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Spatial and Temporal Variability of Selected Trace Metals in Kiel Bight and Mecklenburg Bight

Räumliche und zeitliche Variabilität ausgewählter Spurenmetalle in der Kieler und Mecklenburger Bucht

-- Data report from 1990/92 --

-- Datenbericht von 1990/92 --

by / von

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Summary

Water samples from the surface layer (7 m depth) and from bottom water (2 m above the bottom) were collected on six separate cruises from a network of 27 stations in Kieler Bucht and Mecklenburger Bucht during a three year period (February 1990-July 1992) in order to estimate the spatial and temporal variability of Co, Pb, Cd, Cu, Ni, Fe, Zn, and Mn in the dissolved (< 0.4 µm diameter) and particulate phases. Total Hg in unfiltered water samples was also determined. Standard hydrographic parameters, nutrients, dissolved O_2, particulate organic C and N, and suspended particulate matter (SPM) were also measured. (The entire data base measures a total of approximately 10,200 data points). Results are presented in this report as summary tables of mean data for surface and bottom waters in summer and winter seasons, and in figures showing mean surface and bottom water concentrations seasonally at each station. Statistical differences at the $p= 0.01$ probability level are tabulated for hydrochemical parameters, dissolved metals, and particulate metals in four different comparison types (summer surface water vs summer bottom water, winter surface vs winter bottom, surface water in summer vs winter, and bottom water in summer vs winter). In addition, comparisons of dissolved and particular trace elements to hydrochemical and biological parameters are presented, in order to clarify the biogeochemical processes in the study area.

Zusammenfassung

Über einen Zeitraum von 3 Jahren (Februar 1990 - Juli 1992) wurden auf 6 verschiedenen Fahrten und von 27 Stationen in der Kieler und Mecklenburger Bucht Wasserproben aus der Deckschicht (7 m) und dem Tiefenwasser (2 m über Grund) entnommen, um die räumliche und zeitliche Variabilität der gelösten (< 0.4 µm) und partikulären Konzentrationen von Co, Pb, Cd, Cu, Ni, Fe, Zn, Mn in diesem Gebiet zu untersuchen. Auch die gesamt-Hg Konzentrationen von unfiltrierten Wasserproben wurden bestimmt. Außerdem sind die hydrochemischen Parameter (Temperatur, Salz-, Sauerstoff- und Nährstoffgehalte), der Gehalt an part. organischem C und N (POC/PON), sowie die Konzentrationen von Chlorophyll a und des suspendierten partikulären Materials (SPM) gemessen worden. (Die gesamte Datenbasis dieses Vorhabens umfaßt etwa 10.200 Einzelmessungen). Die Ergebnisse werden in diesem Datenbericht in Form von Tabellen und Abbildungen einmal als Vergleich der Stationsmittelwerte für vier verschiedene Wassermassen-Typen dargestellt (Oberflächenwasser im Sommer gegen Tiefenwasser im Sommer; Oberflächenwasser im Winter gegen Tiefenwasser im Winter; Oberflächenwasser im Sommer gegen Winter sowie Tiefenwasser im Sommer gegen Winter). Dabei wird für die Signifikanz der Differenzen eine Wahrscheinlichkeit von $p = 0.01$ angesetzt. Zum anderen werden die Konzentrationen der gelösten und partikulären Spurenelemente in den einzelnen Wassermassen gegen die hydrochemischen und biologischen Parameter aufgetragen, um die biogeochemischen Prozesse in diesem Gebiet zu verdeutlichen.

Introduction

A thorough understanding of the natural variability of trace metal concentrations in Baltic waters is lacking. Comprehending these fluctuations is of great interest, first, to gain more knowledge of the biogeochemical processes controlling the distribution of these elements in highly dynamic coastal zones, and secondly, in order to identify anthropogenic perturbations of the ecosystem on a medium- or long-term basis. We present here a large set of data collected during a three year program which should improve the understanding of trace metal behavior in this part of the Baltic (Kieler Bucht - Mecklenburger Bucht). An important aim of the investigations described here, a cooperative effort between IfM, Kiel and the Institut für Ostseeforschung, Warnemünde (IOW), is to develop a strategy of trace-metal sampling, i.e., where and how often specific metals should be sampled in continuing monitoring programs (e.g. the "Helsinki Commission Monitoring Programme") in this part of the Baltic. The central scientific questions that will be addressed by this project (in the final analysis) are the following:

1. What metals show conservative behavior, i.e., is there a relationship between trace metal variations and fluctuations of salinity (for example, differences between inflowing "North Sea waters" and outflowing Baltic surface waters) ?

2. How large is the fraction of particulate metals, and what enrichment factors exist during plankton blooms in the study area ?

3. Is there a seasonal fluctuation, similar to that of the nutrients, for dissolved trace metals such as Cd, Cu, Fe, Ni or Zn due to incorporation (or scavenging) into or onto planktonic organisms ?

4. What is the magnitude of the spatial and seasonal trace metal variability due to the special hydrographic circumstances in the western Baltic (i.e., during stagnating periods in summer with strong thermoclines and anaerobic conditions in bottom waters) ?

Water samples from the surface layer (at 7 m depth) and from bottom water (2 m above the bottom) were collected on six separate cruises from a network of 27 stations in the western Baltic Sea during a three year period (February 1990-July 1992) in order to determine the spatial and temporal variability of Co, Pb, Cd, Cu, Ni, Fe, Zn, and Mn in the dissolved and particulate phases (Table 1, Figure 1, Table 2). Standard hydrographic parameters, nutrients, dissolved O_2, particulate organic C and N, and suspended particulate matter were also measured. Previous studies (Kremling, unpublished) have indicated that the largest variability in concentrations occur between summer and winter seasons throughout the study area for most metals. The temporal variability of the metals leads therefore to comparisons of the data after division into four separate data sets: summer surface, summer bottom, winter surface and winter bottom waters. The results are presented here as summary tables and figures.

