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Evaluation of the 1994 Sediment Analyses from the Miramichi Channel



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ABSTRACT

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A close relationship between the concentrations of Cd and Zn and less defined relationships between the concentrations of Cd and TOC, and the concentrations of Cd, Cu, Pb, and Zn and the proportions of sand, silt, and clay in the samples are shown. The concentrations of Cd, Hg, Cu, Pb, and Zn, expressed as percents of the total concentration, vary throughout the estuary, and the composition of samples from the dump area does not correspond to the composition of the samples from the dredge areas, both in terms of metal concentrations and sediment particle profiles. There is no relationship between the concentrations 'oil and grease' and either total PAH or phenanthrene. The analytical techniques for organic compounds must be improved. It is suggested to include Principal Component Analysis and plots of metal concentrations against geographic coordinates in future reports and additional recommendations are given.

RÉSUMÉ

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L'autre relève un rapport étroit entre les concentrations de Cd et de Zn et un rapport moins marqué entre les concentrations de Cd et le COT, et les concentrations de Cd, de Cu, de Pb et de Zn et les proportions de sable, de vase et d'argile dans les échantillons. Les concentrations de Cd, de Hg, de Cu, de Pb et de Zn, exprimées en pourcentages de la concentration totale, varient dans l'estuaire, et la composition des échantillons prélevés dans la zone d'immersion ne correspond pas à la composition des échantillons provenant des zones draguées, au niveau des concentrations de métaux et des profils des particules de sédiments. Il n'y a aucun rapport entre les concentrations d'«huiles et de graisses» et des HAP totaux ou du phénanthrène. Il faut améliorer les techniques d'analyse des composés organiques. On propose d'inclure dans les prochains rapports une analyse en composantes principales et des graphiques des concentrations de métaux en fonction des coordonnées géographiques; l'auteur formule d'autres recommandations.

INTRODUCTION

This report describes Principal Component Analysis (PCA), correlation and regression analysis, and presentation in geographic coordinates, of the composition of sediments from the Miramichi estuary, New Brunswick, Canada. The objective of the report is to detect patterns in, and to assist in the comprehension and interpretation of, the data.

PCA is a technique that reduces with a minimum loss of information, multivariate data into a form suitable for visual presentation. The visual presentation is then used to study the data and, possibly, recognize their patterns. A demonstration of the application of PCA to environmental data has been published (Zitko 1994). Correlation and regression analyses describe the relationships between variables. Data presentation in geographic coordinates emphasizes graphically the relationships between samples and the accurate positions of the sampling stations.

DATA

The 1994 Miramichi Channel sediment samples (Set A, Table 1, samples 144-185) consist of 38 samples taken between March 7 and 11, 1994 (GSC Project Number 2109595), and 143 samples (Set B, Table 1, samples 1-143) taken between May 23 and 26, 1994 (GSC Project Number 2108521). Metals (Cd, Hg, Cu, Pb, and Zn), total inorganic and organic carbon (TIC, TOC), total oil, organochlorine pesticides, and polynuclear aromatic hydrocarbons (PAH) were measured in Set A, only metals and TOC in Set B. Particle size distribution is reported in both cases. The measurements of metals in Set A were performed by the Centre for Mineral Engineering, TUNS, Halifax, and the PAH analyses were done by Enviroclean Ltd, London, Ontario. All other analyses were performed by Seatech Ltd., Halifax, NS. Laboratories involved in the analyses are not stated for Set B.

The partitioning of the sample cores for analyses is not well described for Set A. PAHs were measured in the 'inner' core, and 'grab' samples were collected and put into foil-lined, hexane-rinsed mason jars to be analyzed for all parameters except PAHs. In Set B, sections, mostly 15 cm long, of the core were analyzed separately. The length of the sections is

indicated in Table 1 (for example, 39015 is sample 39, core section 0-15 cm).

Concentrations of metals in the sediments, determined by Ocean Chem Labs and presented in the Miramichi River Environmental Assessment Committee report (93 samples) (MREAC 1989-92), are included for comparison (Set C, samples 186-278). The means and coefficients of variation of heavy metal concentrations in all three sets are given in Table 2.

METALS

A COMPARISON OF THE THREE DATA SETS

Assuming that the proportions of the five metals (the metal concentrations scaled to a sum of 100: the concentrations are in percent), are constant, it can be seen from Fig. 1 that there are systematic differences between the three data sets. As will be shown later, the clustering may be somewhat influenced by the origin of the samples, since the sets do not consist of samples from exactly the same locations. However, it is likely that the differences between the sets are larger than could be accounted for by different sampling localities. The CV's (coefficients of variation, 100 std/mean) are much higher for Set C. Further, one can see from Fig. 1 that there is a number of 'outliers' containing the metals in proportions considerably different from the majority of the samples.

CORRELATIONS OF METAL CONCENTRATIONS AND SEDIMENT PARTICLE SIZES

Table 3 gives the correlation coefficients of metal concentrations and particle sizes in the combined sets A and B. It can be seen that Cd and Zn are highly correlated and Fig. 2 shows this graphically. This relationship provides an additional tool for the detection of gross errors in the reported concentrations of cadmium and zinc.

A somewhat less well defined linear relationship exists between Cd and total organic carbon (Fig. 3). This association between cadmium and organic matter may mean a lower bioavailability of cadmium.

It can be seen further from Table 3 that concentrations of all metals except mercury are negatively correlated with the fraction of sand in the sediment, and positively correlated with the fractions of silt and clay. There is little correlation between the concentration of Hg and sediment particle size distribution.

METALS IN SEDIMENTS IN SECTIONS OF THE ESTUARY

For further evaluation, the estuary was divided into eight districts (Fig. 4) and the samples from all three sets were sorted accordingly (Table 4). The districts were evaluated by PCA to identify samples with significantly different metal profiles (metal concentrations in percent are used for this purpose). Samples identified as 'outliers' were eliminated from further evaluation. The composition of the 'outliers' is different. It may not be wrong, and it is recommended to re-sample their locations at the next opportunity.

The sample #8 (Table 4) was eliminated from the Newcastle section because of unusually high Pb concentration. The samples #3 and #4 (Table 4) were eliminated from the Chatham section for the same reason. The sample #14 (Table 4) was excluded from the Sheldrake section for the opposite reason, a too low concentration of Pb. The sample #35 in the Bay section contains an elevated concentration of Cd but was left in the set, since similar concentrations of Cd were reported elsewhere in the estuary.

Averages and standard deviations of metal concentrations in the eight districts are given in Table 5. All the data, with the means indicated by letters, are presented in Fig. 5-12 as their principal component projections. Metal concentrations for Fig. 5-8 are in mg/kg, those in Fig. 9-12 in percent.

Figures 5-12 draw the attention to, and Table 5 confirms that, the metal profiles of the sediment samples from the Channel are different from that of the dumpsites. Sediments from the latter contain considerably less Cd and more Hg than the samples from the Channel, but the differences remain even when these two metals are not considered. The concentrations and profiles of metals in the dredged and dumped sediments are different. It may be that some of the metals are leached during the dredging operations or that particle-bound metals are not deposited in the dump area. From the data quoted in

the MREAC report, the dumpsite contains sand, silt, and clay in a proportion of 14, 55, and 31%, respectively. On the other hand, the average particle size distribution of the sets A and B is 29, 52, and 19% of sand, silt, and clay, respectively. It appears that some sand and silt may be lost in dredging and dumping. As can be seen from Fig. 13-17, the metal concentrations in the sediments, with the exception of those of Hg, can be approximately estimated from the particle size distribution of the samples. From the same regression coefficients, the expected concentration of metals in the dumpsite sediment would be 0.78, 0.11, 24.8, 32.5 and 168 mg/kg, for Cd, Hg, Cu, Pb, and Zn, respectively. However, this calculated profile is different from the profiles of samples from the dump area (Fig. 18-19, sample # 18).

The discrepancy between the composition of the dredge spoils and the sediment in the dumpsite area requires further attention.

METAL CONCENTRATIONS IN GEOGRAPHIC COORDINATES

The depth profiles of metal concentrations in sediment samples in relation to the exact geographic location of the sampling stations are shown in Fig. 20-49. Since the estuary extends approximately in the west to east direction, the positions of the sampling stations were described only by their 'Easting' coordinates. On a finer grid, it may be necessary to use the 'Northing' coordinates as well. In any case, reports on sediment sampling should always include exact geographic coordinates of the sampling stations, in addition to a map. Only samples 1-143, for which the coordinates were provided in the report, were used in Fig. 20-49. The coordinates and their Northing and Easting values are given in Table 6. For a quick orientation, the approximate Easting value (in thousands) is 322 for Newcastle, 327 for Chatham, 330 for Loggieville, and 335 for Sheldrake Island.

At the top of the estuary (Easting 305, Fig. 20-25), the concentrations of Hg, Pb, and Cu are relatively constant; those of Cd, Zn and TOC are similar in the surface layer, but differ in their depth profile at the station 72. At Easting 312, (Fig. 26-31) Hg is elevated in the surface to 30 cm layer at the station 78 and may deserve a closer look at this 'spot'. Pb concentrations are relatively constant, as are those of Cu. However, the Cu depth profiles show larger and inconsistent differences. The concentrations

of Cd and Zn are also relatively constant and considerably higher in the 15-30 cm layer. The concentration of Cd in the surface of the station 75 seems unusually low. The differences in the profile of TOC at the stations 75 and 77 appear unusually high.

In the Easting 315 area (Fig. 32-37), the concentrations of Pb, Zn, and Hg, except for station 48, are quite constant. On the other hand, the concentrations of Cd, Cu, and TOC show large differences and inconsistent profiles. The situation is similar in the Easting 320 area (Fig. 38-43), again with Hg elevated at one station and those of Zn relatively constant. Cu has quite large differences in profiles and the concentrations are almost always highest in the deepest layer. Cd and TOC have considerable profile variations.

In the Easting 325 area (Fig. 44-49), the concentrations of Hg, Pb, and Zn are relatively constant. Cu and Zn show profile variations, and those for TOC are particularly large.

The presentation of the results in geographic coordinates gives a better appreciation of the situation than a simple tabular listing of values. It may help to identify 'hot spots', to detect analytical or transcription errors, and it complements the data presentation by PCA.

ORGANIC CONTAMINANTS

HYDROCARBONS

There is no correlation between the total PAH (SPA) concentration and total oil concentration (Fig. 50). Similarly, there is no correlation between the concentration of phenanthrene and total oil concentration (Fig. 51). The determined 'PAH profiles' are extremely variable. This indicates problems in the analytical technique. At the same time, the reported concentrations of 'oil' are considerable in many samples. This brings up the question of what is actually measured and reported as 'oil and grease'. This material must be further characterized, at least by its infrared spectrum.

ORGANOCHLORINE COMPOUNDS

DDT and metabolites are reported as 'not detectable', but no documentation of performance of

the laboratories in analyzing sediments for organochlorine compounds is provided.

CONCLUSIONS

On the whole, the quality of the analyses for metals seems to have improved, but there still are not good estimates of analytical as well as sampling errors. The measurements of organic contaminants are below the current state of the art.

RECOMMENDATIONS

1. Several sediment standard reference materials should be analyzed by laboratories participating in the analyses of the Miramichi sediments.
2. Station locations should be identified by geographic coordinates.
3. Analyses of 'outliers' should be repeated as a routine procedure.
4. For the purposes of environmental quality assessment, more sediment samples from the Newcastle - Chatham area should be analyzed.
5. Analytical techniques for PAH must be improved and state-of-the-art techniques for organochlorine compounds must be implemented.
6. Infrared spectra of the 'oil' extracts should be provided.
7. 'Material balance' of dredging and dumping should be evaluated.
8. Data should be routinely evaluated as described in this report.

ACKNOWLEDGMENTS

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Table 1. Sample set A (144-185) and B (1-143).

1	39015	38	494563	75	59015	112	681530	149	5
2	391530	39	50015	76	591530	113	683045	150	6
3	393043	40	501530	77	593045	114	69015	151	7
4	40015	41	503045	78	594557	115	691530	152	8
5	401530	42	504563	79	60015	116	693045	153	9
6	403041	43	51015	80	601530	117	694548	154	10
7	41015	44	511530	81	603045	118	70015	155	11
8	411519	45	513045	82	604556	119	701530	156	12
9	42015	46	514560	83	61015	120	703045	157	12R
10	421519	47	52015	84	611530	121	704560	158	13
11	43015	48	521530	85	613045	122	706078	159	14
12	431530	49	523045	86	614561	123	7105	160	15
13	433045	50	524562	87	62015	124	72015	161	16
14	434552	51	53015	88	621530	125	721530	162	17
15	44015	52	531530	89	623045	126	723045	163	18
16	441530	53	533045	90	624562	127	724557	164	19
17	443045	54	534558	91	63015	128	7405	165	20
18	444554	55	54015	92	631530	129	75015	166	21
19	45015	56	541530	93	633045	130	751530	167	21R
20	451530	57	543045	94	634560	131	753046	168	22
21	453043	58	544564	95	64015	132	76015	169	23
22	46015	59	55015	96	641530	133	761530	170	24
23	463530	60	551530	97	643045	134	763045	171	25
24	463045	61	553045	98	644554	135	764560	172	26
25	464551	62	554564	99	65015	136	766075	173	27
26	47015	63	56015	100	651530	137	77015	174	28
27	471530	64	561530	101	653045	138	771523	175	28R
28	473045	65	563045	102	654560	139	78015	176	29
29	474549	66	564558	103	656074	140	781530	177	30
30	48015	67	57015	104	66015	141	783045	178	31
31	481530	68	571530	105	661530	142	784560	179	32
32	483045	69	573045	106	663045	143	786073	180	33
33	484560	70	574556	107	664566	144	1	181	34
34	486074	71	58015	108	67015	145	2	182	35
35	49015	72	581530	109	671530	146	3	183	36
36	491530	73	583045	110	673040	147	4	184	37
37	493045	74	584558	111	68015	148	4R	185	38

Table 2. Means and coefficients of variation (CV). Symbols from Fig. 1: o - Set A; + - Set B; . - Set C.

		Set A	Set B	Set C
		144-185	1-143	186-278
		Mean		
Cadmium	Cd	0.317	0.340	0.251
Mercury	Hg	0.006	0.056	0.057
Copper	Cu	9.946	10.617	10.080
Lead	Pb	17.143	13.847	16.877
Zinc	Zn	72.588	75.141	72.734
		CV		
Cadmium	Cd	11.010	17.784	35.293
Mercury	Hg	55.748	31.742	96.441
Copper	Cu	11.301	18.756	21.105
Lead	Pb	13.323	14.418	41.464
Zinc	Zn	3.322	3.859	10.326

Table 3. Correlation coefficients of metals and particle sizes in sets A and B.

Cd	Hg	Cu	Pb	Zn	Sand	Silt	Clay
1.0000	0.3683	0.6455	0.6049	0.8858	-0.6863	0.6642	0.6671
0.3683	1.0000	0.3379	0.0007	0.3433	-0.2759	0.2367	0.2876
0.6455	0.3379	1.0000	0.5801	0.7391	-0.5867	0.5301	0.5958
0.6049	0.0007	0.5801	1.0000	0.7551	-0.5301	0.5140	0.5224
0.8858	0.3433	0.7391	0.7551	1.0000	-0.6976	0.6708	0.6755
-0.6863	-0.2759	-0.5867	-0.5301	-0.6976	1.0000	-0.9782	-0.9274
0.6642	0.2367	0.5301	0.5140	0.6708	-0.9782	1.0000	0.8557
0.6671	0.2876	0.5958	0.5224	0.6755	-0.9274	0.8557	1.0000

Table 4. Combined data sets A, B, C, sorted by location of station in the estuary.

No.	Cd mg/kg	Hg mg/kg	Cu mg/kg	Pb mg/kg	Zn mg/kg	Original designation	Local number
Newcastle							
1	0.15	0.21	34.6	72.8	372.5	76 S6-UPPER cbr	1
2	0.77	0.3	32.9	57.7	271.1	77 S7-UPPER mbr	2
3	0.88	0.43	53.4	57.6	272.5	78 S8-UPPER nw	3
4	0.16	0.23	55	57.3	379.8	84 S6-MIDDLE cbr	4
5	0.98	0.27	50	70.4	357.8	85 S7-MIDDLE mbr	5
6	0.21	0.19	14.4	24.3	82.3	86 S8-MIDDLE nw	6
7	0.15	0.09	18.6	29.9	80.6	91 S6-LOWER cbr	7
8	0.44	0.21	92.4	382.9	176.5	92 S7-LOWER mbr	8XXXXXXXXX
9	0.39	0.35	15.4	29.7	91.1	93 S8-LOWER nw	8
10	0.34	0.04	19.6	24	130	039 Newcastle	9
11	0.38	0.03	14.9	40.1	179	40	10
12	0.51	0.07	14	17	108	S19 Newcastle	11
13	0.93	0.1	21	33	158	20	12
14	0.32	0.12	34	25	95	7105	13
15	0.88	0.12	33	37	207	72015	14
16	0.73	0.07	21	27	151	721530	15
17	0.58	0.09	20	28	148	723045	16
18	0.72	0.11	30	61	187	724557	17
19	0.48	0.1	34.0	28.0	123.0	7405	18
Douglastown							
20	0.5	0.02	16	27	122	1	1
21	0.32	0.01	12	22	92	2	2
22	0.32	0.01	13	18	90	3	3
23	0.61	0.02	16	27	127	4	4
24	0.79	0.02	21	32	160	4R	5
25	0.26	0.05	6	6	46	21 Douglastown	6
26	0.31	0.09	8	7	58	22	7
27	1.1	0.07	25	39	206	23	8
28	0.56	0.1	20	21	117	24	9
29	0.47	0.06	15	34.9	150	41	10
30	0.44	0.05	15.3	23.4	112	42	11
31	0.23	0.02	6.9	12.5	71.5	43	12
32	0.18	0.01	6.4	10.1	58.9	44 Douglastown	13
33	0.16	0.01	6.9	10.1	60.9	45	14
34	0.71	0.07	19.1	36.4	181	46	15
35	0.21	0.01	7	11.2	72.1	47	16
36	0.18	0.01	7.1	11.6	66.4	48	17
37	0.28	0.1	11	18	82	39015	18
38	0.14	0.08	11	11	58	391530	19
39	0.23	0.08	9	12	64	393043	20
40	0.22	0.07	11	12	62	40015	21
41	0.24	0.08	10	15	63	401530	22
42	0.22	0.07	8.0	12.0	60.0	403041	23

Table 4. (cont'd)

No.	Cd mg/kg	Hg mg/kg	Cu mg/kg	Pb mg/kg	Zn mg/kg	Original designation	Local number
Chatham							
43	0.99	0.12	27.5	44	246	49 below CH.	1
44	0.65	0.12	29	223.0	146	50	3XXXXXXXXX
45	0.48	0.11	20	84	127	51	4XXXXXXXXX
46	0.62	0.05	13	23.4	138	52	2
47	0.48	0.11	35	25	147	75015	3
48	0.97	0.12	33	33	220	751530	4
49	0.93	0.12	26	34	180	753046	5
50	0.95	0.14	21	32	226	76015	6
51	1.06	0.1	28	36	217	761530	7
52	0.94	0.08	30	36	207	763045	8
53	1.1	0.07	28	38	200	764560	9
54	1.05	0.07	39	36	210	766075	10
55	0.98	0.18	22	33	176	77015	11
56	1	0.08	35	40	217	771523	12
57	1.05	0.32	30	40	204	78015	13
58	1.06	0.32	27	40	224	781530	14
59	1.03	0.15	38	40	211	783045	15
60	0.91	0.08	30	37	180	784560	16
61	1.06	0.08	26.0	40.0	191.0	786073	17
'Middle'							
62	0.46	0.08	13	21	91	25 Midw Ch/L.N	1
63	0.48	0.1	15	22	101	26	2
64	0.8	0.1	18	27	154	27	3
65	0.2	0.07	7	12	56	28	4
66	0.15	0.03	7	7	52	29	5
67	0.28	0.06	10	12	81	30	6
68	0.62	0.04	17	25	140	31	7
69	0.25	0.05	8	10	68	32	8
70	0.45	0.08	12	20	104	41015	9
71	0.58	0.13	15	15	122	411519	10
72	0.26	0.06	8	16	70	42015	11
73	0.13	0.08	7	16	49	421519	12
74	0.61	0.09	15	21	126	43015	13
75	0.76	0.08	22	26	161	431530	14
76	0.65	0.06	18	28	161	433045	15
77	0.89	0.07	28	32	177	434552	16
78	0.62	0.08	18	27	132	44015	17
79	0.66	0.09	15	18	131	441530	18
80	0.6	0.1	19	26	143	443045	19
81	0.62	0.09	20	22	141	444554	20
82	0.53	0.09	14	14	100	45015	21
83	0.6	0.1	17	16	129	451530	22
84	0.62	0.1	22	21	146	453043	23
85	0.31	0.09	8	13	74	46015	24
86	0.47	0.1	10.0	15.0	100.0	461530	25

Table 4. (cont'd)

No.	Cd mg/kg	Hg mg/kg	Cu mg/kg	Pb mg/kg	Zn mg/kg	Original designation	Local number
'Middle'							
87	0.47	0.08	13	18	110	463045	26
88	0.96	0.12	24	25	214	464551	27
89	0.35	0.08	12	11	90	47015	28
90	0.57	0.09	15	20	114	471530	29
91	0.67	0.12	25	30	168	473045	30
92	0.49	0.08	17	21	110	474549	31
93	0.65	0.12	20	28	145	48015	32
94	0.76	0.11	20	33	163	481530	33
95	0.85	0.08	21	33	181	483045	34
96	0.78	0.2	24	30	170	484560	35
97	0.83	0.12	22	28	160	486074	36
98	0.51	0.005	12	21	100	5	37
99	0.71	0.005	19	26	141	6	38
100	0.34	0.005	11	13	84	7	39
101	0.72	0.02	21	23	150	8	40
102	0.37	0.005	12	23	93	9	41
103	0.71	0.005	19	36	145	10	42
104	0.35	0.005	15	28	89	11	43
105	0.56	0.01	18	32	137	12	44
106	0.73	0.01	21	33	158	12R	45
107	0.22	0.005	9	12	58	13	46
108	0.43	0.005	15	36	106	14	47
109	0.48	0.01	17	29	105	15	48
110	0.52	0.01	15	26	110	16	49
111	0.46	0.02	14	27	107	17	50
112	0.5	0.005	17	27	112	18	51
113	0.75	0.005	22	37	158	19	52
114	0.48	0.005	16	26	106	20	53
115	0.23	0.04	10	17	67	33	54
116	0.24	0.02	8	9	65	34	55
117	0.65	0.09	14	21	118	35	56
118	0.25	0.05	11	13	70	36	57
119	0.14	0.02	8.1	20.5	61.7	53	58
120	1.31	0.15	42.2	58.2	350	54	59
121	0.66	0.11	18.9	33.4	158	55	60
122	0.24	0.02	9.1	19.5	84.3	56	61
Loggieville							
123	0.48	0.05	12.1	28.7	118	57 Loggieville	1
124	0.43	0.05	14.1	23.7	114	58	2
125	0.3	0.02	9.4	20.6	89.9	59	3
126	0.45	0.04	13.2	25	120	60	4
127	0.44	0.04	13	26.4	118	61	5
128	0.78	0.09	23.7	37.5	194	62	6
129	0.61	0.19	16.9	30	142	63	7
130	0.63	0.04	18.2	29.4	146.0	64	8

Table 4. (cont'd)

No.	Cd mg/kg	Hg mg/kg	Cu mg/kg	Pb mg/kg	Zn mg/kg	Original designation	Local number
Loggieville							
131	0.47	0.04	14.1	22.5	121	65	9
132	0.79	0.08	23.2	38.6	198	66	10
133	0.57	0.005	19	36	125	21	11
134	0.6	0.005	20	34	141	21R	12
135	0.43	0.01	21	33	101	22	13
136	0.47	0.01	14	25	110	23	14
137	0.56	0.01	20	33	126	24	15
138	1.01	0.02	22	91	317	25	16
139	0.49	0.02	16	23	118	26	17
140	0.65	0.01	22	31	158	27	18
141	0.68	0.005	21	32	155	28	19
142	0.72	0.005	19	33	148	28R	20
143	0.57	0.02	16	32	122	29	21
144	0.7	0.005	18	35	146	30	22
145	0.77	0.005	21	38	164	31	23
146	0.81	0.005	22	40	164	32	24
147	0.73	0.09	21	29	148	49015	25
148	0.8	0.11	22	31	155	491530	26
149	0.75	0.12	20	28	161	493045	27
150	0.76	0.1	23	30	169	494563	28
151	0.79	0.11	16	26	139	50015	29
152	0.75	0.1	18	27	147	501530	30
153	0.7	0.13	16	26	124	503045	31
154	0.57	0.11	21	25	140	504563	32
155	0.58	0.1	14	22	118	51015	33
156	0.82	0.11	19	24	155	511530	34
157	0.78	0.12	20	32	167	513045	35
158	0.73	0.1	24	28	175	514560	36
159	0.61	0.12	18	25	137	52015	37
160	0.68	0.14	18	25	160	521530	38
161	0.66	0.11	19	25	162	523045	39
162	0.78	0.12	23	25	172	524562	40
163	0.58	0.12	16	25	130	53015	41
164	0.76	0.13	20	30	153	531530	42
165	0.84	0.11	20	36	170	533045	43
166	0.62	0.1	23	29	176	534558	44
167	0.6	0.12	16	25	128	54015	45
168	0.77	0.1	18	26	150	541530	46
169	0.84	0.12	19	30	175	543045	47
170	0.65	0.1	22	25	163	544564	48
171	0.92	0.13	20	31	171	55015	49
172	0.6	0.12	18	28	140	551530	50
173	0.92	0.12	21	29	166	553045	51
174	0.72	0.04	16	26	123	554564	52
175	0.75	0.11	20	29	155	56015	53
176	0.76	0.1	19.0	27.0	147.0	561530	54

Table 4. (cont'd)

No.	Cd mg/kg	Hg mg/kg	Cu mg/kg	Pb mg/kg	Zn mg/kg	Original designation	Local number
Loggieville							
177	0.86	0.11	21	31	160	563045	55
178	0.67	0.1	23	26	153	564558	56
179	0.8	0.1	16	24	135	57015	57
180	0.61	0.09	20	29	177	571530	58
181	0.78	0.1	22	34	175	573045	59
182	0.84	0.1	25	36	183	574556	60
183	0.72	0.1	20	21	146	58015	61
184	0.83	0.09	24	28	184	581530	62
185	0.7	0.07	22	35	173	583045	63
186	0.93	0.09	23	32	186	584558	64
187	0.65	0.1	20	26	147	59015	65
188	0.73	0.08	21	26	181	591530	66
189	0.81	0.09	23	30	174	593045	67
190	0.82	0.12	23	29	166	594557	68
191	0.61	0.1	18	20	121	60015	69
192	0.75	0.12	19	24	154	601530	70
193	0.28	0.06	14	14	82	603045	71
194	0.39	0.12	15	18	97	604556	72
195	0.49	0.01	16	35	125	33	73
196	0.57	0.02	17	29	123	34	74
197	0.55	0.01	19	30	138	35	75
198	0.5	0.01	16	25	114	36	76
199	0.54	0.01	17	35	129	37	77
200	0.53	0.01	17.0	33.0	129.0	38	78
Sheldrake							
201	0.19	0.02	9.3	12.7	73.2	67 Sheldr I	1
202	0.65	0.06	18.5	34.4	161	68	2
203	0.39	0.04	12.7	26.9	105	69	3
204	0.35	0.04	12	27.7	102	70	4
205	0.61	0.06	17	26	124	37	5
206	0.64	0.06	17	25	131	38 SheldrI	6
207	0.84	0.04	21.1	49.3	177	1 off Sheldr	17
208	0.66	0.03	16.8	29.1	147	2 "	18
209	0.26	0.02	9.3	18	74.6	3 "	19
210	0.52	0.04	16.2	29.8	116	4 Oak Pt	10
211	0.51	0.05	20.8	27.3	146	5	11
212	0.6	0.03	19.1	33.1	146	6	12
213	0.34	0.03	14.8	19.7	102	7	13
214	0.38	0.02	9.7	10.5	118	8 Grab sample	14XXXXXXXXXX
215	0.55	0.05	17.7	35.1	131	9	14
216	0.51	0.04	19.3	31.8	137	10 Grand Dune I	15
217	0.31	0.04	17.1	30.6	102	11 "	16
218	0.41	0.04	20.1	31.8	146	12	17
219	0.26	0.04	21.2	29.1	118	13	18
220	0.35	0.04	19.4	34.2	124.0	14	19

Table 4. (cont'd)

No.	Cd mg/kg	Hg mg/kg	Cu mg/kg	Pb mg/kg	Zn mg/kg	Original designation	Local number
Bay							
225	0.6	0.08	19	23	132	61015	1
226	0.58	0.12	19	23	131	611530	2
227	0.74	0.1	22	30	166	613045	3
228	0.63	0.11	24	30	152	614561	4
229	0.6	0.1	20	26	139	62015	5
230	0.68	0.09	19	29	160	621530	6
231	0.65	0.1	20	26	147	623045	7
232	0.69	0.1	20	27	153	624562	8
233	0.55	0.09	17	25	133	63015	9
234	0.67	0.1	22	28	152	631530	10
235	0.71	0.11	22	29	168	633045	11
236	0.48	0.09	17	20	109	634560	12
237	0.7	0.1	23	27	154	64015	13
238	0.69	0.09	30	32	152	641530	14
239	0.59	0.1	22	27	149	643045	15
240	0.64	0.09	20	27	151	644564	16
241	0.55	0.1	22	25	147	65015	17
242	0.6	0.1	20	30	146	651530	18
243	0.67	0.1	20	36	145	653045	19
244	0.4	0.1	18	37	118	654560	20
245	0.75	0.08	18	36	134	656074	21
246	0.66	0.12	27	30	156	66015	22
247	0.71	0.11	22	28	153	661530	23
248	0.8	0.1	21	30	145	663045	24
249	0.77	0.1	22	28	160	664566	25
250	0.7	0.09	19	27	141	67015	26
251	0.65	0.11	19	23	140	671530	27
252	0.59	0.12	20	23	133	673040	28
253	0.54	0.14	18	24	119	68015	29
254	0.7	0.12	21	24	139	681530	30
255	0.63	0.07	21	24	143	683045	31
256	0.47	0.07	14	16	108	69015	32
257	0.9	0.06	23	32	174	691530	33
258	0.52	0.1	29	40	149	693045	34
259	0.76	0.1	13	22	76	694548	35
260	0.3	0.11	28	40	168	70015	36
261	0.34	0.08	18	21	98	701530	37
262	0.34	0.08	14	10	71	703045	38
263	0.38	0.08	11	18	113	704560	39
264	0.3	0.07	27.0	18.0	81.0	706078	40

Table 4. (cont'd)

No.	Cd mg/kg	Hg mg/kg	Cu mg/kg	Pb mg/kg	Zn mg/kg	Original designation	Local number
Dumpsite							
221	0.47	0.04	16.6	28.5	117	15 Dumps 6B	1
222	0.35	0.03	14.7	19	93.8	16 7B	2
223	0.26	0.03	16.8	17.5	99.4	17 10B	3
224	0.26	0.02	14.6	12.4	79.4	18 13A	4
265	0.19	0.27	12.6	23.9	97.6	71 S1-UPPER db	5
266	0.14	0.21	19.8	28	107.3	72 S2-UPPER db	6
267	0.13	0.24	22.3	30	125.7	73 S3-UPPER db	7
268	0.23	0.3	24.3	36.8	166.3	74 S4-UPPER db	8
269	0.25	0.18	18.1	26.4	124.5	75 S5-UPPER db	9
270	0.17	0.2	17.8	21.1	69.1	80 S2-MIDDLE db	10
271	0.14	0.2	16.8	24.3	83.8	81 S3-MIDDLE db	11
272	0.17	0.15	19.8	26.3	91.6	82 S4-MIDDLE db	12
273	0.16	0.08	11.2	17.6	69.6	83 S5-MIDDLE db	13
274	0.12	0.13	18.2	21.8	80.1	87 S2-LOWER db	14
275	0.13	0.15	18.2	20.6	78.4	88 S3-LOWER db	15
276	0.11	0.15	11	17.1	46.6	89 S4-LOWER db	16
277	0.15	0.08	9.1	14.4	69.2	90 S5-LOWER db	17

XXXXXXX = eliminated 'outliers'.

