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Mercury and organochlorine compounds in eels (*Anguilla rostrata* L.) from the Miramichi watershed

by

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ABSTRACT

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Eels (*Anguilla rostrata* L.) were obtained from two stations in the Miramichi, New Brunswick, Canada, watershed. The eels were divided into 'large' (mean weight 1092 and 1205 g), 'medium' (771 and 776 g), and small (226 and 442 g) groups, and analyzed for mercury, organochlorine pesticides and PCB, and 'toxic' (2378 chlorine substituted) chlorinated dibenzodioxins and dibenzofurans (CDDF). Levels of mercury were low (overall mean 0.089 µg/g wet weight). Of organochlorine pesticides, only p,p'-DDE was detectable in all samples (overall mean 15 ng/g wet weight). p,p'-DDD was detected in some samples, and PCB were not detectable. Very low levels of CDDF were detected and the reproducibility of the analyses was poor. All samples contained chlorinated diphenyl ethers (CDE). The quality of the determination of organochlorine pesticides and PCB must be improved. Low levels of CDDF do not warrant additional analyses, but the presence of CDE should be investigated further. Samples submitted for analysis should contain 'latent' duplicates, in addition to standard reference materials.

RÉSUMÉ

Zitko, V., and H. Collins. 1997. Mercury and organochlorine compounds in eels (*Anguilla rostrata* L.) from the Miramichi watershed. Can. Manuscr. Rep. Fish. Aquat. Sci. iii + 31 p.

Les anguilles (*Anguilla rostrata* L.) ont été obtenues à deux stations dans le bassin hydrographique de la Miramichi (Nouveau-Brunswick), au Canada. Les anguilles ont été classées en "grandes" (poids moyen de 1 092 et 1 205 g), "moyennes" (771 et 776 g) et "petites" (226 et 442 g), et analysées pour le mercure, les pesticides organochlorés, les PCB, ainsi que les dibenzodioxines (chlorées en 2,3,7,8) et les dibenzofuranes chlorés (CDDF). Les concentrations de mercure étaient faibles (moyenne globale de 0,089 µg/g de poids humide). De tous les pesticides organochlorés, seul le p,p'-DDE a été décelé dans tous les échantillons (moyenne globale de 15 ng/g de poids humide). Le p,p'-DDD a été décelé dans certains échantillons, et on n'a pas pu déceler de PCB. Il y a eu détection de très faibles concentrations de CDDF, mais la reproductibilité des analyses était médiocre. Tous les échantillons renfermaient des oxydes de diphényle chlorés (ODC). Il faudra améliorer la qualité des analyses de pesticides organochlorés et de PCB. Les faibles concentrations de CDDF ne justifient pas d'analyses supplémentaires, mais la présence d'ODC doit faire l'objet de recherches plus poussées. Les échantillons soumis à l'analyse doivent comporter des doubles "latents" en plus des matières de référence normalisées.

INTRODUCTION

The objectives of this study were to determine the levels of the title compounds in eels and to estimate the reproducibility of analyses performed by commercial laboratories.

The eels were obtained from Brander's Cove (BC), a site on the Northwest Miramichi River, just west (upstream) of the Eel Ground First Nations Reserve, and from the mouth of Bay du Vin River (BV) on the south shore of Miramichi Inner Bay. Both sites are in the Miramichi River estuary (see Map). Miramichi River Environmental Assessment Committee was able to secure the samples at Brander's Cove by direct purchase from the fishers on December 7, 1995, and from Bay du Vin indirectly through specimens purchased on a commercial fish market in January 2, 1996. The eels were taken by spearing them through the ice after the "mud-up" in late fall.

Specimens from both locations were divided into three groups (Table 1). Approximately 50 g of muscle were taken from the dorsal part of the body behind the head of each eel. The samples were pooled and homogenised in a Sorvall Omnimixer. Two samples were taken from each homogenate and submitted for analysis. The analyses were performed by the Research and Productivity Council (Arsenault and Silk 1996). RPC did not know which samples were duplicates.

MERCURY

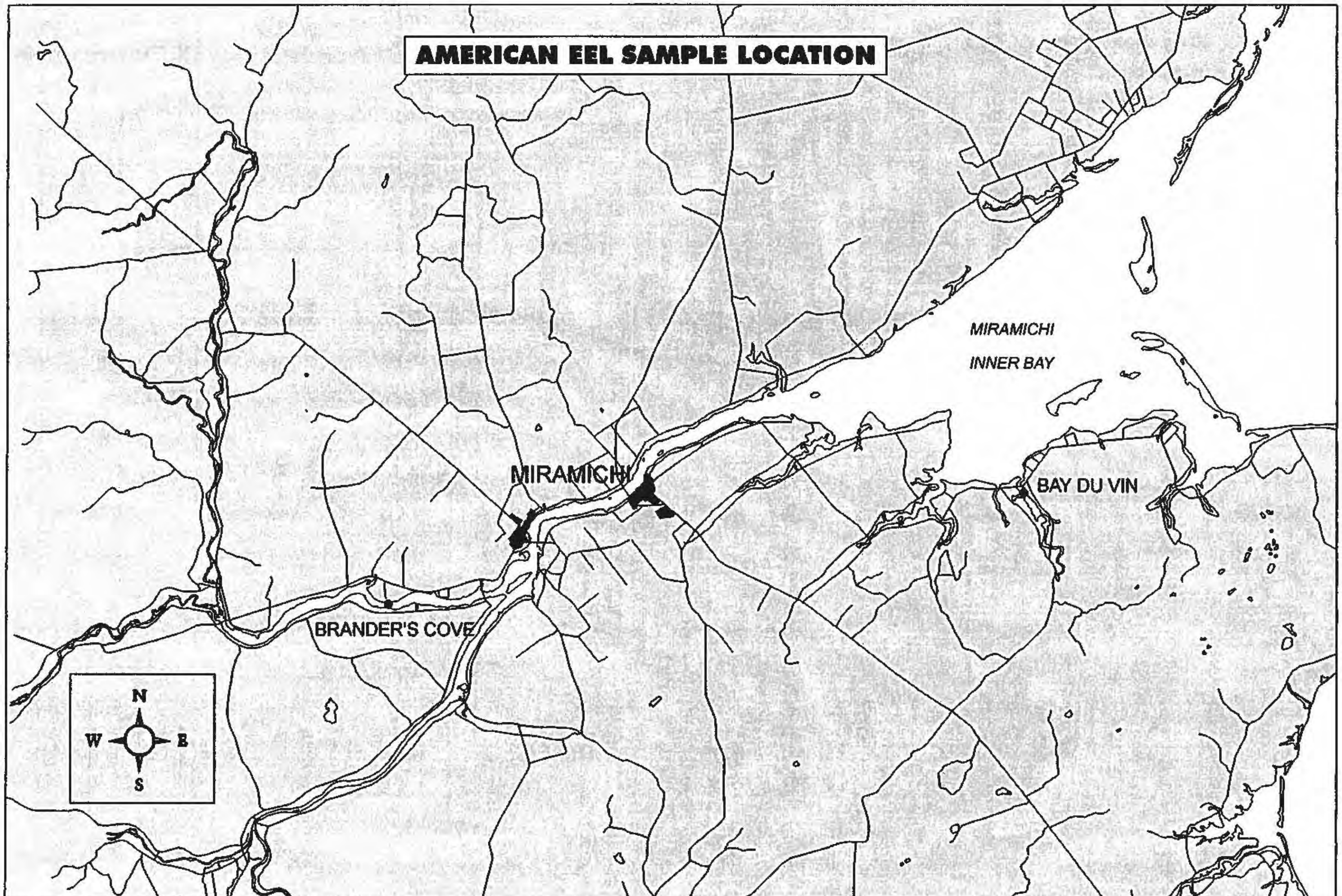
The levels of mercury are low and, with one exception, the agreement between known and 'latent' duplicates is reasonable (Fig. 1). The levels do not depend on the weight of the eels and are on the average lower in eels from Brander's Cove (BC, mean 0.070, std 0.034, cv 48.8%) than in eels from Bay du Vin (BV, mean 0.108, std 0.011, cv 9.95%). The values are much less uniform in the former than in the latter. The difference between BC and BV is statistically significant at P=0.05, provided the assumptions of the t-test are met.

ORGANOCHLORINE PESTICIDES AND PCB

Only p,p'-DDE and, in some instances, p,p'-DDD are detectable (Table 2, Fig. 2). The difference in the DDE concentration between the BC and the BV samples is not statistically significant. The levels are about 30% of the values reported by Zitko for an eel homogenate prepared in 1990 (Zitko 1995), and the differences between latent duplicates are considerable. PCB are reported as not detectable (the eel homogenate contained the chlorobiphenyls # 153 and 138 at 11 and 19 ng/g, respectively). It may be that peaks of some chlorobiphenyls are hidden in the 'noisy' baseline. A detailed analysis of this possibility awaits the delivery of the data as computer text files, by RPC. If some chlorobiphenyls are present, their

Table 1. Weight (g) of eels and pooling of samples.

	Locality					
	Brander's Cove, NW Miramichi			Bay du Vin		
	Large	Medium	Small	Large	Medium	Small
	1348	903	385	1093	863	610
	1239	795	298	1444	664	619
	1012	894	215	1375	749	564
	1158	583	249	1143	856	280
	1038	681	166	1277	935	304
	988		156	1101	665	276
	953		114	1005	702	
	1003					
Mean	1092	771	226	1205	776	442
Std	132	124	86	150	100	157
CV, %	12	16	38	12	13	35
	Sample code					
	BC2	BC1	BC3	BV1	BV5	BV3
	BC$	BC6	BC5	BV2	BV6	BV4



AMERICAN EEL SAMPLE LOCATION
MIRAMICHI
INNER BAY
MIRAMICHI
BAY DU VIN
BRANDER'S COVE
N
W
E
S

Table 2. Concentration of p,p'-DDE and p.p'-DDD (ng/g) in eels.

Sample	DDE	DDD
BC2*	16	5
BC4*	17	5
BC1+	17	6
BC6+	15	5
BC6 DUPL	13	0
BC3#	18	0
BC5#	8	0
BV1^	12	0
BV2^	16	0
BV5@	17	0
BV6@	12	0
BV3&	29	0
BV4&	9	0

*, +, #, ^, @, & - latent duplicates.

levels are very low. Somewhat more disturbing are the variations in gas chromatograms between the latent duplicates. The variations may indicate contamination problems in the analytical laboratory (Fig. 3-15). Because of different methods and no intercalibration, it is impossible to tell whether the difference between the present and the 1990 data is significant.

CHLORINATED DIBENZODIOXINS AND DIBENZOFURANS (CDDF)

The concentrations of the 'toxic' CDDF (the '2378' chlorine substitution pattern) are very low (Table 3). For further evaluation, the 'non-detectable' values are arbitrarily replaced by 50% of the method detection limit. The concentrations of five congeners increase with weight of eels from Brander's Cove. On the other hand, nine congeners (predominantly dibenzofurans) are present in higher concentrations in heavier eels from Bay du Vin. The concentrations of CDDF in all 'small' eels and in most 'medium' eels are higher in eels from Brander's Cove than in those from Bay du Vin. In the 'large' class the differences are distributed almost equally (concentrations of 10 congeners are higher in eels from Brander's Cove).

The agreement between latent duplicates is poor. This may be largely due to the low levels of CDDF in the eels. With a few exceptions the measured values are less than twice the method detection limit (Table 4). In view of the large variations between duplicates, the significance of the size and site relationships is uncertain.

It is difficult to comprehend relationships in multicomponent mixtures of compounds such as CDDF (Table 3). Principal Component Analysis (PCA) is a technique for visualizing the patterns by reducing the number of components to a few

Table 3. Concentration of chlorinated dibenzodioxins and dibenzofurans in eels (pg/g).

	Large		Medium		Small		Large		Medium		Small	
Compound	BC2	BC4	BC1	BC6	BC3	BC5	BV1	BV2	BV5	BV6	BV3	BV4
2378	0.70	1.40	1.10	0.90	0.90	0.45	0.25	0.50	0.35	0.35	0.40	0.80
12378	1.20	1.10	1.80	2.45	1.80	3.80	1.75	2.10	1.55	1.95	1.45	0.95
123478	0.65	1.30	0.25	0.80	0.65	0.50	0.40	0.80	0.55	0.60	0.65	0.50
123678	1.30	1.10	0.60	1.50	0.55	1.30	0.35	0.70	0.45	0.50	0.60	0.45
123789	0.60	1.20	0.25	1.70	1.50	1.90	0.35	0.80	0.50	0.55	0.65	0.50
234678	1.40	2.80	1.20	3.00	1.60	2.50	0.90	2.20	2.00	1.75	1.35	1.25
ocdd	3.70	2.40	1.40	8.20	3.80	11.10	1.15	7.00	2.30	0.80	3.30	1.90
2378f	0.85	1.70	2.50	2.25	2.80	2.60	1.05	2.35	1.65	1.70	2.15	1.50
12378f	2.30	1.30	1.30	3.10	1.85	3.60	2.40	1.55	2.75	2.00	2.25	1.75
23479f	2.70	1.30	1.30	3.10	1.45	3.60	2.40	1.30	2.75	2.00	2.25	1.75
123478f	0.90	0.90	0.65	2.20	1.00	2.70	1.10	1.05	1.05	0.20	0.75	0.90
123678f	1.60	0.80	0.60	2.10	0.90	2.30	1.00	0.95	0.95	1.00	0.70	0.80
234678f	1.50	1.00	0.70	1.00	1.05	1.90	1.20	1.15	1.15	0.40	0.80	0.95
123789f	2.00	1.10	0.80	1.20	1.20	1.05	1.40	1.30	1.35	0.25	0.95	1.10
1234678f	1.50	1.30	0.55	2.90	3.10	4.60	1.25	2.40	0.65	0.80	0.65	0.70
1234789f	0.85	1.70	0.75	0.90	1.35	1.20	1.70	0.90	0.90	1.05	0.90	0.95
ocdf	2.15	4.30	0.70	3.30	2.60	1.30	0.60	0.75	0.55	0.65	0.55	0.90

Table 4. Concentration divided by method detection limit.

