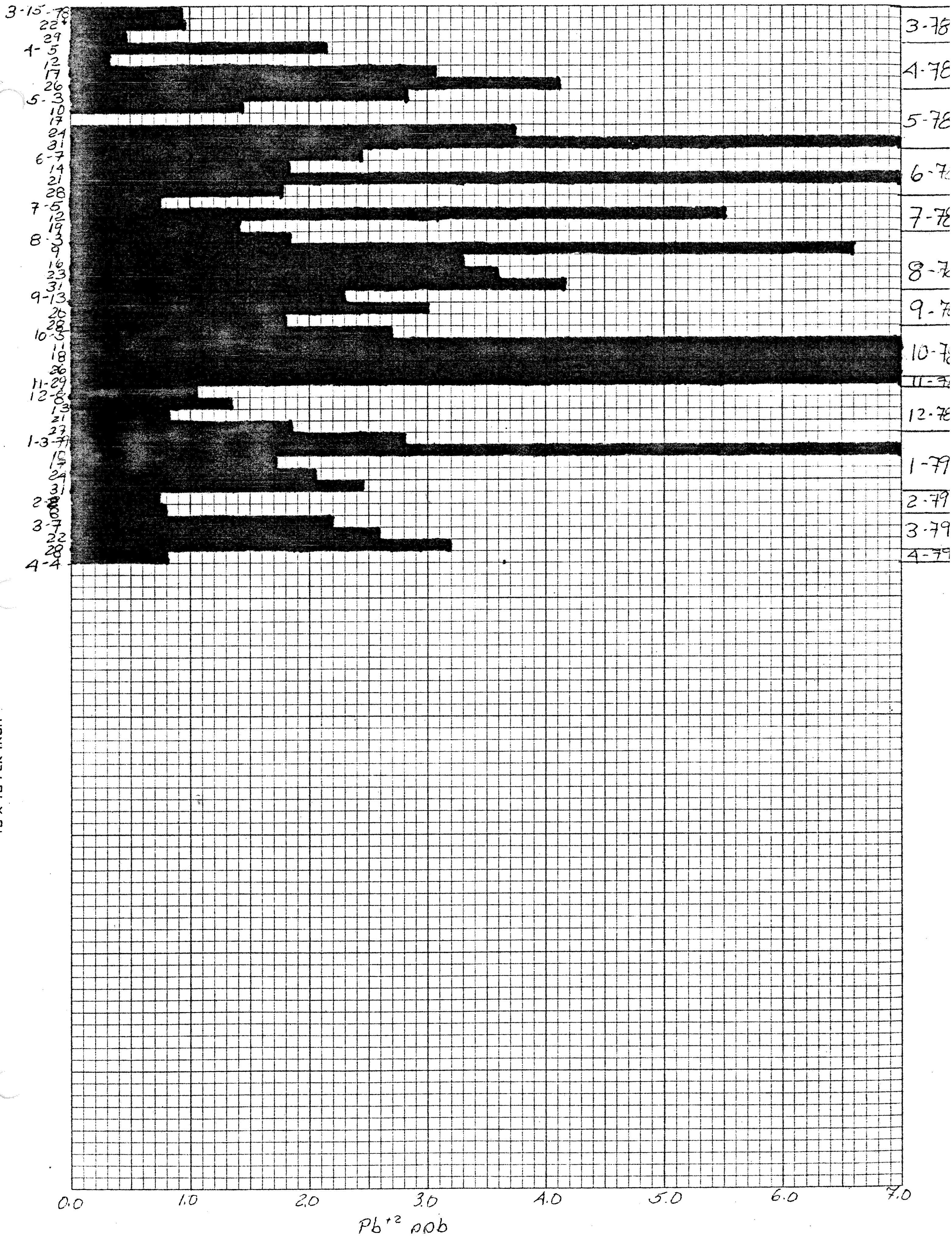


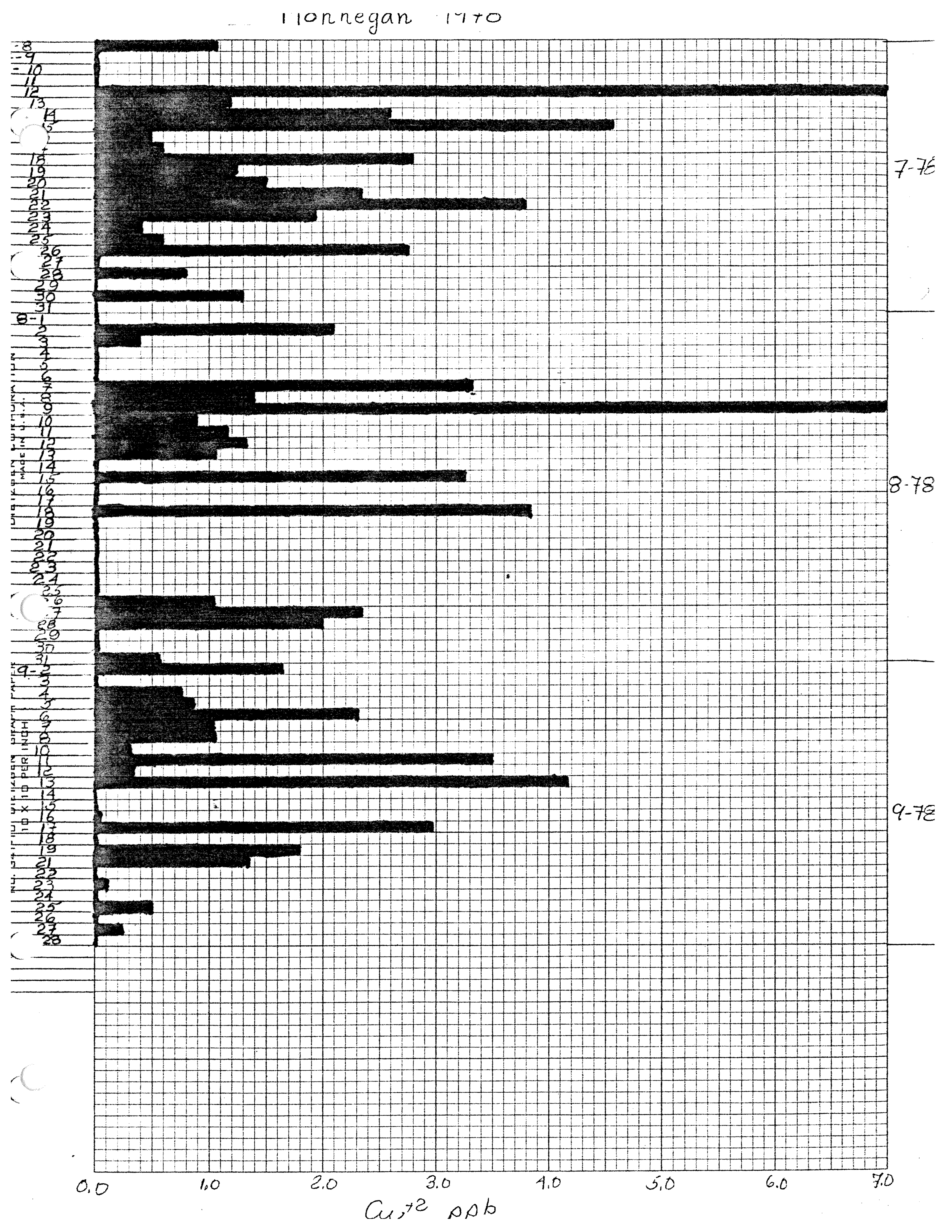
NO. 341-10 DIETZGEN GRAPH PAPER 10 X 10 PER INCH
DIETZGEN CORPORATION MADE IN U.S.A.