Table 5. Means and standard deviations of metal concentrations in parts of Miramichi estuary.

Cd	Hg	Cu	Pb	Zn	Portion of estuary
Mean concentrations in mg/kg					
0.5867	0.1622	28.6556	39.9889	188.5389	N Newcastle
0.3774	0.0483	12.2043	18.6609	94.7739	D Douglastown
0.9518	0.1288	28.7353	35.7294	199.6471	C Chatham
0.5334	0.0632	15.9066	23.0426	120.7705	M 'Middle'
0.6691	0.0756	18.9744	29.3897	148.5115	L Loggieville
0.4711	0.0405	16.8105	29.0316	124.3579	S Sheldrake
0.6057	0.0970	20.5250	26.7750	137.6250	B Bay
0.2018	0.1447	16.5824	22.6882	94.0824	V Dumpsite
Standard deviations					
0.3048	0.1135	13.3972	17.7282	100.8047	N Newcastle
0.2406	0.0331	5.3629	9.8640	44.4632	D Douglastown
0.1625	0.0792	6.4520	5.3940	28.2178	C Chatham
0.2283	0.0455	6.1649	8.7812	48.0056	M 'Middle'
0.1482	0.0465	3.2329	8.6125	31.5132	L Loggieville
0.1717	0.0118	3.6789	7.6317	27.2413	S Sheldrake
0.1409	0.0162	4.0445	6.1748	24.6490	B Bay
0.0947	0.0873	4.0429	6.2517	28.2257	V Dumpsite
Mean concentrations in %					
0.2417	0.0695	11.6875	16.1070	71.8943	N Newcastle
0.2885	0.0458	9.8696	14.3892	75.4069	D Douglastown
0.3586	0.0483	10.8523	13.4832	75.2575	C Chatham
0.3246	0.0412	9.9184	14.5890	75.1268	M 'Middle'
0.3386	0.0386	9.6892	14.8883	75.0454	L Loggieville
0.2709	0.0239	9.8777	16.9460	72.8814	S Sheldrake
0.3298	0.0537	11.1766	14.3913	74.0486	B Bay
0.1545	0.1090	12.6174	17.1244	69.9947	V Dumpsite
Standard deviations					
0.0957	0.0571	3.6875	3.3820	5.2518	N Newcastle
0.0717	0.0385	1.6670	1.9944	2.4040	D Douglastown
0.0441	0.0278	2.3192	1.1366	2.4326	C Chatham
0.0540	0.0284	0.9380	3.1647	3.2053	M 'Middle'
0.0463	0.0241	1.0777	2.2806	2.2832	L Loggieville
0.0609	0.0057	1.0910	2.1562	2.3184	S Sheldrake
0.0766	0.0123	2.0955	2.1809	3.0154	B Bay
0.0631	0.0605	2.1340	2.5955	3.9242	V Dumpsite

Table 6. Geographical coordinates of stations 39-77.

Station	Easting	Northing	Reach
39	310138	5210265	6
40	310620	5210386	7 widener
41	315701	5215053	12
42	315884	5215095	12
43	315941	5215131	12
44	315991	5215124	12
45	316088	5215173	12
46	316134	5215175	12
47	316182	5215199	12
48	316461	5215226	13 widener
49	320586	5217134	16 widener
50	320904	5217027	16
51	321144	5217006	16
52	321150	5216995	16
53	321214	5216984	16
54	321366	5216948	16
55	321408	5216978	16
56	321358	5216989	16
57	321478	5216938	16
58	321563	5216914	16
59	321630	5216902	16
60	321755	5216880	16
61	325520	5216958	17
62	325016	5216763	17
63	325076	5216776	17
64	325263	5216859	17
65	325266	5216850	17
66	325422	5216910	17
67	325469	5216940	17
68	325861	5217037	18 widener
69	326222	5217891	18
70	327240	5219182	19
71	305215	5208480	Newcastle berth
72	305245	5208240	Newcastle berth
73	305220	5208412	Newcastle berth
74	312535	5212015	Chatham berth
75	312610	5212180	Chatham berth
76	312570	5212100	Chatham berth
77	312595	5212143	Chatham berth

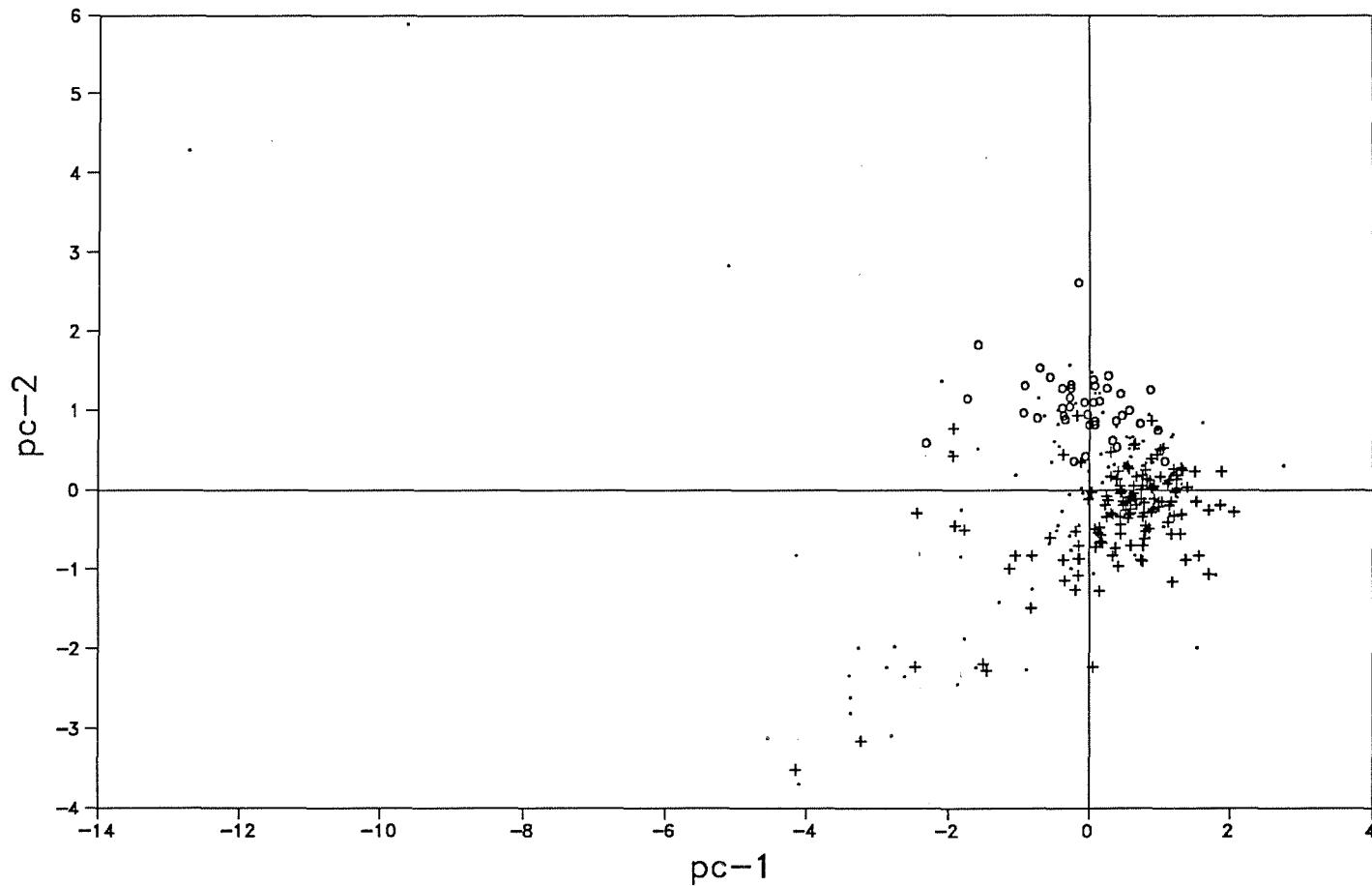
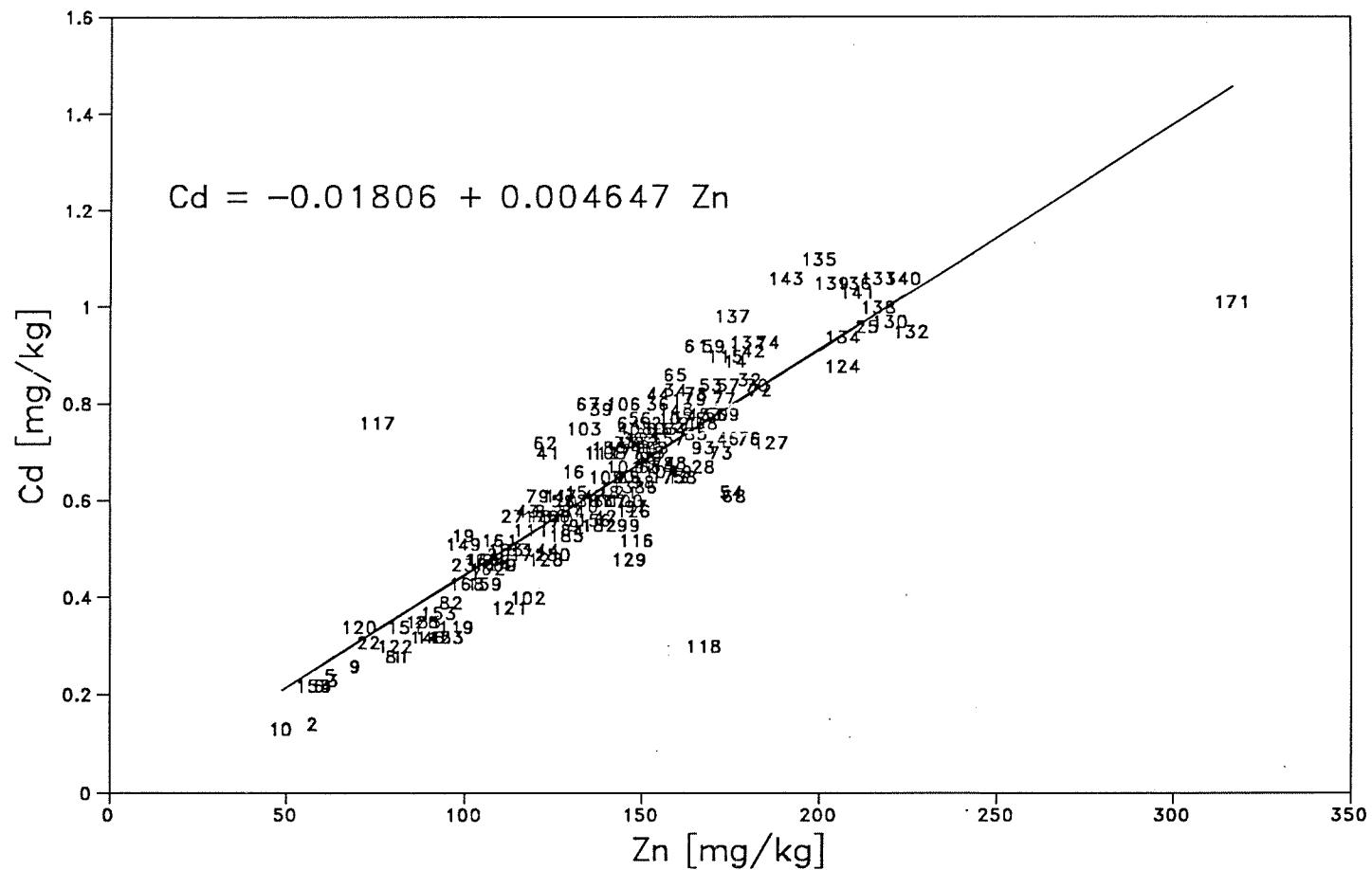
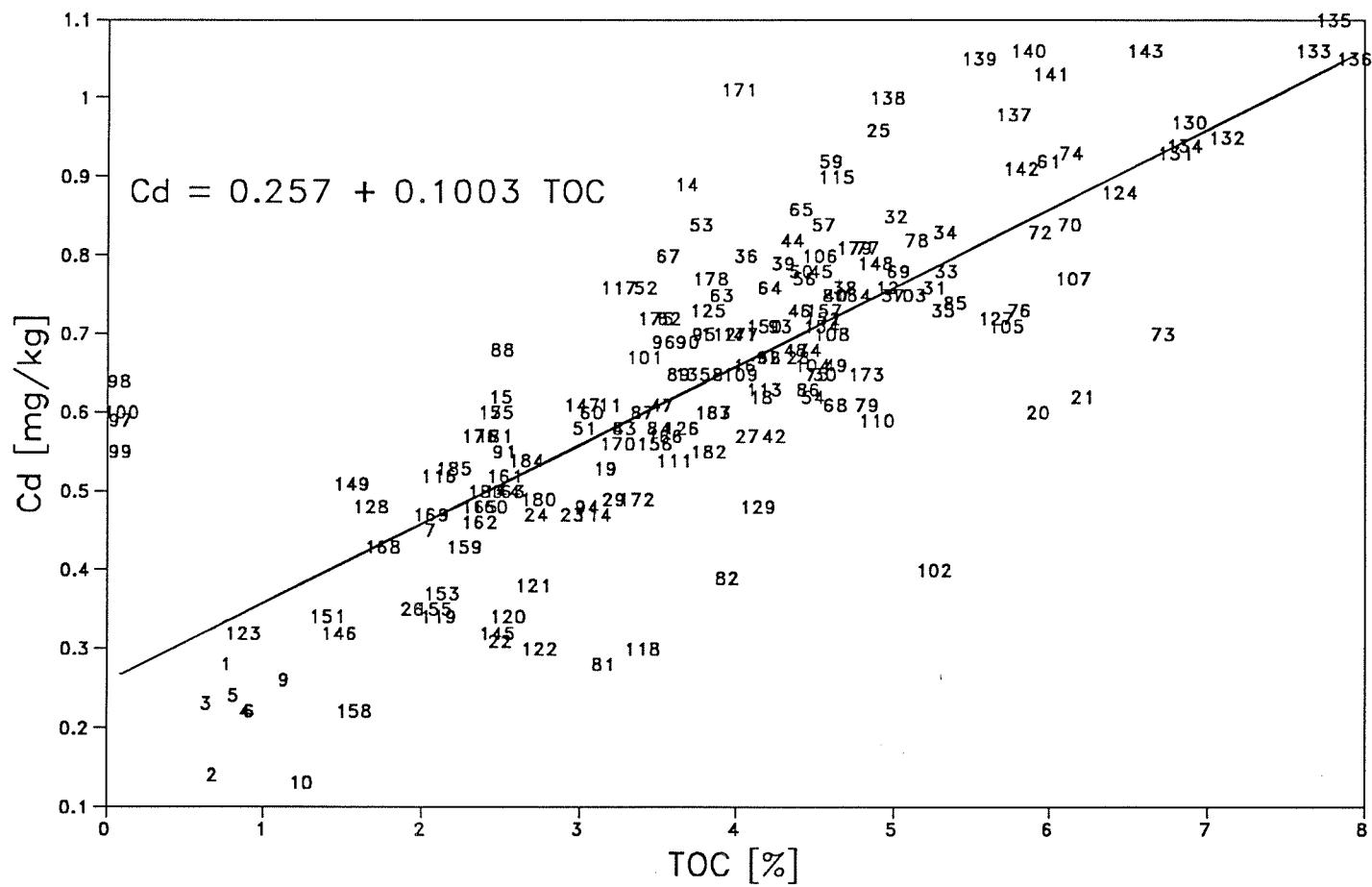


Fig. 1. Concentration of Cd, Hg, Cu, Pb, and Zn expressed in percent of their total, projected on the plane of the principal components pc1 and pc2. Samples from sets A, B and C are indicated by 'o', '+' and '.', respectively.





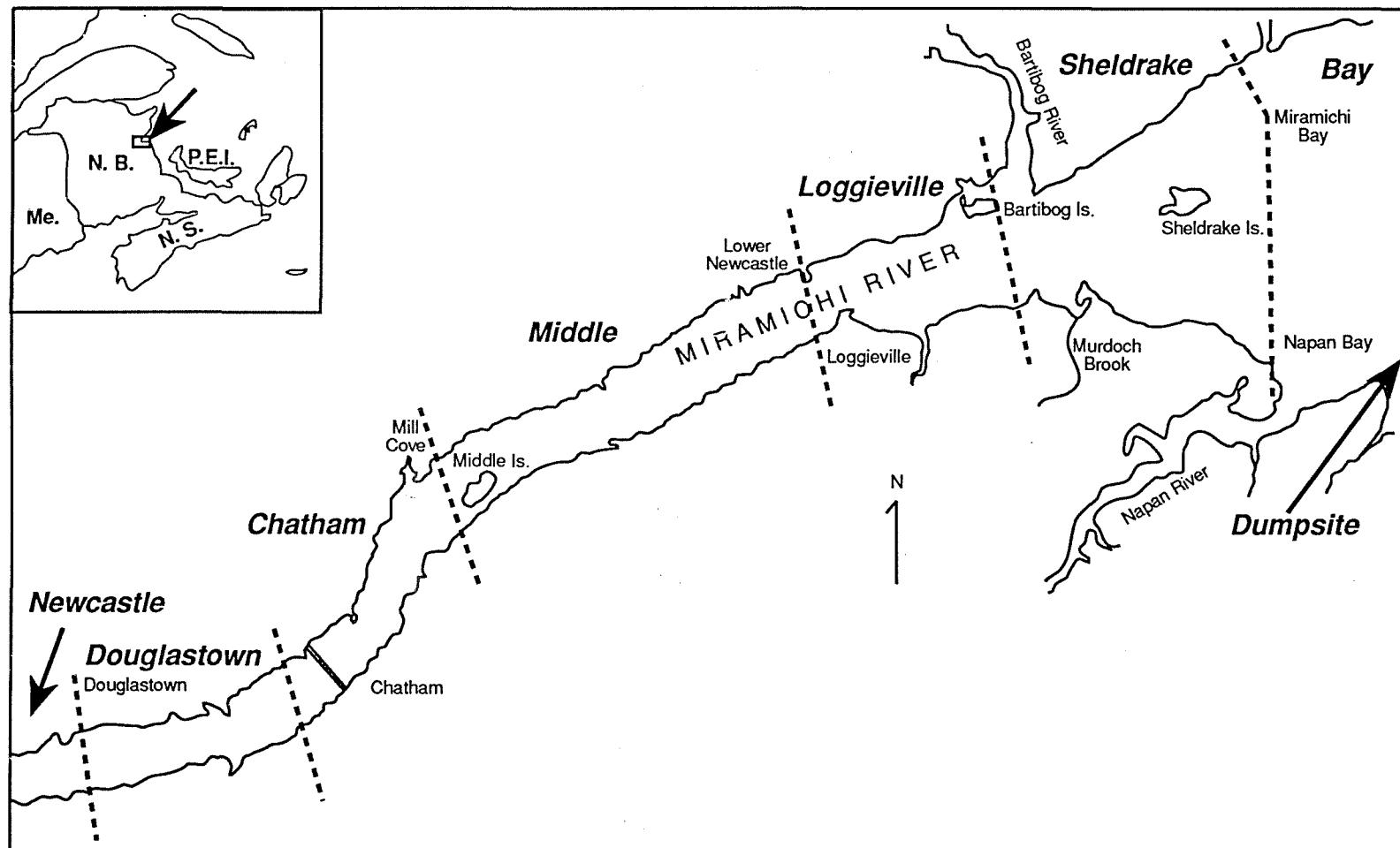


Fig. 4. Sections of the Miramichi estuary.

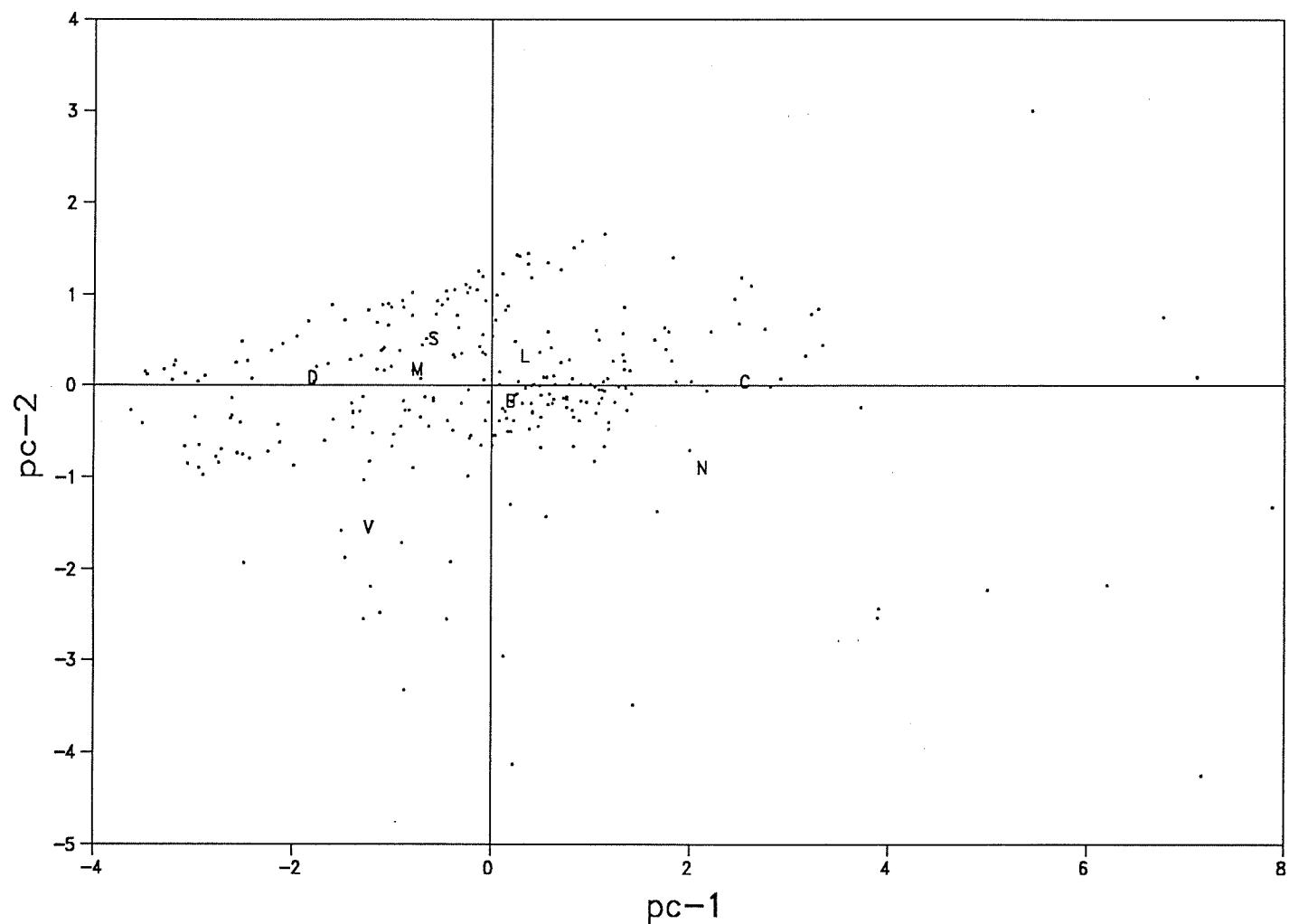


Fig. 5. Concentration of Cd, Hg, Cu, Pb, and Zn in combined sets A, B, and C, projected on the plane of the principal components pc1 and pc2. Letters indicate means for the sections of the estuary: N = Newcastle, D = Douglastown, C = Chatham, M = 'Middle', L = Loggieville, S = Sheldrake, B = Bay, V = Dumpsite. See also Table 5.

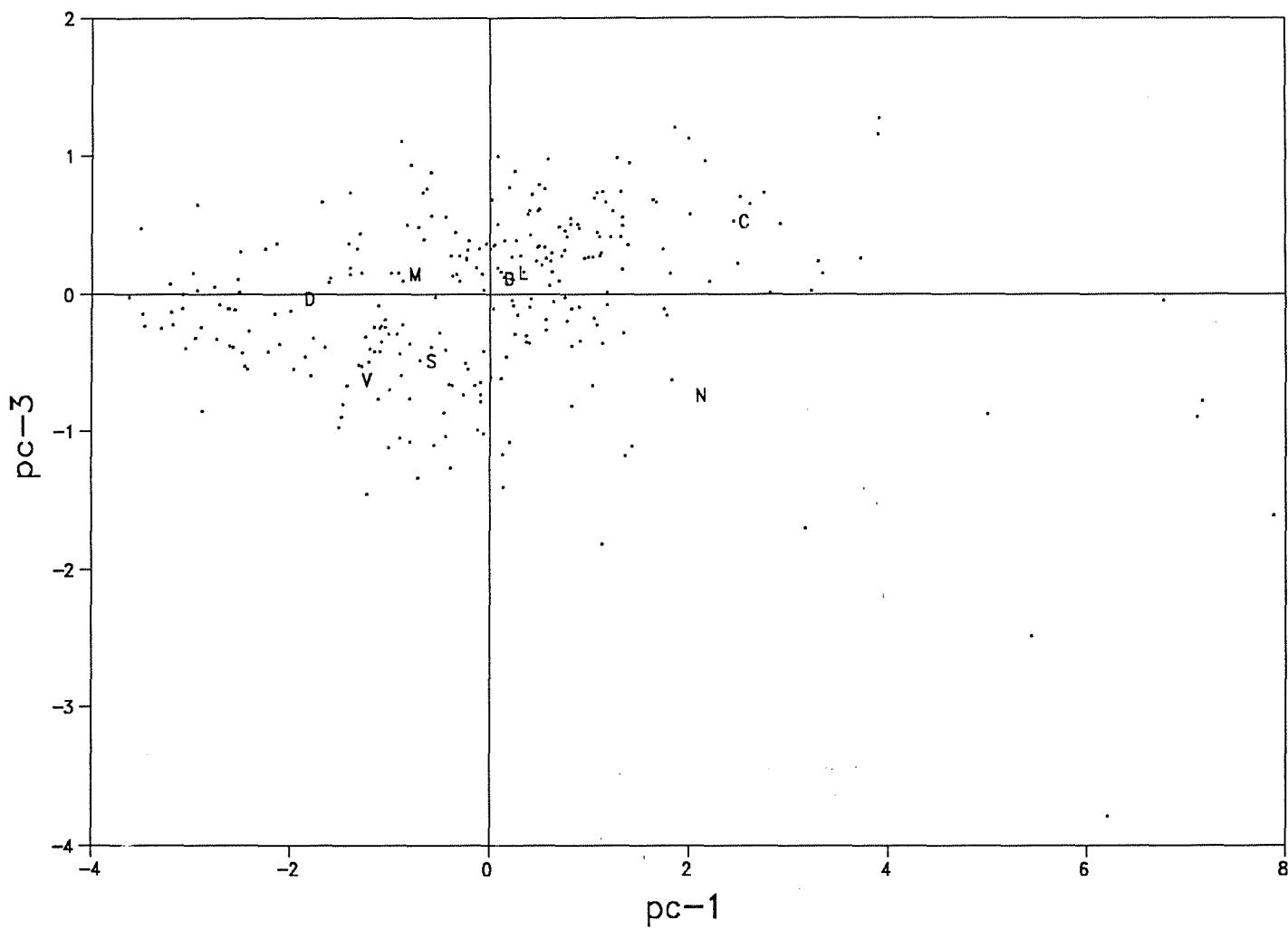


Fig. 6. Concentration of Cd, Hg, Cu, Pb, and Zn in combined sets A, B, and C, projected on the plane of the principal components pc1 and pc3. For further details see Fig. 5.