Methods

SAMPLE COLLECTION

All surface water samples were collected at 7 m depth using the underway, continuous pumping system of Schüßler and Kremling (1993). Uncontaminated surface water was supplied to laminar-flow clean benches installed on either F/S ALKOR or F/S POSEIDON by the pumping system. Samples for the determination of trace metals were pressure filtered through acid-cleaned 0.4 µm Nuclepore filters into acid cleaned quartz-glass bottles using pure N_2 gas, and acidified with quartz-distilled HNO_3 (1 ml / 500 ml sample). Details of the filtration procedure may be found in Kremling and Petersen (1984). Bottom-water samples (1-2 m above the bottom) were collected using acid cleaned 10 l Go-Flo samplers (General Oceanics). Water from the Go-Flo samplers was forced to the clean benches through acid cleaned plastic tubing by filtered pure N_2 gas. Standard hydrochemical parameters (temperature, salinity, nutrients) were collected by CTD-rosette, and from the bypass outflow of the underway pumping system. Samples for the determination of trace metal contents of SPM were collected on acid cleaned 0.4 µm Nuclepore filters, rinsed with deionized-distilled water, and frozen until analysis at IOW, Warnemünde. Spatially integrated SPM samples from 1 - 3 m^3 of surface seawater were also collected in each of the study areas (Kieler Förde. Eckernförder Bucht, Flensburger Bucht, Fehmarn Belt, and Mecklenburger Bucht/Lübecker Bucht) over 2-3 hour periods while steaming along the cruise track using a high speed, flow-through centrifuge connected to the underway pumping system (Schüßler and Kremling, 1993).

ANALYSES

Hydrographic and hydrochemical parameters:

Salinity and temperature profiles were obtained on each cruise by CTD. Profile data is available for each station, however, only data from the surface and bottom water layers are presented in this report. Nutrient concentrations were determined on-board by standard wet-chemical methods methods (Grasshoff, Ehrhardt, and Kremling, 1983). POC/PON samples were processed using a total CHN analyzer at IfM, Kiel. Chlorophyll a concentration was determined by fluorometric analysis of the acetone extracts of particulate material trapped on glass fiber filters.

Dissolved trace metals:

Co, Pb, Cd, Cu, Ni, Fe and Zn were extracted from the filtered seawater samples using the carbamate (APDC/DDDC) freon method of Danielsson et al. (1979). A similar oxine (8-hydroxyquinoline) chloroform extraction method (Bender et al., 1977; Kremling et al., 1983) was used for Mn in surface waters. Metals were analyzed by graphite furnace, Zeeman atomic absorption spectrometry

(AAS) using a Perkin-Elmer Model 5000 in a Class 100 cleanroom. Precision and accuracy of the AAS analysis are presented in Tables 3 and 4. Precisions typically ranged from 6 - 25 % for all elements. Accuracy of the extraction method was assessed by extractions performed on NASS-2 and CASS-2 certified seawater standards (National Research Council Canada). There were no statistical differences ($p = 0.01$) between measured and certified concentration for any of the metals investigated. Samples collected in bottom waters using Go-Flo samplers were analyzed for Mn either by the oxine-chloroform extraction method, or by injecting samples directly into the AAS after diluting 1:6 or more in 0.1-0.5 M quartz distilled HNO_3 (Schultz Tokos, unpublished). Accuracy was ≥ 80% based on recovery of Mn from standard seawater reference material (CASS-2, National Research Council Canada). Multiple analysis of samples yielded precision ranging from 2 - 23 %.

Particulate metals:

Trace metals in SPM were determined by the Institut für Ostseeforschung, Warnemünde, from suspended particulate material collected on precleaned Nuclepore filters by leaching with 0.5 N HCl for time periods ≥ 3 weeks (Brügmann, 1986; Brügmann et al., 1992). Leaching was followed by complete digestion in teflon bombs by ashing with 2 ml HNO_3 and 100 µl HF for two hours at 180 °C, evaporating to dryness and then redissolving in 1 ml HNO_3. The acid solutions were analyzed using a Perkin-Elmer model 3030 AA spectrophotometer with Zeeman correction. Data for SPM, Co, Pb, Cd, Cu, Ni, Fe, Zn, Mn, and Al collected on 0.4 µm Nuclepore filters is reported as total particulate concentration (nmol/l) or total metal content of the particulate matter (µg/g). Precision of the analyses ranged from 9% for Cu to 30% for Al. The accuracy of the filter digestion procedure was tested by measurements of the BCSS-1 standard for trace metals in marine sediments (National Research Council Canada). Results were in full agreement with the certified values (better than 95% recovery for most elements). Total Hg in unfiltered water samples was determined at IOW by permanganate oxidation and a cold-vapor reduction technique.

SPM collected by the flow-through centrifuge was analyzed for total trace metal contents (µg/g dry weight) at IfM after digestion following the method of Loring and Rantala (1989). Acidic solutions from the digested samples were analyzed for Co, Ni, Cu, Fe, Zn, and Mn by inductively coupled plasma-emission spectrometry (ICP) at IfM. Additional elements were also measured by ICP as supporting data (e.g. P, Na, Ti, Ca, Al). Pb, Cd, and Co were measured by GF-AAS. Results reported here are corrected for digestion efficiencies < 100% by comparison to recoveries of metals from coastal-zone sediments (BCSS-1, National Research Board Canada). Method development for the complete digestion of suspended matter was being performed simultaneously by another group in our laboratory. The method to be used in the future (yielding recoveries of > % 90 for most of the metals studied here) is:

1. Grind an aliquot of dried sample to a fine powder in an agate mortar. Weigh 100-200 mg sample into a teflon bomb.

2. Add 1 ml deionized-distilled H_2O and 3 ml concentrated quartz-distilled HNO_3. Bring to dryness on a hotplate.

3. Add 3 ml hot concentrated distilled HNO_3, 1 ml deionized-distilled H_2O, 3 ml Suprapur HCl and 3 ml Suprapur HF. Close bomb and cook at 165 °C for 12 hours.

4. Allow samples to cool to room temperature. Add 1 ml Suprapur $HClO_4$ and bring to dryness on a hotplate. Repeat this step if necessary.

5. Add 2 ml HNO_3 and 1 ml deionized-distilled H_2O and bring to dryness on a hotplate.

6. Add 1 ml hot HNO_3 and enough deionized-distilled H_2O to reach the desired end volume (12 ml H_2O for this work). Place into clean tubes for analysis.