Compound	BC2	BC4	BC1	BC6	BC3	BC5	Mean	Max
2378	0.50	2.20	1.13	1.13	0.50	0.50	0.99	2.20
12378	1.09	0.50	0.50	0.50	0.50	0.50	0.60	1.09
123478	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
123678	1.18	1.50	1.07	0.50	1.44	0.50	1.03	1.50
123789	0.50	0.50	1.13	1.25	1.90	0.50	0.96	1.90
234678	0.50	1.00	2.00	0.50	0.50	0.50	0.83	2.00
ocdd	1.54	0.50	4.56	0.50	2.92	0.50	1.75	4.56
2378f	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
12378f	1.77	0.50	0.50	0.50	0.50	0.50	0.71	1.77
23479f	2.08	0.50	0.50	0.50	0.50	0.50	0.76	2.08
123478f	1.00	0.50	1.16	0.50	1.59	0.50	0.87	1.59
123678f	2.00	0.50	1.24	0.50	1.44	0.50	1.03	2.00
234678f	1.50	0.50	0.50	0.50	1.06	0.50	0.76	1.50
123789f	1.82	0.50	0.50	0.50	0.50	0.50	0.72	1.82
1234678f	1.15	0.50	2.23	1.55	2.71	0.50	1.44	2.71
1234789f	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
ocdf	0.50	1.40	2.36	2.00	0.50	0.50	1.21	2.36
Mean	1.10	0.74	1.23	0.73	1.06	0.50		
	BV1	BV2	BV5	BV6	BV3	BV4	Mean	Max
2378	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
12378	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
123478	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
123678	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
123789	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
234678	0.50	1.00	0.50	0.50	0.50	0.50	0.58	1.00
ocdd	0.50	6.36	2.87	0.50	3.30	2.37	2.65	6.36
2378f	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
12378f	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
23479f	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
123478f	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
123678f	0.50	0.50	0.50	3.33	0.50	0.50	0.97	3.33
234678f	0.50	0.50	0.50	1.00	0.50	0.50	0.58	1.00
123789f	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
1234678f	0.50	1.85	0.50	0.50	0.50	0.50	0.72	1.85
1234789f	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
ocdf	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Mean	0.50	0.98	0.65	0.71	0.68	0.62		

'principal' ones, without a considerable loss of information (Zitko 1994). This simplifies graphical presentation and visual examination of the data. The result is 'scores' plots. In these, sample positions are plotted in new 'principal component' coordinates. Samples similarity is inversely proportional to their distance. On the other hand, 'loadings' plots indicate the effect the original variables have on the principal components. A high level of a variable will affect most the principal component on which this variable has the highest loading. The concentrations of the components of the mixture (sometimes referred to as 'profile') can be used as such or can be expressed as percents of total, to eliminate the effect of widely different concentrations.

Figure 16 is the scores plot in the plane of first two principal components. Latent duplicates are connected by lines. It can be seen that with one exception the agreement between the latent duplicates is poor and the situation is the same in the pc-1 and pc-3 plane (Fig. 17). Elimination of concentration differences by expressing the concentrations as percents shows equally poor similarity of latent duplicates (Fig. 18, 19). The agreement is somewhat better when the results are corrected for recovery (Fig. 20, 21).

A comparison of the profiles of CDDF in fish and shellfish has been published (Zitko 1992). To compare the present data with published ones, the positions of the Miramichi eel data were calculated in the principal component coordinates of the published set. Since the published set does not contain 1,2,3,4,6,7,8- hepta-, and octachlorodibenzodioxin, 1,2,3,4,6,7,8- hepta-, 1,2,3,4,6,7,9-hepta- and octachlorodibenzofuran, their concentrations could not be used in the calculations. The Miramichi eel CDDF profiles fall, with one exception, well within the published data set (Fig. 22, 23).

Effects of pulpmills are particularly expressed by elevated levels of 2,3,7,8-tetrachlorodibenzofuran. As can be seen from the loadings plots (Fig. 24, 25), such samples would be located in the upper left-hand corner of the scores plots. Consequently, the CDDF profile of the Miramichi eels is only slightly, if at all, affected by chlorine bleaching pulpmill effluent.

Arsenault and Silk noted that all eel samples contain chlorinated diphenyl ethers (CDE) which interfere in the determination of the homologue totals of chlorinated dibenzofurans, but do not affect the values of the individual '2378' congeners. However, the differences in the numbers of CDDF isomers in the latent duplicates (Table 5) should not occur. The presence of CDE deserves a further study.

CONCLUSIONS

1. The levels of mercury, organochlorine pesticides, PCB, and chlorinated dibenzodioxins and dibenzofurans in eels from Brander's Cove and Bay du Vin are low.

2. The quality of the mercury determinations is good.

3. The determination of organochlorine pesticides and PCB must be improved, particularly the detectability of chlorobiphenyls. If additional analyses are contemplated, the laboratory must analyze several standard reference materials to establish competence.

4. The quality of the determination of chlorinated dibenzodioxins and dibenzofurans is poor because of the extremely low levels encountered. The situation is not likely to improve much by analyzing standard reference materials. There is no need to analyze additional samples of eels from the given locations, in the near future.

Table 5. Number of isomers of chlorinated dibenzodioxins and dibenzofurans identified.

	Brander's Cove						Bay du Vin					
	Large		Medium		Small		Large		Medium		Small	
	BC2	BC4	BC1	BC6	BC3	BC5	BV	BV2	BV5	BV6	BV	BV
tetra	0	1	1	1	0	0	0	0	0	0	0	0
penta	0	0	0	0	0	0	0	0	0	0	0	0
hexa	1	1	2	1	4	0	0	0	0	0	0	0
hepta	1	1	2	1	1	0	0	1	0	0	0	0
octa	1	0	1	0	1	0	0	1	1	0	1	1
tetraf	3	3	3	3	3	3	3	3	3	3	3	3
pentaf	7	4	3	6	3	2	3	5	3	2	3	3
hexaf	8	4	4	2	6	2	2	3	3	6	2	2
heptaf	1	1	2	2	1	0	0	2	1	1	1	1
octaf	0	1	1	1	0	0	0	0	0	0	0	0

5. A survey of the levels of chlorinated diphenyl ethers in aquatic biota should be carried out.

6. The samples submitted for analysis should always contain latent duplicates.

ACKNOWLEDGMENTS

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REFERENCES

Arsenault, T., S.J. Silk. 1996. Chemical analyses of eel samples. Research and Productivity Council, Fredericton, NB E3B 6Z9, Report Number ES/95/0184.

Zitko, V. 1989. A graphical presentation of the composition and properties of chlorinated dibenzodioxins and dibenzofurans. Sci. Total Environ. 84: 191-194.

Zitko, V. 1992. Patterns of 2,3,7,8-substituted chlorinated dibenzodioxins and dibenzofurans in aquatic fauna. Sci. Total Environ. 111: 95-108.

Zitko, V. 1994. Principal Component Analysis in the evaluation of environmental data. Mar. Poll. Bull. 28: 718-722.

Zitko, V. 1995. Fifty years of research on the Miramichi River, p. 29-41. In Chadwick, E.M.P. (ed.). Water, science, and the public: the Miramichi ecosystem. Can. Spec. Publ. Fish. Aquat. Sci. 123: 330p.

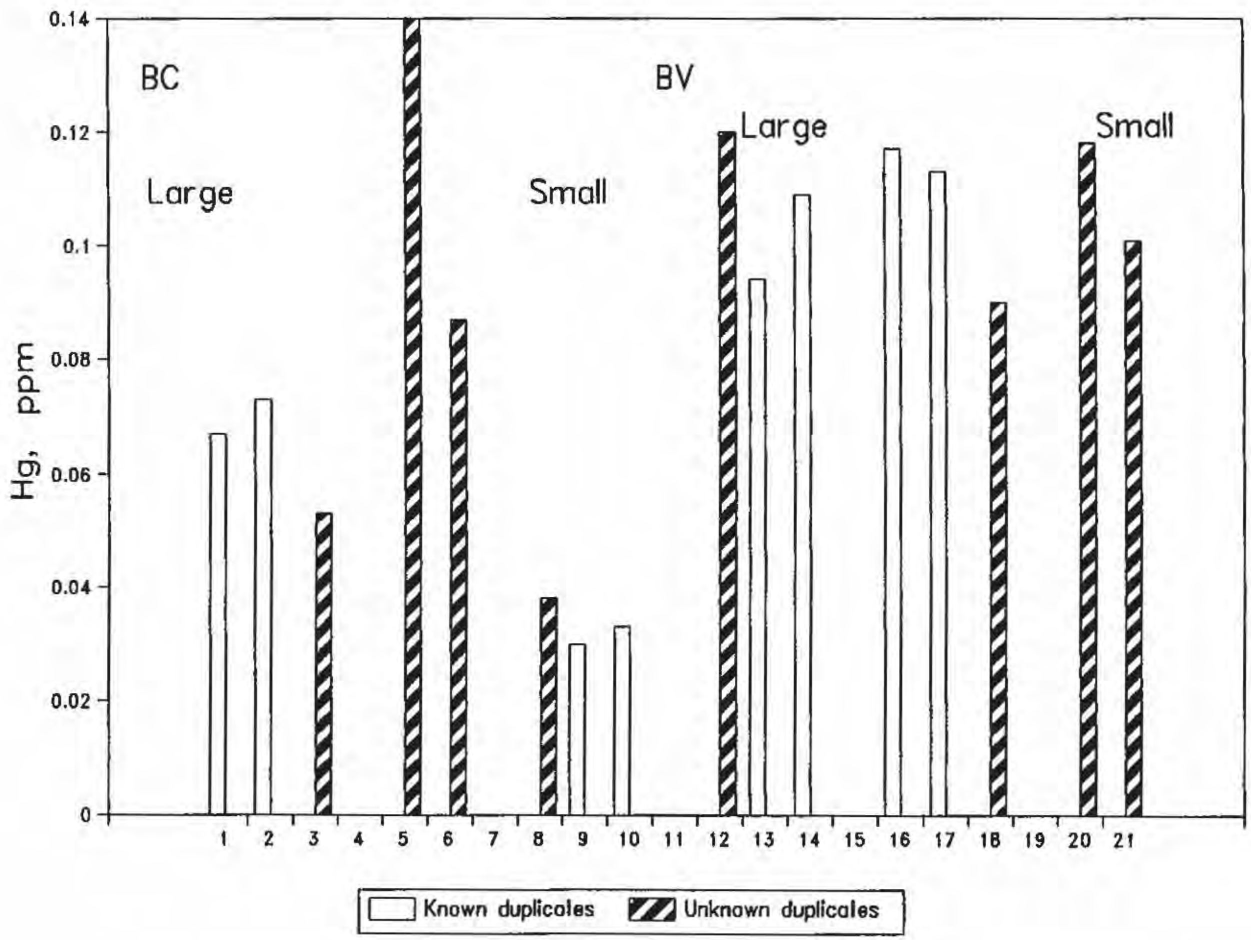

Fig. 1. Concentration of mercury levels in eels (ppm = μg/g wet weight).

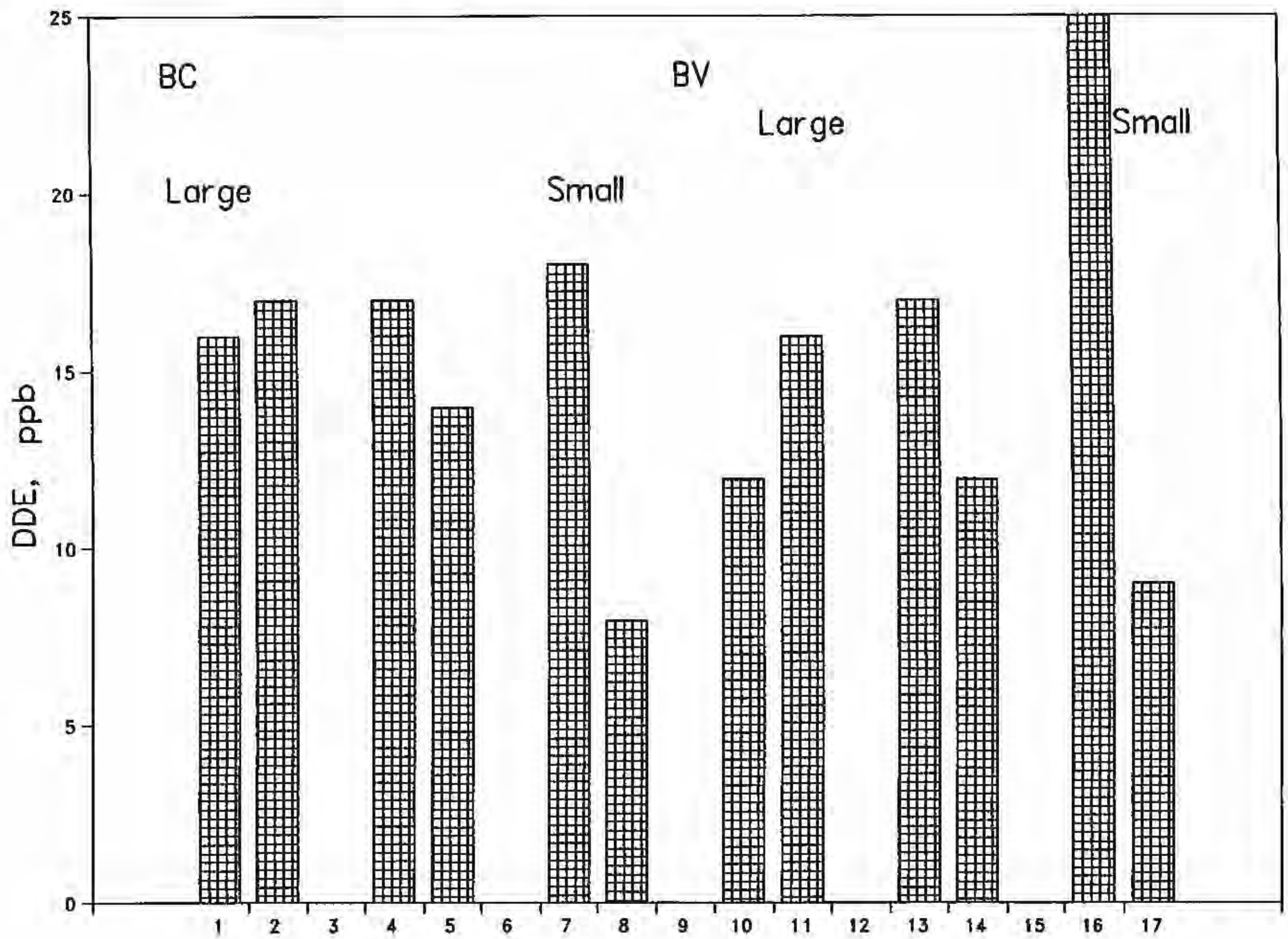

Fig. 2. Concentration of p,p'-DDE in eels (ppb = ng/g wet weight).