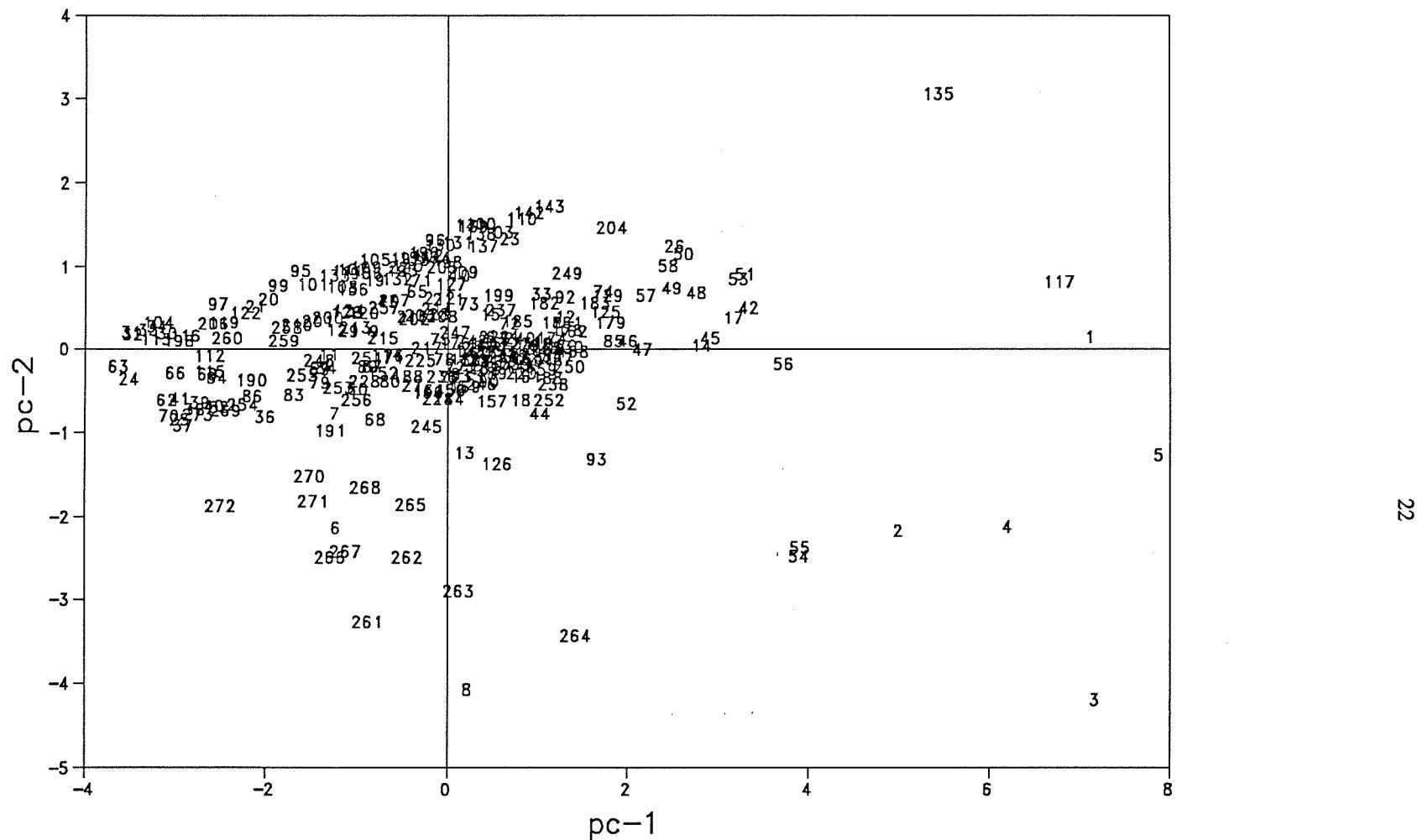


Fig. 7. Concentration of Cd, Hg, Cu, Pb, and Zn in combined sets A, B, and C, projected on the plane of the principal components pc1 and pc2. Samples are identified by numbers in Table 4.

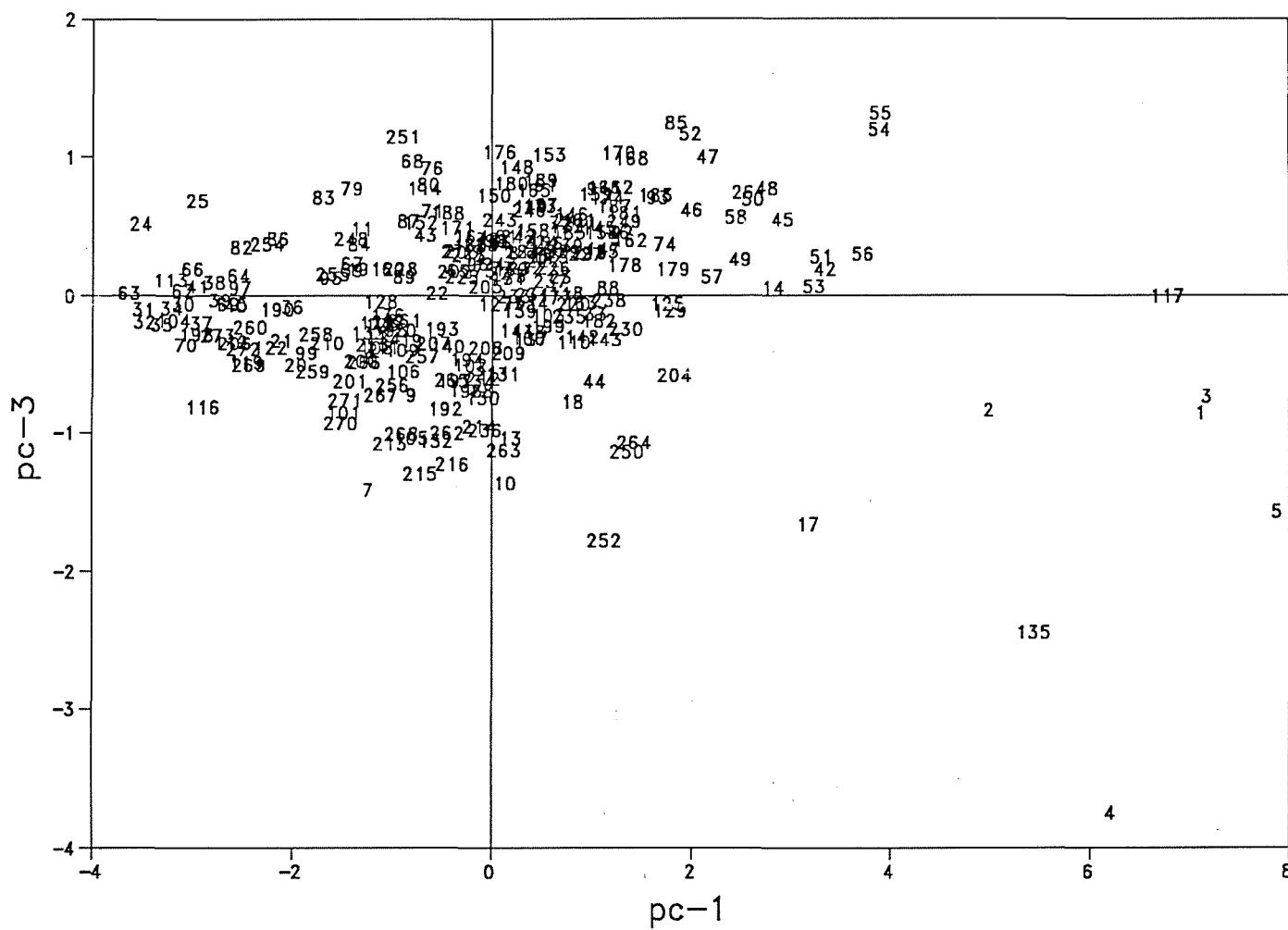


Fig. 8. Concentration of Cd, Hg, Cu, Pb, and Zn in combined sets A, B, and C, projected on the plane of the principal components pc1 and pc3. Samples are identified by numbers in Table 4.

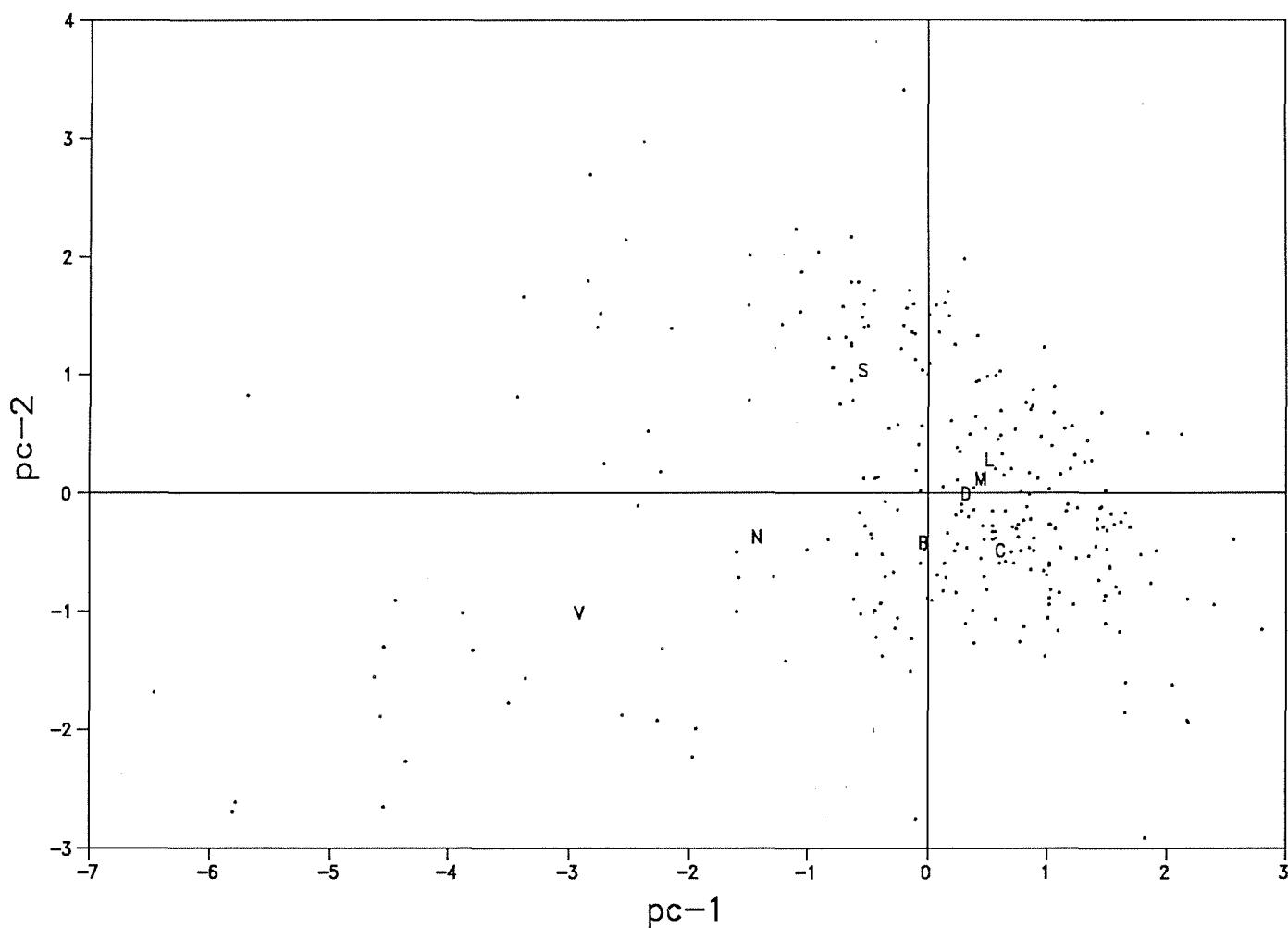


Fig. 9. Concentration of Cd, Hg, Cu, Pb, and Zn in combined sets A, B, and C, projected on the plane of the principal components pc1 and pc2. Same as Fig. 5, except that the concentrations of metals are expressed in percent of the total concentration.

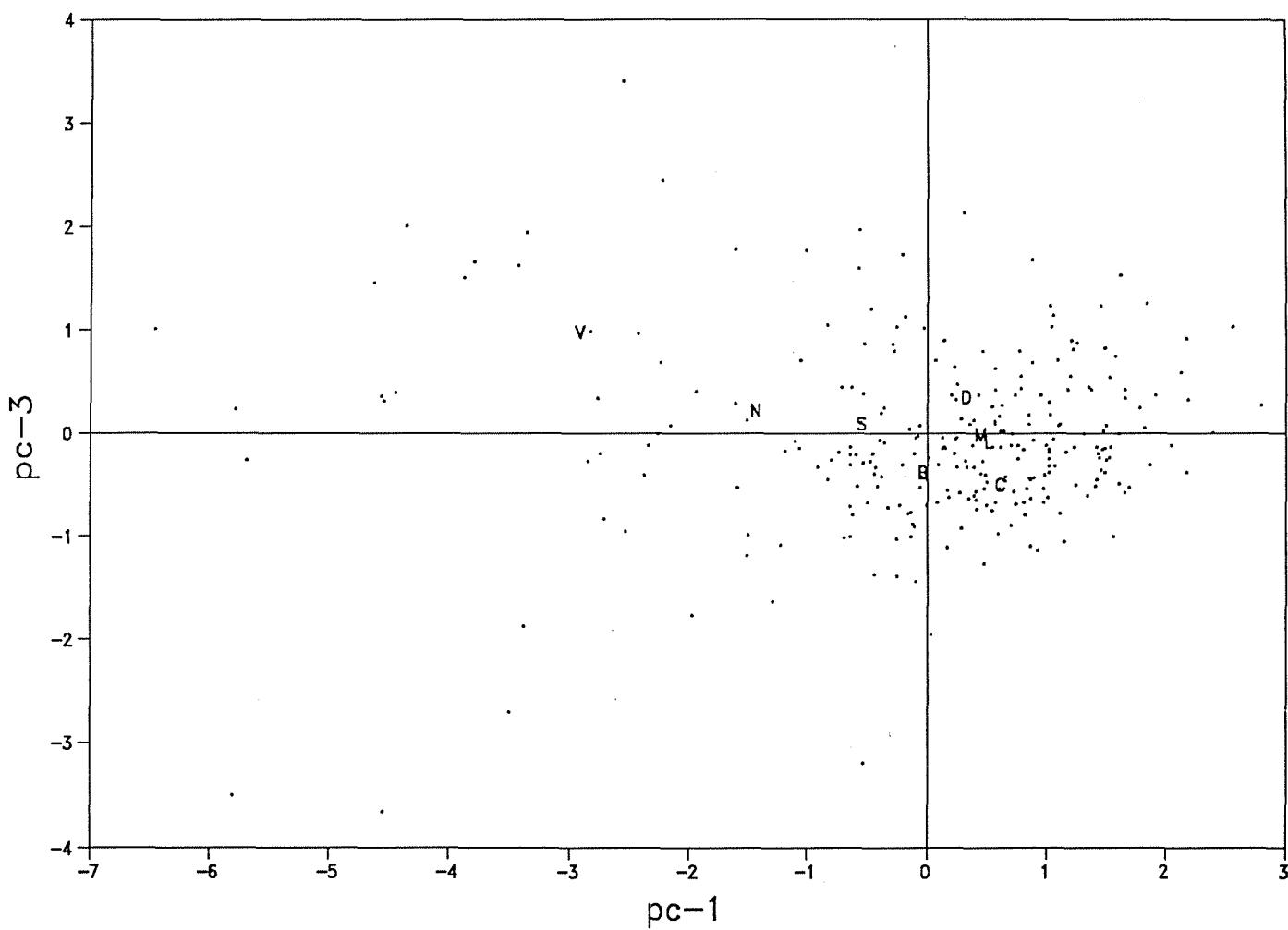


Fig. 10. Concentration of Cd, Hg, Cu, Pb, and Zn in combined sets A, B, and C, projected on the plane of the principal components pc1 and pc3. Same as Fig. 5, except that the concentrations of metals are expressed in percent of the total concentration.

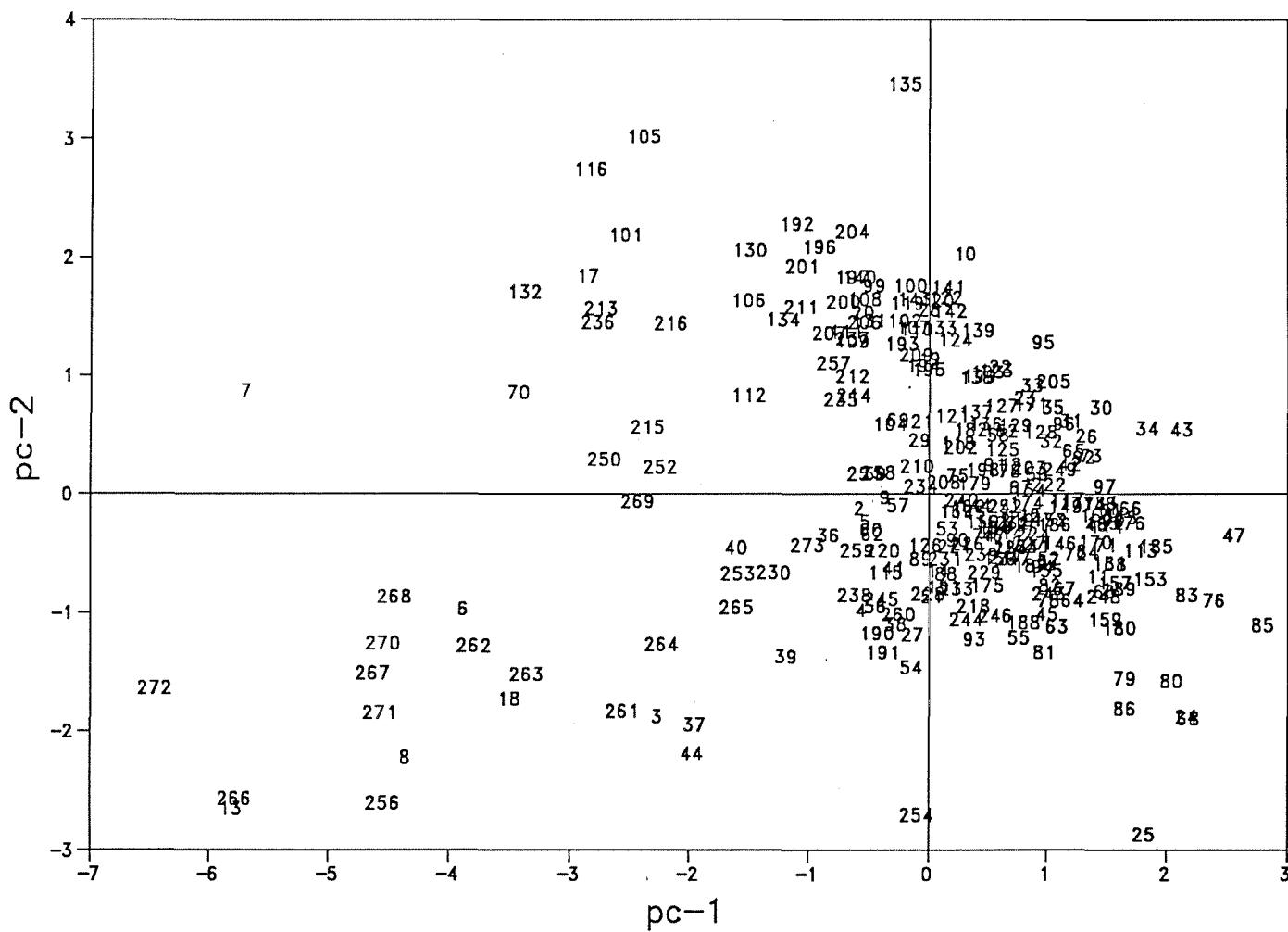


Fig. 11. Concentration of Cd, Hg, Cu, Pb, and Zn in combined sets A, B, and C, projected on the plane of the principal components pc1 and pc2. Same as Fig. 5, except that the concentrations of metals are expressed in percent of the total concentration. Samples are identified by numbers in Table 4.

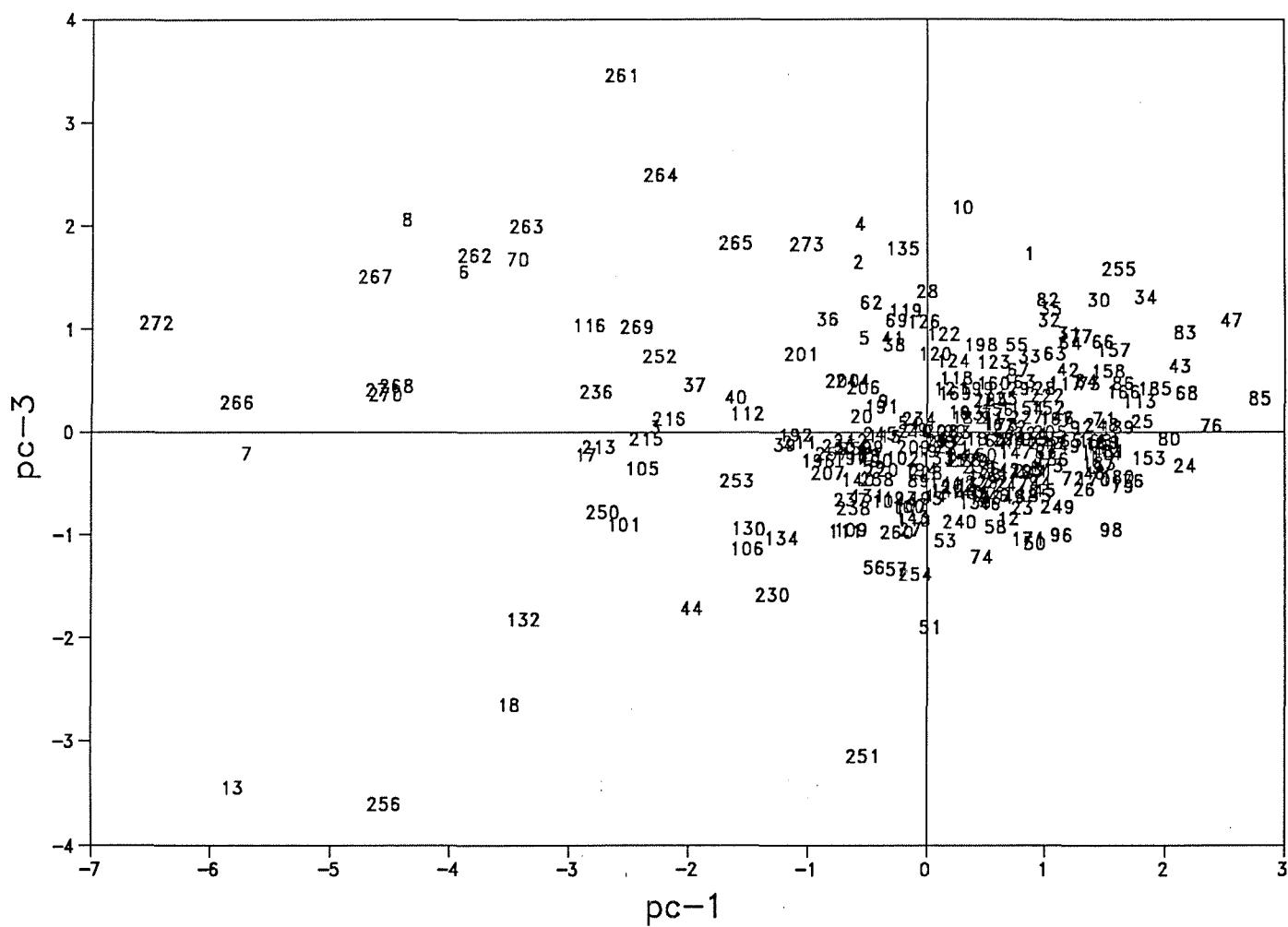


Fig. 12. Concentration of Cd, Hg, Cu, Pb, and Zn in combined sets A, B, and C, projected on the plane of the principal components pc1 and pc3. Same as Fig. 5, except that the concentrations of metals are expressed in percent of the total concentration. Samples are identified by numbers in Table 4.

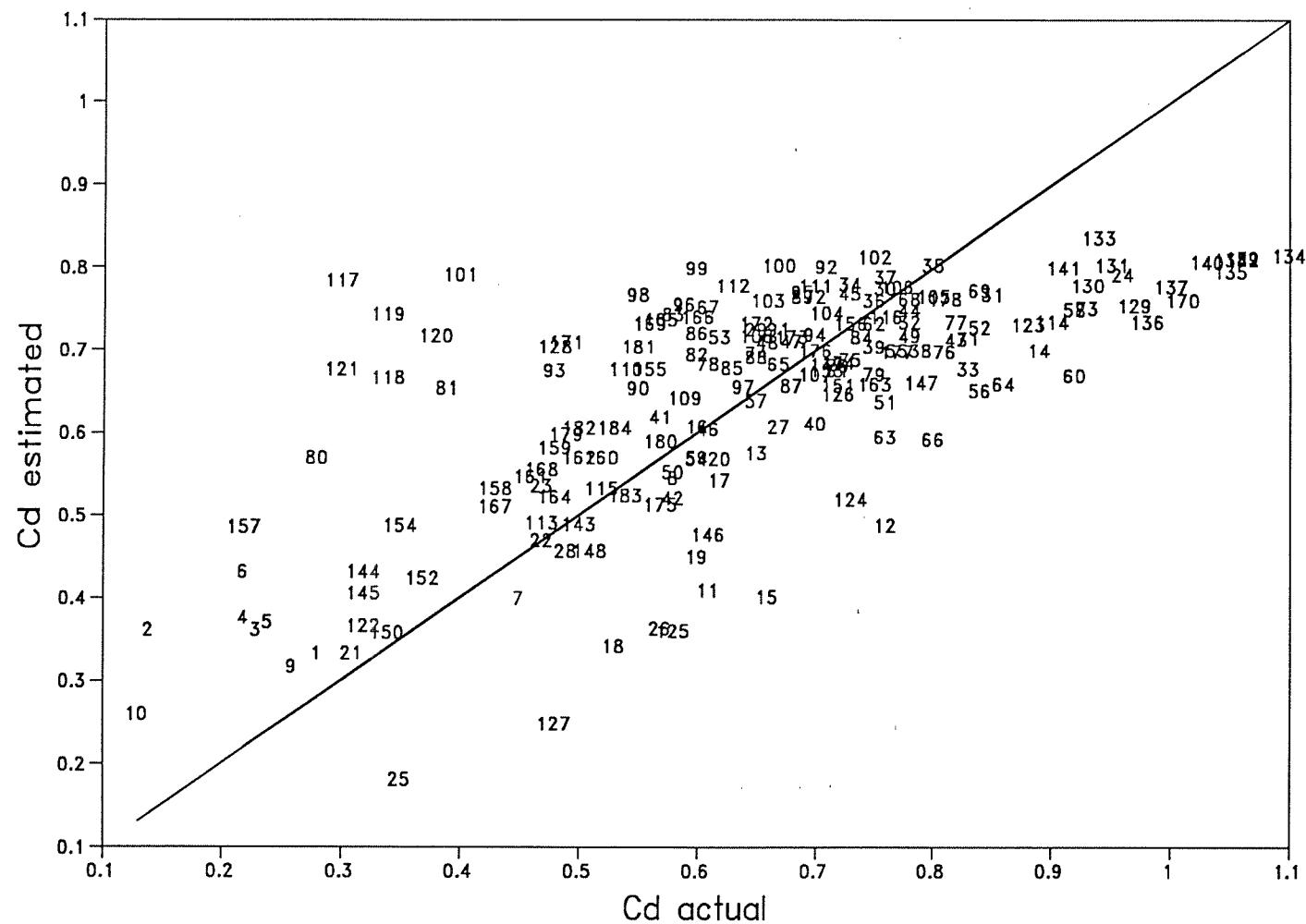
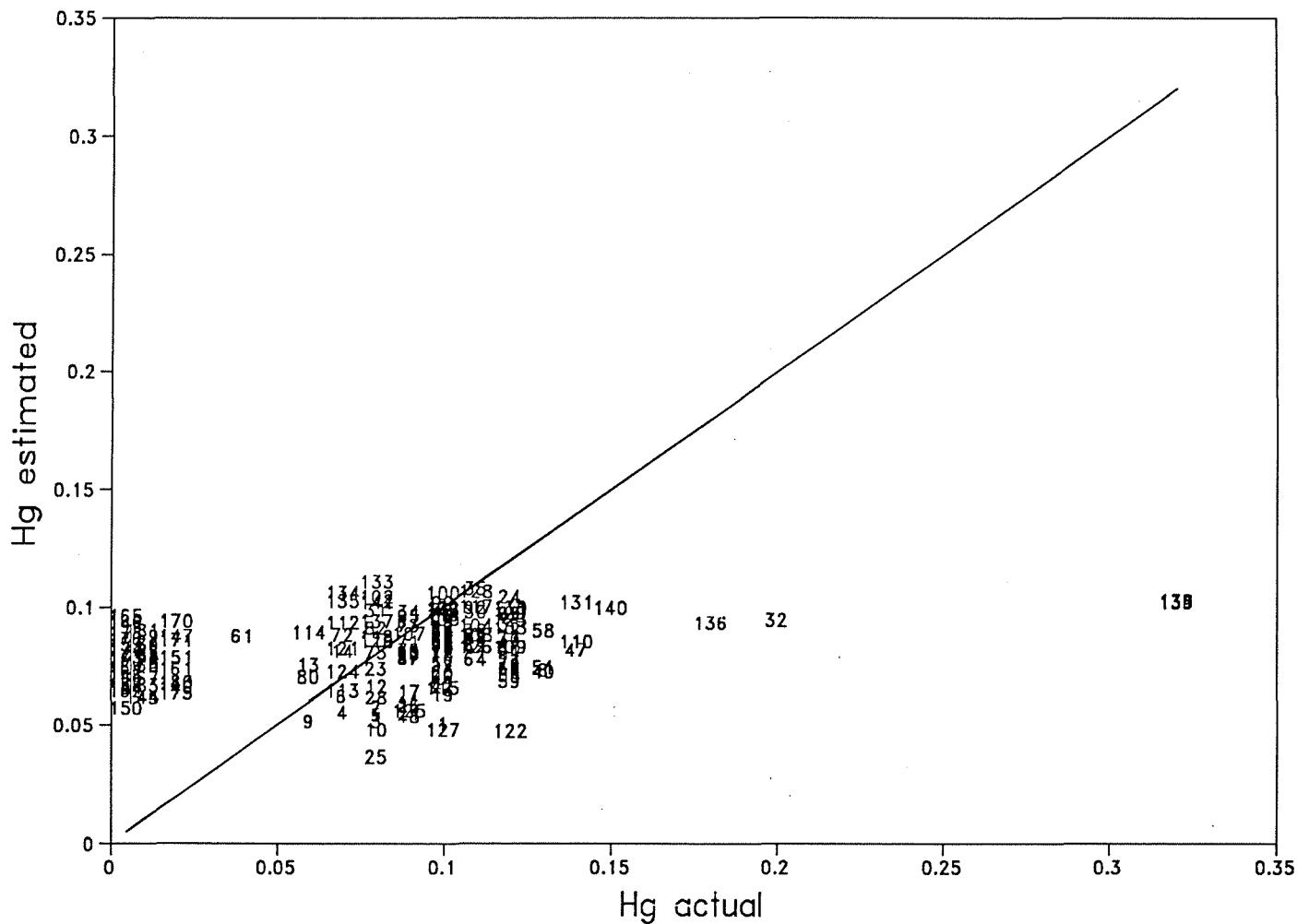


Fig. 13. The relationship between actual concentration of Cd and concentration estimated from the proportions of sand, silt, and clay in the sample. Samples are identified by their numbers in Table 1. Samples to be estimated are not present in the calibration set.