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Table 1. Station locations

Station (see Fig. 1)	°N	°E	Water depth (m)	Locale
1	54° 28.0	9° 51.9	17	Eckernförder Bucht
2	54° 29.2	9° 57.1	24	"
3	54° 30.7	10° 01.8	24	"
4	54° 32.5	10° 07.0	22	"
5	54° 34.5	10° 13.0	21	"
8	54° 51.8	9° 37.5	24	Flensburger Förde
9	54° 49.6	9° 42.5	26	"
10	54° 50.0	9° 52.0	30	"
11	54° 47.7	10° 02.0	26	"
12	54° 44.5	10° 05.5	23	"
13	54° 39.5	10° 11.0	23	"
18	54° 25.0	12° 03.0	16	Mecklenburger Bucht
19	54° 28.0	11° 47.0	20	"
20	54° 33.0	11° 24.0	25	Fehmarn Belt
21	54° 36.0	11° 01.0	26	"
22	54° 38.5	10° 47.0	>20	Kieler Bucht
23	54° 41.5	10° 30.0	>20	"
24	54° 17.0	11° 45.0	ca. 20	Mecklenburger Bucht
25	54° 21.0	11° 34.0	ca. 20	"
26	54° 16.0	11° 26.0	ca. 20	"
27	54° 09.0	11° 14.0	ca. 20	Lübecker Bucht
28	54° 05.0	11° 00.0	ca. 20	"
33	Kieler Leuchtturm		ca. 13	Kieler Förde
34	54° 28.5	10° 13.3	18	"
35	54° 23.1	10° 11.6	17	"
36	54° 21.4	10° 10.0	14	"
37	Schwentine Mündung		12	"

Table 2. Cruise information and summary of weather conditions.

CRUISE	DATES	AIR TEMP. (°C)	ATMOSPHERIC PRESSURE (mb)	WIND SPEED AND DIRECTION	COMMENTS
F/S POSEIDON 169 (P 169) "winter"	6 - 9 February 1990	min. 6 - max. 10	min. 989 - max. 1025	light (SW) rising to Bft. 9-10 (SW)	latter part of cruise under winter storm conditions
F/S ALKOR 8 (A 8) "summer"	15 - 20 August 1990	min. 12 - max. 23	min. 996 - max. 1018	light (SW) rising to Bft. 6 (SW), higher at end of cruise	summertime conditions, water column stratified
F/S POSEIDON 176 (P 176) "winter"	6 - 9 November 1990	min. 2 - max. 9	min. 1023 - max. 1028	maximum Bft 5 (W)	water column partially stratified
F/S ALKOR 19 (A 19) "summer"	19 - 30 August 1991	min. 12 - max. 22	min. 1011 - max. 1017	maximum Bft. 7 (W)	upwelling observed in Flensburger Förde.
F/S ALKOR 26 (A 26) "winter"	3 - 7 February 1992	min. 2 - max. 6	min. 1000 - max. 1010	light (W) rising to Bft. 5 (SW), then back to Bft. 2 (SW)	overall conditions mild, water column mixed except at deepest stations
F/S ALKOR 32 (A 32) "summer"	30 June - 7 July 1992	min. 16 - max. 32	min. 1007 - max. 1015	maximum Bft. 6 (W)	summertime conditions, water column strongly stratified

Table 3. Analytical precision (the % deviation) of trace metal analysis by GF-AAS. Number of separate samples analyzed in duplicate = n. Data from all cruises is included.

Surface waters (depth = 7 m):

A. Summer cruises (A8, A19, A32)

Metal	Co	Pb	Cd	Cu	Ni	Fe	Zn	Mn
n samples	25	26	32	25	28	24	20	8
precision ± σ	10.9 ± 9.9	31.4 ± 20.7	9.1 ± 7.1	9.2 ± 7.9	7.8 ± 6.8	12.3 ± 12.7	14.4 ± 17.2	7.6 ± 9.4

B. Winter cruises (P169, P176, A26)

Metal	Co	Pb	Cd	Cu	Ni	Fe	Zn	Mn
n samples	11	10	11	12	10	12	11	13
precision ± σ	6.4 ± 6.9	27.2 ± 19.6	6.2 ± 6.6	8.0 ± 8.4	7.9 ± 8.6	16.4 ± 19.8	16.8 ± 10.9	35.9 ± 15.2

Bottom waters (2 m above bottom):

A. Summer cruises (A8, A19, A32)

Metal	Co	Pb	Cd	Cu	Ni	Fe	Zn	Mn	Mn&
n samples	7	7	7	7	7	6	8	2	12
precision ± σ	9.4 ± 9.0	20.2 ± 23.0	18.2 ± 23.9	8.6 ± 4.3	4.2 ± 3.0	7.9 ± 5.0	9.8 ± 9.8	3.5 ± 1.2	17.6 ± 15.0

B. Winter cruises (P169, P176, A26)

Metal	Co	Pb	Cd	Cu	Ni	Fe	Zn	Mn	Mn&
n samples	7	7	7	7	7	7	7	3	8
precision ± σ	26.4 ± 10.9	20.2 ± 20.8	6.3 ± 4.7	5.4 ± 4.3	11.3 ± 8.7	16.7 ± 17.0	10.8 ± 9.1	20.6 ± 27.0	26.5 ± 20.0

& Analyses by direct injection technique (no extraction performed; see text).

Table 4. Recovery of trace-metals from standard seawater reference materials by solvent extraction.

NASS-2 (North Atlantic Seawater Standard)&

Metal	Co	Pb	Cd	Cu	Ni	Fe	Mn
certified conc. (nmol/l ± σ)	0.068 ± 0.017	0.188 ± 0.029	0.258 ± 0.036	1.72 ± 0.17	4.38 ± 0.46	4.01 ± 0.61	0.40 ± 0.13
Measured ($\bar{x}$ ± σ)	0.071 ± 0.008	0.174 ± 0.021	0.240 ± 0.062	1.75 ± 0.14	4.44 ± 1.02	7.00 ± 0.72	0.39 ± 0.06
n	5	14	16	10	12	3	4

CASS-2 (Coastal Atlantic Seawater Standard)&

Metal	Co	Pb	Cd	Cu	Ni	Fe	Zn
certified conc. (nmol/l ± σ)	0.424 ± 0.102	0.092 ± 0.029	0.169 ± 0.036	10.62 ± 0.61	5.07 ± 0.61	21.5 ± 2.15	35.8 ± 2.18
Measured ($\bar{x}$ ± σ)	0.411 ± 0.085	0.071 ± 0.019	0.144 ± 0.021	9.33 ± 1.82	4.90 ± 0.42	16.4 ± 2.18	31.6 ± 6.21
n	5	4	5	5	5	4	5

& Reference materials from National Research Council Canada,

Table 5. Mean hydrographic and hydrochemical parameters by layer and season (± σ). All stations.