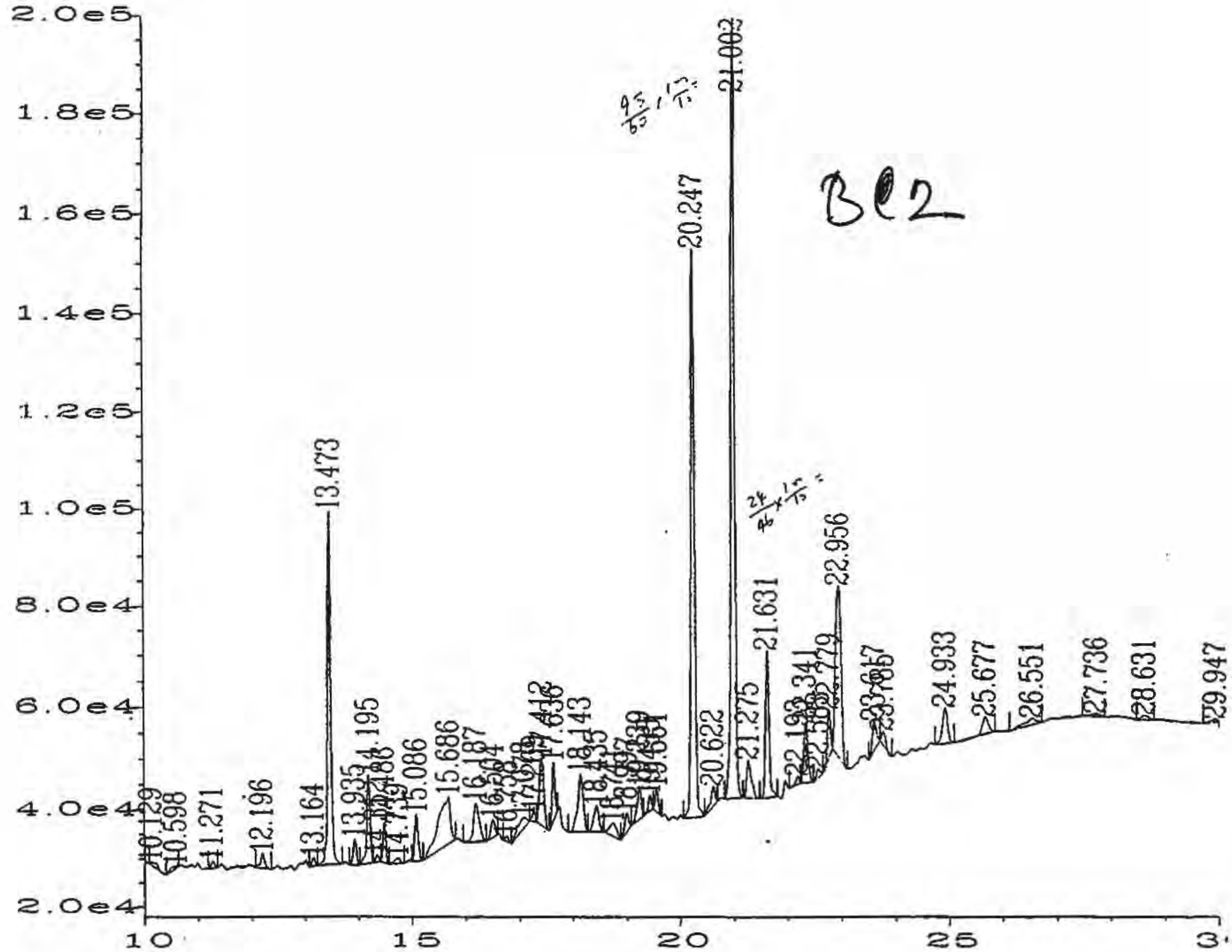

Fig.3. Gas chromatogram with electron capture detector, sample BC2
(latent duplicate of BC4)

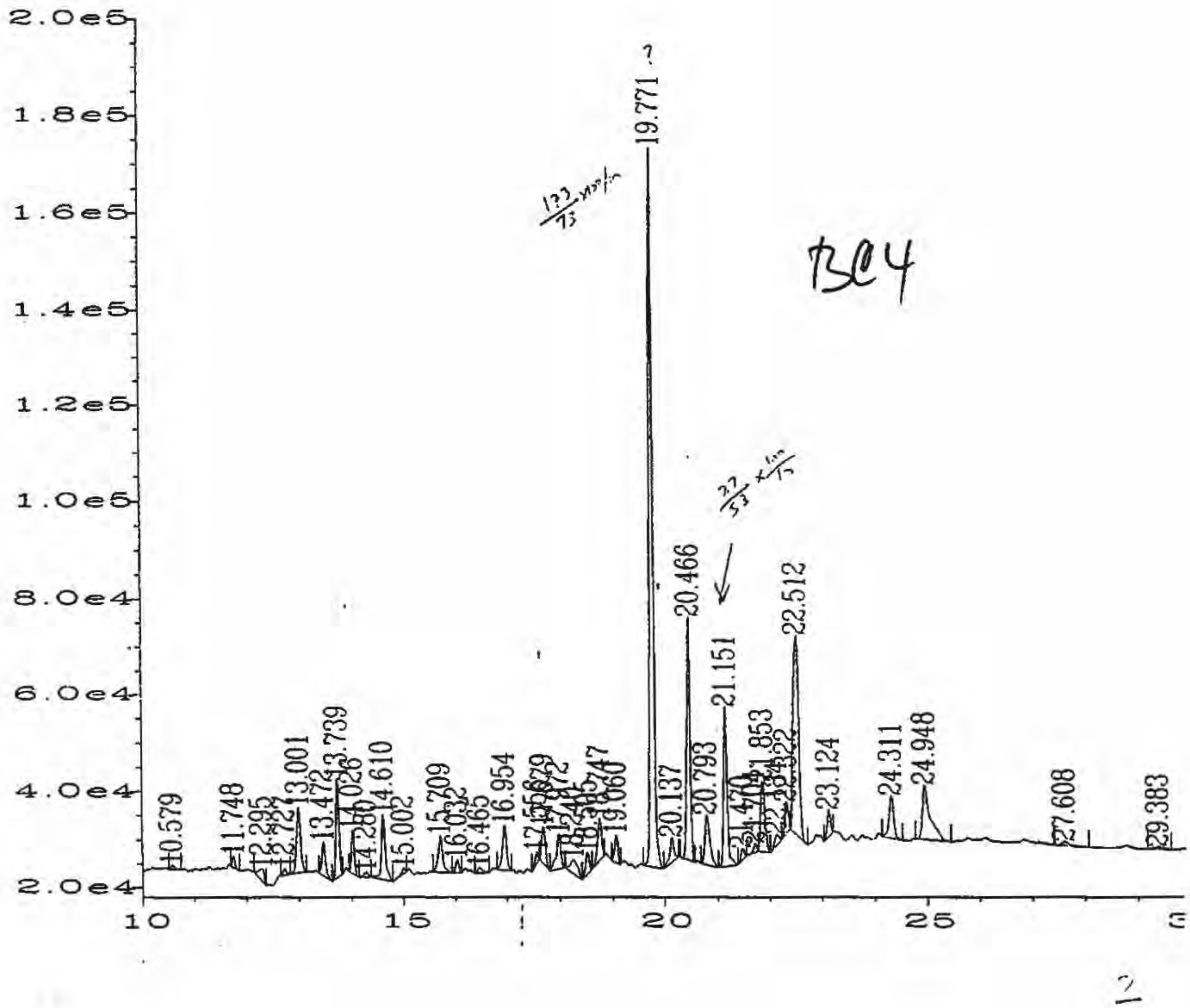

Fig.4. Gas chromatogram with electron capture detector, sample BC4
(latent duplicate of BC2)

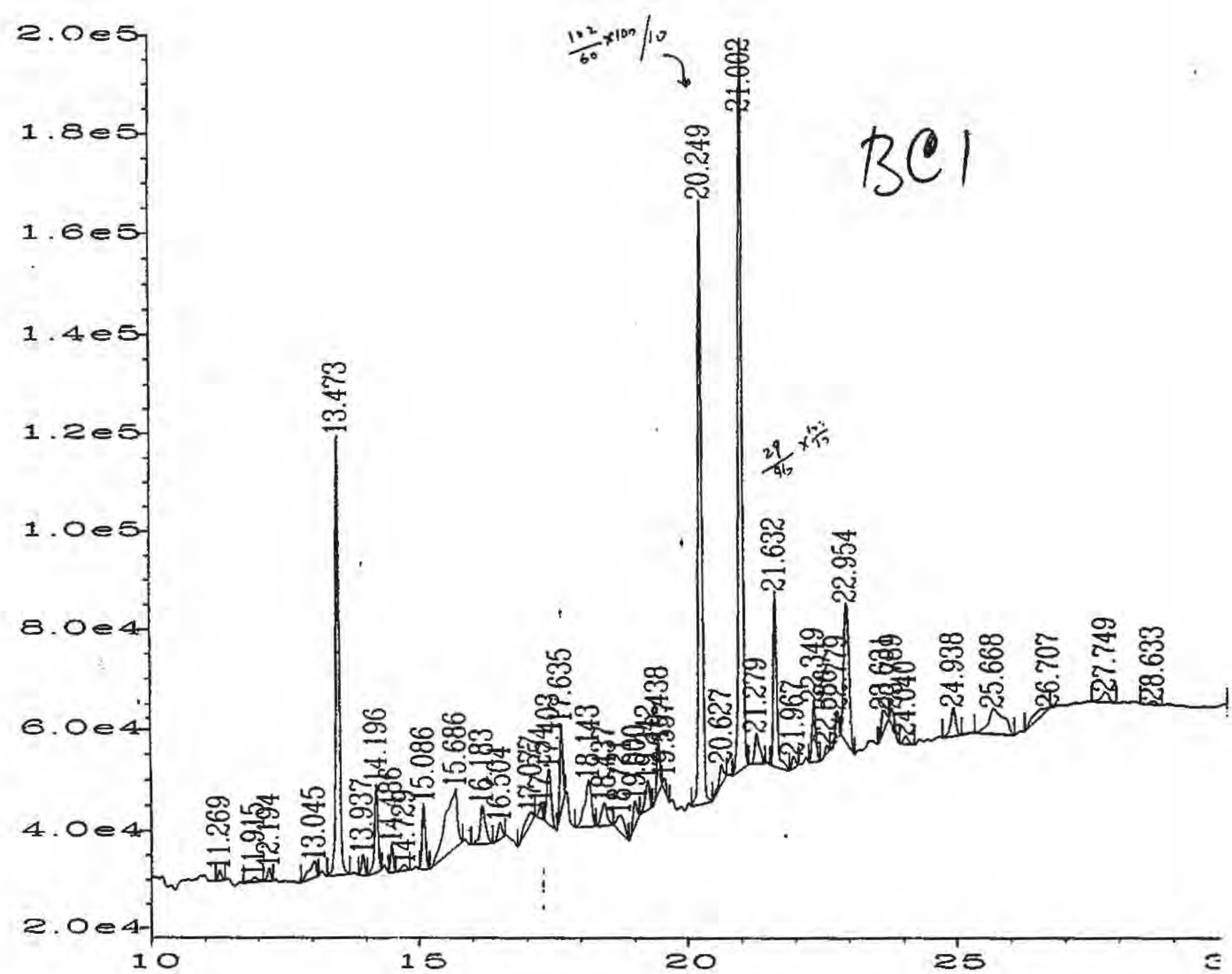

Fig.5. Gas chromatogram with electron capture detector, sample BC1
(latent duplicate of BC6)

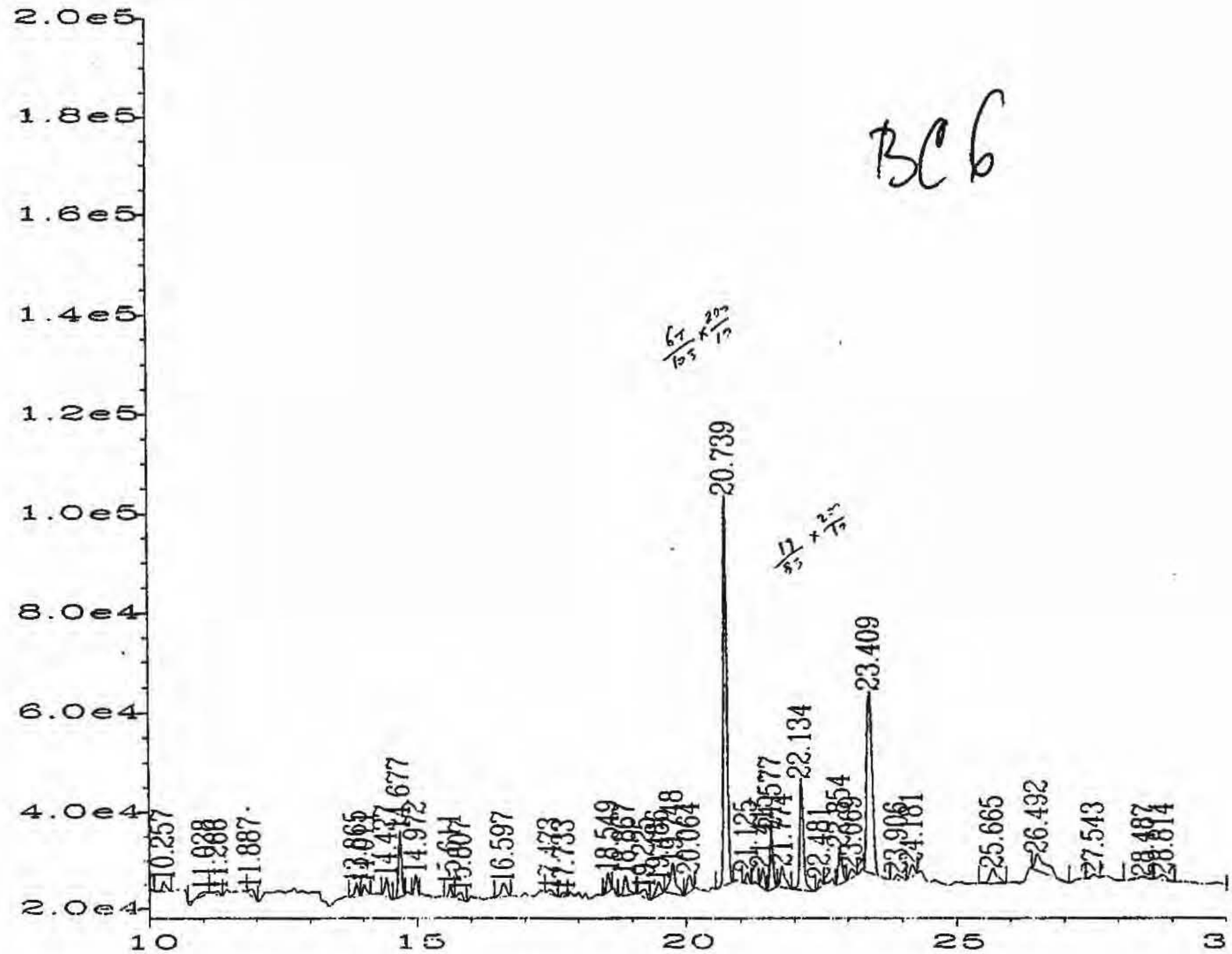

Fig.6. Gas chromatogram with electron capture detector, sample BC6
(latent duplicate of BC1)