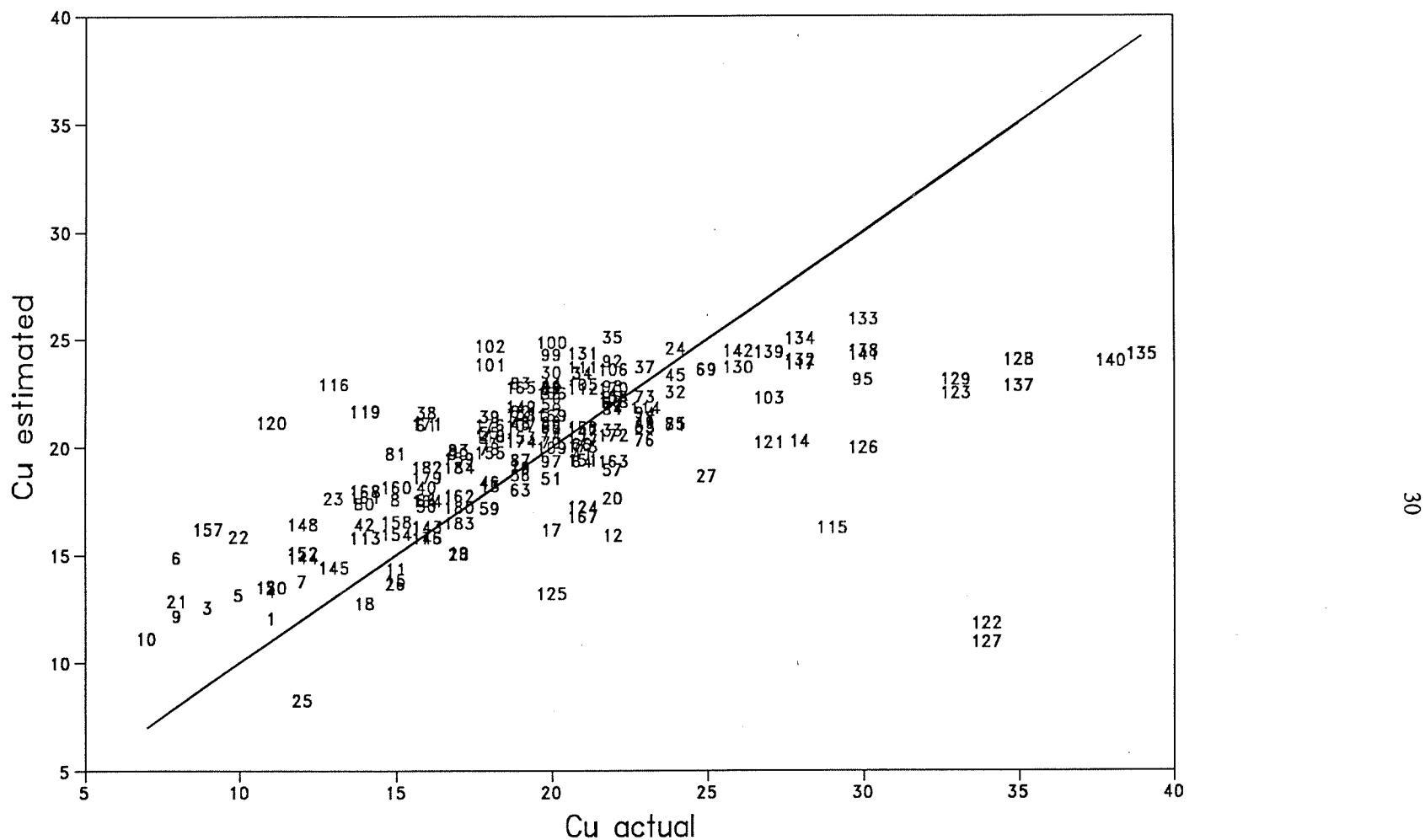
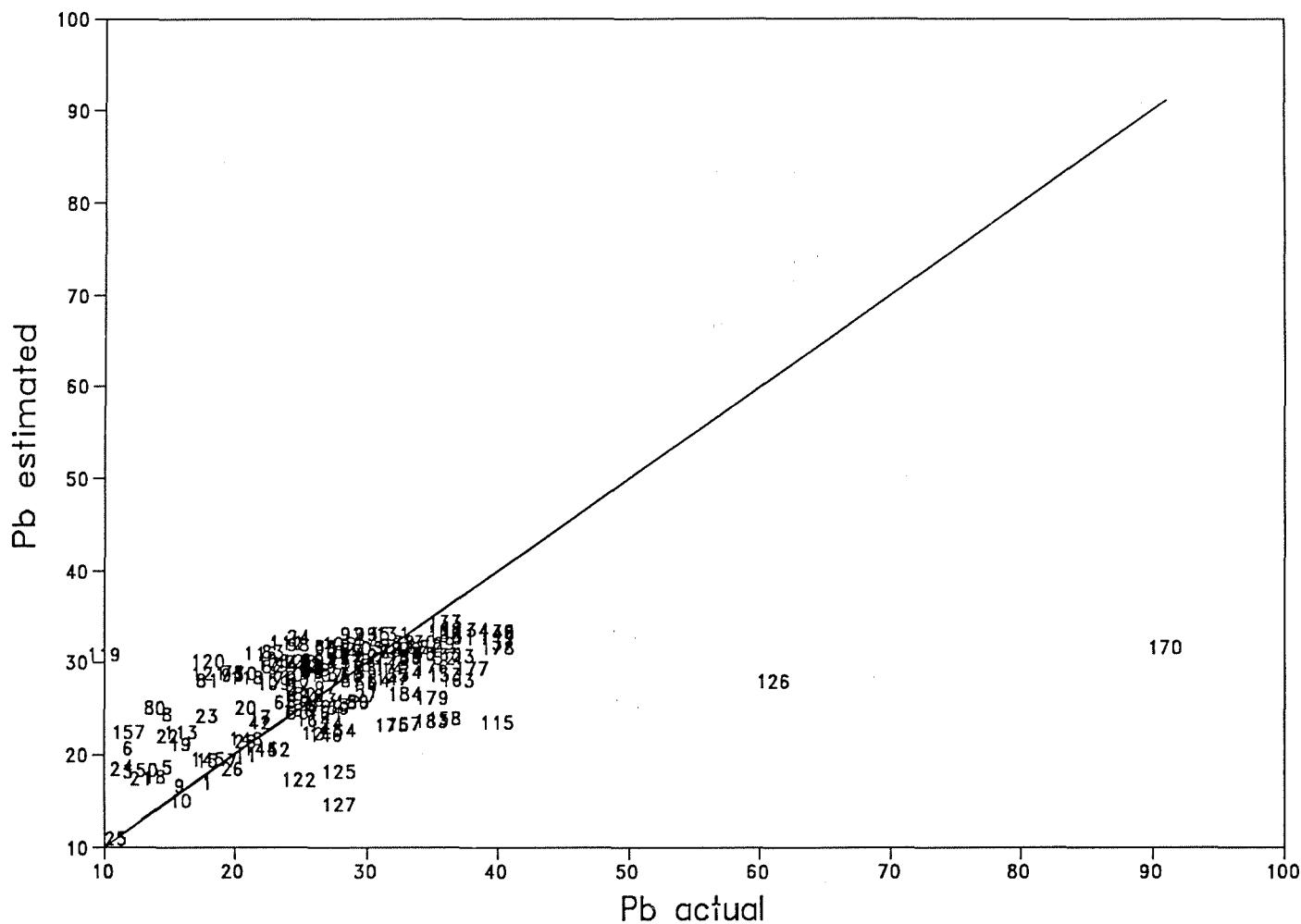
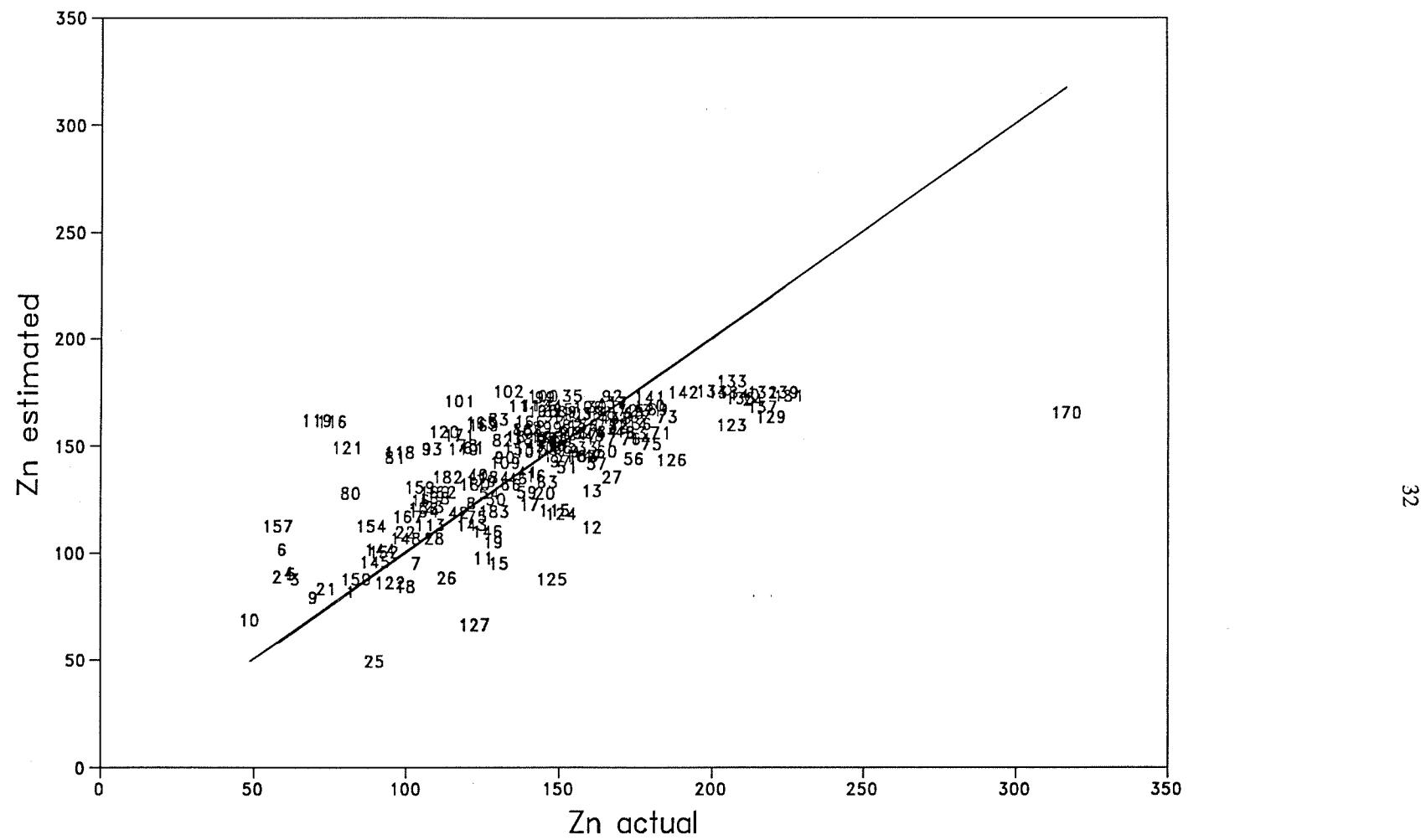


Fig. 15. The relationship between actual concentration of Cu and concentration estimated from the proportions of sand, silt, and clay in the sample. Samples are identified by their numbers in Table 1. Samples to be estimated are not present in the calibration set.





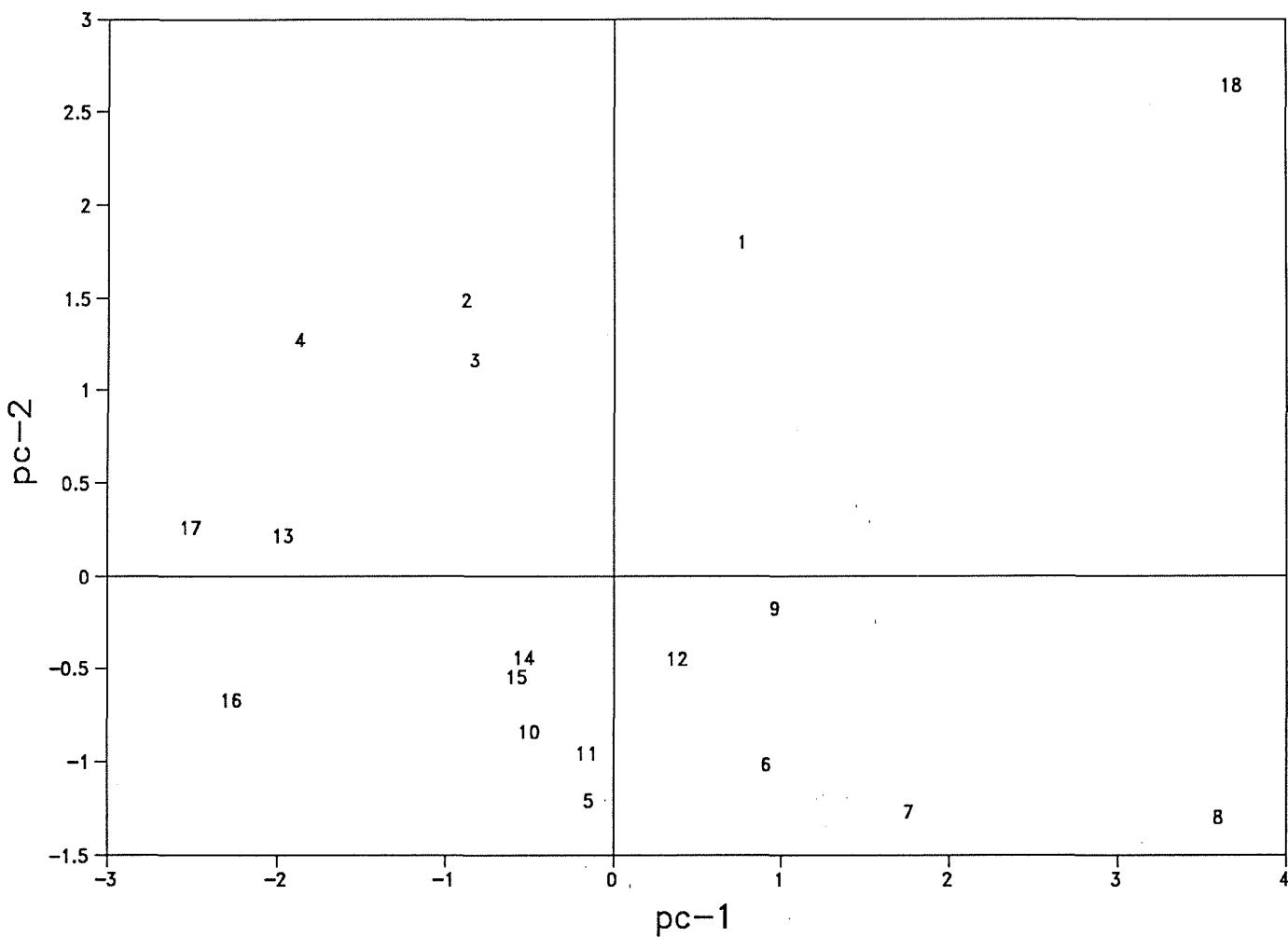


Fig. 18. Concentrations of Cd, Hg, Cu, Pb, and Zn in samples from the 'Dump' area (# 1-17), and the concentrations calculated from the average proportion of sand, silt, and clay in the area (#18), projected on the pc1-pc2 plane.

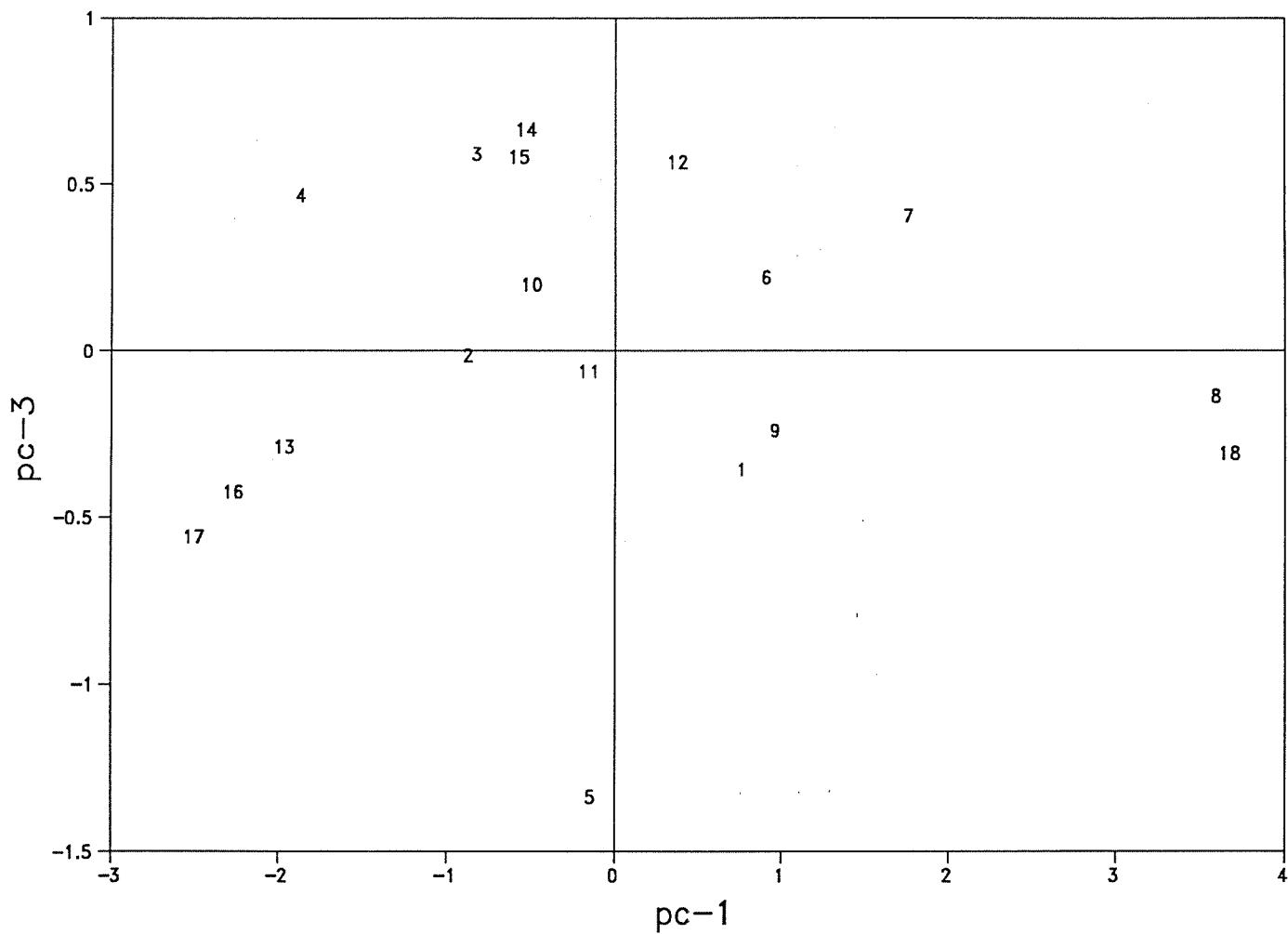
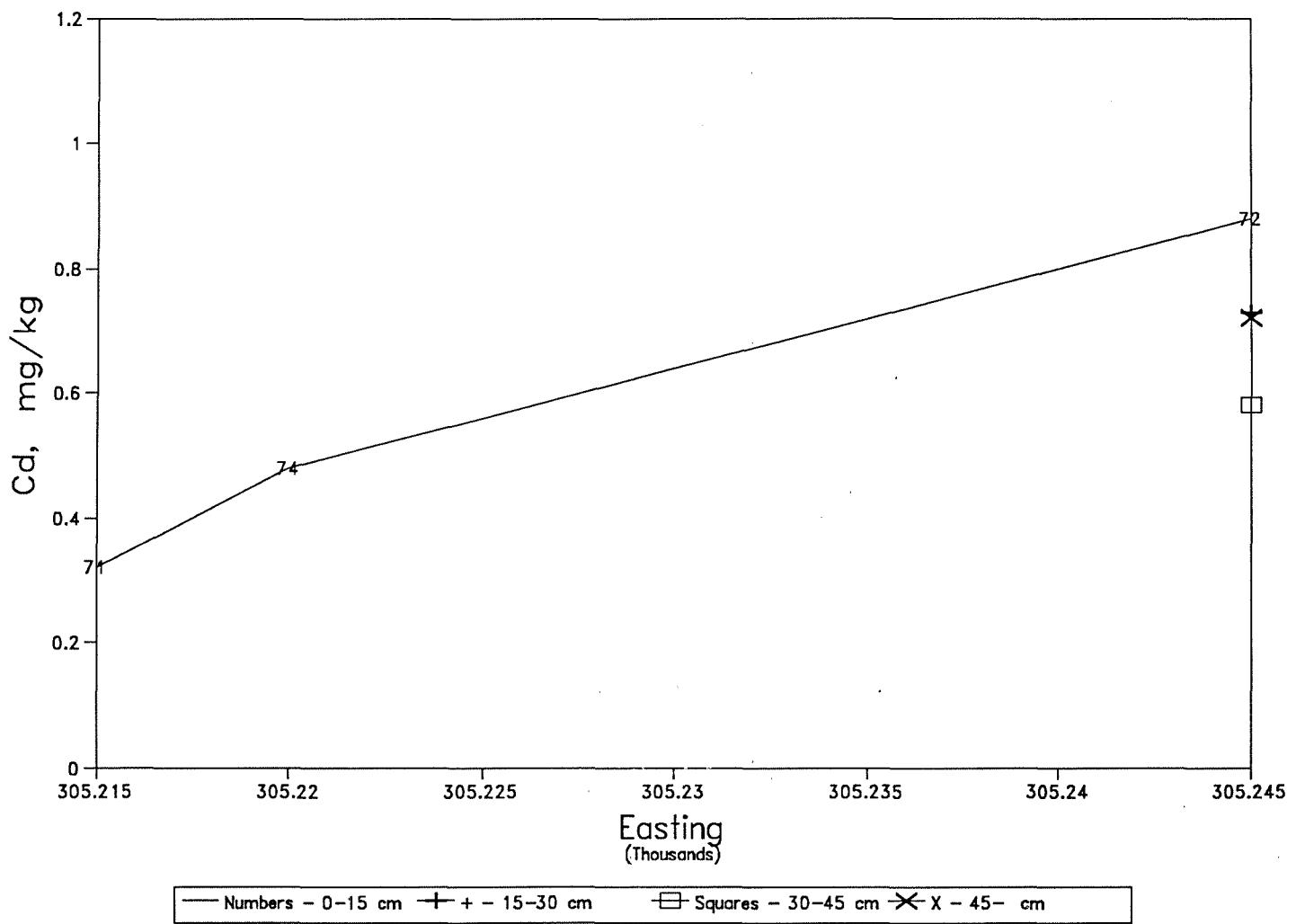


Fig. 19. Concentrations of Cd, Hg, Cu, Pb, and Zn in samples from the 'Dump' area (# 1-17), and the concentrations calculated from the average proportion of sand, silt, and clay in the area (#18), projected on the pc1-pc3 plane.



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Fig. 20. Concentrations of Cd plotted against Eastings of sampling stations (see Tables 1 and 6).

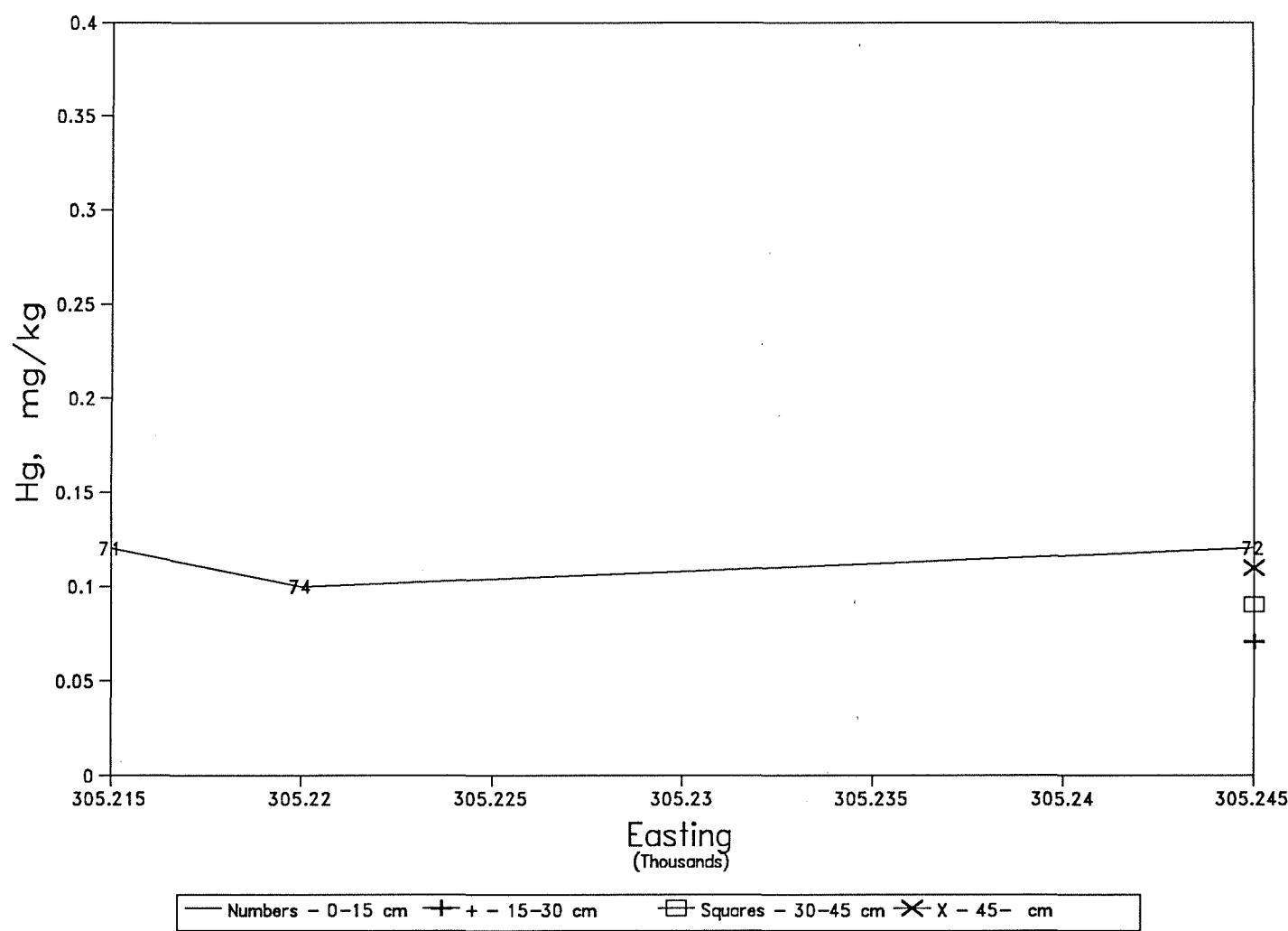


Fig. 21. Concentrations of Hg plotted against Eastings of sampling stations (see Tables 1 and 6).