A. Surface water (depth = 7 m):

Summer cruises (A8, A19, A32). See Table 2 for cruise dates.

	Temp °C	Salin. PSU	NO2 µmol/l	NO3 µmol/l	NH4 µmol/l	SiO µmol/l	PO4 µmol/l	O2 %-Sat.	POC µg/l	PON µg/l	chl-a µg/l
$\bar{x}$	18.19	14.333	0.06	0.16	0.22	7.88	0.40	92.0	453.06	83.97	1.43
± σ	2.22	2.835	0.10	0.14	0.45	9.24	0.49	21.7	173.90	134.40	1.72
n	78	79	77	73	74	78	76	27	79	79	78

Winter cruises (P169, P176, A26)

	Temp °C	Salin. PSU	NO2 µmol/l	NO3 µmol/l	NH4 µmol/l	SiO µmol/l	PO4 µmol/l	O2 %-Sat.	POC µg/l	PON µg/l	chl-a µg/l
$\bar{x}$	5.47	17.580	0.44	6.02	1.87	15.01	0.99	------------	161.00	31.28	------------
± σ	2.45	2.780	0.29	5.94	1.51	6.49	2.14	------------	109.80	22.82	------------
n	66	71	73	71	73	73	73	------------	56	56	------------

B. Bottom water (2 m above bottom):

Summer cruises (A8, A19, A32)

	Temp °C	Salin. PSU	NO2 µmol/l	NO3 µmol/l	NH4 µmol/l	SiO µmol/l	PO4 µmol/l	O2 %-Sat.	POC µg/l	PON µg/l	chl-a µg/l
$\bar{x}$	11.61	20.150	0.20	2.67	2.07	34.00	1.67	33.6	228.20	39.21	0.95
± σ	2.68	3.350	0.15	3.07	2.58	17.50	1.08	25.6	118.00	33.80	1.49
n	79	76	77	75	77	78	77	78	71	71	77

Winter cruises (P169, P176, A26)

	Temp °C	Salin. PSU	NO2 µmol/l	NO3 µmol/l	NH4 µmol/l	SiO µmol/l	PO4 µmol/l	O2 %-Sat.	POC µg/l	PON µg/l	chl-a µg/l
$\bar{x}$	6.55	19.440	0.40	5.05	3.21	16.69	1.26	85.8	60.65	83.20	------------
± σ	3.20	2.200	0.20	2.39	2.08	4.67	0.34	7.3	104.80	4.25	------------
n	47	64	65	65	65	65	65	25	35	35	------------

Table 6. Significant differences (*) at the p= 0.01 probability level for mean hydrographic and hydrochemical data of Table 5.
"0" = significant difference not provable.

A. Winter vs Summer Comparisons: Surface or Bottom Waters

	Temp.	Salinity	NO2	NO3	NH4	SiO	PO4	O2	POC	PON	chl-a
Surface	*	*	*	*	*	*	0	------------	*	*	------------
Bottom	*	0	*	*	*	*	*	*	*	*	------------

B. Surface vs Bottom Comparisons: Winter or Summer

	Temp	Salinity	NO2	NO3	NH4	SiO	PO4	O2	POC	PON	chl-a
Winter	0	*	0	0	*	0	0	------------	*	*	------------
Summer	*	*	*	*	*	*	*	*	*	*	0

Table 7. Mean dissolved (0.4 μm filtered) metal concentrations (nmol/kg ± σ *) in surface and bottom waters by season. (All stations).

A. Surface waters (depth = 7 m):

Summer cruises (A8, A19, A32). See Table 2 for cruise information.

Metal	Co	Pb	Cd	Cu	Ni	Fe	Zn	Mn
n samples	78	78	78	77	78	78	76	78
$\bar{x} \pm \sigma$	0.192 ± 0.129	0.082 ± 0.105	0.124 ± 0.052	8.36 ±3.36	11.07 ± 1.83	26.10 ± 33.21	19.37 ± 21.11	60.6 ± 155.3
NV& (% of $\bar{x}$)	66.3	124.2	40.9	39.1	14.6	126.6	108.0	256.2

Winter cruises (P169, P176, A26)

Metal	Co	Pb	Cd	Cu	Ni	Fe	Zn	Mn
n samples	71	68	71	71	71	71	71	72
$\bar{x} \pm \sigma$	0.229 ± 0.096	0.066 ± 0.054	0.138 ± 0.075	7.81 ± 1.94	10.95 ± 1.43	32.03 ± 43.29	16.69 ± 8.54	30.09 ± 28.48
NV (% of $\bar{x}$)	41.4	77.1	54.0	23.5	10.4	134.1	55.6	92.9

B. Bottom waters (2 m above bottom):

Summer cruises (A8, A19, A32)

Metal	Co	Pb	Cd	Cu	Ni	Fe	Zn	Mn
n samples	76	76	76	76	76	75	76	75
$\bar{x} \pm \sigma$	1.32 ± 1.86	0.081 ± 0.062	0.173 ± 0.069	7.77 ± 2.30	11.99 ± 2.35	196.9 ± 563	40.54 ± 49.11	2137 ± 2783
NV (% of $\bar{x}$)	140.6	73.8	35.5	28.3	19.1	285.8	120.7	130.2

Winter cruises (P176, A26)

Metal	Co	Pb	Cd	Cu	Ni	Fe	Zn	Mn
n samples	50	50	50	50	50	50	50	50
$\bar{x} \pm \sigma$	0.320 ± 0.177	0.127 ± 0.083	0.119 ± 0.027	8.29 ± 1.63	12.35 ± 2.52	49.00 ± 54.32	17.71 ± 9.59	104.0 ± 109.4
NV (% of $\bar{x}$)	53.7	62.2	21.8	18.9	17.0	109.6	53.1	103.2

* σ = total uncertainty = natural variability + analytical uncertainty(precision).