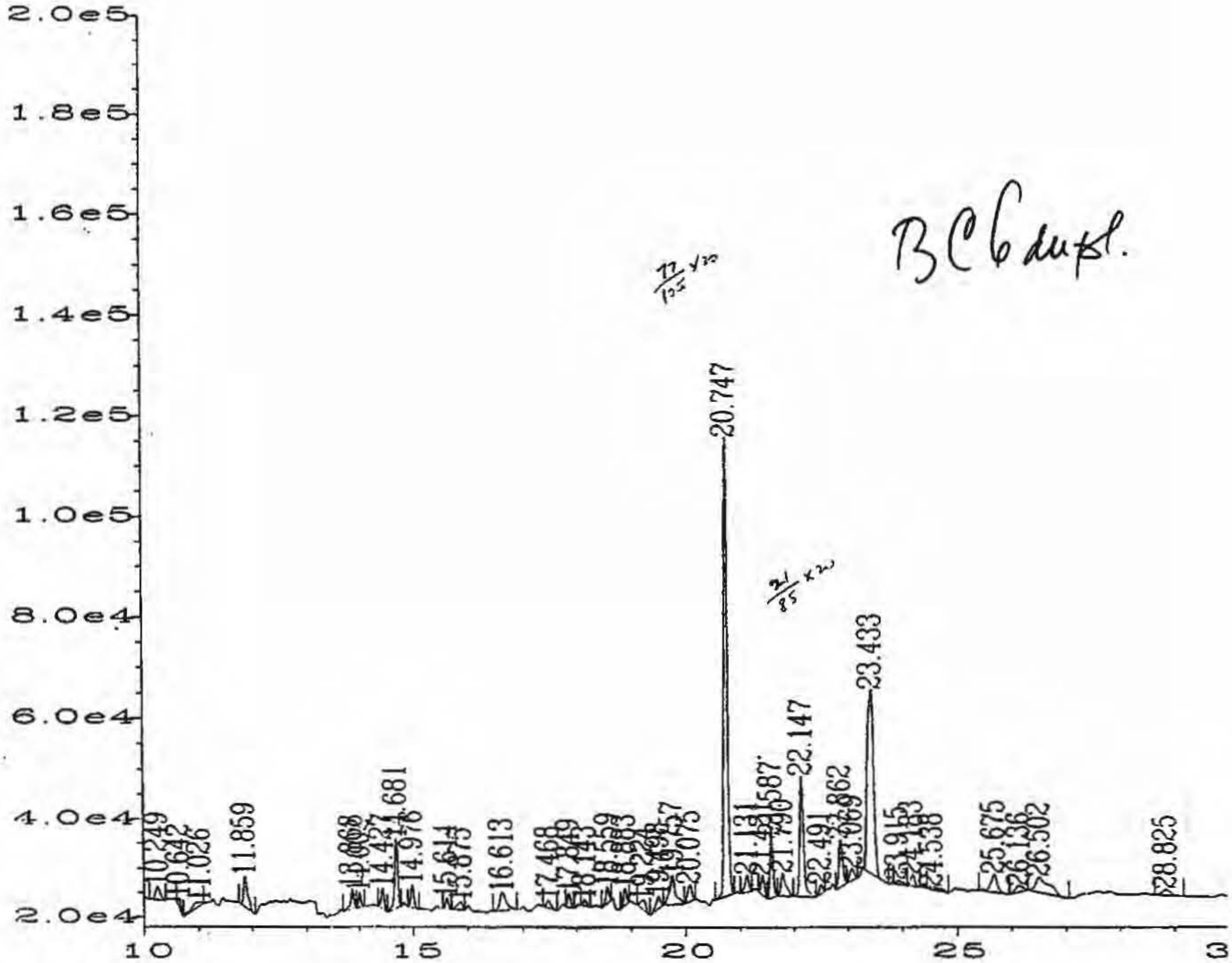

Fig.7. Gas chromatogram with electron capture detector, sample BC6, (latent duplicate of BC1), duplicate analysis

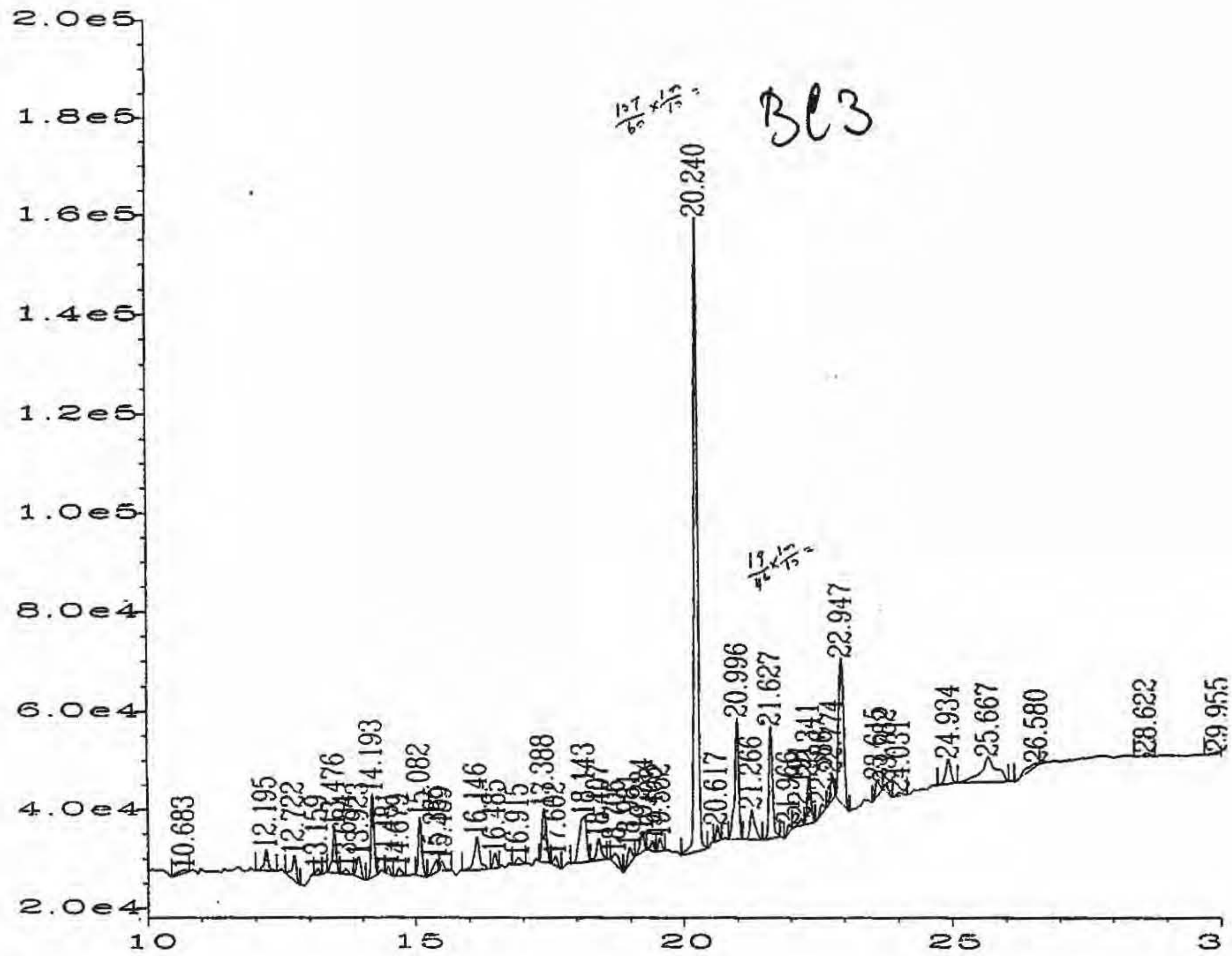

Fig.8. Gas chromatogram with electron capture detector, sample BC3
(latent duplicate of BC5)

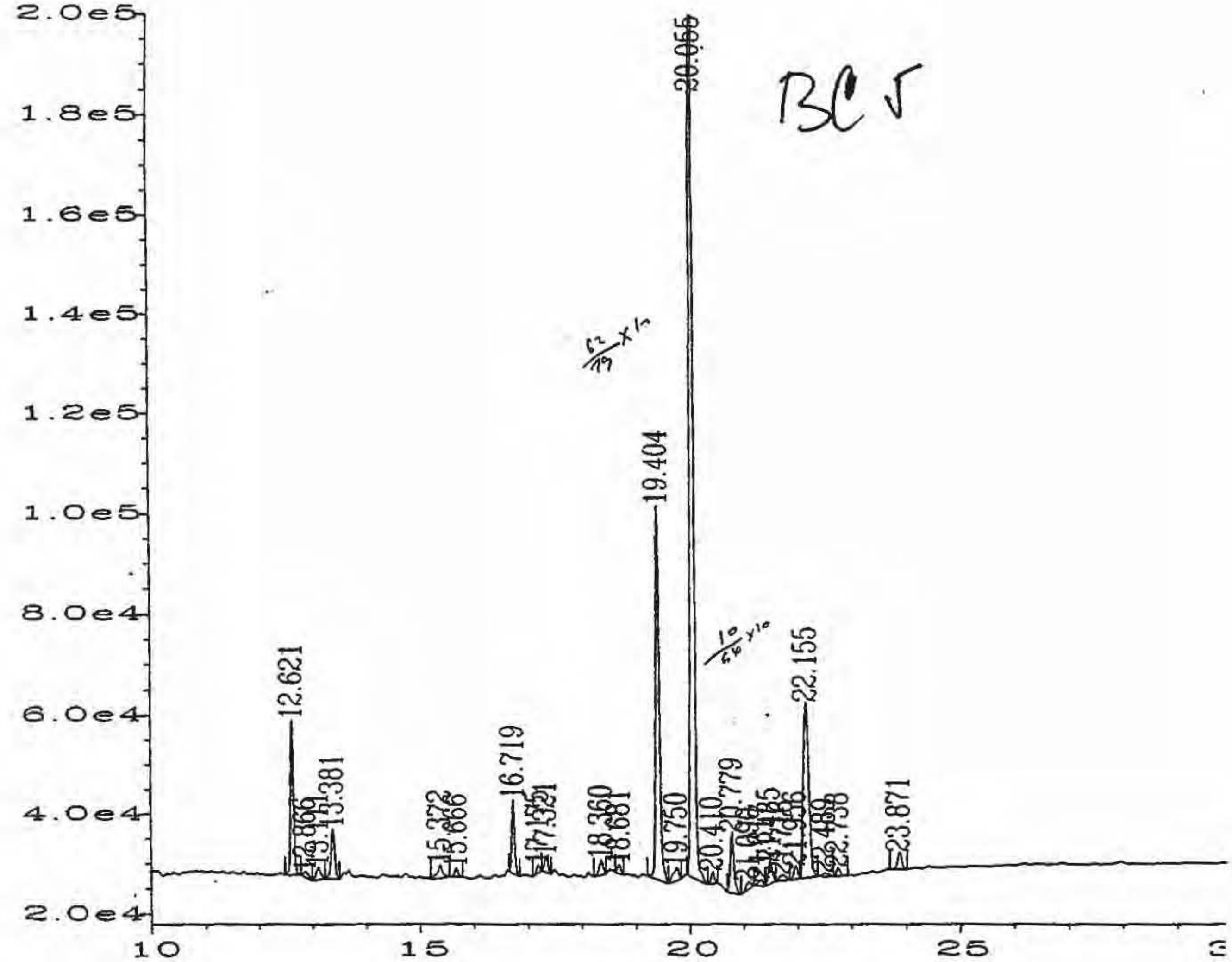

Fig.9. Gas chromatogram with electron capture detector, sample BC5
(latent duplicate of BC3)

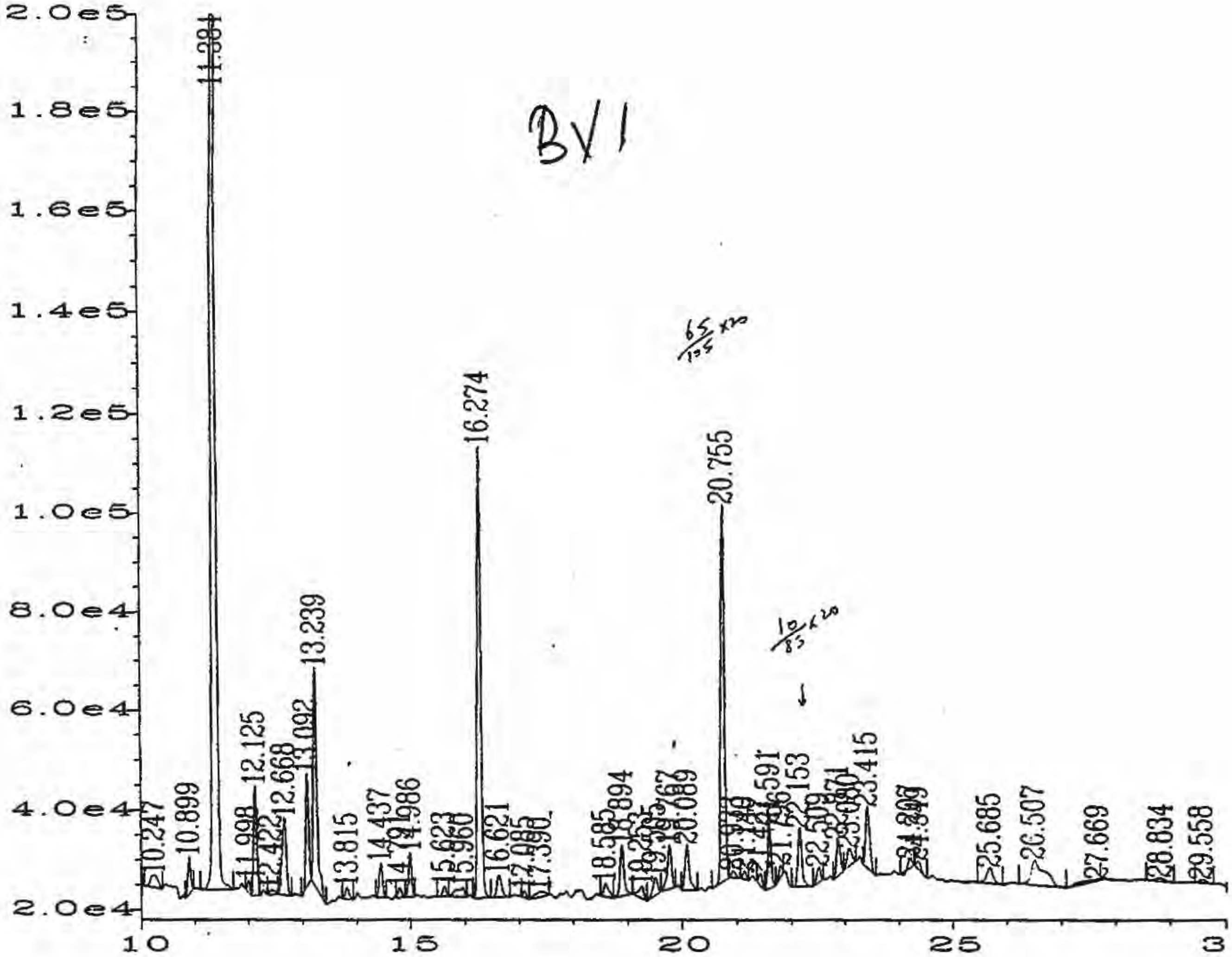

Fig.10. Gas chromatogram with electron capture detector, sample BV1
(latent duplicate of BV2)