Petit Manan Pt. 1978



Provincetown 1978 + 1979




Monnegan 1978
7-78
8-78
9-78
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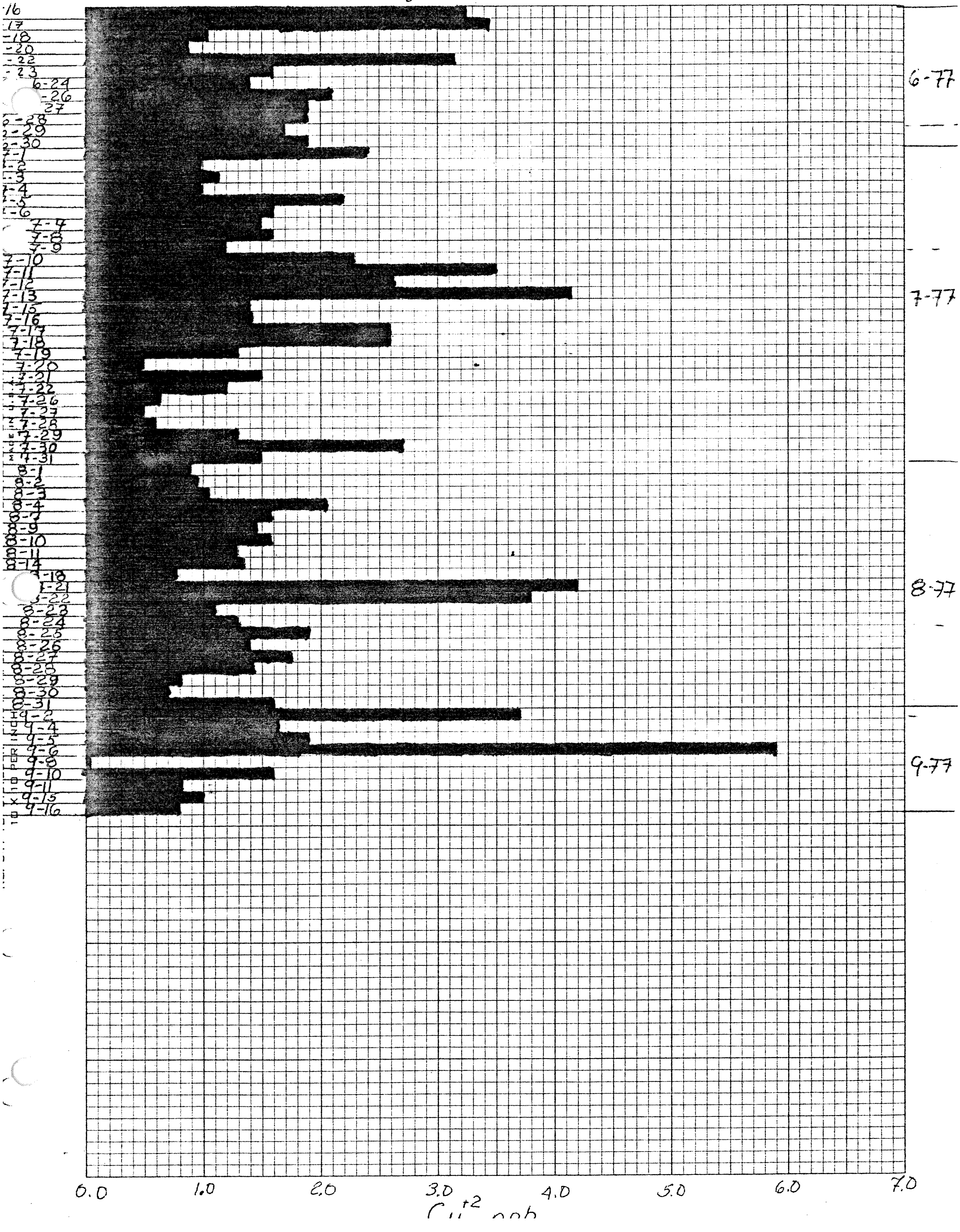
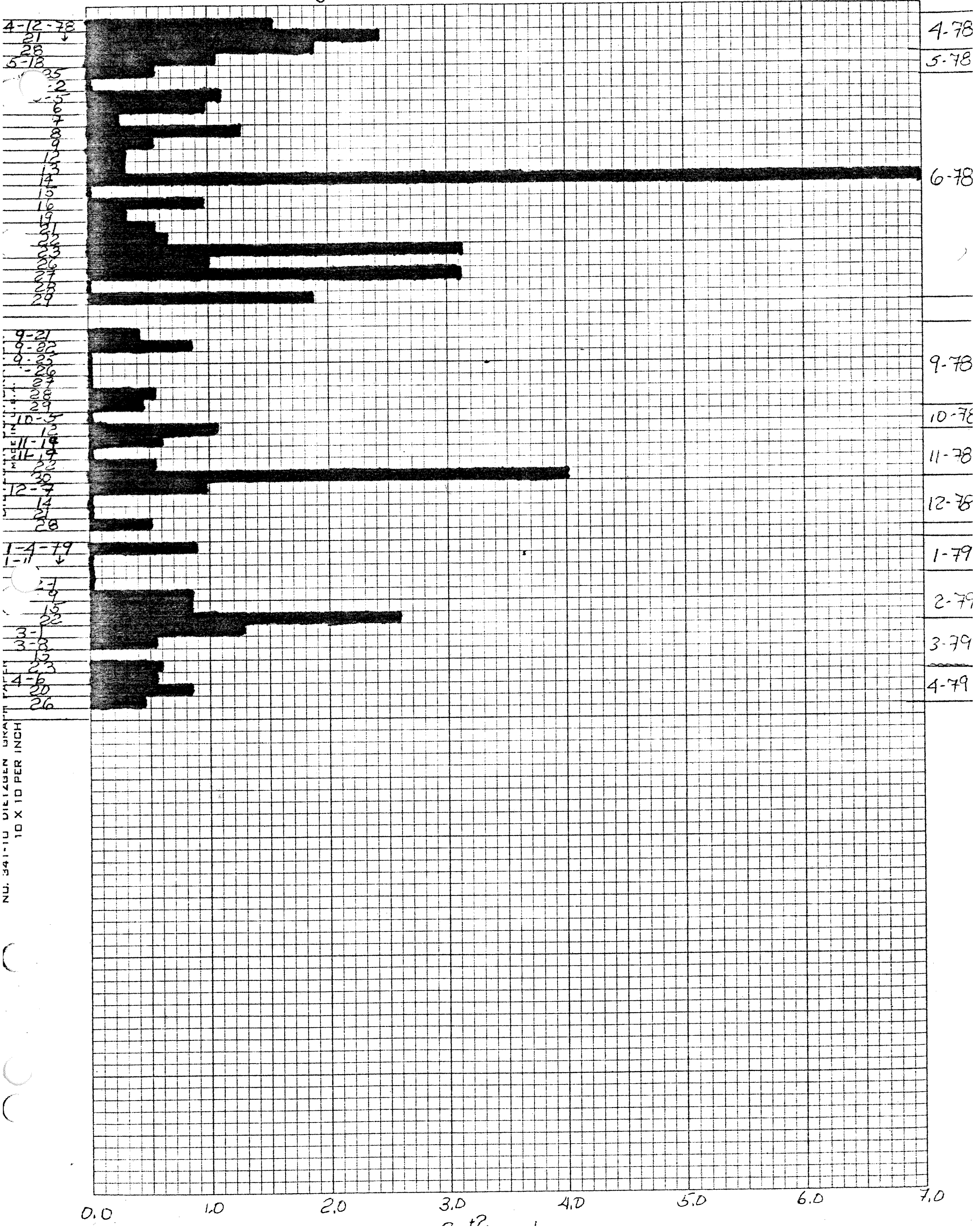
1.0