& NV = natural variability (± % of $\bar{x}$) = $(([\sigma / \bar{x}] \times 100)^2$ - (precision from Table 3.$)^2)^{0.5}$

Table 8. Significant differences (*) at the p= 0.01 probability level for dissolved metal concentration data ($\bar{x}$ ± natural variability data of Table 7). "0" = a significant difference is not provable.

A. Winter vs Summer Comparisons: Surface or Bottom Waters

	Co	Pb	Cd	Cu	Ni	Fe	Zn	Mn
Surface	0	0	0	0	0	0	0	0
Bottom	*	*	*	0	0	0	*	*

B. Surface vs Bottom Comparisons: Winter or Summer

	Co	Pb	Cd	Cu	Ni	Fe	Zn	Mn
Winter	*	*	0	0	*	0	0	*
Summer	*	0	*	0	*	*	*	*

Table 9. Mean SPM and total particulate metal concentrations on 0.4 µm filters (± σ*). All stations. Units: nmol/l = mass particulate metal / l; µg/g = metal content of particulate matter.

A. Surface waters (depth = 7 m):

Summer cruises (A8, A19, A32)

	SPM mg/l	Co nmol/l	Co µg/g	Pb nmol/l	Pb µg/g	Cd nmol/l	Cd µg/g	Cu nmol/l	Cu µg/g
n	79	53	53	79	79	79	79	79	79
$\bar{x}$ ± σ	0.542 ± 0.314	0.028 ± 0.028	3.10 ± 2.65	0.071 ± 0.145	18.56 ± 20.73	0.011 ± 0.006	2.88 ± 3.04	0.13 ± 0.17	15.35 ± 19.21
&NV (% of $\bar{x}$)	54.9		166		227		134		210

Winter cruises (P176, A26)

	SPM mg/l	Co nmol/l	Co µg/g	Pb nmol/l	Pb µg/g	Cd nmol/l	Cd µg/g	Cu nmol/l	Cu µg/g
n	64	51	51	51	51	51	51	49	49
$\bar{x}$ ± σ	0.78 ± 0.82	0.046 ± 0.051	5.24 ± 3.02	0.111 ± 0.126	47.43 ± 34.32	0.004 ± 0.003	0.96 ± 0.47	0.10 ± 0.15	11.45 ± 10.84
NV (% of $\bar{x}$)	104		53.3		70.3		114		181

B. Bottom waters (2 m above bottom):

Summer cruises (A8, A19, A32)

	SPM mg/l	Co nmol/l	Co µg/g	Pb nmol/l	Pb µg/g	Cd nmol/l	Cd µg/g	Cu nmol/l	Cu µg/g
n	71	49	49	71	71	69	69	71	71
$\bar{x}$ ± σ	0.53 ± 0.34	0.113 ± 0.132	13.31 ± 9.24	0.085 ± 0.101	35.39 ± 24.80	0.006 ± 0.004	1.61 ± 1.01	0.16 ± 0.16	21.37 ± 20.08
NV (% of $\bar{x}$)	61.5		65.8		67.1		59.4		93.5

Winter cruises (P176, A26)

	SPM mg/l	Co nmol/l	Co µg/g	Pb nmol/l	Pb µg/g	Cd nmol/l	Cd µg/g	Cu nmol/l	Cu µg/g
n	50	50	50	50	50	49	49	50	50
$\bar{x}$ ± σ	0.43 ± 0.30	0.059 ± 0.052	7.61 ± 2.96	0.144 ± 0.146	66.22 ± 36.02	0.004 ± 0.003	0.96 ± 0.66	0.25 ± 0.47	22.61 ± 29.67
NV (% of $\bar{x}$)	67.3		32.1		51.7		65.8		152

* σ = total uncertainty = natural variability + analytical uncertainty(precision).

& NV = natural variability (± % of $\bar{x}$) = $(([\sigma\ /\ \bar{x}] \times 100)^2$ - (precision; see text)$^2)^{0.5}$

Table 9 (Cont.). Total particulate metal concentrations on 0.4 µm filters (± σ*). Data from all stations. Units: nmol/l = mass particulate M^{+} / l; µg/g = metal content in particulate matter.

A. Surface waters (depth = 7 m):

Summer cruises (A8, A19, A32)

	Fe nmol/l	Fe µg/g	Ni nmol/l	Ni µg/g	Zn nmol/l	Zn µg/g	Mn nmol/l	Mn µg/g	Al nmol/l	Al µg/g	total Hg nmol/l
n	79	79	79	79	79	79	7978	78	79	79	79
$\bar{x}$ ± σ	38.6 ± 56.5	3400 ± 4090	0.11 ± 0.04	15.08 ± 13.33	2.36 ± 1.75	339 ± 538	38.4 ± 77.9	3600 ± 6050	61.7 ± 146	2480 ± 4660	0.025 ± 0.014
&NV (% of $\bar{x}$)		215		118		162		269		431	

Winter cruises (P176, A26)

	Fe nmol/l	Fe µg/g	Ni nmol/l	Ni µg/g	Zn nmol/l	Zn µg/g	Mn nmol/l	Mn µg/g	Al nmol/l	Al µg/g	total Hg nmol/l
n	51	51	51	51	50	50	50	50	51	51	50
$\bar{x}$ ± σ	88.6 ± 95.7	9700 ± 5600	0.21 ± 0.28	22.08 ± 18.62	1.20 ± 1.11	193 ± 264	17.6 ± 16.2	2070 ± 980	94.7 ± 103	4700 ± 2800	0.023 ± 0.009
NV (% of $\bar{x}$)		55.7		118		136		45.1		76.8	

B. Bottom waters (2 m above bottom):

Summer cruises (A8, A19, A32)