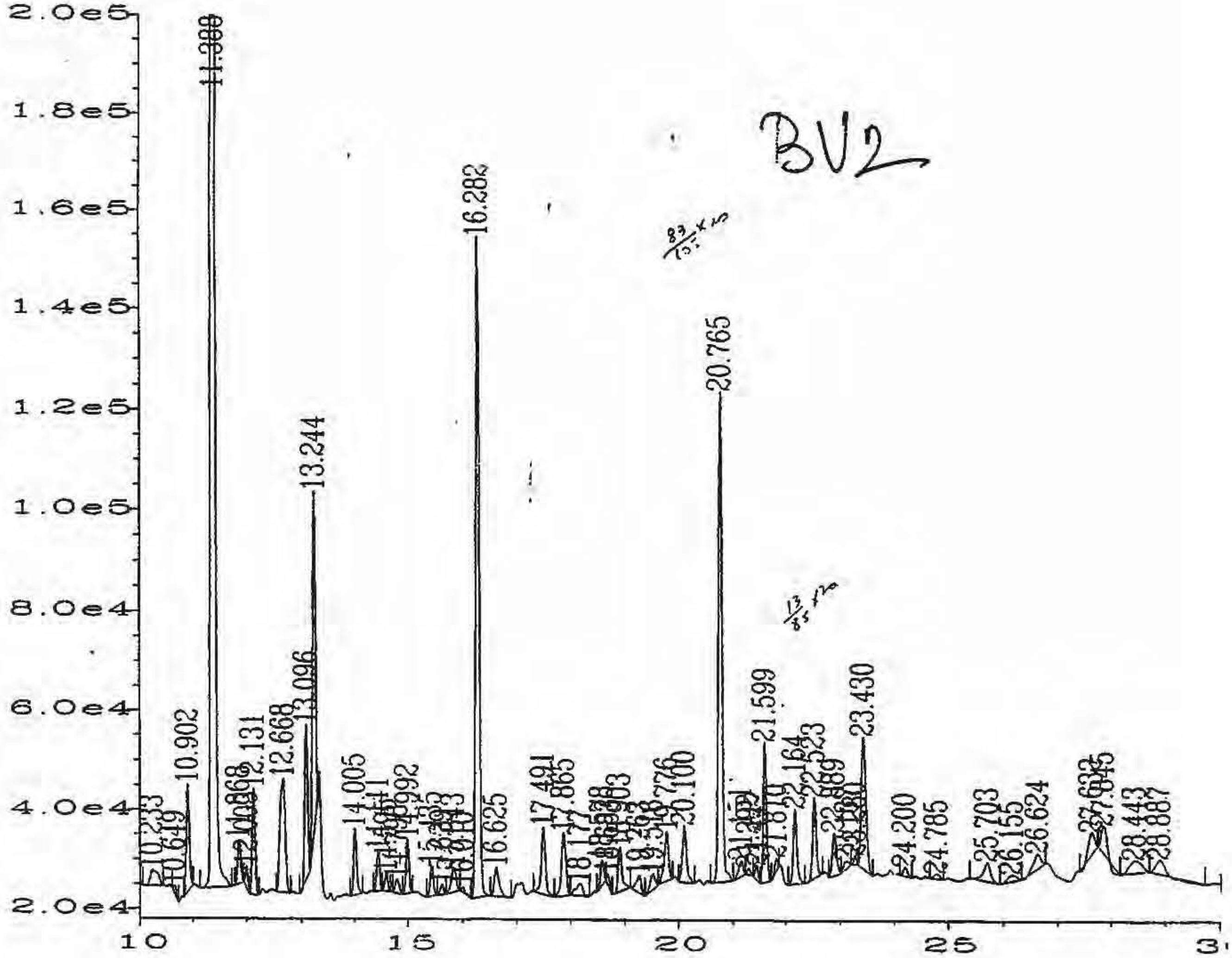

Fig.11. Gas chromatogram with electron capture detector, sample BV2 (latent duplicate of BV1)

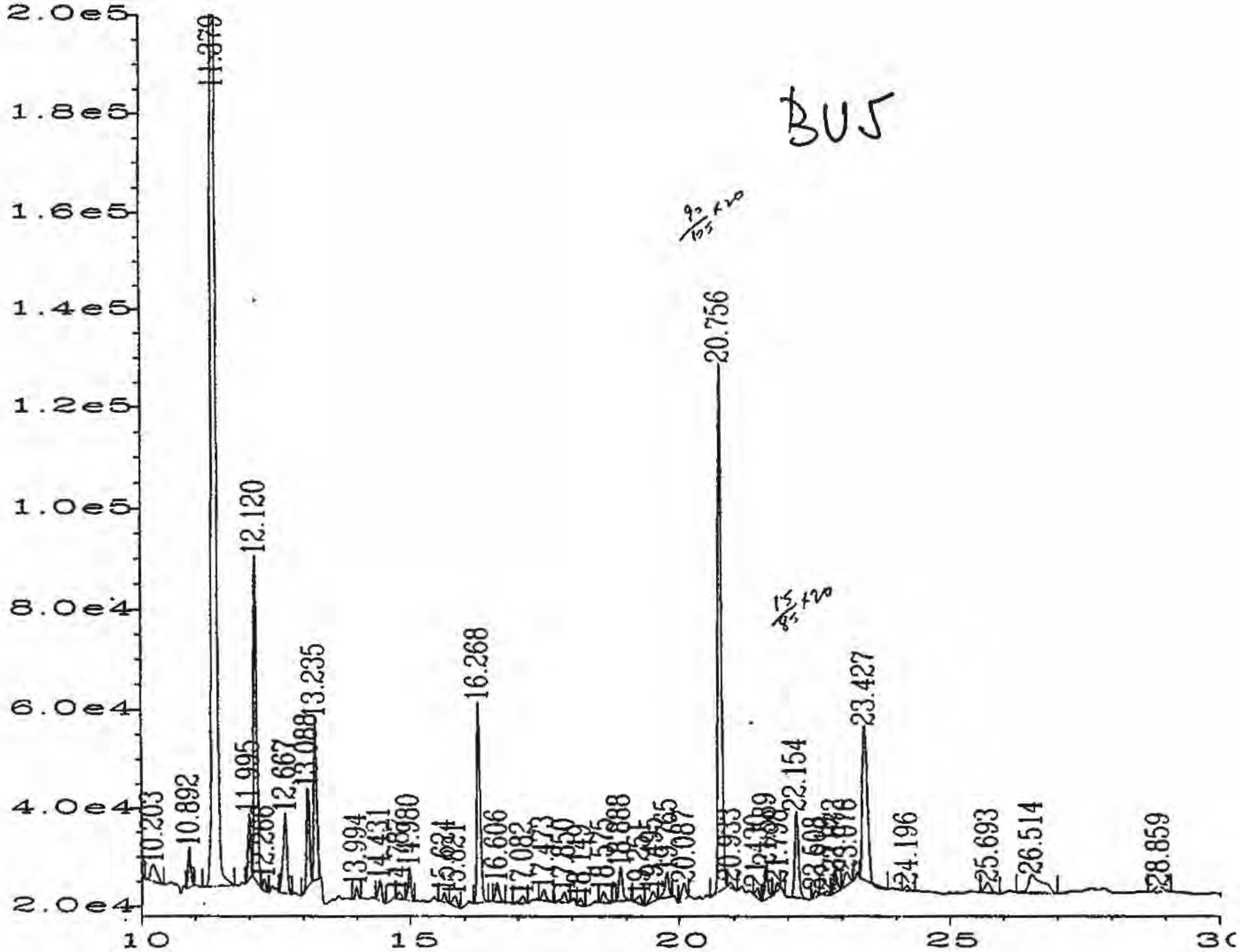

Fig.12. Gas chromatogram with electron capture detector, sample BV5 (latent duplicate of BV6)

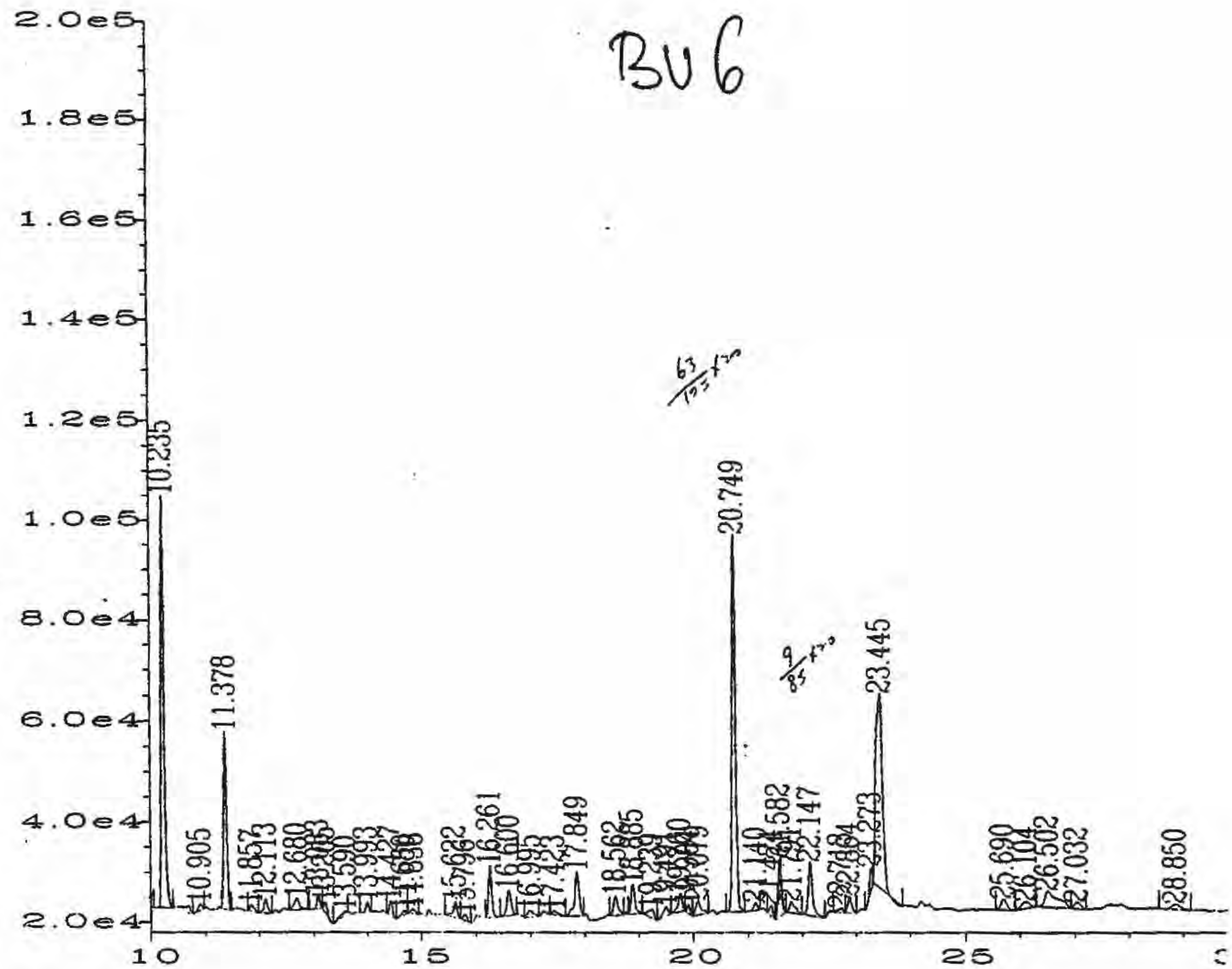

Fig.13. Gas chromatogram with electron capture detector, sample BV6 (latent duplicate of BV5)

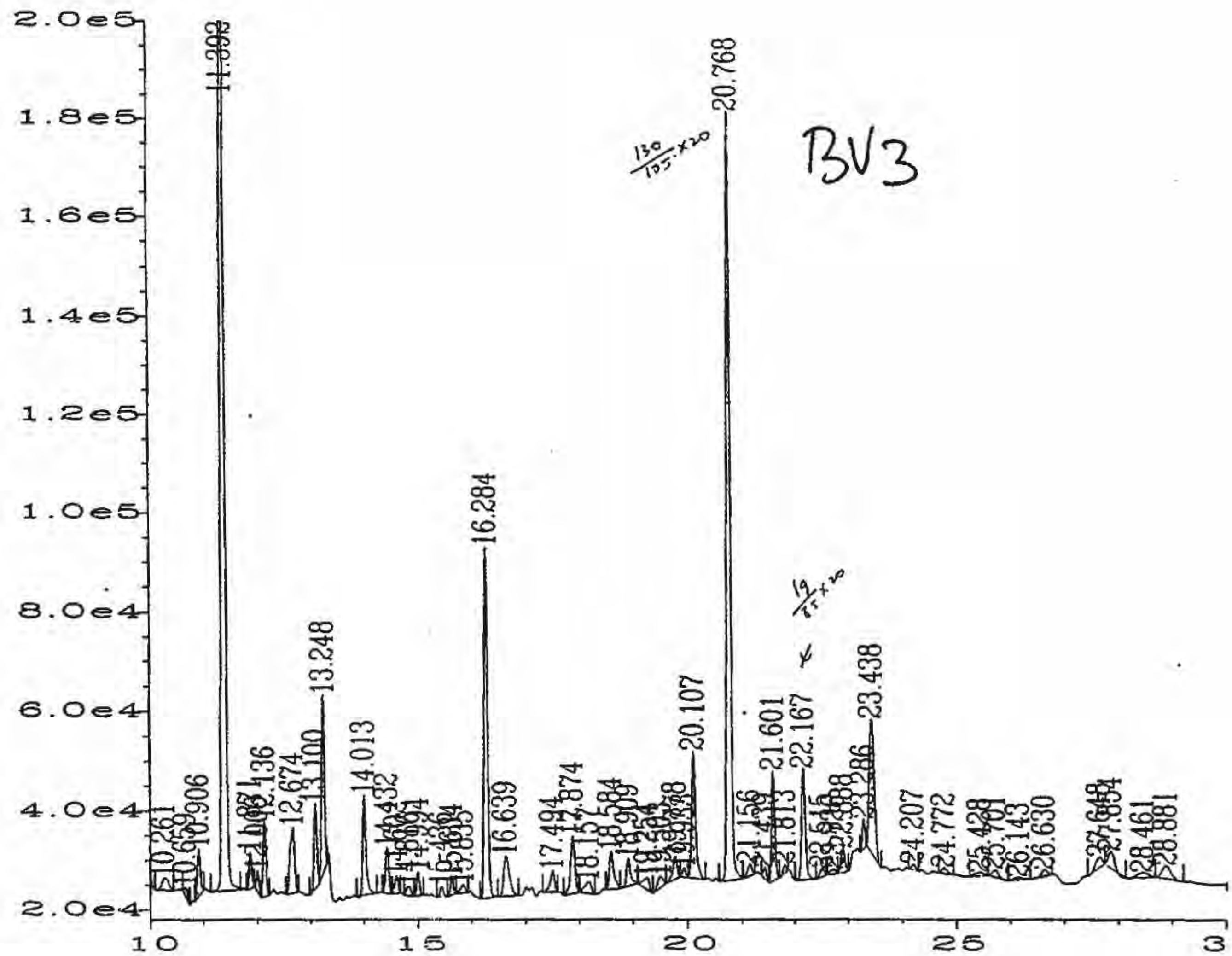

Fig.14. Gas chromatogram with electron capture detector, sample BV3
(latent duplicate of BV4)