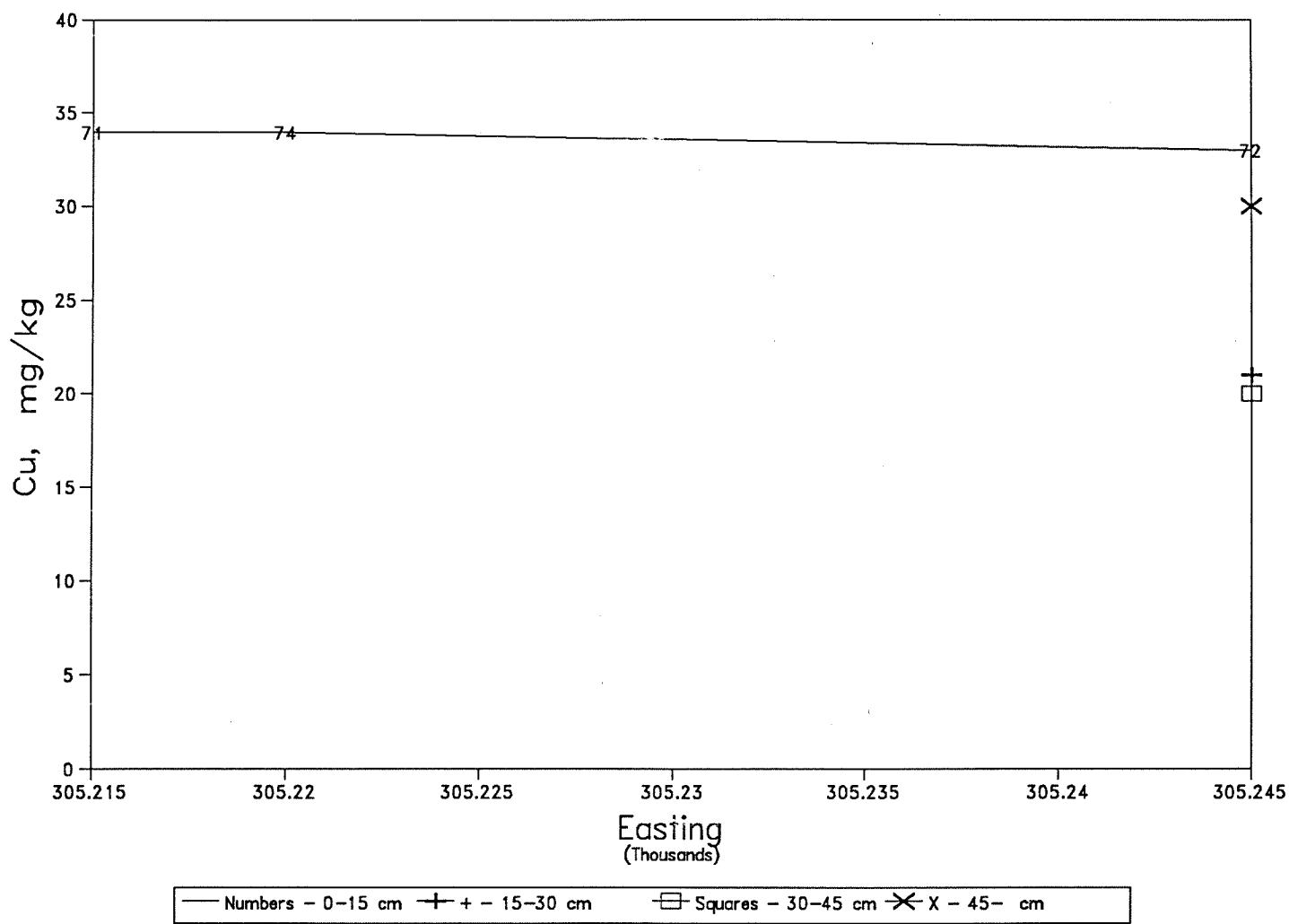


Fig. 22. Concentrations of Cu plotted against Eastings of sampling stations (see Tables 1 and 6).

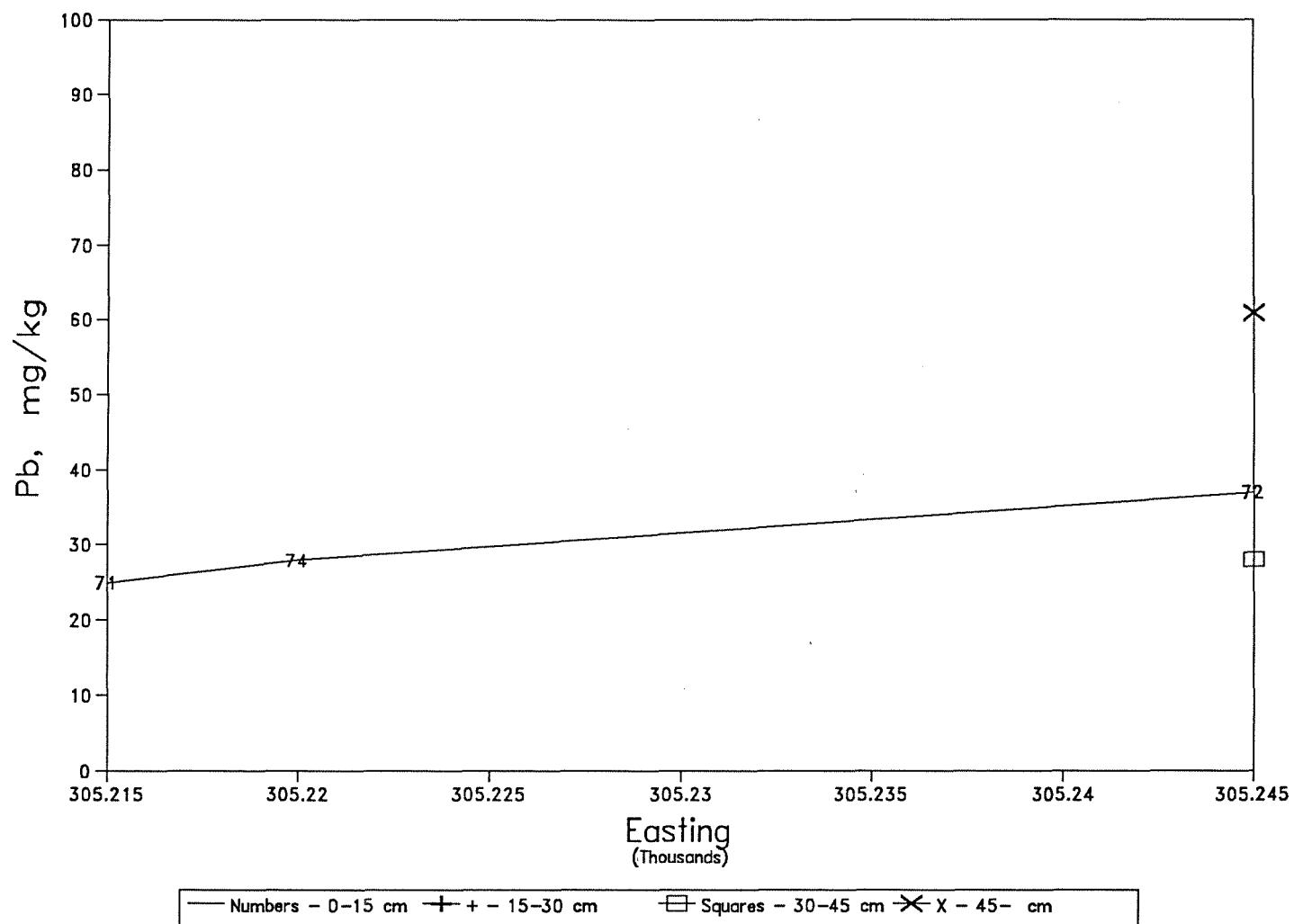


Fig. 23. Concentrations of Pb plotted against Eastings of sampling stations (see Tables 1 and 6).

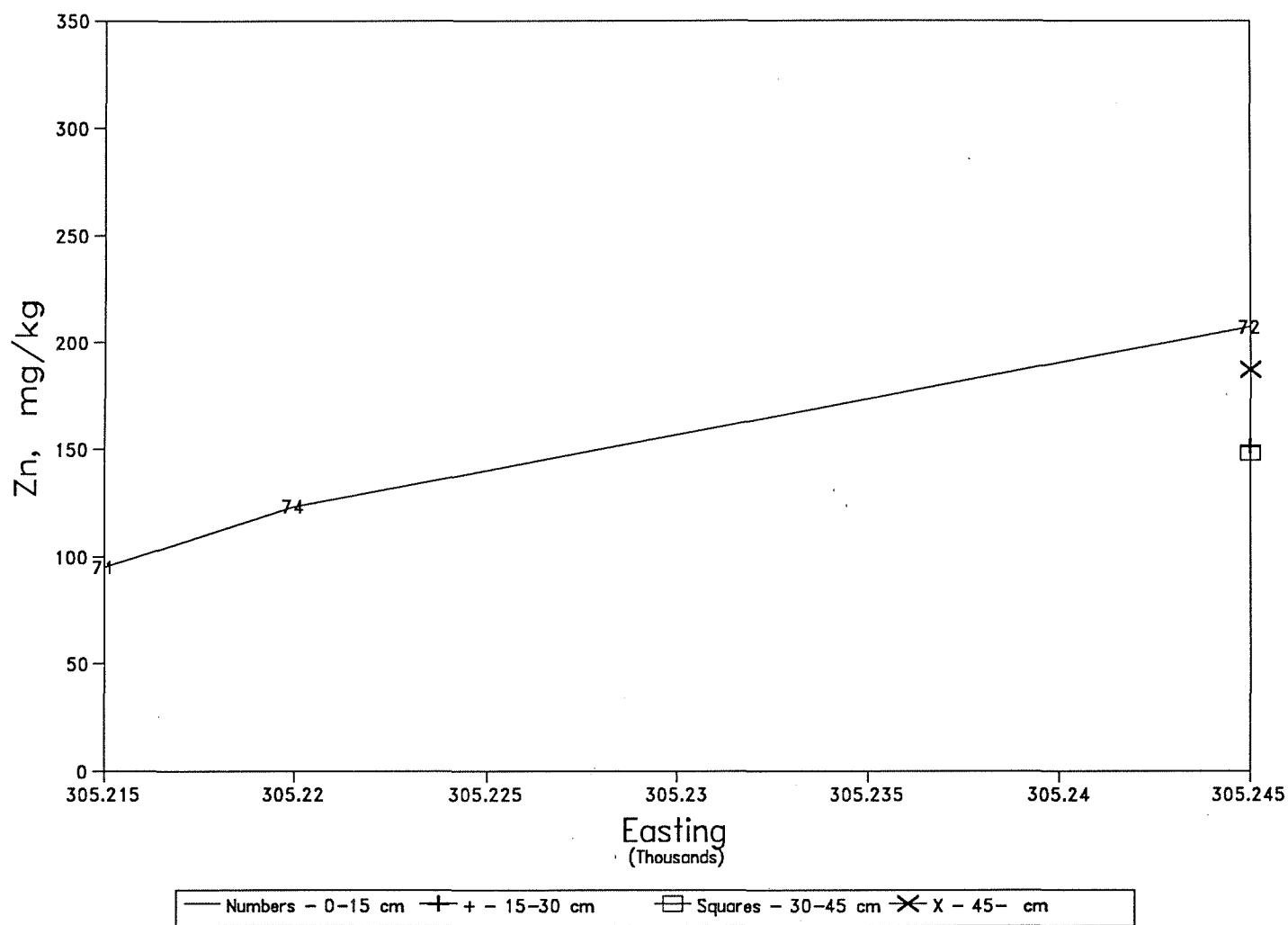


Fig. 24. Concentrations of Zn plotted against Eastings of sampling stations (see Tables 1 and 6).

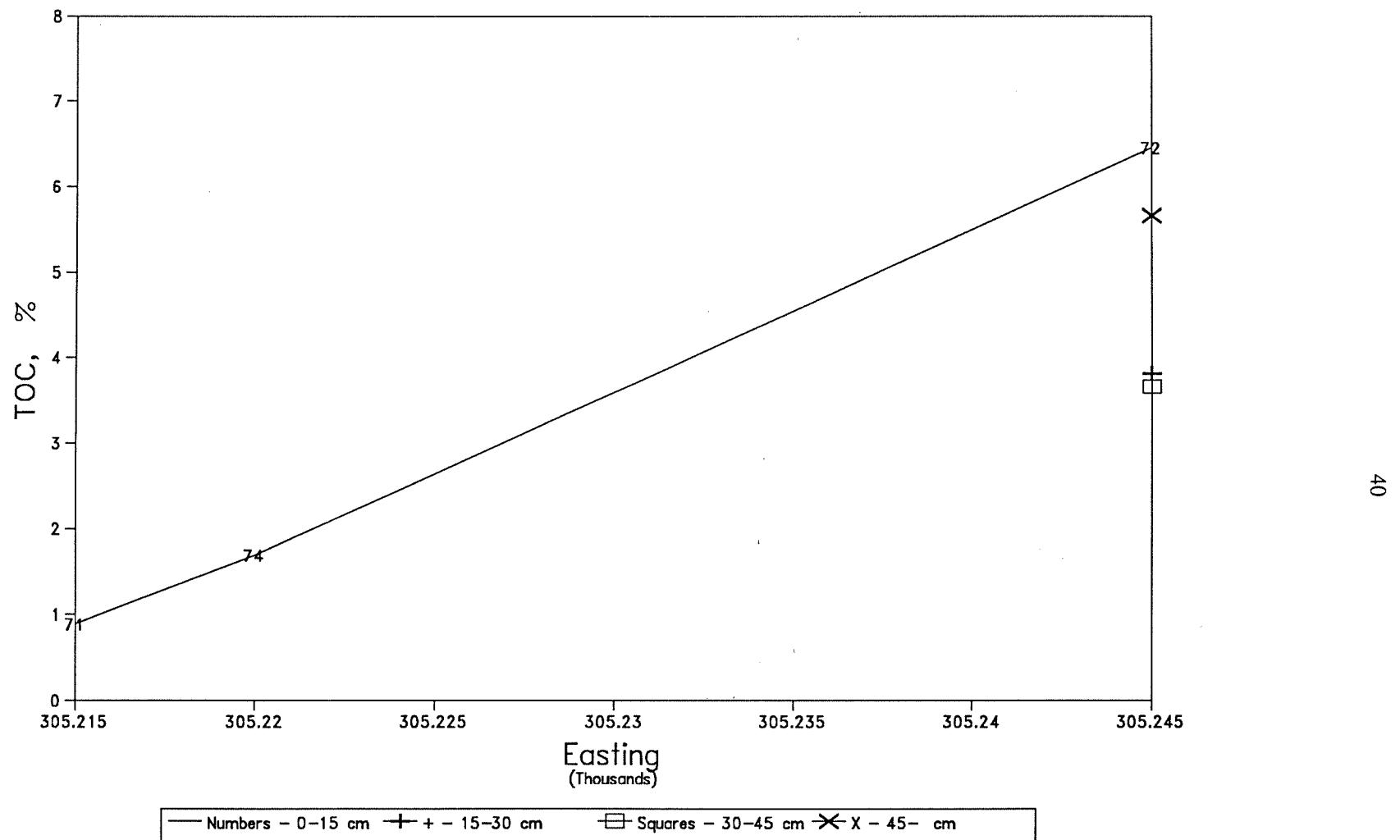


Fig. 25. Concentrations of TOC plotted against Eastings of sampling stations (see Tables 1 and 6).

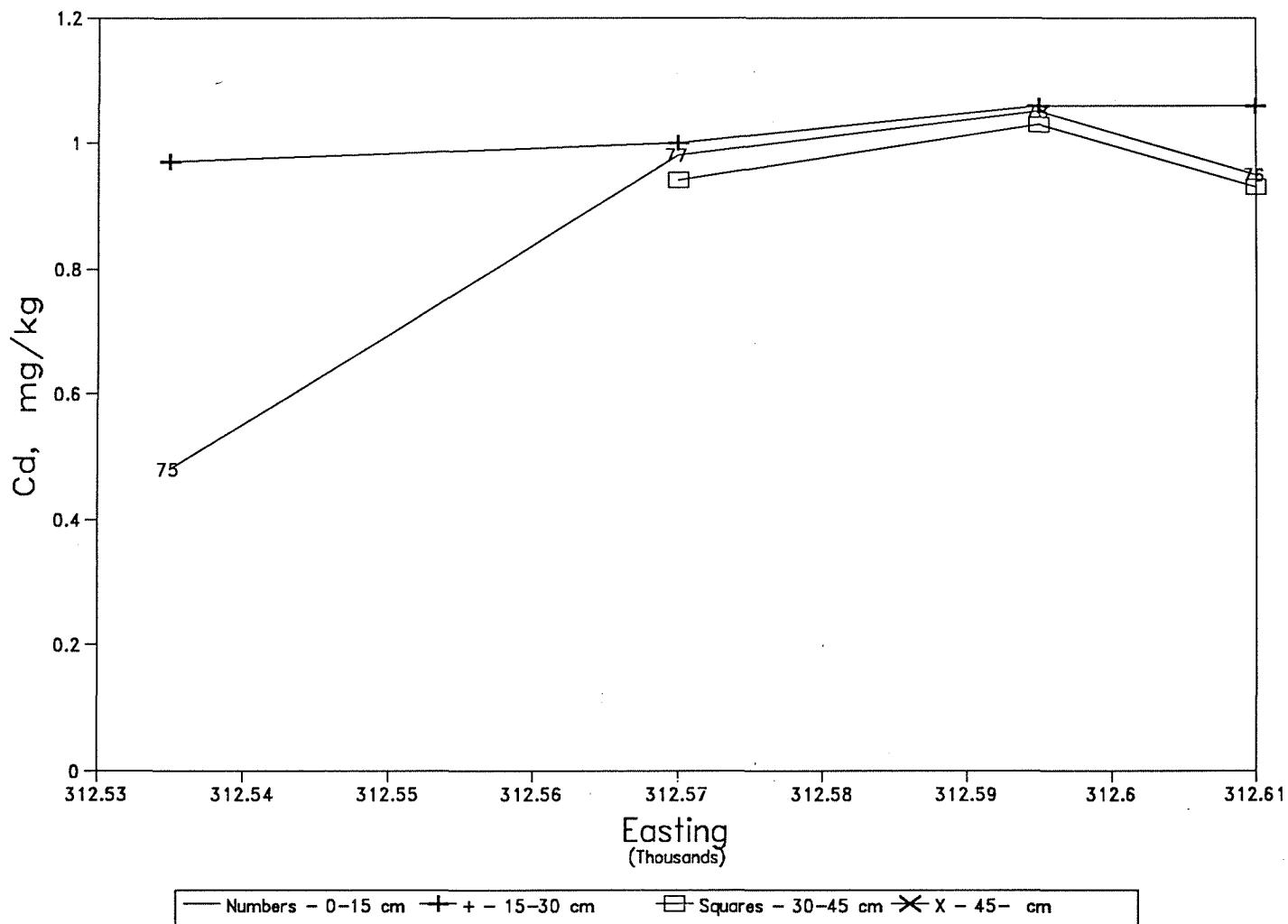


Fig. 26. Concentrations of Cd plotted against Eastings of sampling stations (see Tables 1 and 6).

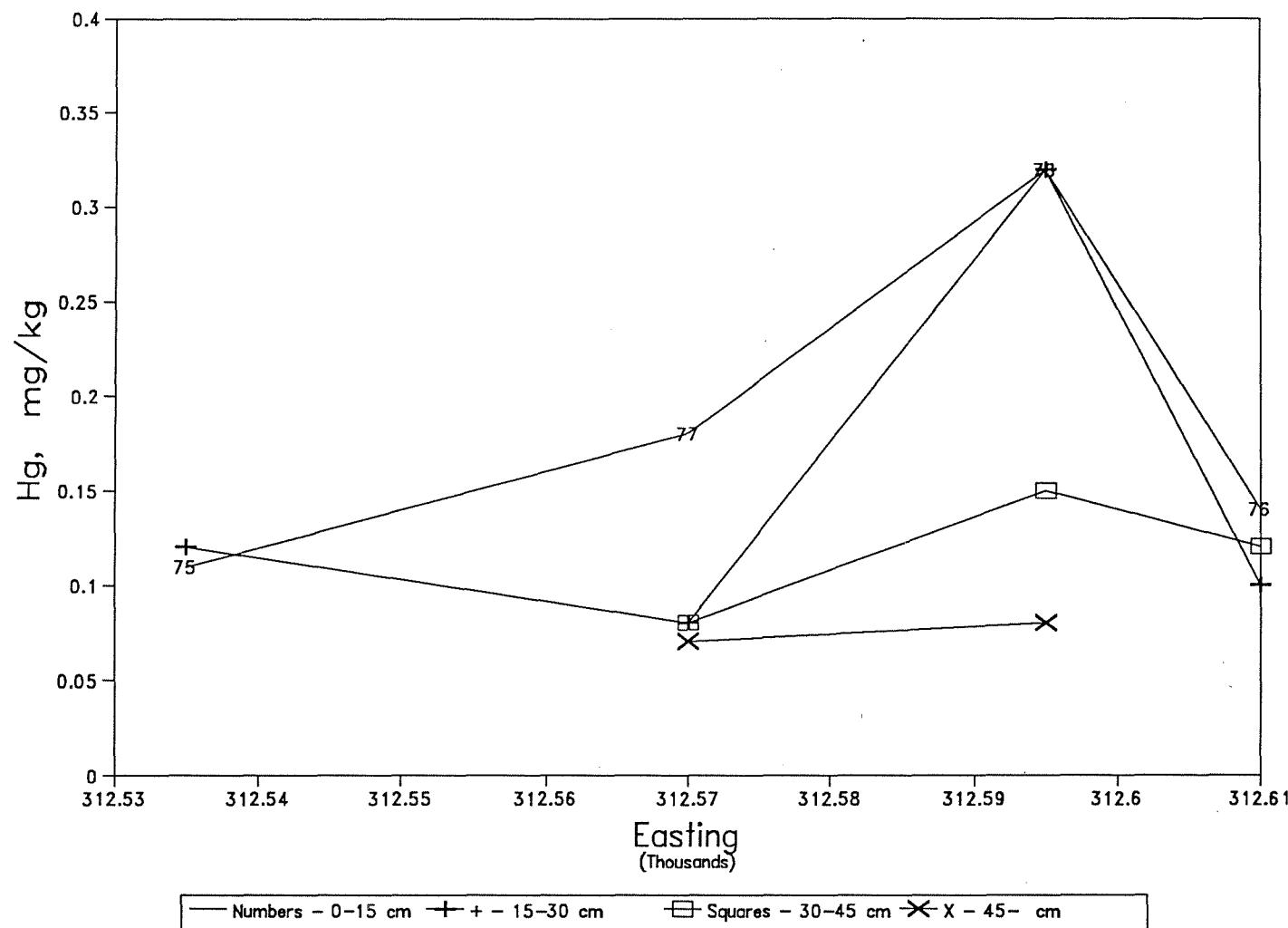


Fig. 27. Concentrations of Hg plotted against Eastings of sampling stations (see Tables 1 and 6).

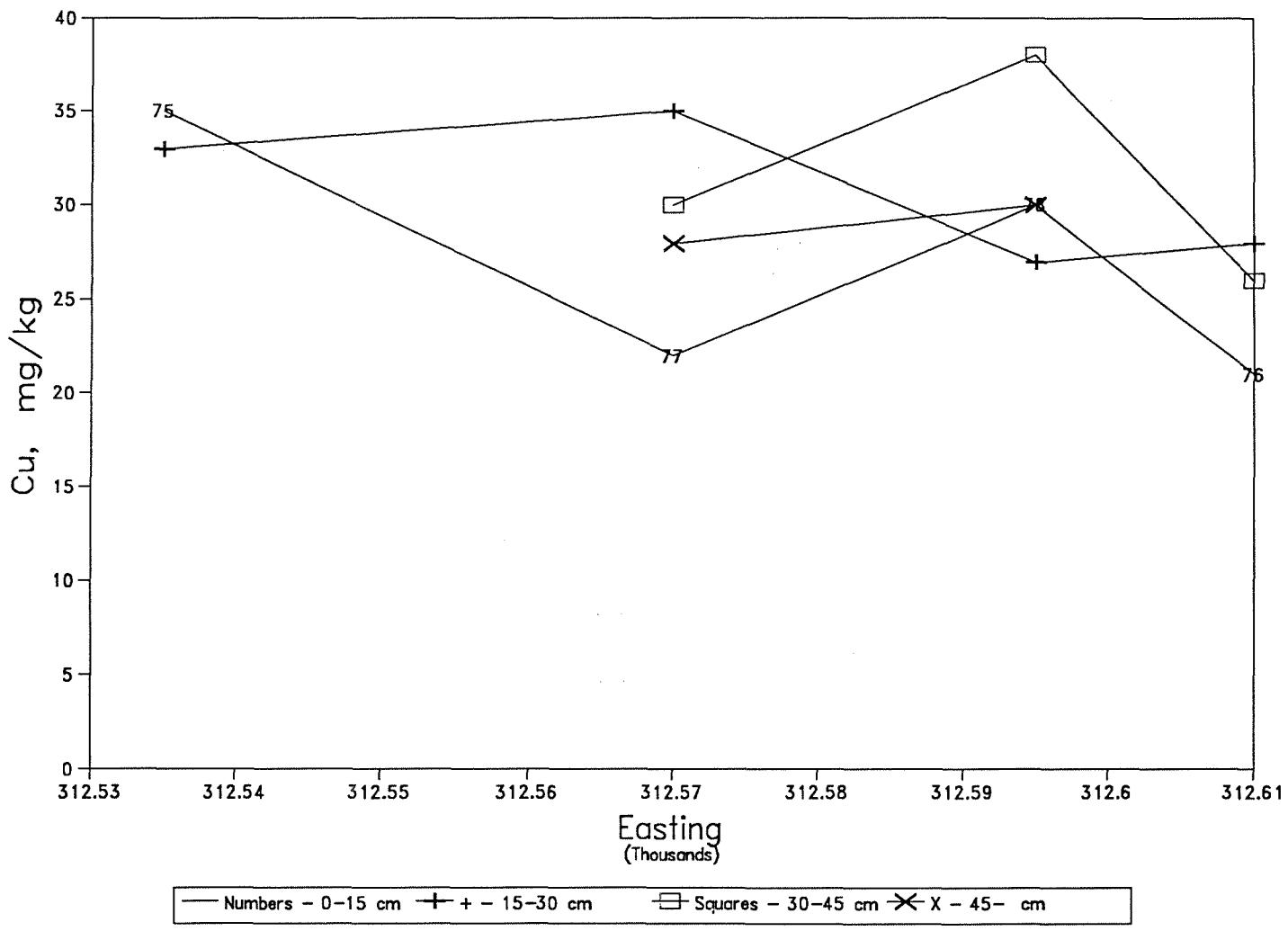


Fig. 28. Concentrations of Cu plotted against Eastings of sampling stations (see Tables 1 and 6).