	Fe nmol/l	Fe µg/g	Ni nmol/l	Ni µg/g	Zn nmol/l	Zn µg/g	Mn nmol/l	Mn µg/g	Al nmol/l	Al µg/g	total Hg nmol/l
n	71	71	67	68	68	68	71	71	71	71	70
$\bar{x}$ ± σ	324 ± 541	27400 ± 34000	0.10 ± 0.12	12.89 ± 7.25	1.79 ± 1.04	261 ± 107	283 ± 544	24400 ± 33200	61.1 ± 116	2850 ± 3050	0.028 ± 0.018
NV (% of $\bar{x}$)		124		56.1		39.8		269		134	

Winter cruises (P176, A26)

	Fe nmol/l	Fe µg/g	Ni nmol/l	Ni µg/g	Zn nmol/l	Zn µg/g	Mn nmol/l	Mn µg/g	Al nmol/l	Al µg/g	total Hg nmol/l
n	50	50	50	50	46	46	49	49	50	50	48
$\bar{x}$ ± σ	115 ±84	15400 ± 9600	0.22 ± 0.24	29.59 ± 21.80	1.19 ± 1.12	166 ± 96	28.8 ± 22.0	4190 ± 3020	134 ± 125	7740 ± 3850	0.025 ± 0.012
NV (% of $\bar{x}$)		60.0		72.8		56.8		70.5		39.5	

* σ = total uncertainty = natural variability + analytical uncertainty(precision).

& NV = natural variability (± % of $\bar{x}$) = $(([\sigma \ / \ \bar{x}] \times 100)^2$ - (precision; see text)$^2)^{0.5}$

Table 10. Significant differences (*) at the $p = 0.01$ probability level for mean particulate metal data (µg/g) of Table 9.
"0" = a significant difference is not provable.

A. Winter vs Summer Comparisons: Surface or Bottom Waters

	SPM	Co	Pb	Cd	Cu	Fe	Ni	Zn	Mn	Al
Surface	0	0	0	*	0	0	0	0	0	0
Bottom	0	*	0	*	0	0	0	0	*	*

B. Surface vs Bottom Comparisons: Winter or Summer

	SPM	Co	Pb	Cd	Cu	Fe	Ni	Zn	Mn	Al
Winter	*	*	*	0	0	*	0	0	*	*
Summer	0	*	0	*	0	*	0	0	*	0

Table 11. Summary table of suspended particulate matter (µg/g ± σ) collected with a high-speed centrifuge. Differences significant at the p = 0.01 level are indicated by *. (+ = significant difference at p = 0.10).

Location	Season	Co (n)	Pb (n)	Cd (n)	Ni (n)	Cu (n)	Fe (n)	Zn (n)	Mn (n)
Kiel. Förde	Summer	(2) 4.0 ± 0.27	(2) 14.5 ± 16.4	(2) 1.6 ± 1.1	(2) 12.0 ± 1.1	(2) 30.9 ± 7.8	(2) 5630 ± 3460	(2) 350 ± 38	(2) 5480 ±1050
								+	+
	Winter	(2) 5.2 ± 3.8	(2) 55.7 ± 47.0	(2) 0.9 ± 0.1	(2) 17.1 ± 4.2	(2) 44.5 ± 21.5	(2) 19360 ± 7160	(2) 178 ± 48	(2) 2200 ± 300
Eck. Bucht.	Summer	(3) 1.6 ± 0.6	(3) 4.7 ± 3.2	(3) 2.4 ± 1.1	(3) 11.7 ± 7.9	(3) 12.1 ± 9.3	(3) 1870 ± 910	(3) 171 ± 71	(3) 1250 ± 730
			+			+			
	Winter	(2) 7.2 ± 7.4	(2) 58.0 ± 27.8	(2) 1.1 ± 0.1	(2) 20.8 ± 16.0	(2) 38.3 ± 18.0	(2) 24490 ±13410	(2) 147 ± 62	(2) 1500 ±1540
Flensburger Förde	Summer	(2) 2.3 ± 0.4	(3) 3.9 ± 1.4	(3) 2.0 ± 0.9	(3) 8.2 ± 7.1	(3) 11.0 ± 5.1	(3) 2570 ± 1570	(3) 166 ± 33	(3) 2870 ± 3200
			+		+	+	*		
	Winter	(2) 6.8 ± 0.7	(2) 45.2 ± 18.0	(2) 1.0 ± 0.1	(2) 28.6 ± 7.3	(2) 40.2 ± 10.1	(2) 24870 ± 4320	(2) 150 ± 21	(2) 2390 ± 440
Meckl. Bucht/Fehm Belt	Summer	(3) 2.2 ± 0.7	(3) 9.9 ± 1.9	(3) 1.5 ± 0.5	(3) 16.5 ± 13.4	(3) 15.0 ± 3.8	(3) 4360 ± 2480	(3) 145 ± 17	(3) 874 ± 643
		+	+						
	Winter	(3) 6.9 ± 4.1	(3) 52.0 ± 37.7	(3) 1.0 ± 0.2	(3) 21.1 ± 12.1	(3) 30.8 ± 18.5	(3) 21370 ±13090	(3) 139 ± 48	(3) 815 ± 175
Lübecker Bucht	Summer	(3) 1.9 ± 1.0	(3) 13.5 ± 11.3	(3) 2.1 ± 0.2	(3) 15.0±14.0	(3) 10.0 ± 5.9	(3) 1680 ± 1140	(3) 149 ± 51	(3) 640 ± 375
			*				*		
	Winter	(3) 6.1 ± 4.0	(3) 52.6 ± 40.2	(3) 1.2 ± 0.2	(3) 17.0±11.6	(3) 30.2 ± 20.0	(3) 29500 ± 7830	(3) 145 ± 52	(3) 928 ± 522

Table 12. Significant differences (*) at the p = 0.01 level between particulate metal contents (µg/g) of SPM collected by centrifuge and on 0.4 µm Nuclepore filters in the study areas by season (individual sample data not included in this report). "0" indicates a significant difference cannot be proven.

Location	Season	Co	Pb	Cd	Ni	Cu	Fe	Zn	Mn
Kiel. Förde	Summer	0	0	0	0	0	0	0	0
	Winter	0	0	0	0	0	0		0
Eck. Bucht.	Summer	0	0	0	0	0	0	0	0
	Winter	0	0	0	0	0	*	0	0
Flensburger Förde	Summer	0	0	0	0	0	0	0	0
	Winter	0	0	0	0	0	*	0	0
Meckl. Bucht/Fehm. Belt	Summer	0	0	0	0	0	0	0	0
	Winter	0	0	0	0	0	*	0	0
Lübecker Bucht	Summer	0	0	0	0	0	0	0	0
	Winter	0	0	0	0	0	*	0	0

Figure 1. Map of station locations.