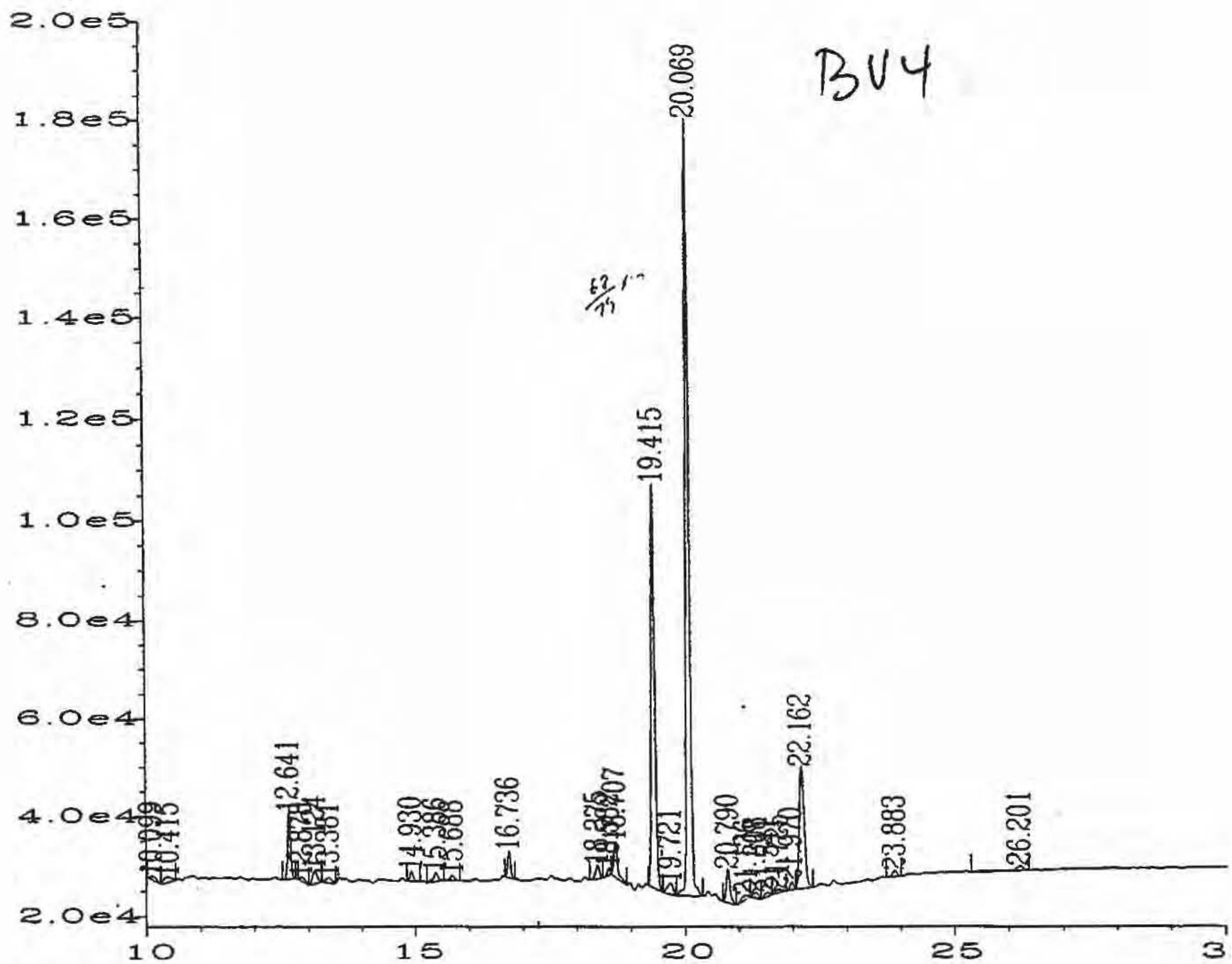

Fig.15. Gas chromatogram with electron capture detector, sample BV4
(latent duplicate of BV3)

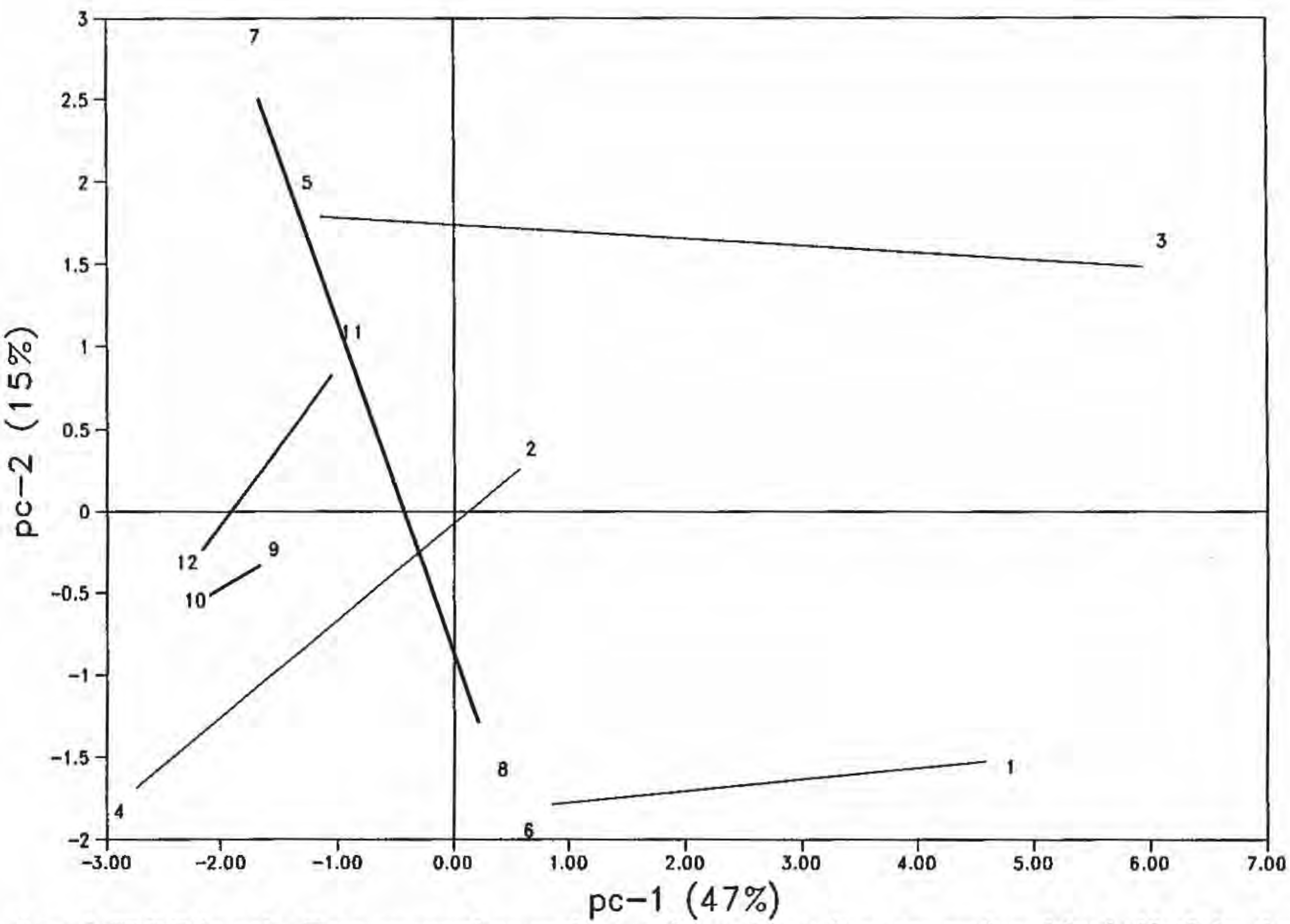

Fig. 16. Scores plot of CDDF in eels. Data are used as such, not-detectable values are replaced by half of the detection limit. Data are plotted in the plane of the first two principal components (pc-1 and pc-2). Amount of original variance accounted for by the principal components is indicated on the respective axes. The positions of samples in the plot are indicated by numbers: 1 - BC2, 2 - BC4, 3 - BC1, 4 - BC6, 5 - BC3, 6 - BC5, 7 - BV1, 8 - BV2, 9 - BV5, 10 - BV6, 11 - BV3, 12 - BV4. Latent duplicates are connected by lines. The distances between samples are inversely proportional to sample similarity.

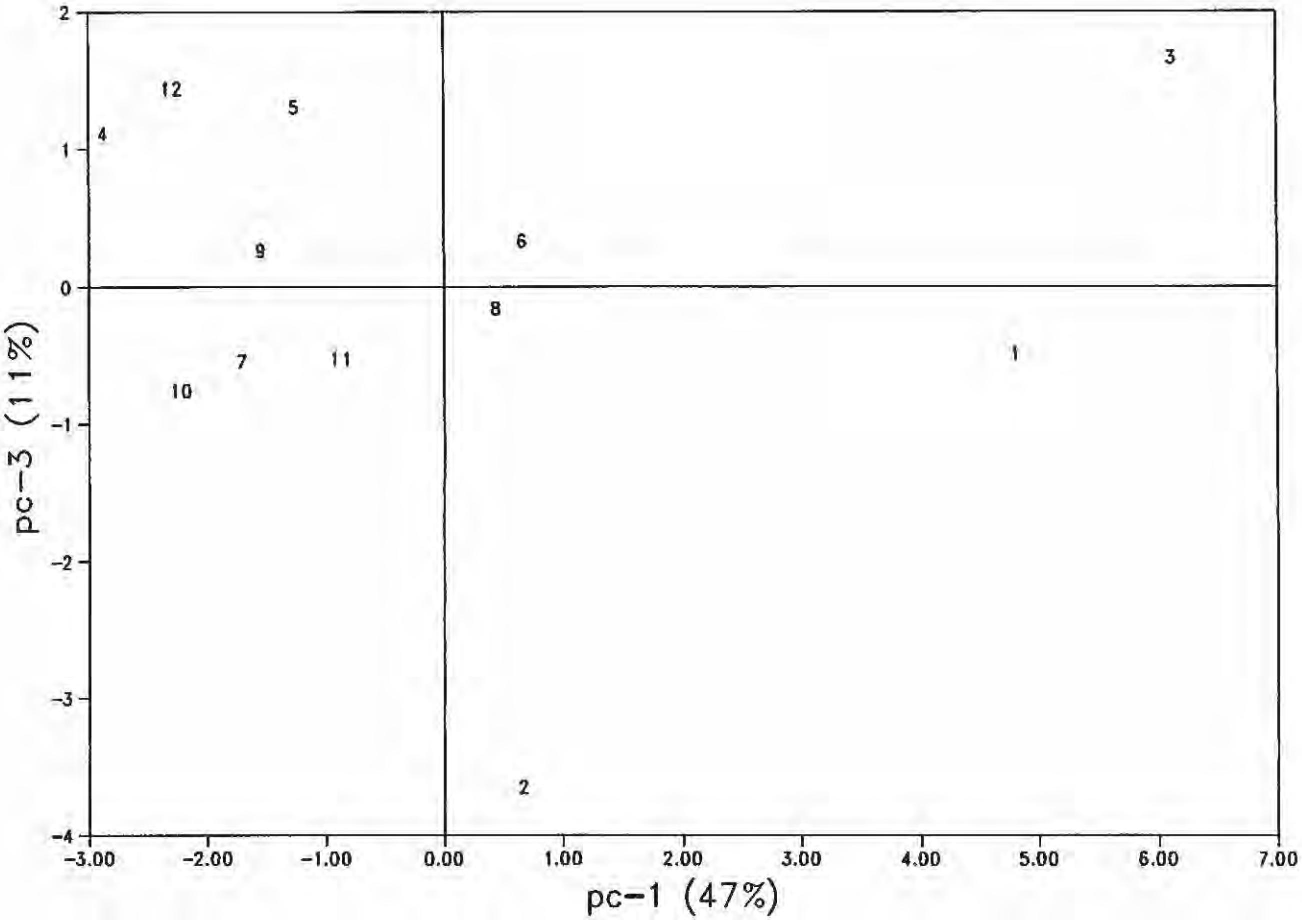

Fig. 17. Scores plot of CDDF in eels. Data are used as such, not-detectable values are replaced by half of the detection limit. Data are plotted in the plane of the two principal components pc-1 and pc-3. Amount of original variance accounted for by the principal components is indicated on the respective axes. For additional details see Fig.16.