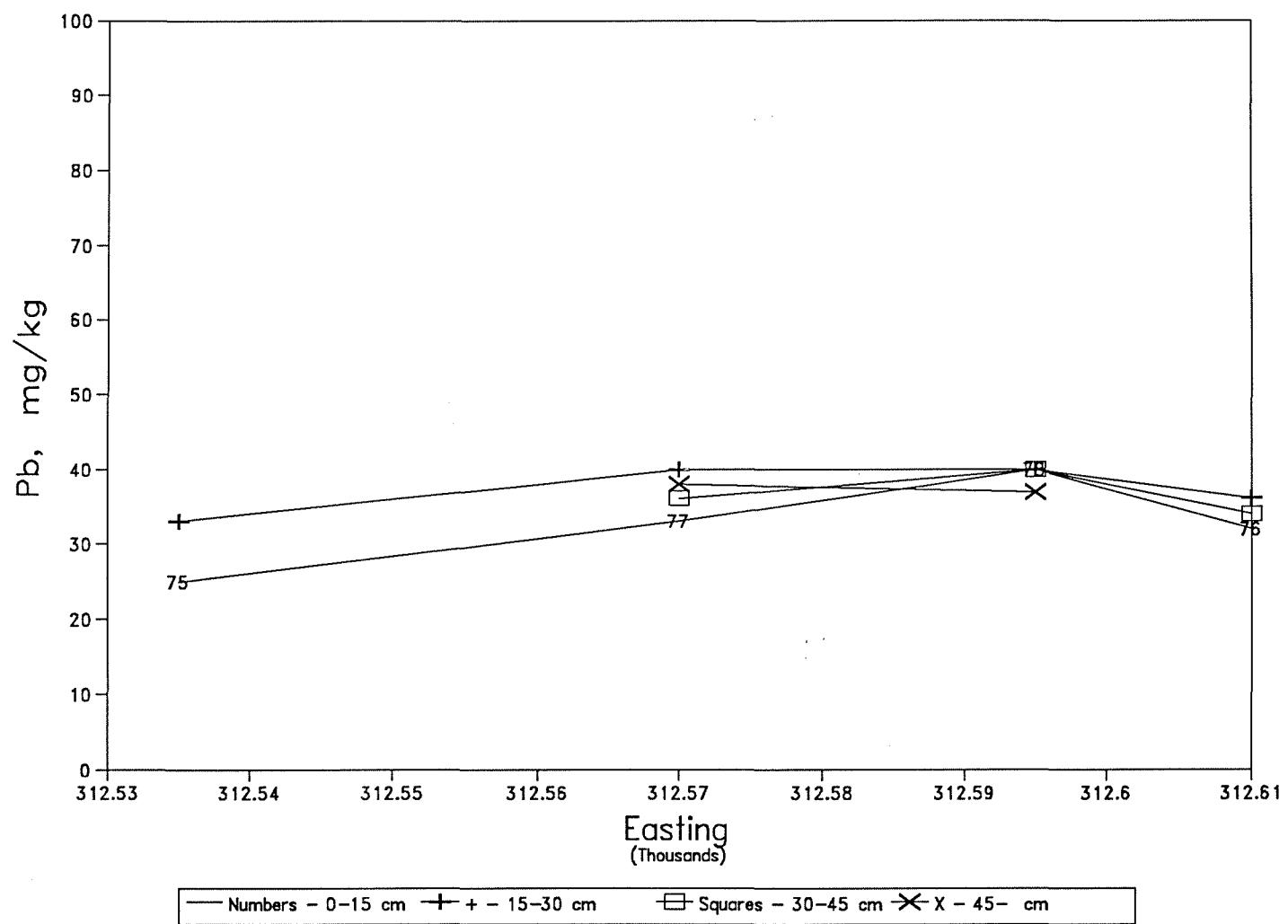


Fig. 29. Concentrations of Pb plotted against Eastings of sampling stations (see Tables 1 and 6).

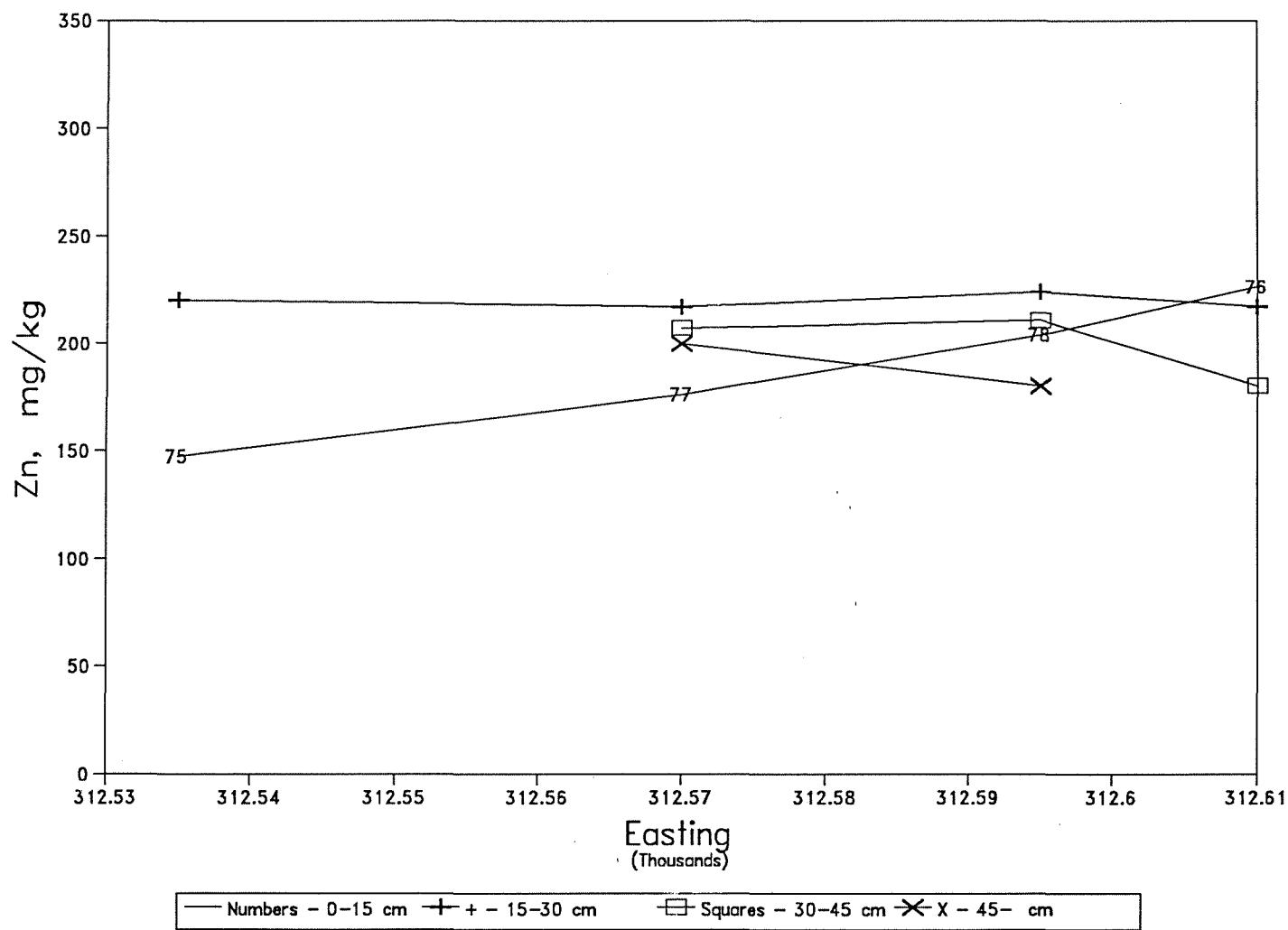


Fig. 30. Concentrations of Zn plotted against Eastings of sampling stations (see Tables 1 and 6).

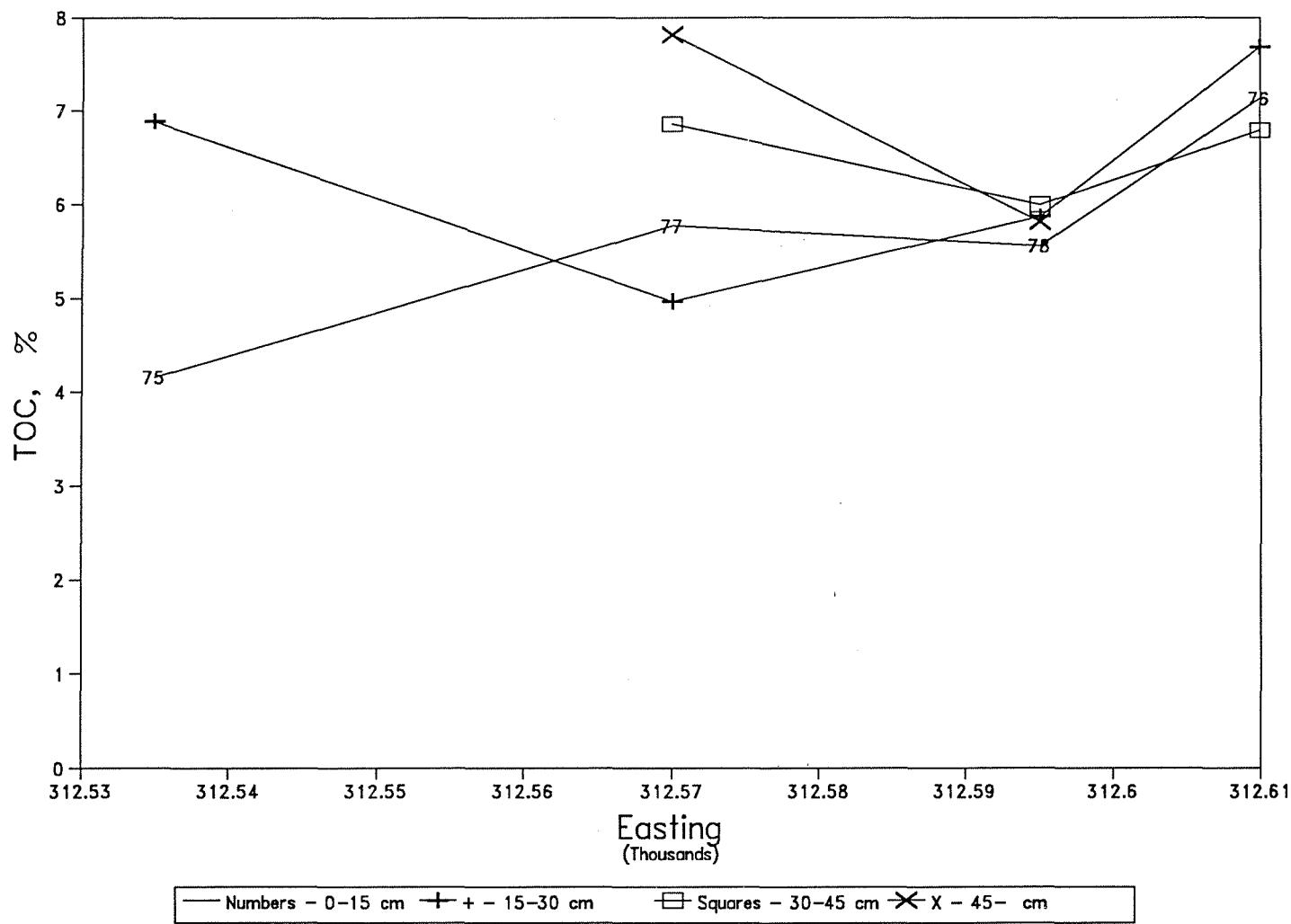


Fig. 31. Concentrations of TOC plotted against Eastings of sampling stations (see Tables 1 and 6).

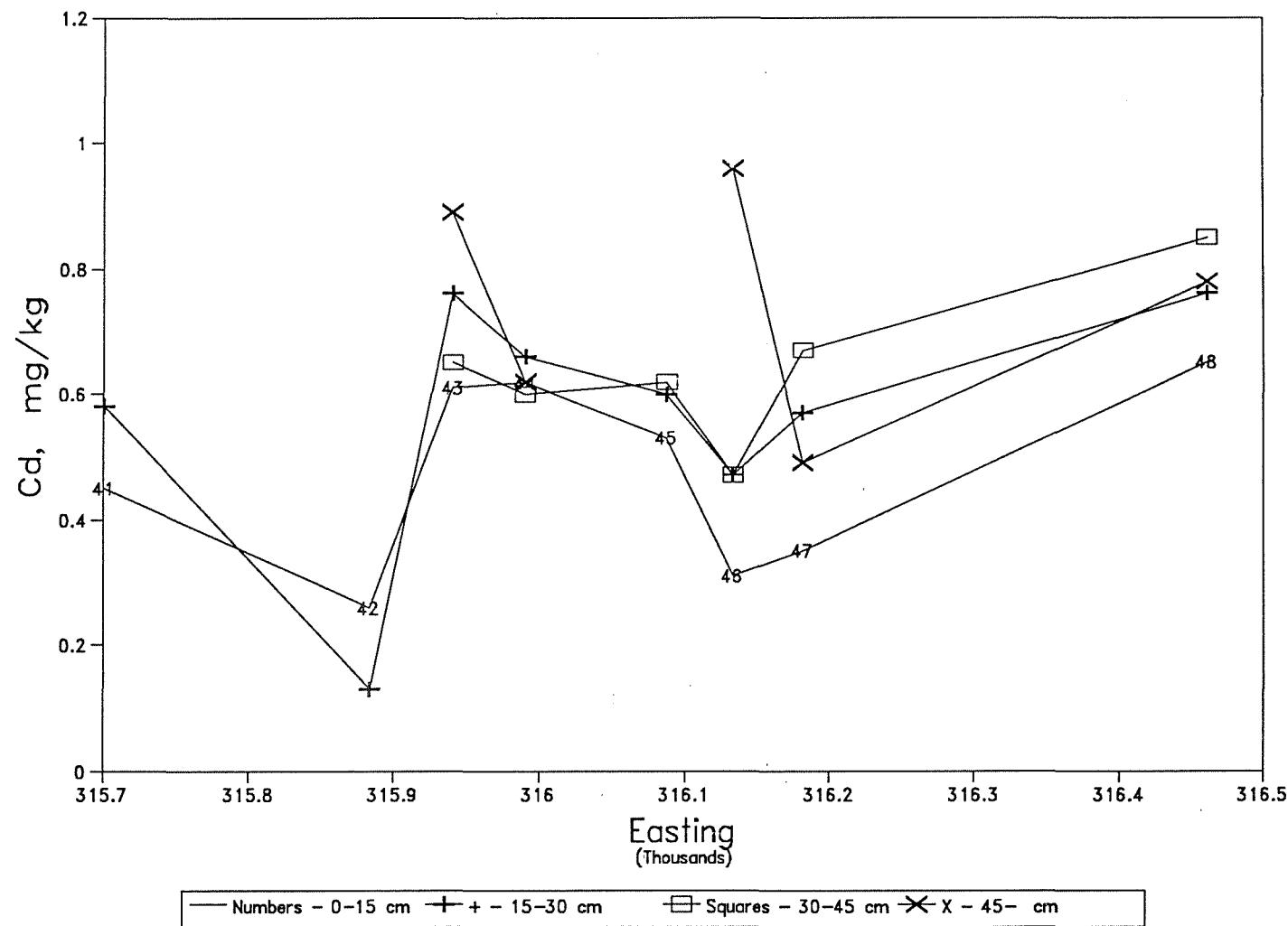


Fig. 32. Concentrations of Cd plotted against Eastings of sampling stations (see Tables 1 and 6).

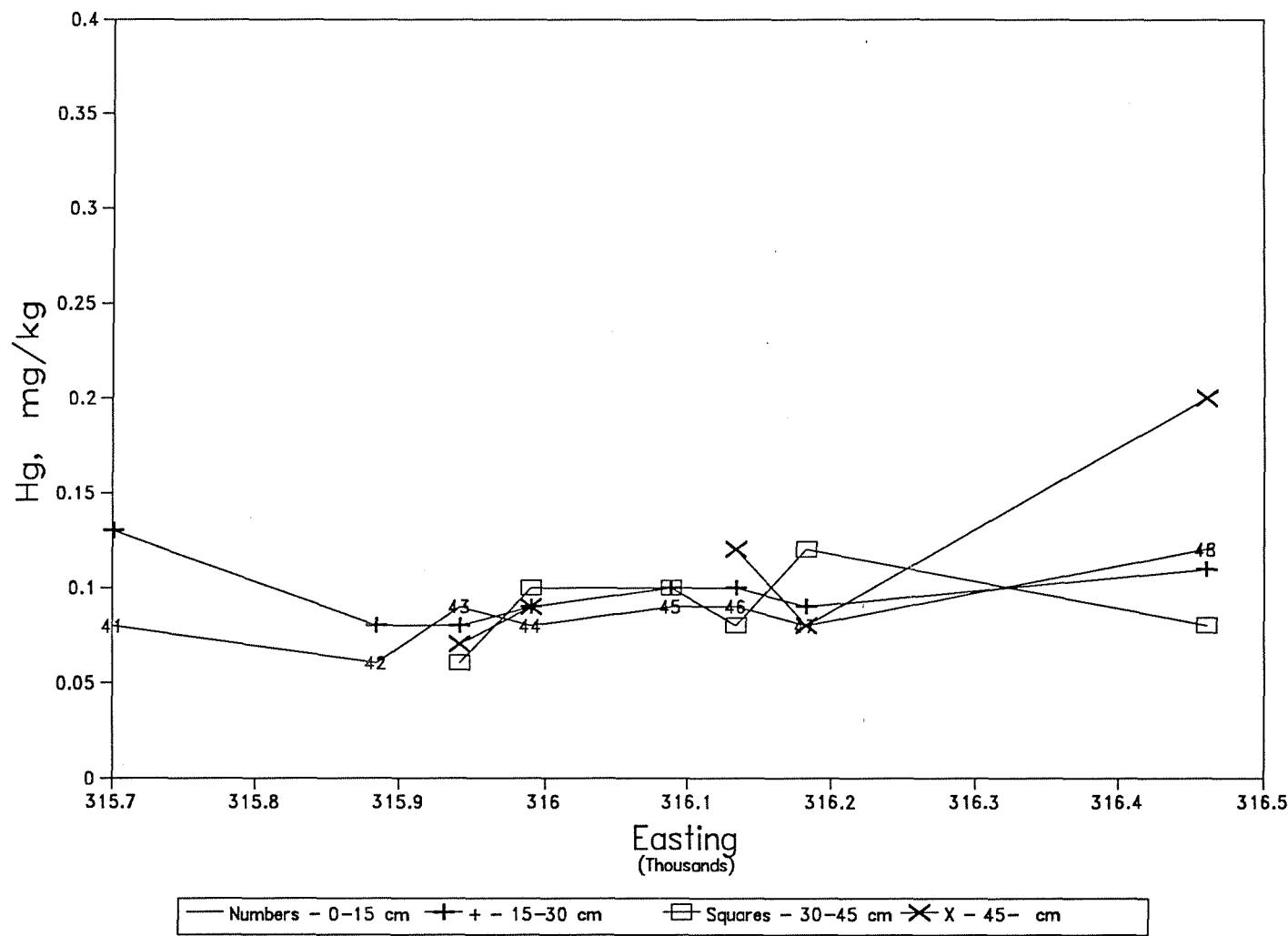


Fig. 33. Concentrations of Hg plotted against Eastings of sampling stations (see Tables 1 and 6).

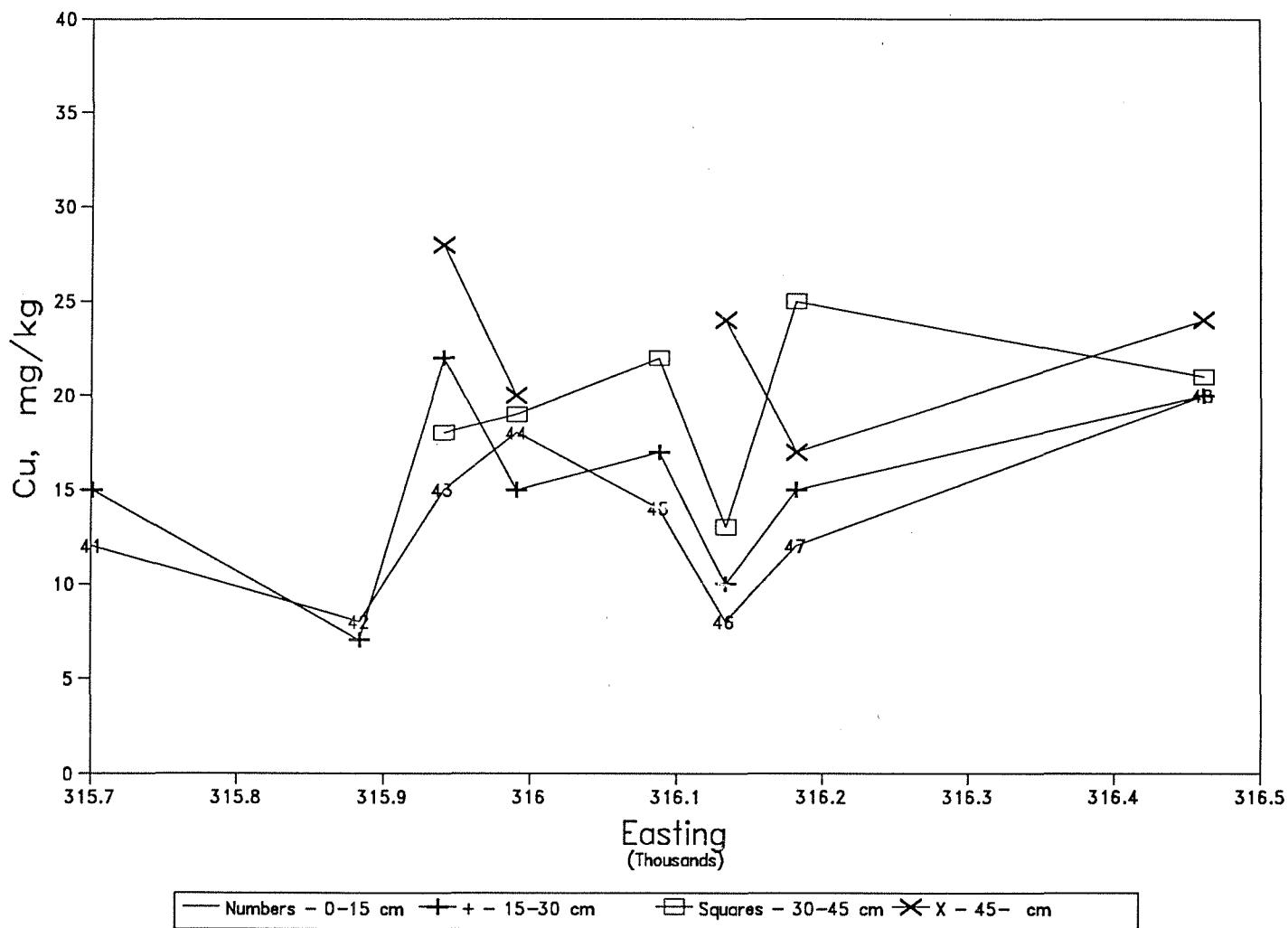


Fig. 34. Concentrations of Cu plotted against Eastings of sampling stations (see Tables 1 and 6).

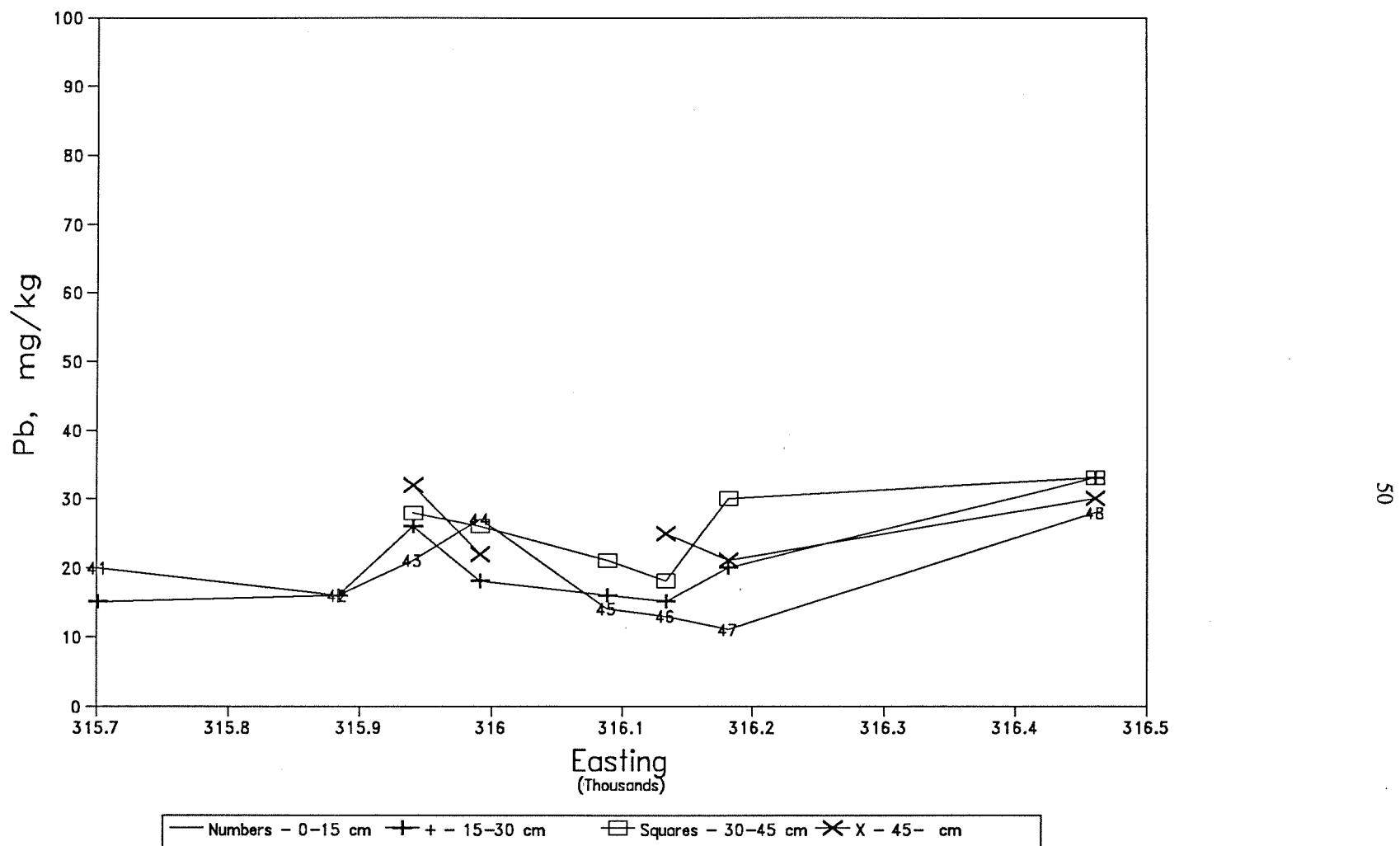


Fig. 35. Concentrations of Pb plotted against Eastings of sampling stations (see Tables 1 and 6).

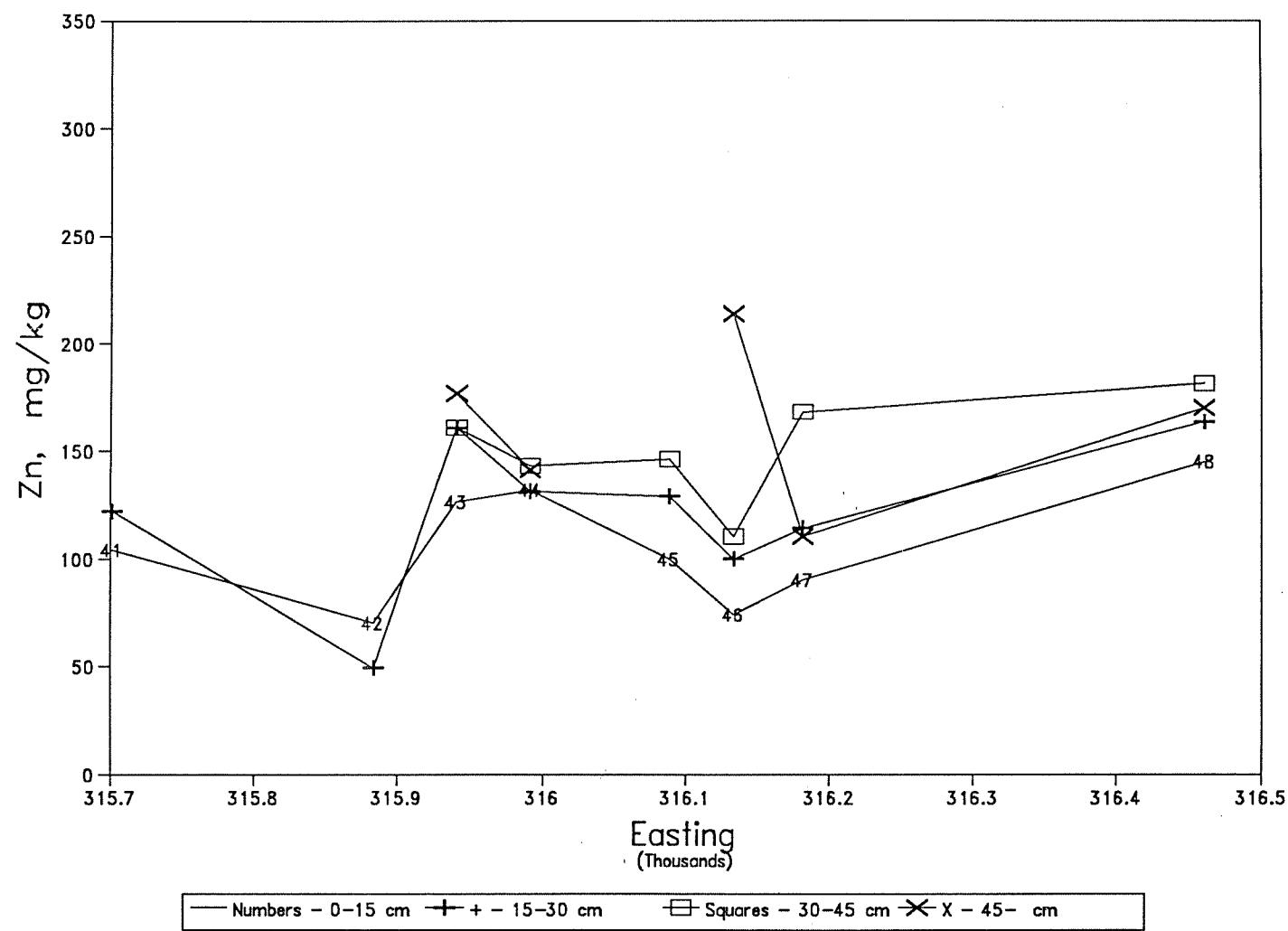


Fig. 36. Concentrations of Zn plotted against Eastings of sampling stations (see Tables 1 and 6).