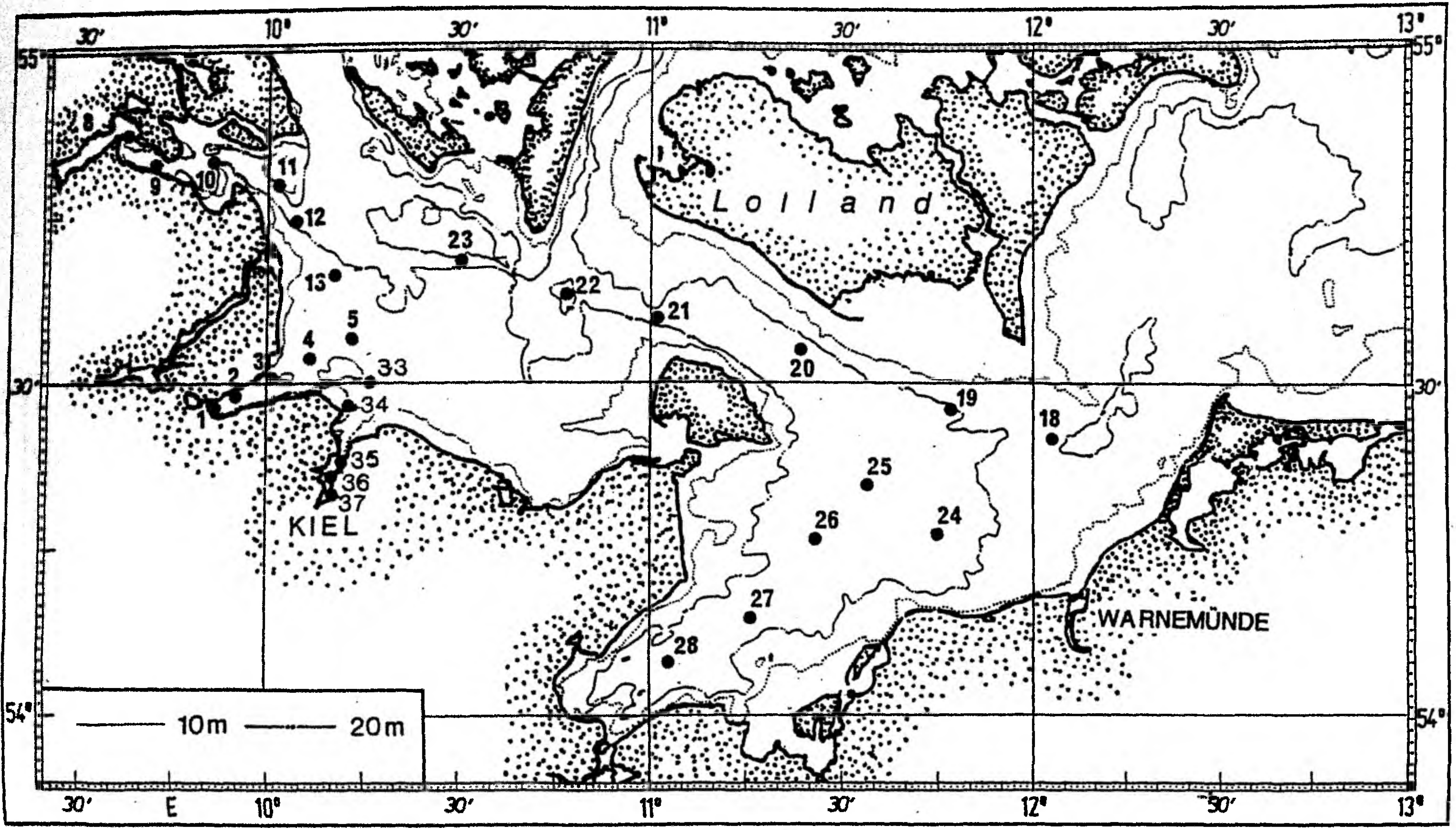


Figure 2. Water temperature versus station number in surface and bottom waters by season. I, O, E, and W in the area names indicate inner, outer, eastern, and western directions for orientation.