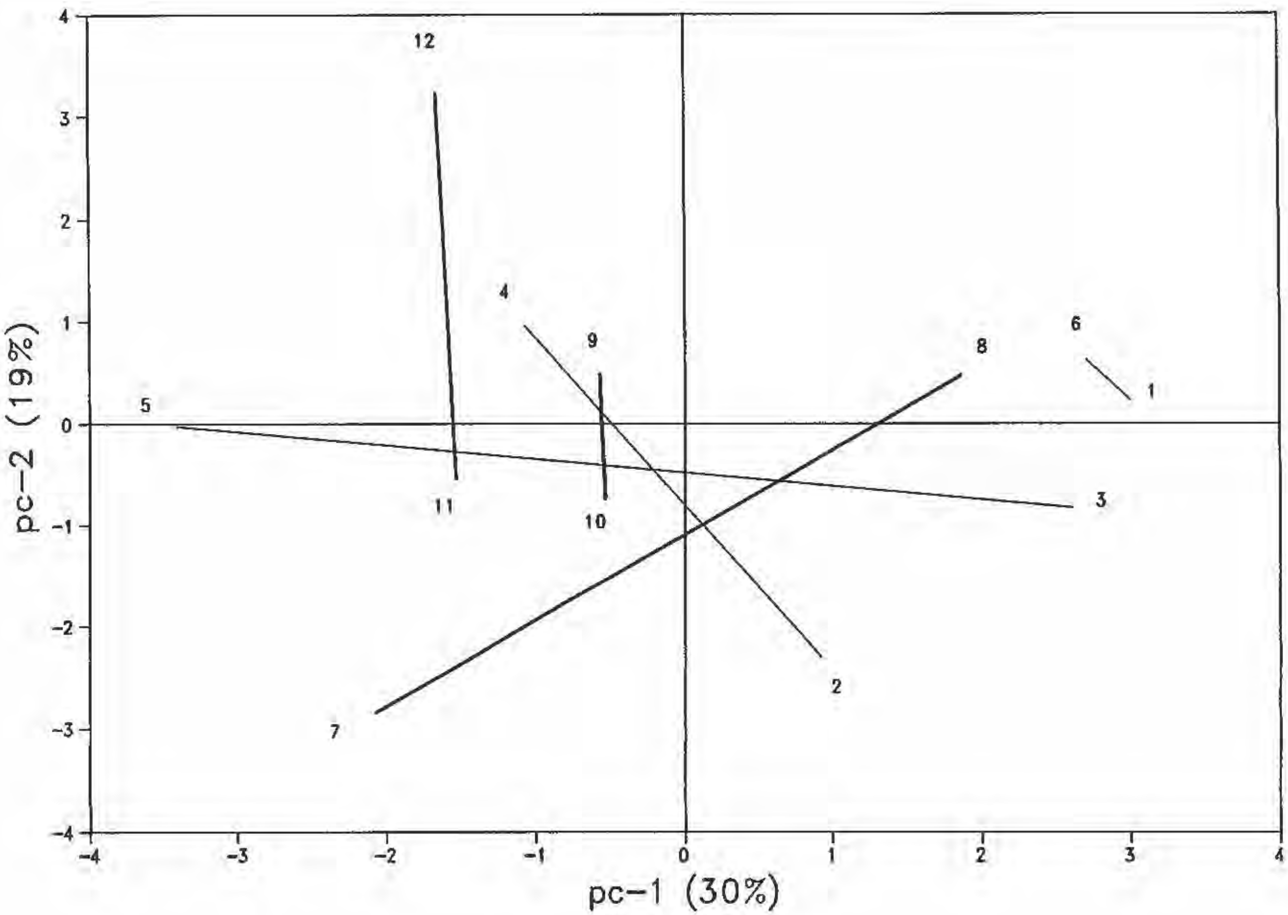

Fig. 18. Scores plot of CDDF in eels. Data are expressed as percents of total and plotted in the plane of pc-1 and pc-2. For additional details see Fig. 16.

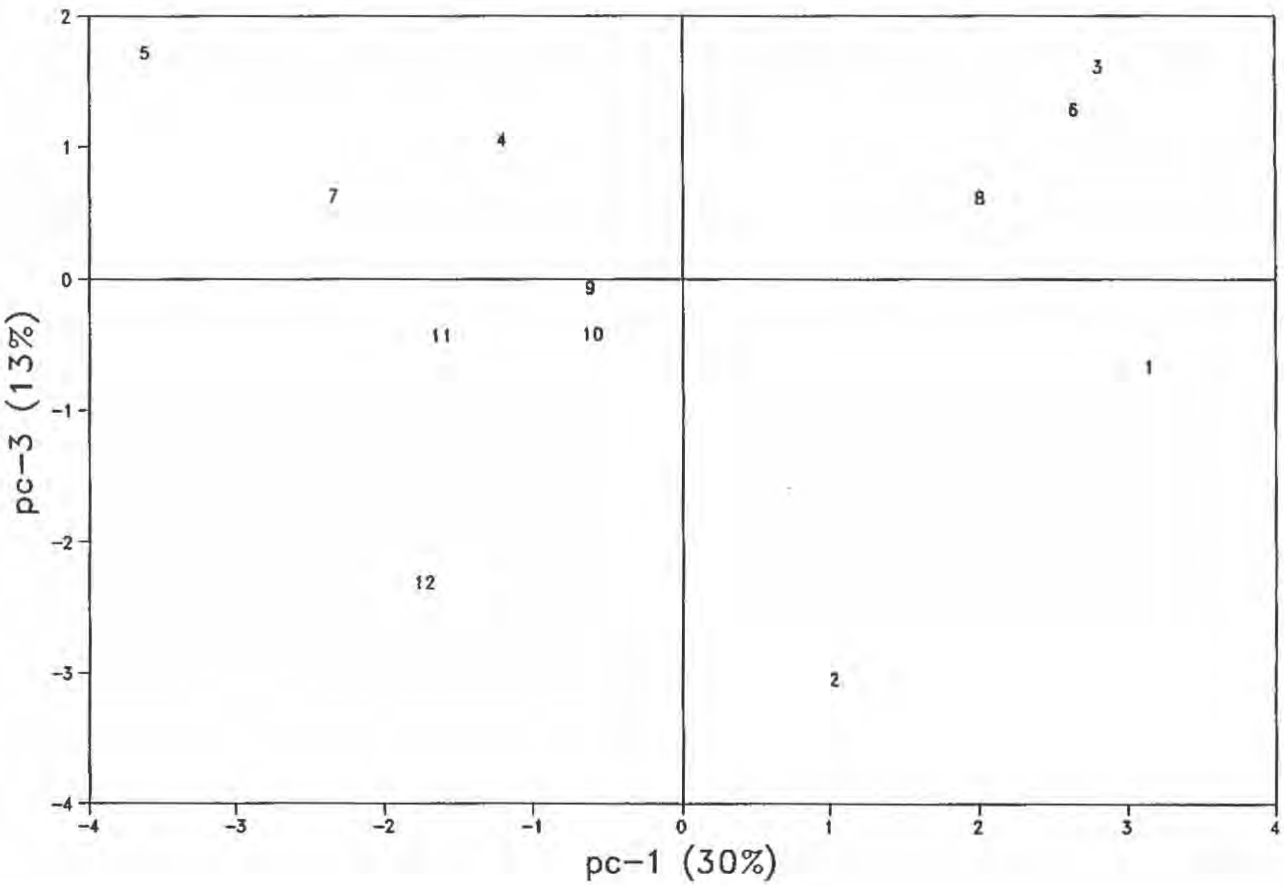

Fig. 19. Scores plot of CDDF in eels. Data are expressed as percents of total and plotted in the plane of pc-1 and pc-3. For additional details see Fig. 16.

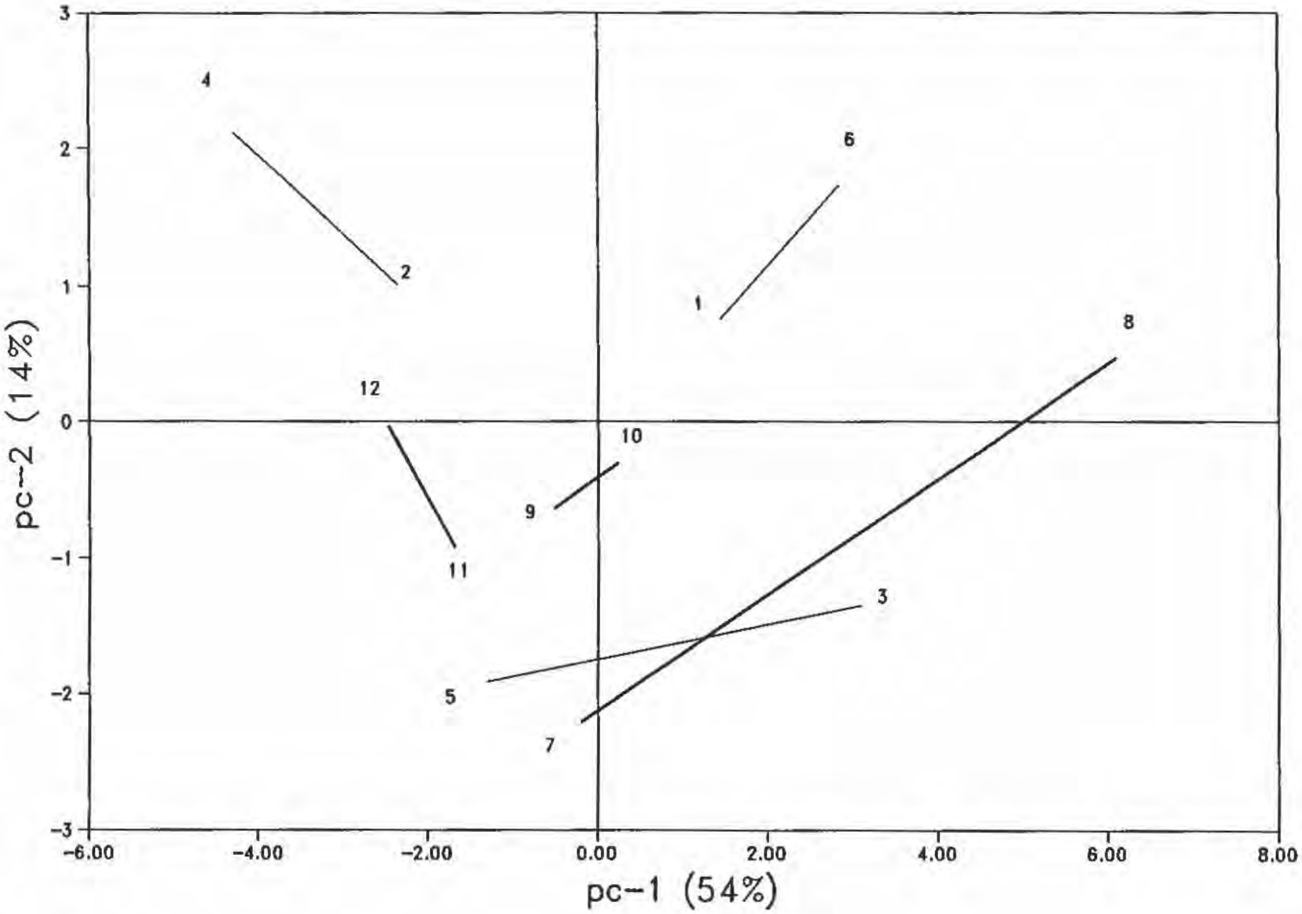

Fig. 20. Scores plot of CDDF in eels. Data are corrected for recovery and plotted in the plane of pc-1 and pc-2. For additional details see Fig. 16.

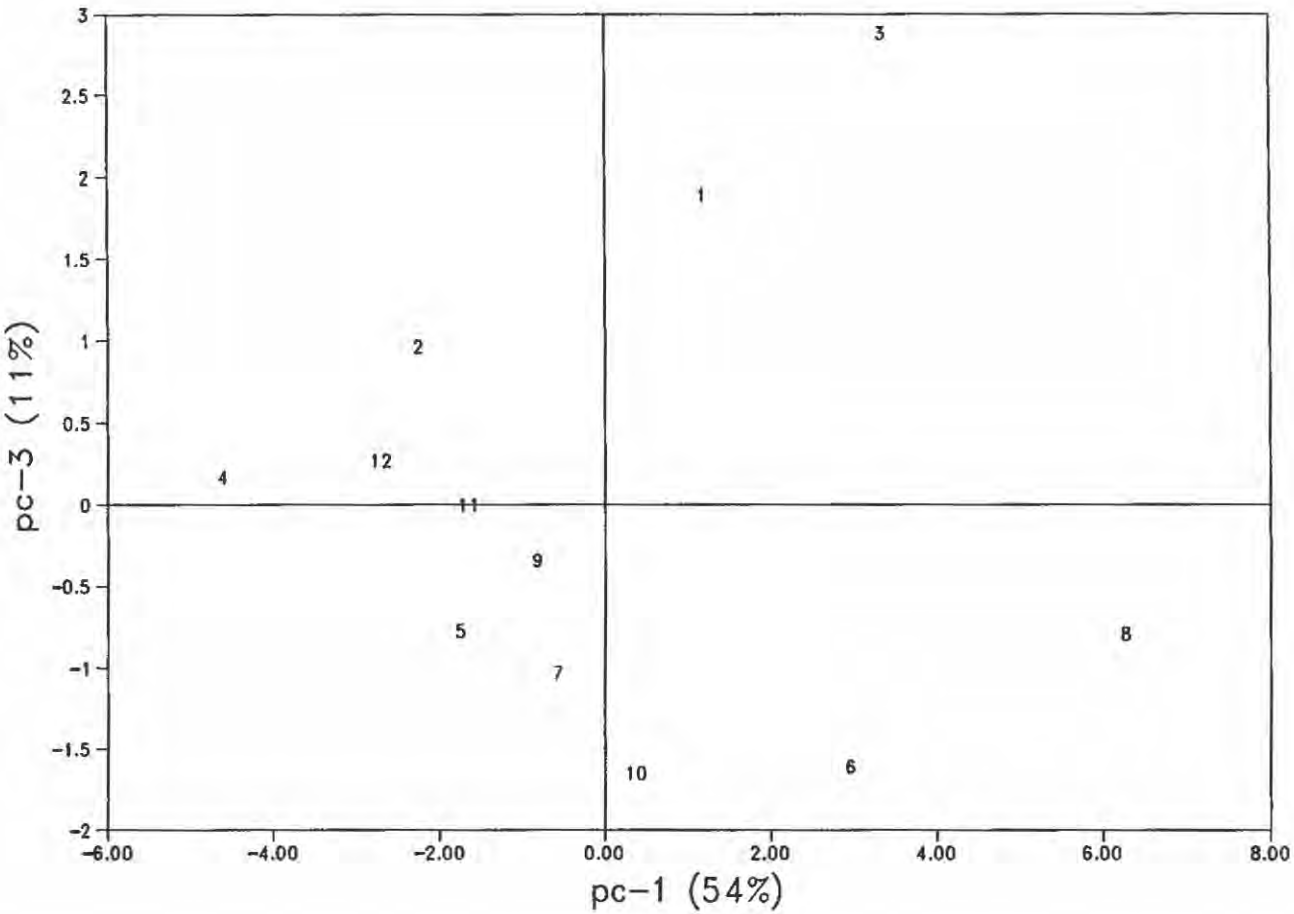

Fig. 21. Scores plot of CDDF in eels. Data are corrected for recovery and plotted in the plane of pc-1 and pc-3. For additional details see Fig. 16.