2.0
3.0
4.0
5.0
6.0
7.0
Cu+2 ppb

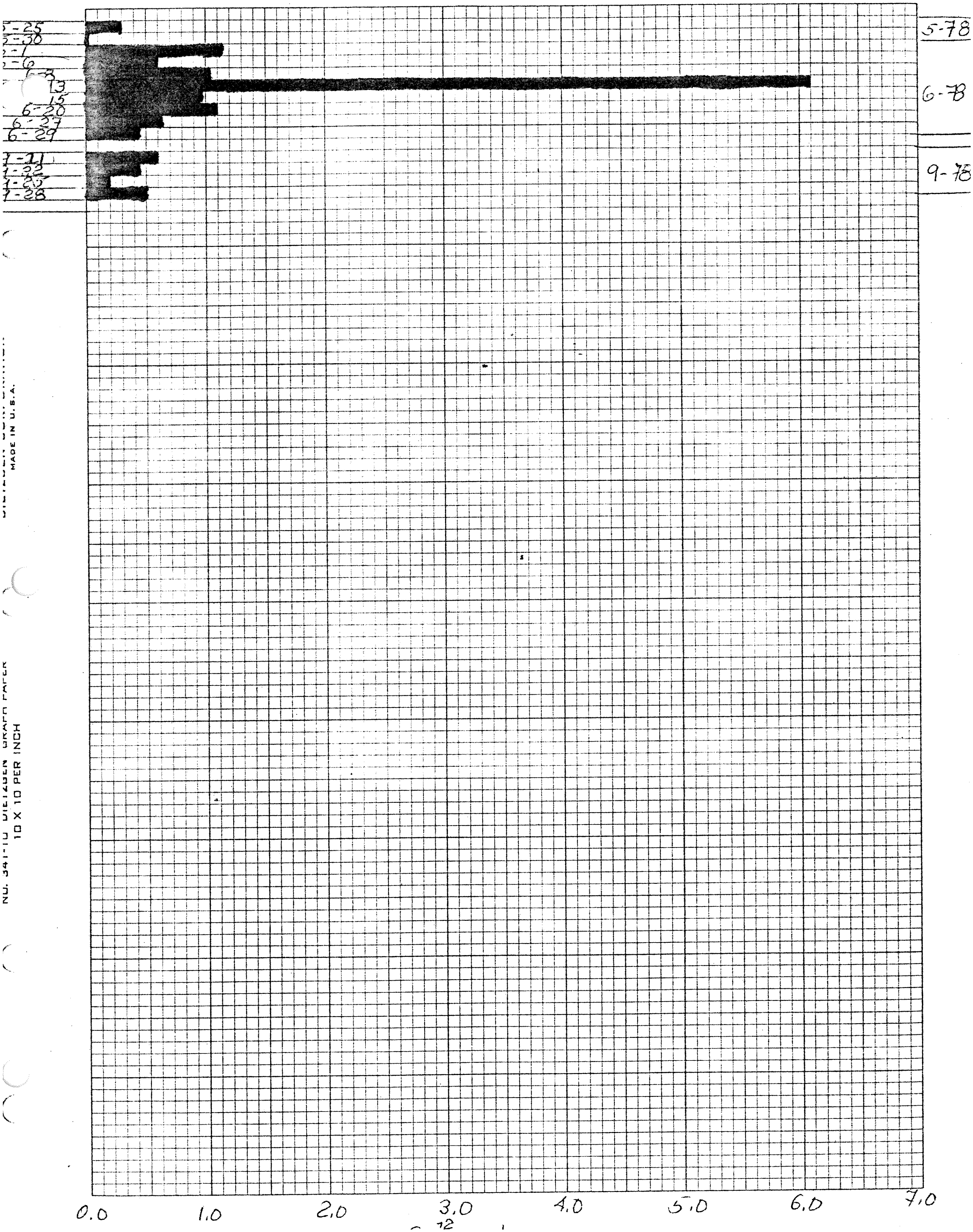
Monhegan 1977