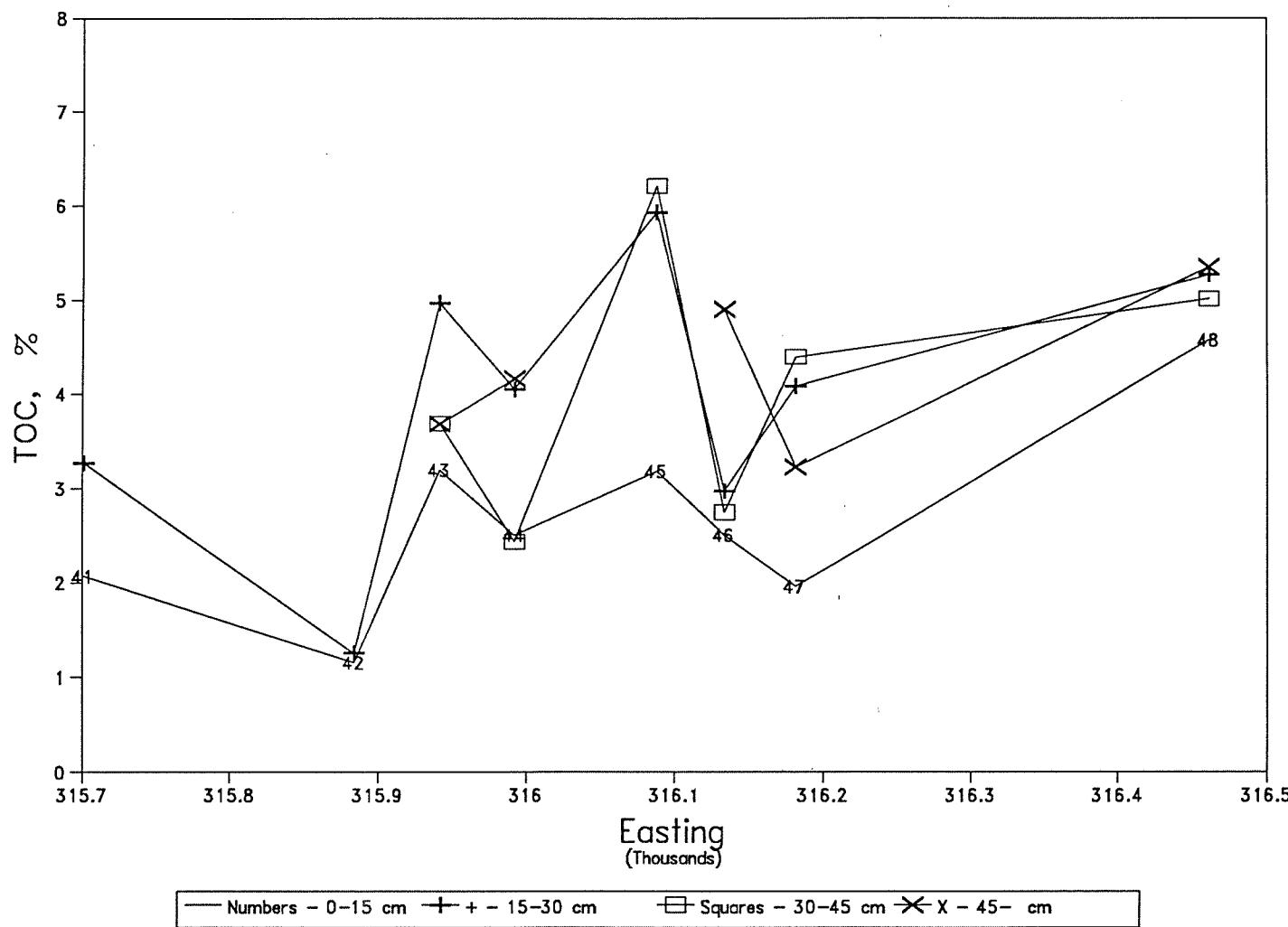


Fig. 37. Concentrations of TOC plotted against Eastings of sampling stations (see Tables 1 and 6).

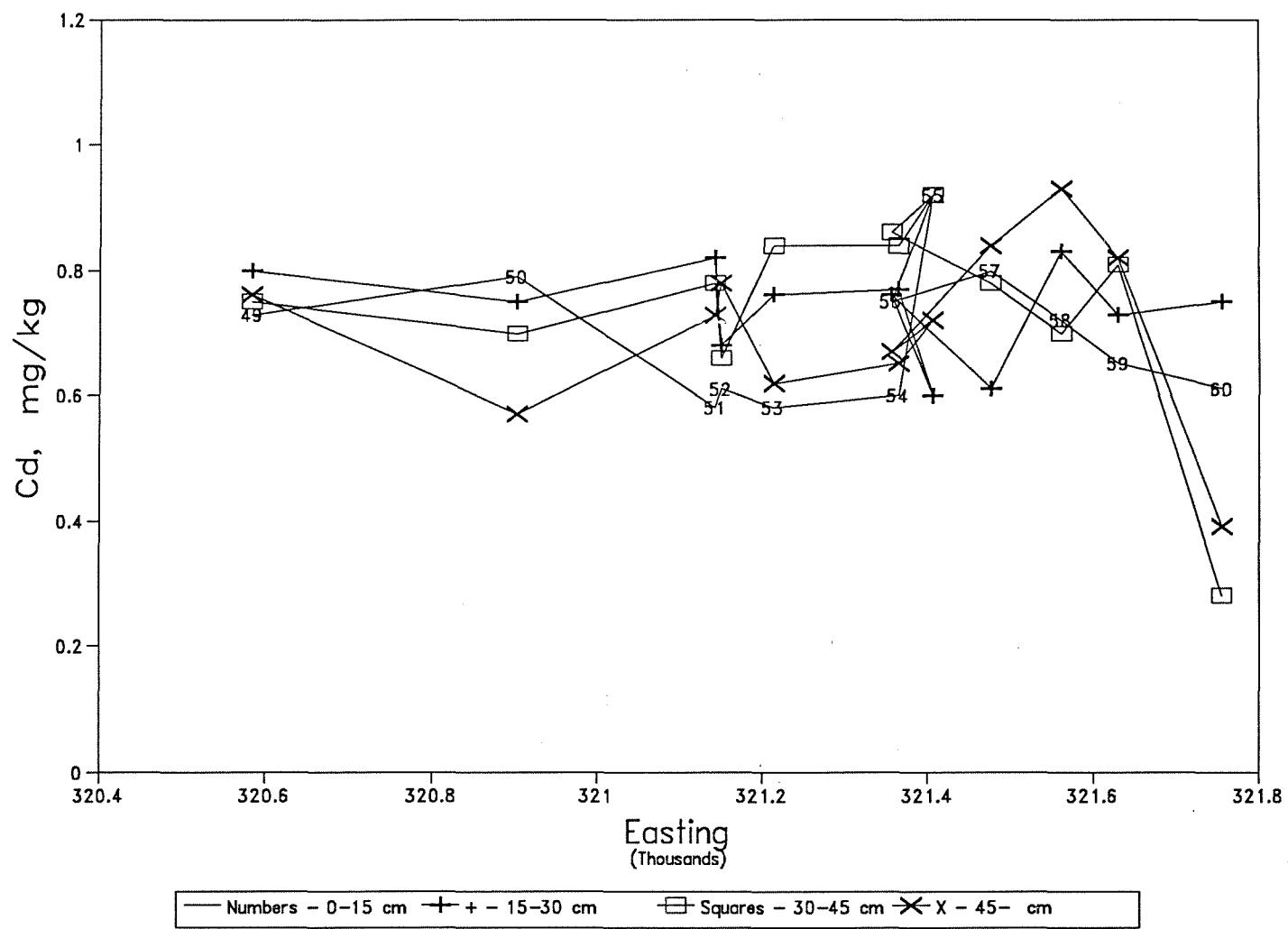


Fig. 38. Concentrations of Cd plotted against Eastings of sampling stations (see Tables 1 and 6).

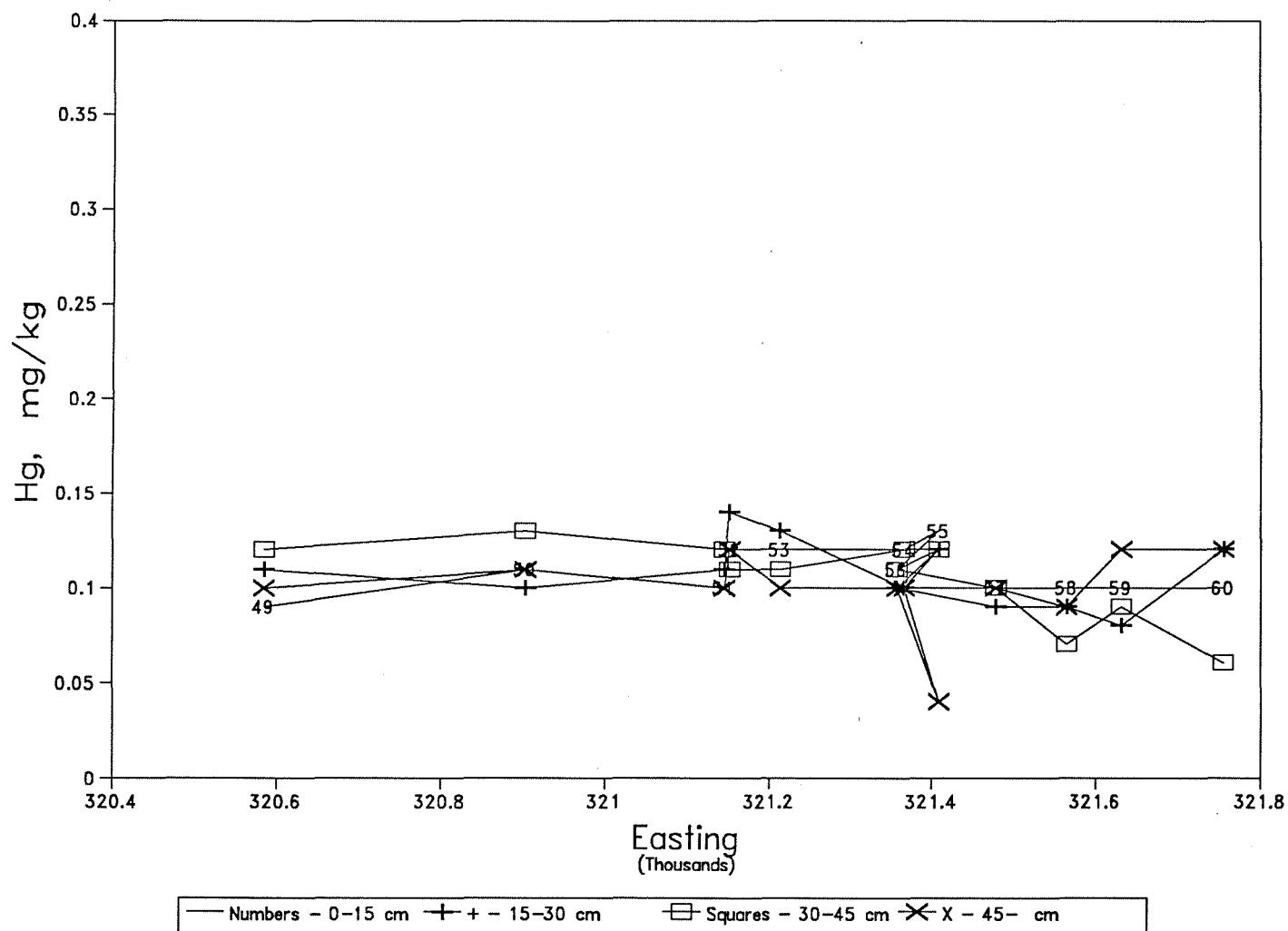


Fig. 39. Concentrations of Hg plotted against Eastings of sampling stations (see Tables 1 and 6).

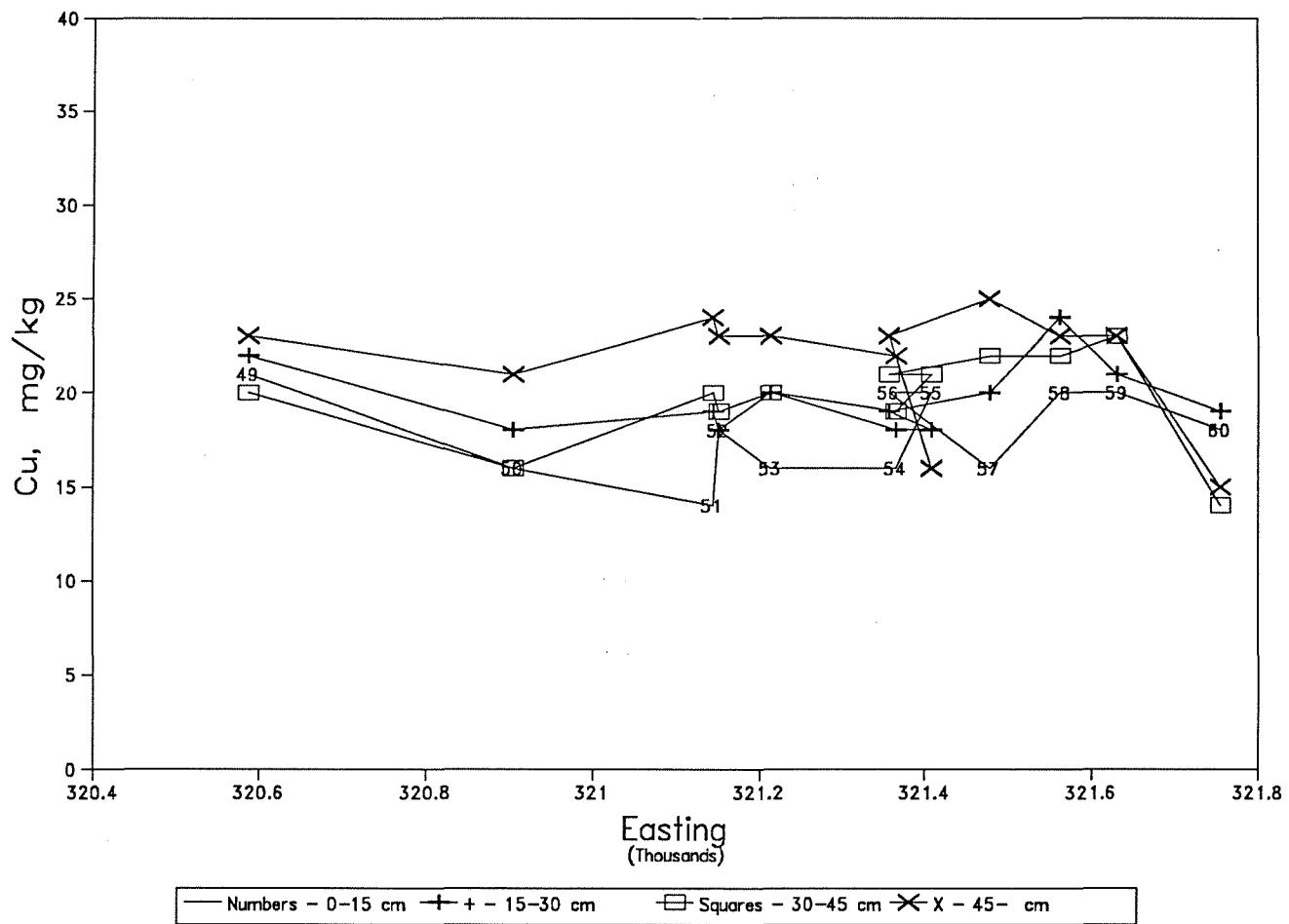


Fig. 40. Concentrations of Cu plotted against Eastings of sampling stations (see Tables 1 and 6).

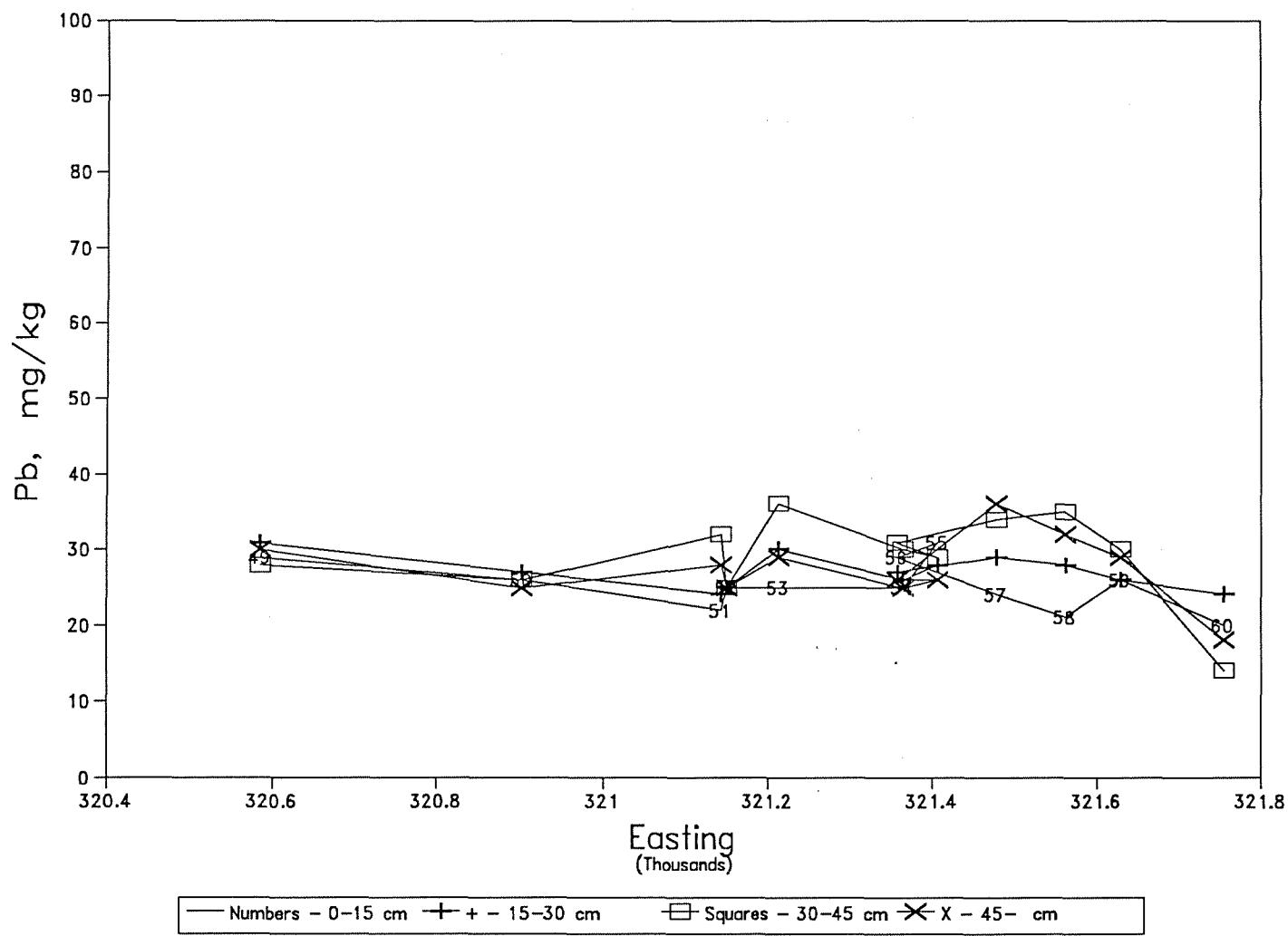


Fig. 41. Concentrations of Pb plotted against Eastings of sampling stations (see Tables 1 and 6).

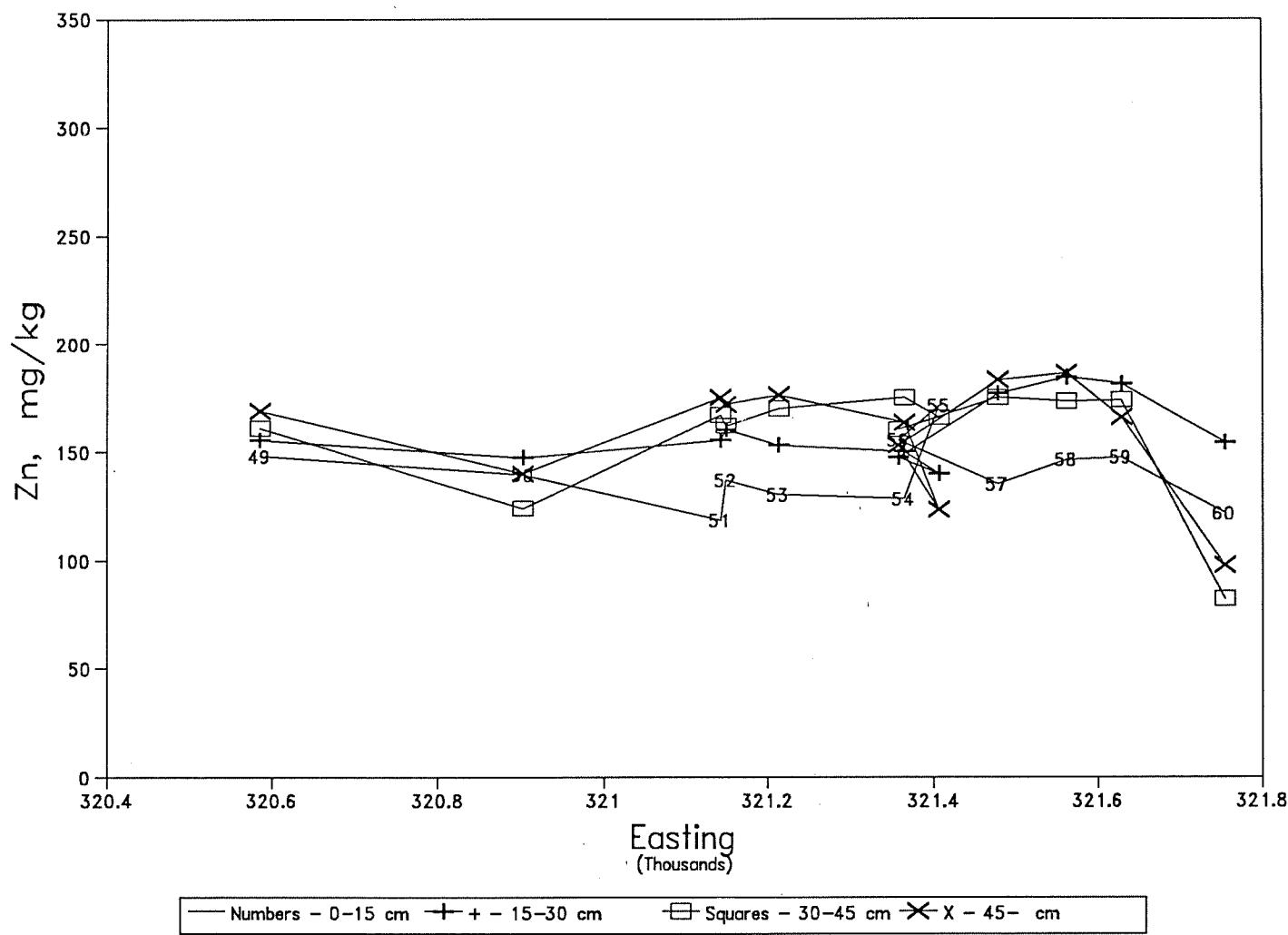


Fig. 42. Concentrations of Zn plotted against Eastings of sampling stations (see Tables 1 and 6).

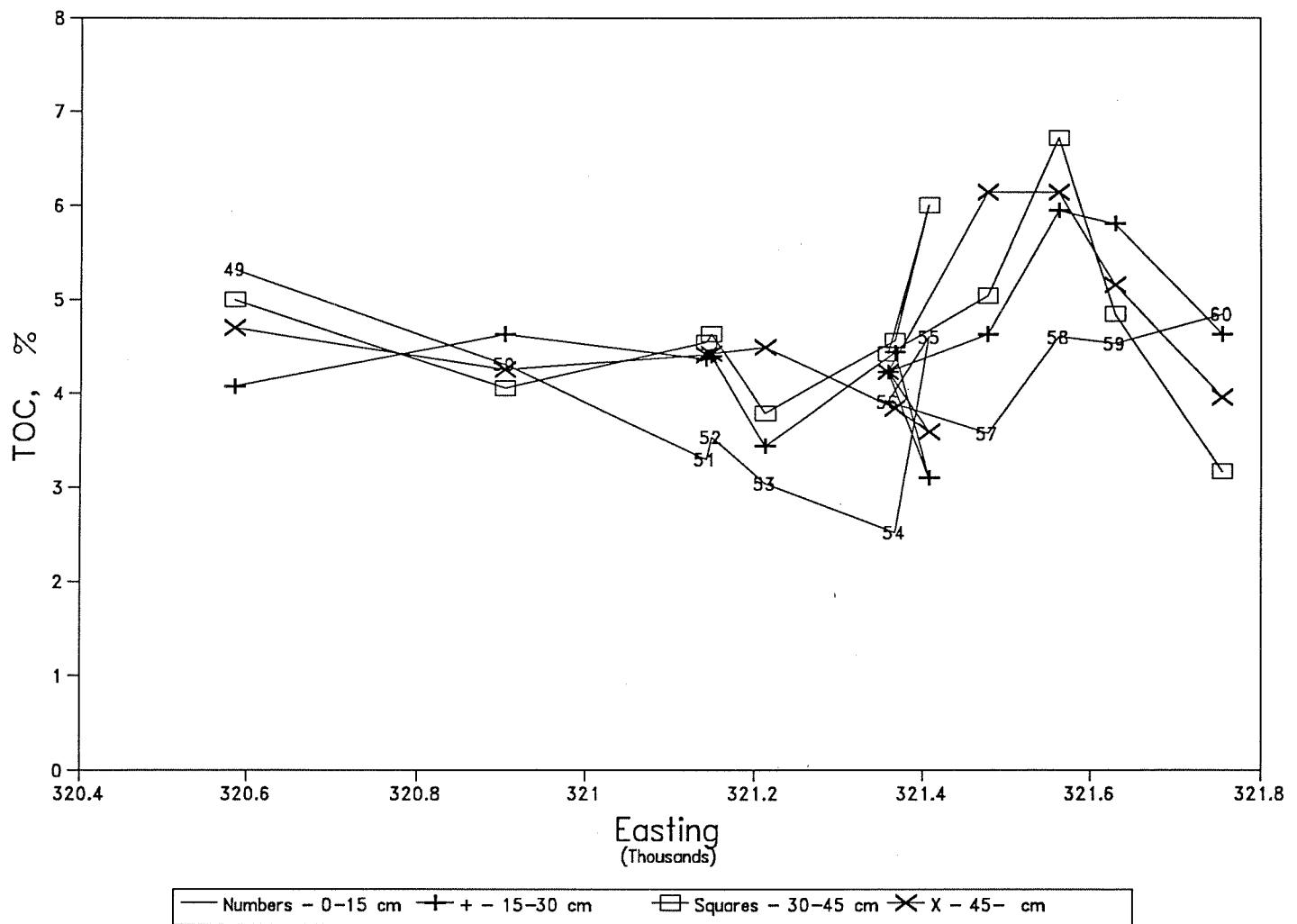


Fig. 43. Concentrations of TOC plotted against Eastings of sampling stations (see Tables 1 and 6).