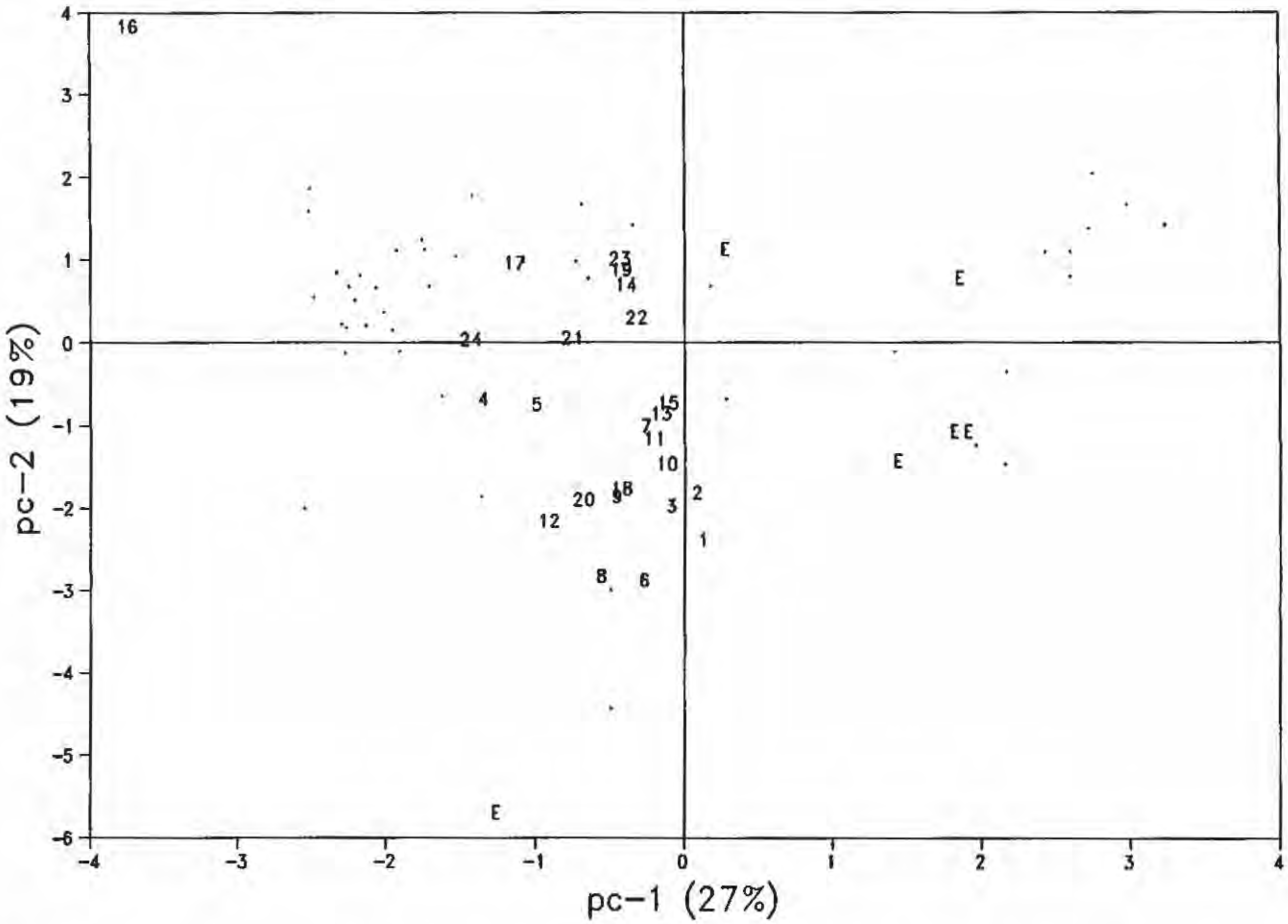

Fig. 22. CDDF in eels data are expressed as percents of total and are plotted in pc-1 and pc-2 coordinates of a published data set [4]. Literature data on fish are indicated by '.' and 'E' for eels. Miramichi data are numbered 1-6 and 7-12 for the BC and BV series, and 13-18, and 19-24 for the respective recovery-corrected data.

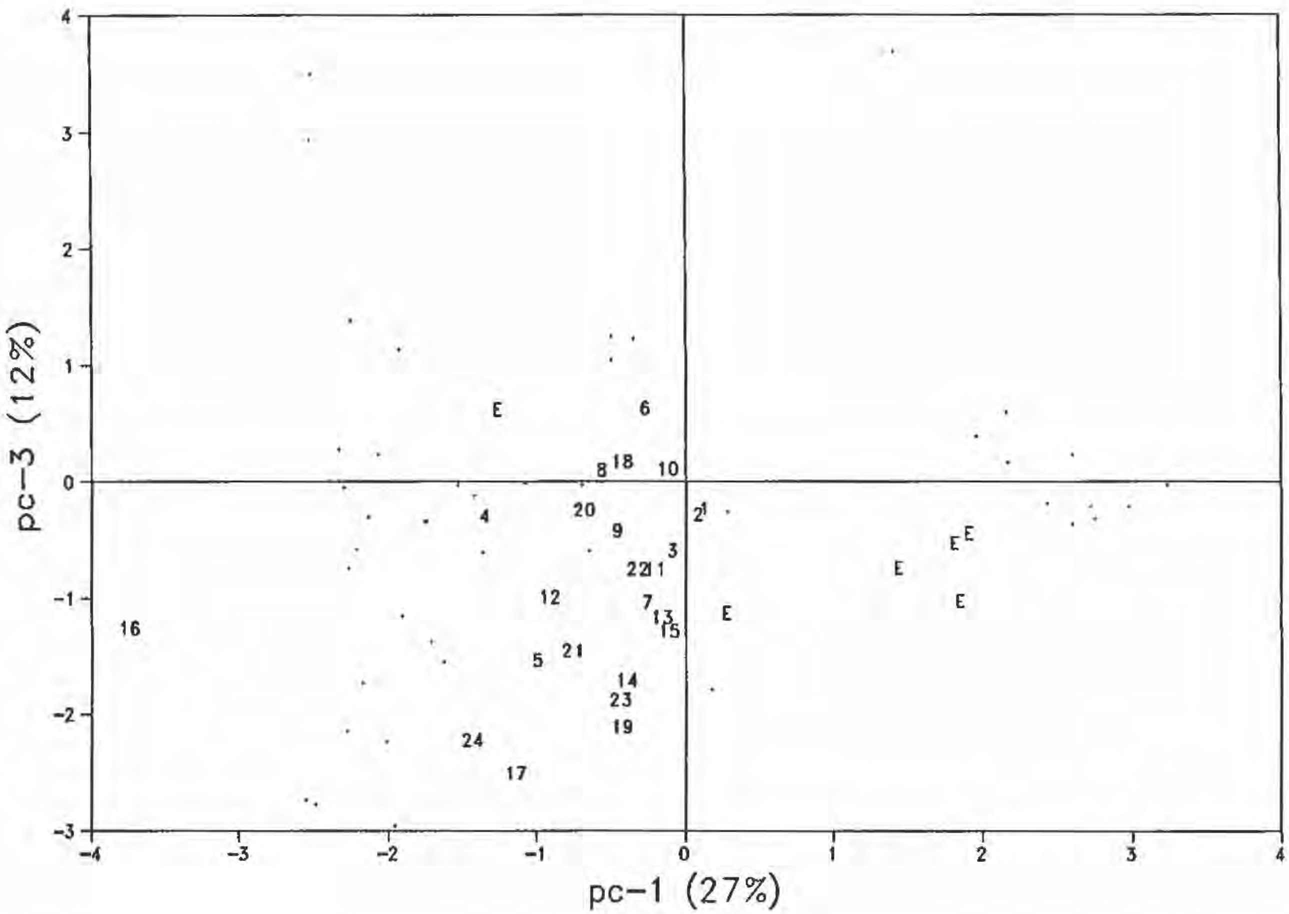

Fig. 23. CDDF in eels data are expressed as percents of total and are plotted in pc-1 and pc-3 coordinates of a published data set (Zitko 1992). For other details see Fig. 22.

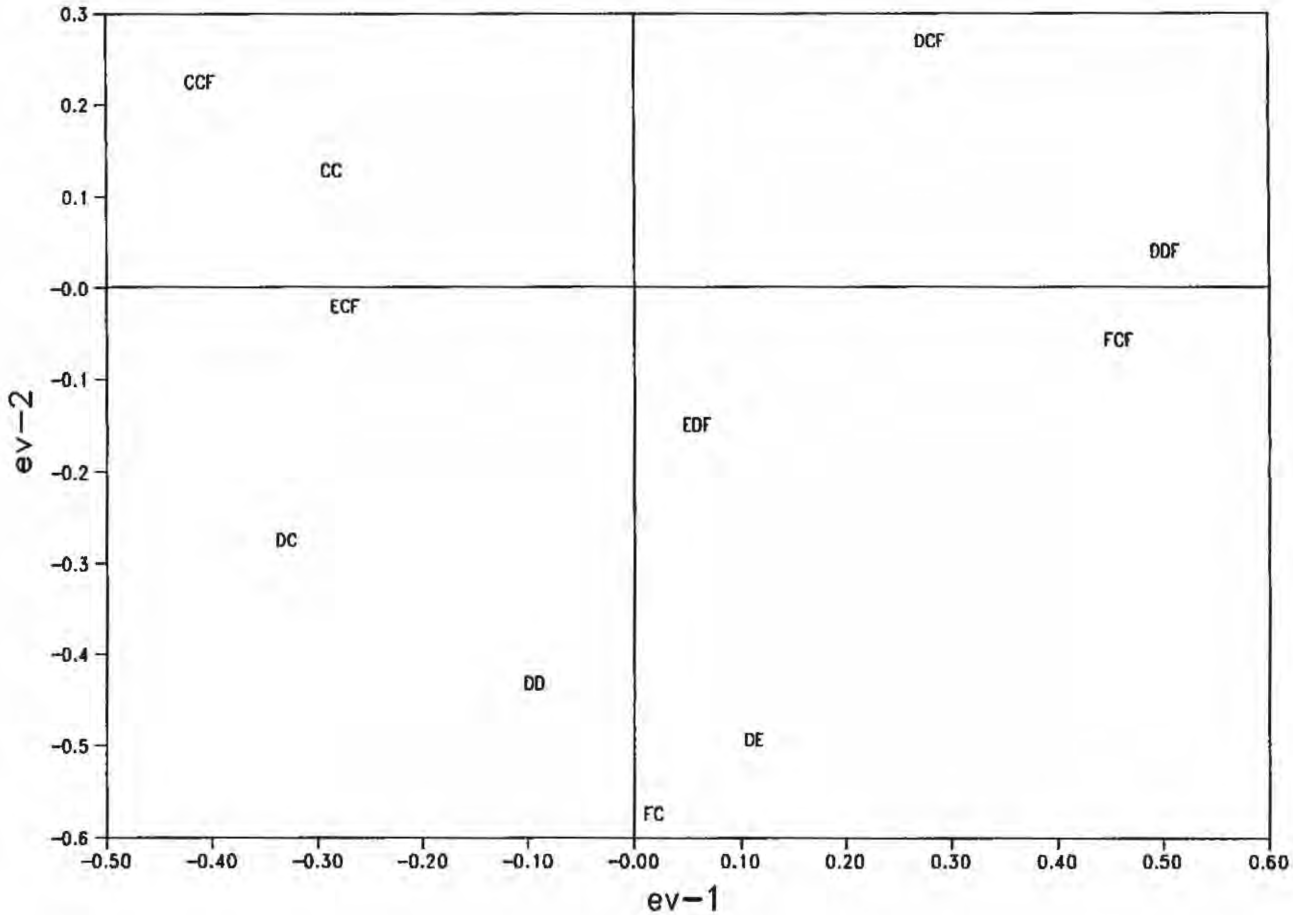

Fig.24. Loading plot ev-1 and ev-2 of the principal components pc-1 and pc-2 of the published data set (Zitko 1989). Letters indicate positions of variables: CC, DC, FC, DD, and DE are compounds with the substitution patterns 2378, 12378, 123478, 123678, and 123789, with 'F' suffix indicating the respective dibenzofuran; ECF and EDF are 23478 and 234678 substituted dibenzofurans (Zitko 1989).

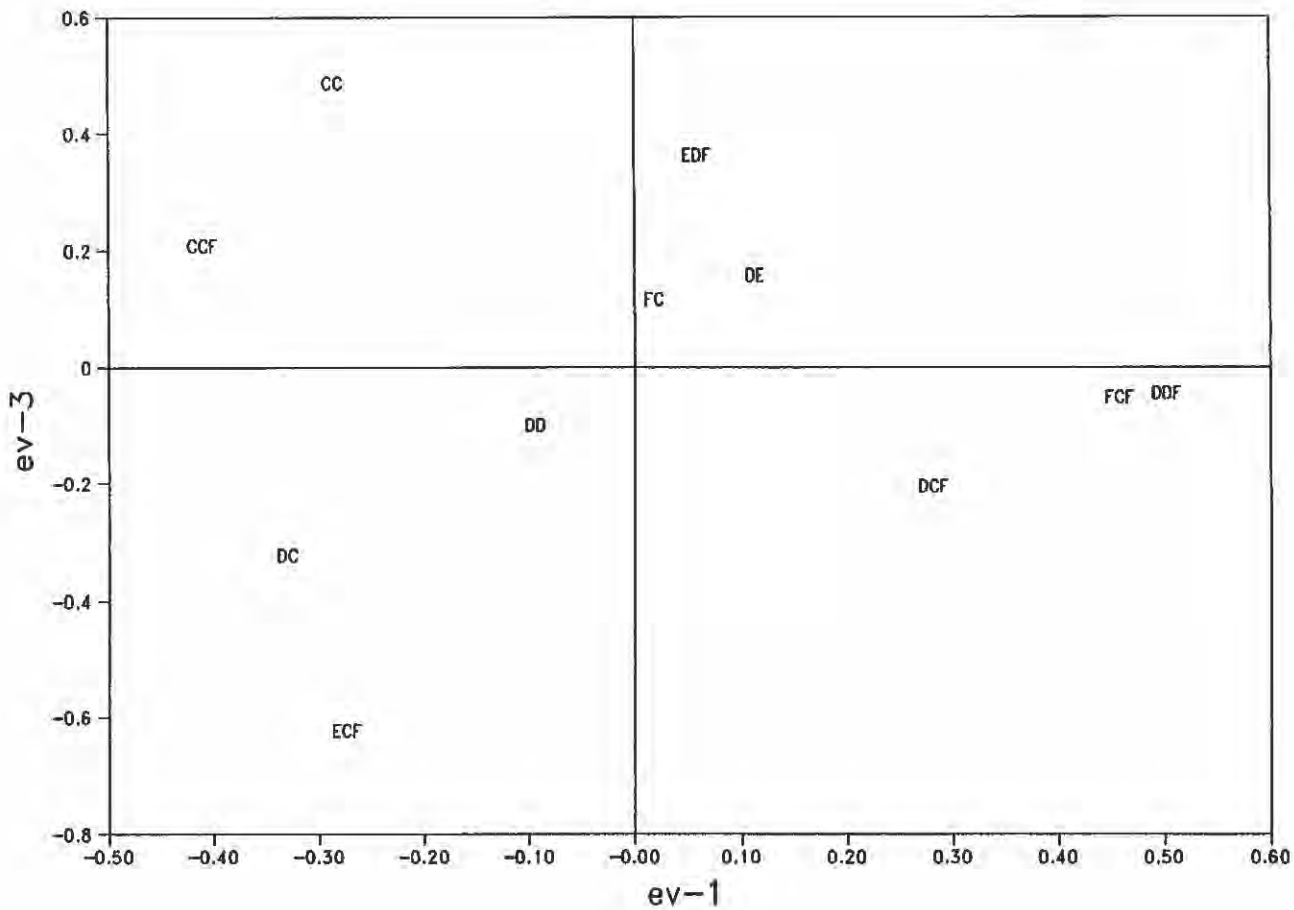

Fig. 25. Loading plot ev-1 and ev-3 of the principal components pc-1 and pc-3 of the published data set (Zitko 1992). See Fig. 24 for details.