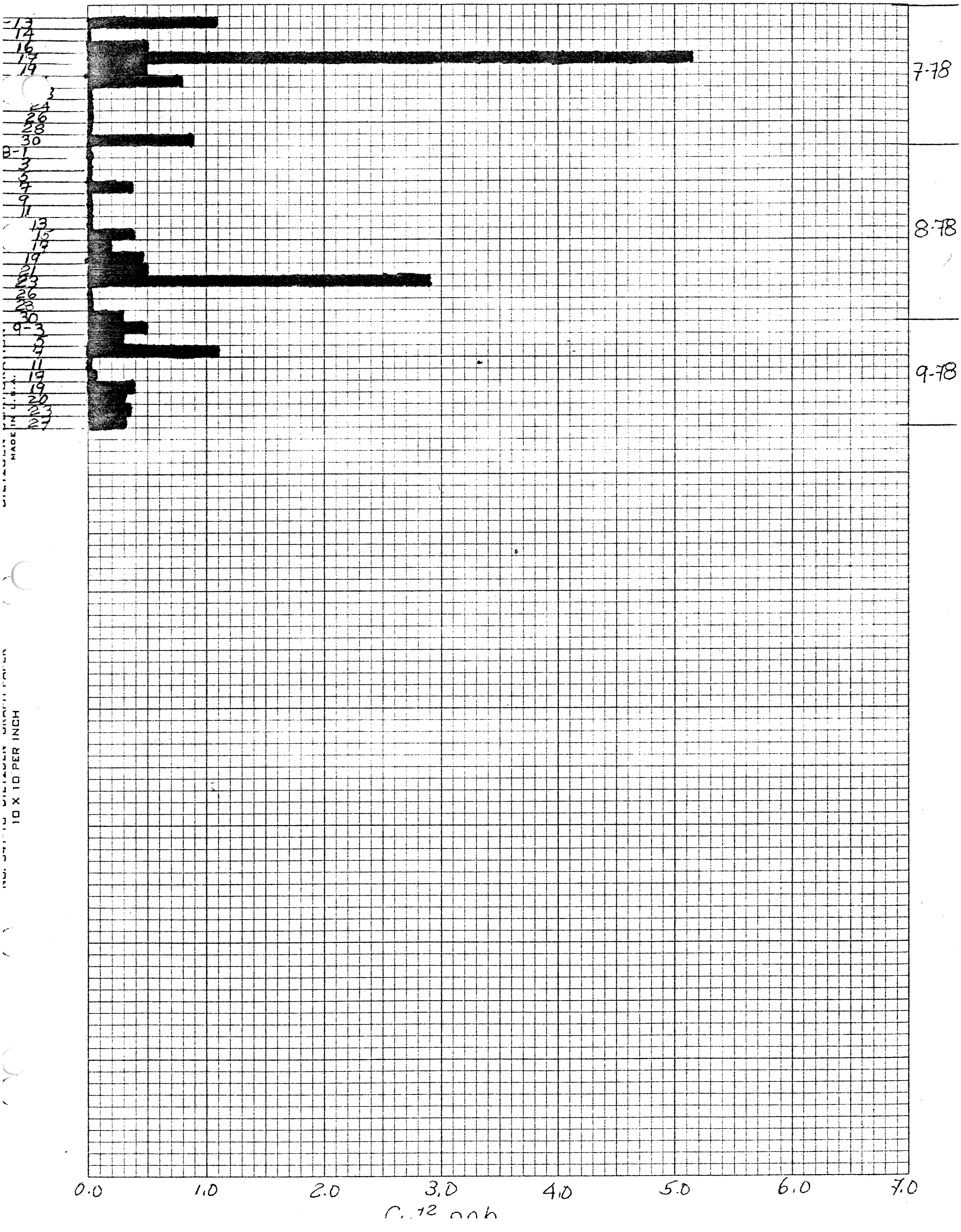
Newagen 1978 + 1979



McKown Pt. 1978



Petit Manan Pt. 1978



Provincetown 1978 + 1979