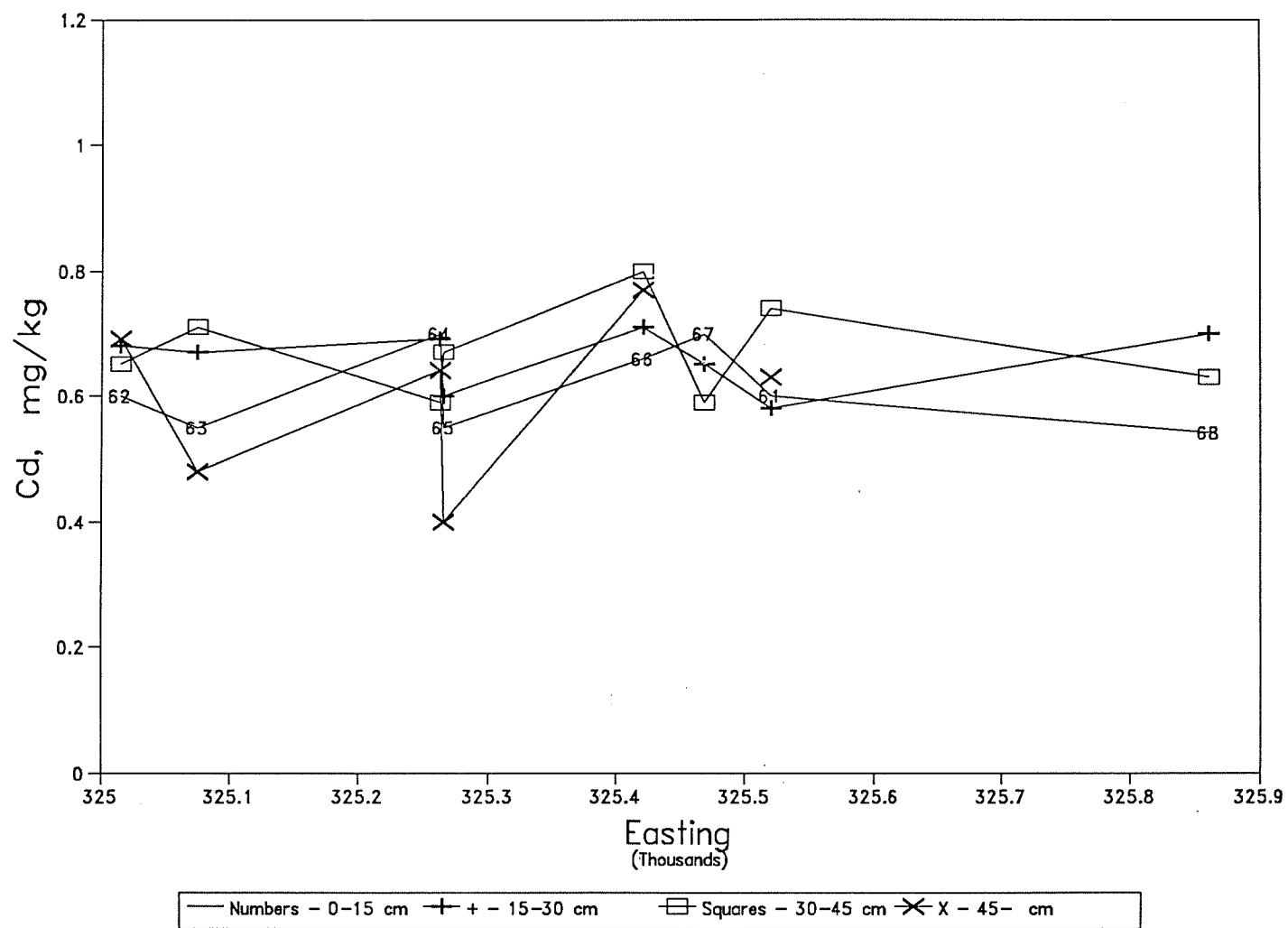


Fig. 44. Concentrations of Cd plotted against Eastings of sampling stations (see Tables 1 and 6).

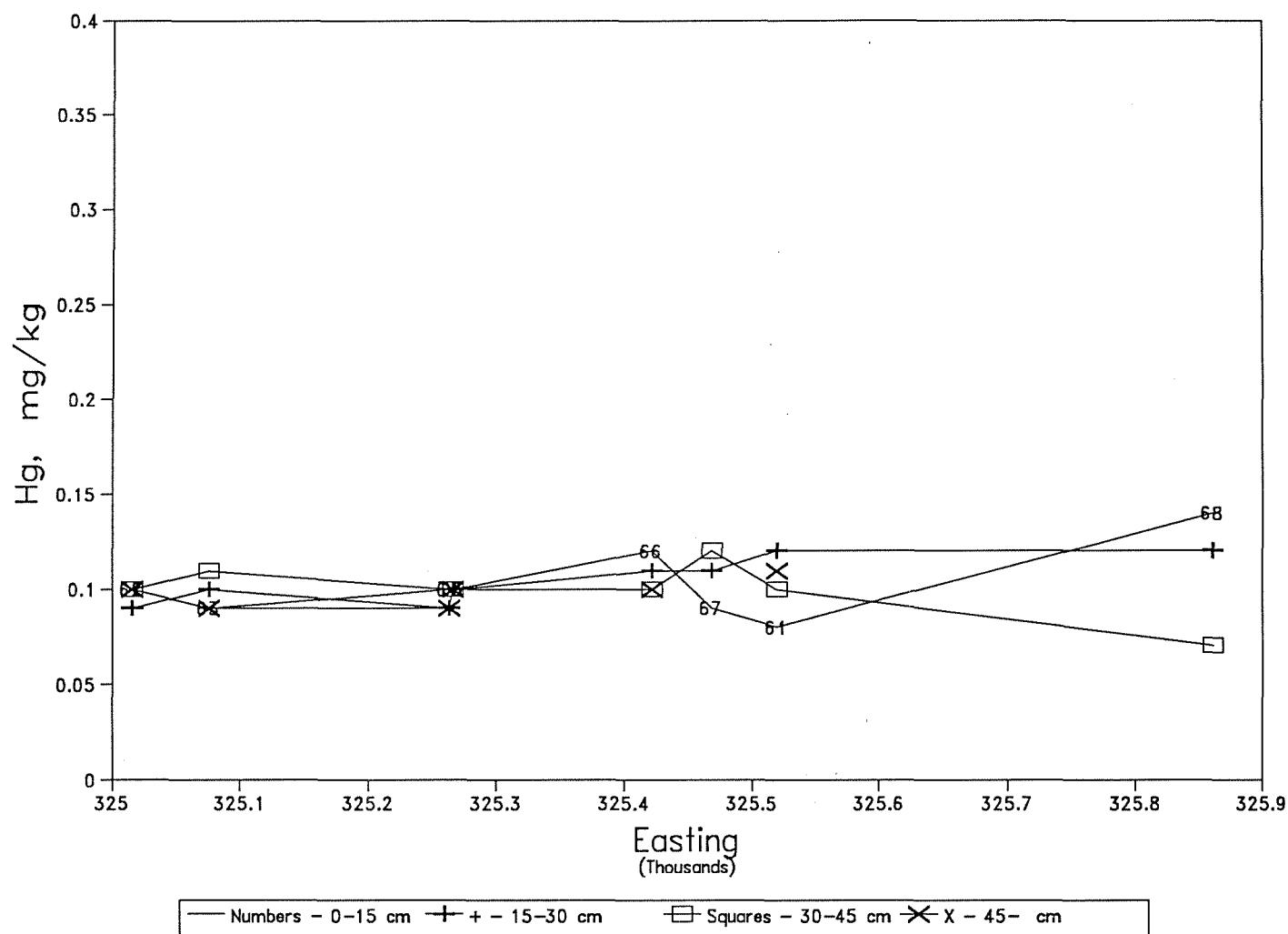


Fig. 45. Concentrations of Hg plotted against Eastings of sampling stations (see Tables 1 and 6).

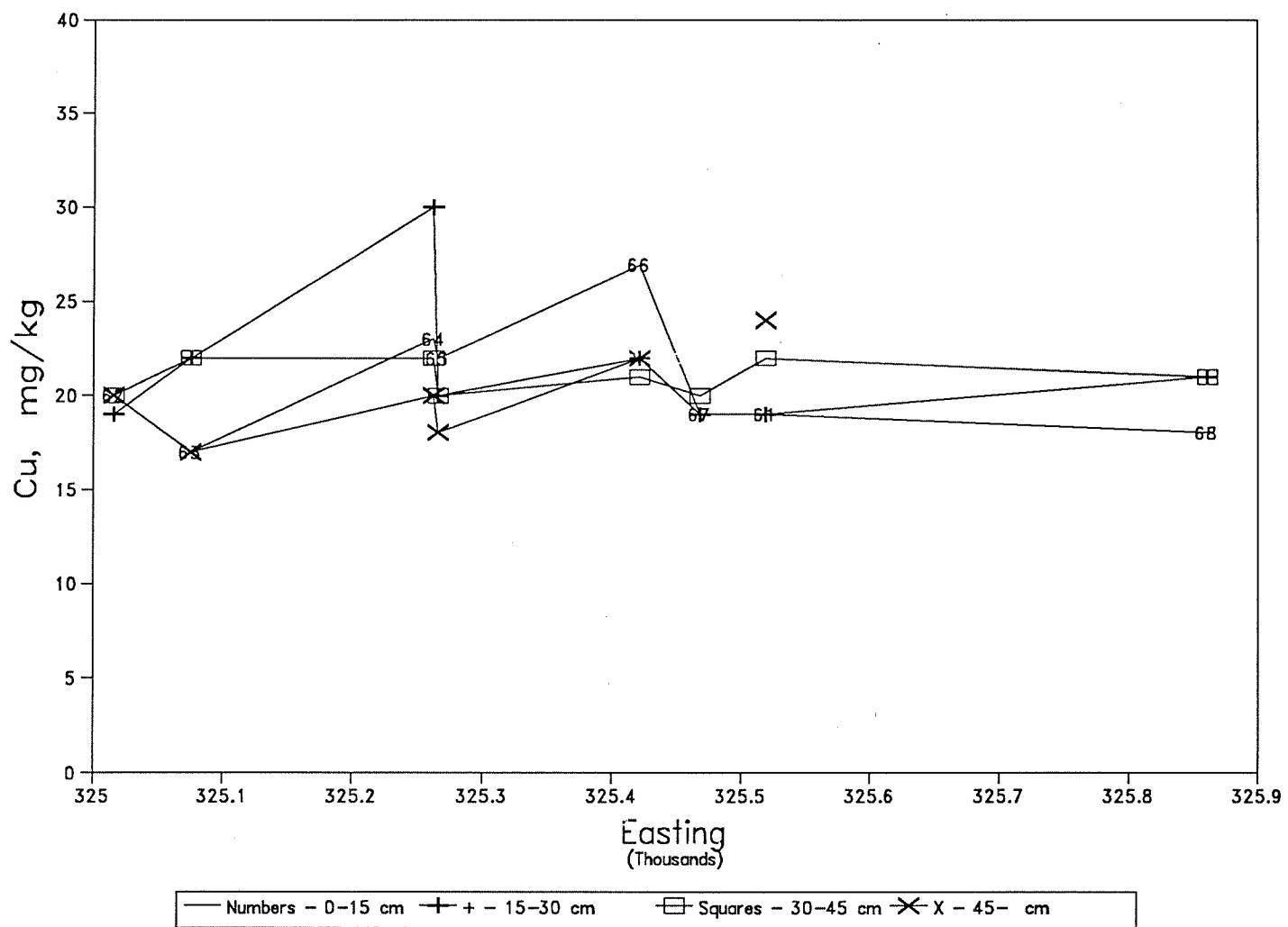


Fig. 46. Concentrations of Cu plotted against Eastings of sampling stations (see Tables 1 and 6).

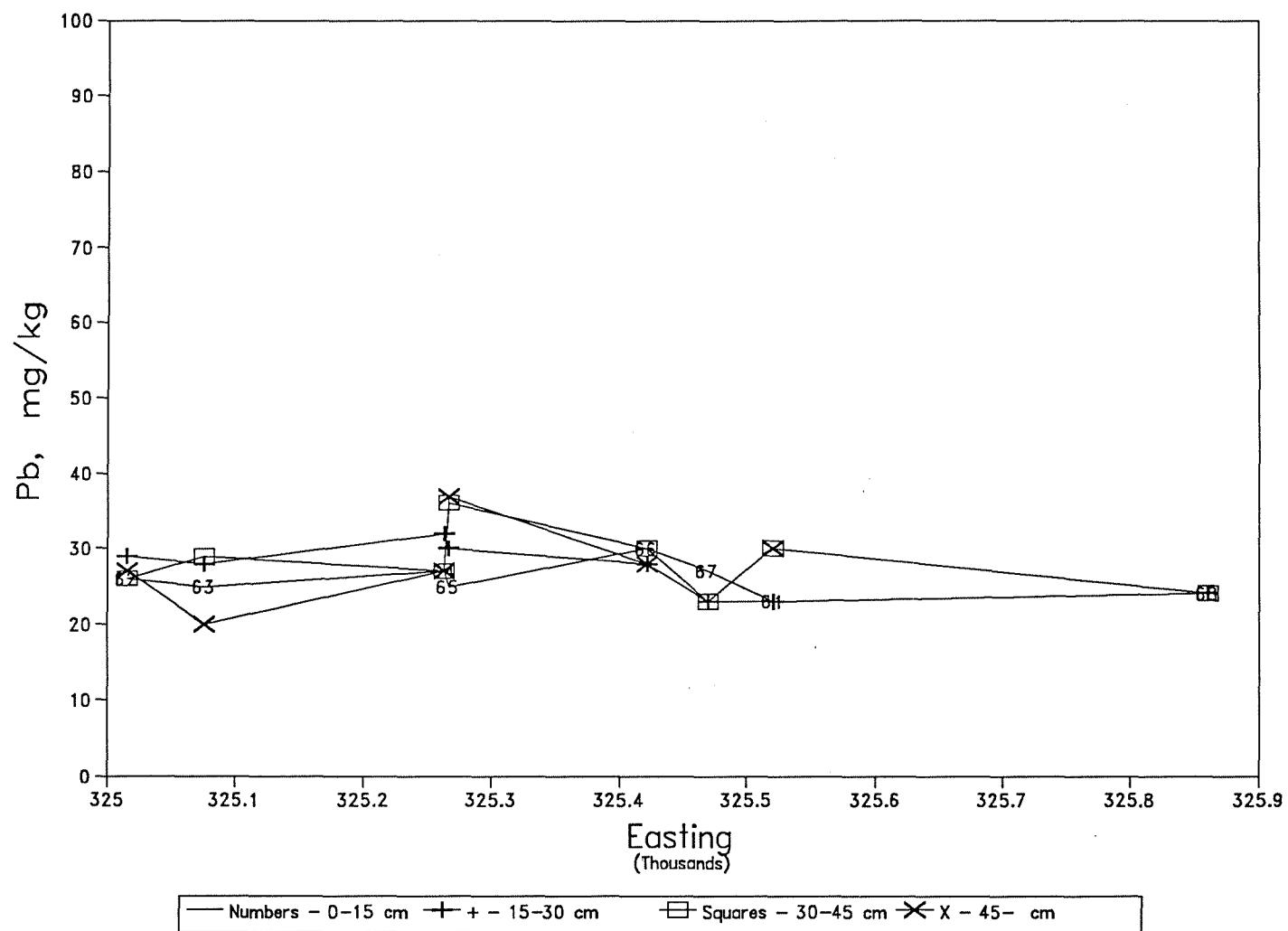


Fig. 47. Concentrations of Pb plotted against Eastings of sampling stations (see Tables 1 and 6).

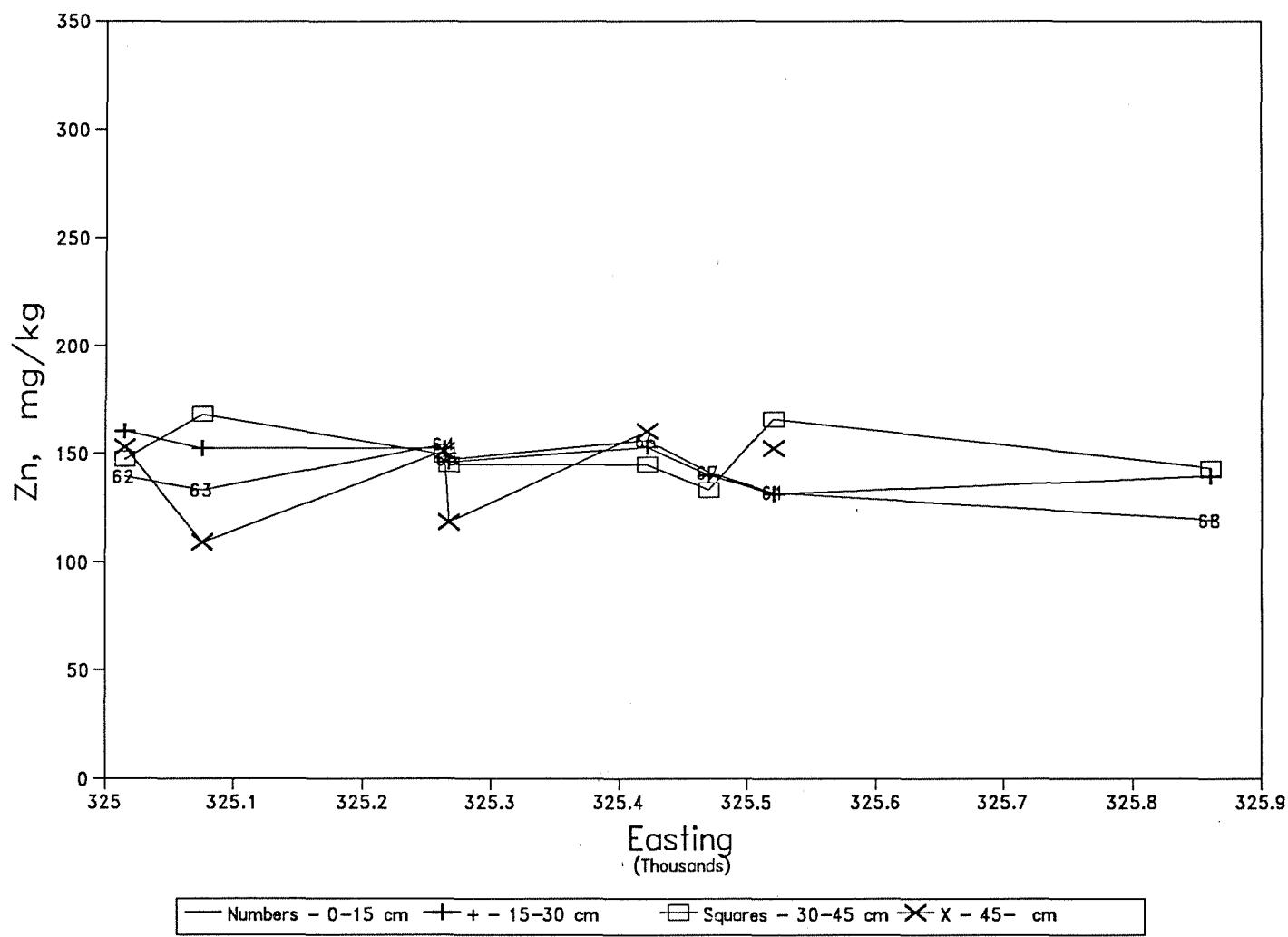


Fig. 48. Concentrations of Zn plotted against Eastings of sampling stations (see Tables 1 and 6).

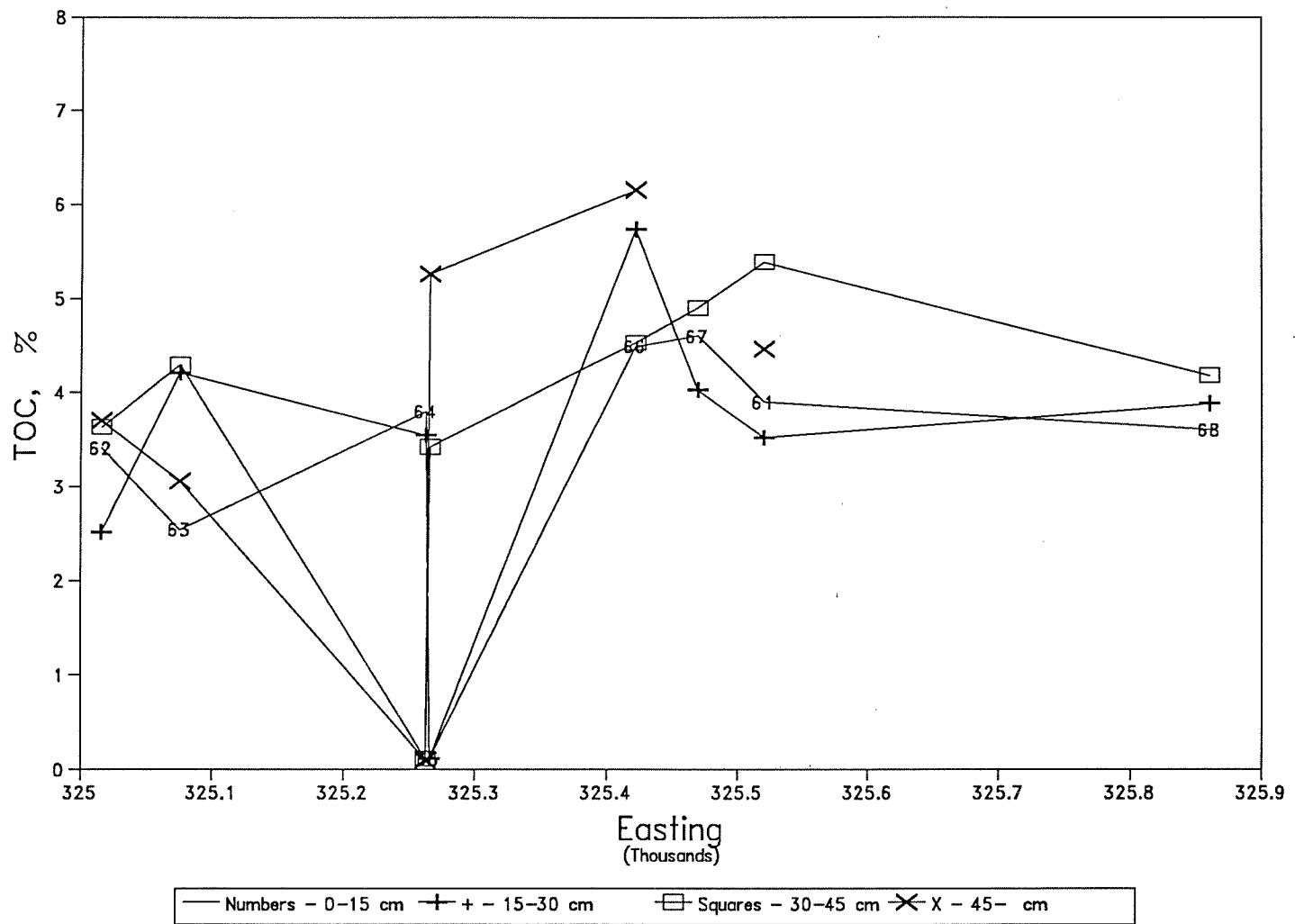


Fig. 49. Concentrations of TOC plotted against Eastings of sampling stations (see Tables 1 and 6).

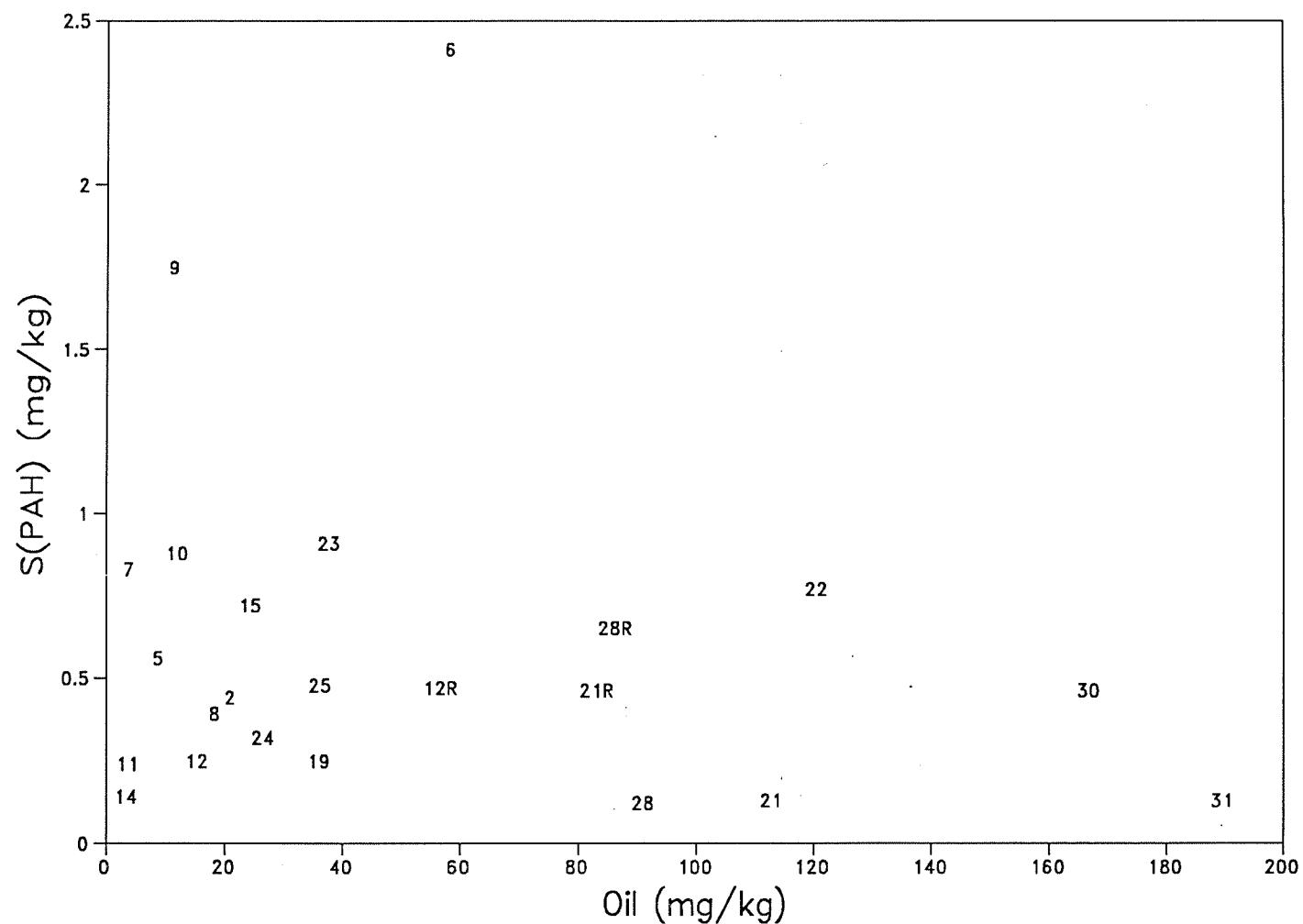


Fig. 50. The lack of relationship between the concentrations of oil and total PAH. Sample numbers refer to Table 1.

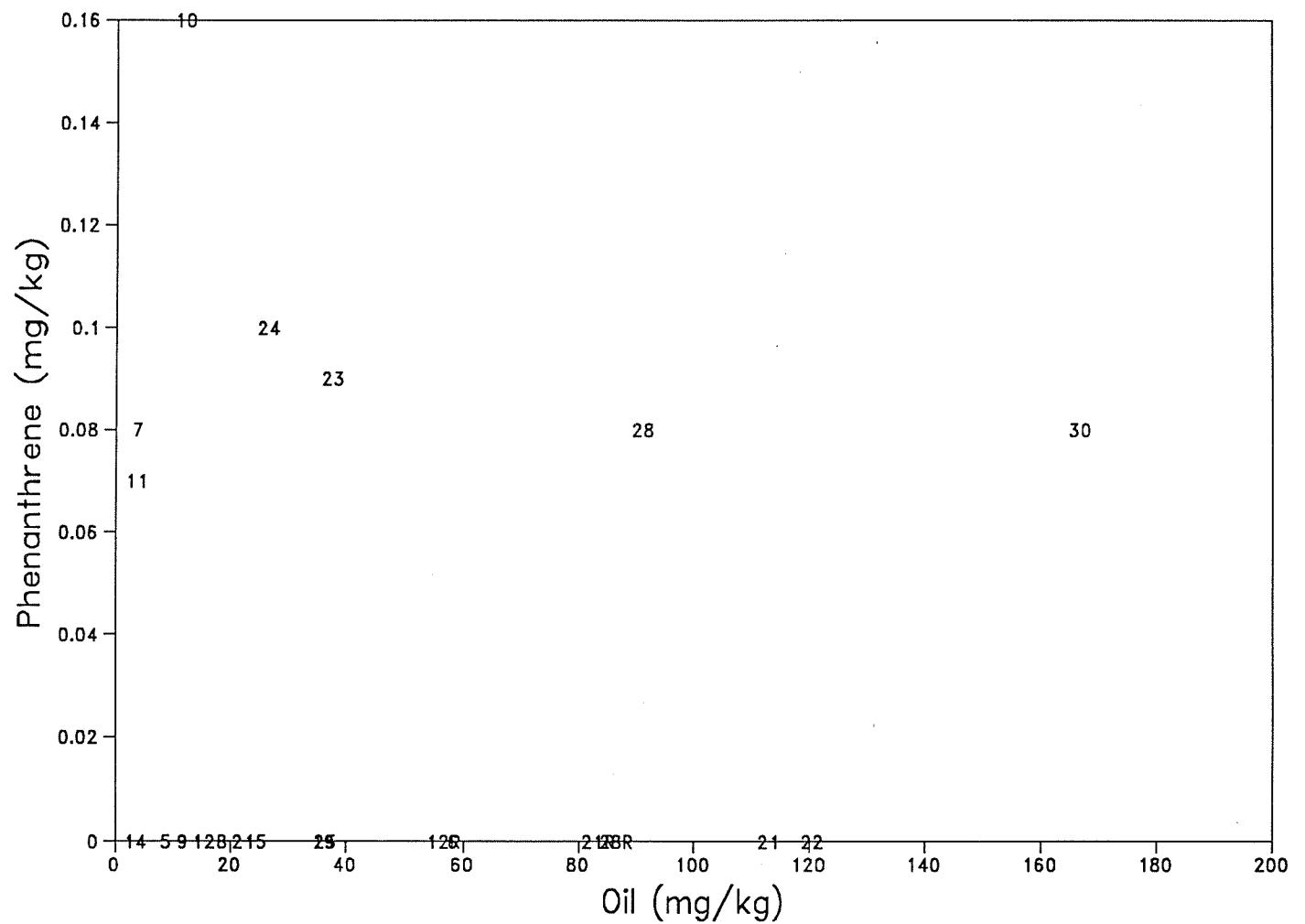


Fig. 51. The lack of relationship between the concentrations of oil and phenanthrene. Sample numbers refer to Table 1.