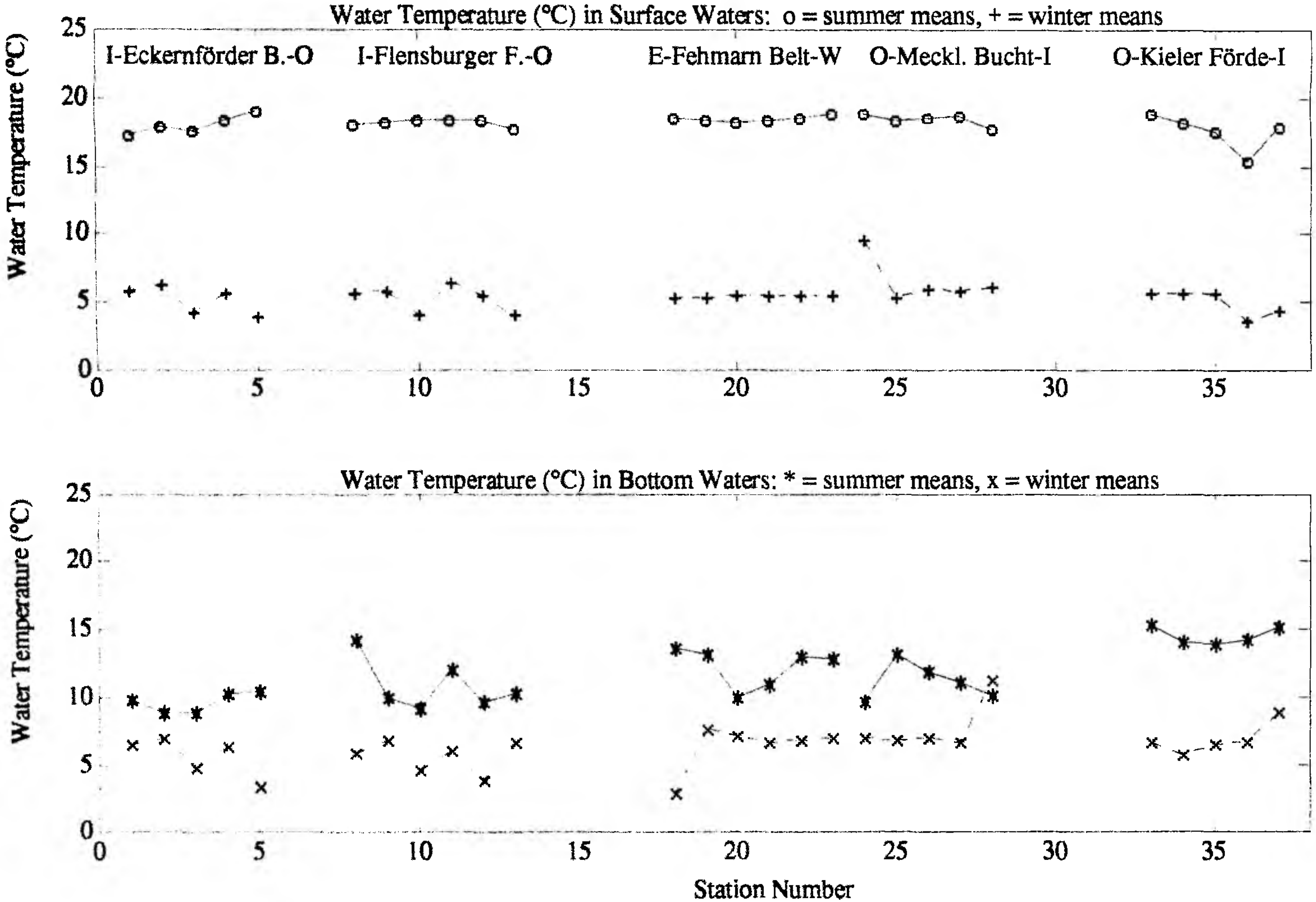


Figure 3. Salinity versus station number in surface and bottom waters by season. I, O, E, and W in the area names indicate inner, outer, eastern, and western directions for orientation.

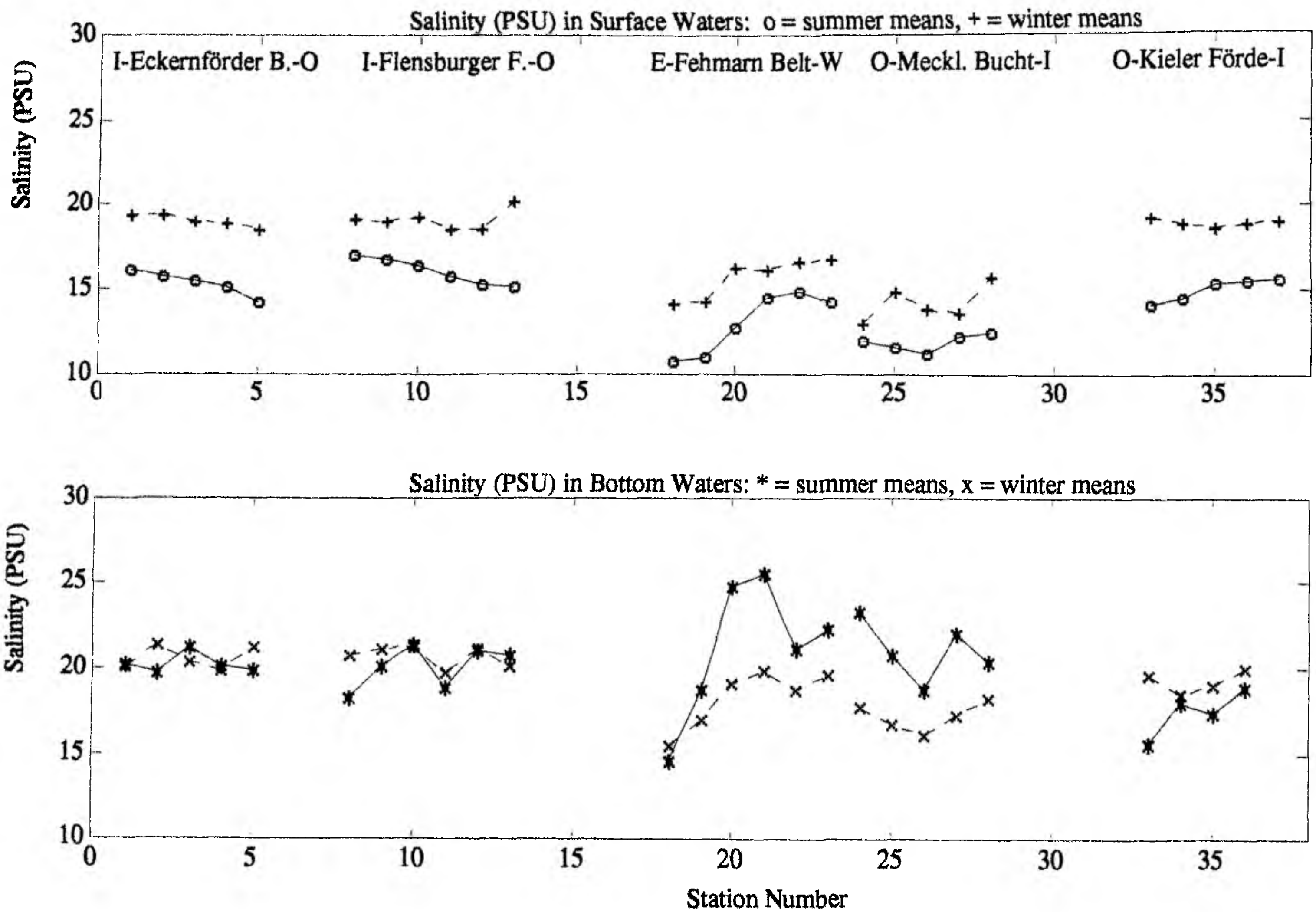


Figure 4. Nitrate versus station number in surface and bottom waters by season. I, O, E, and W in the area names indicate inner, outer, eastern, and western directions for orientation.

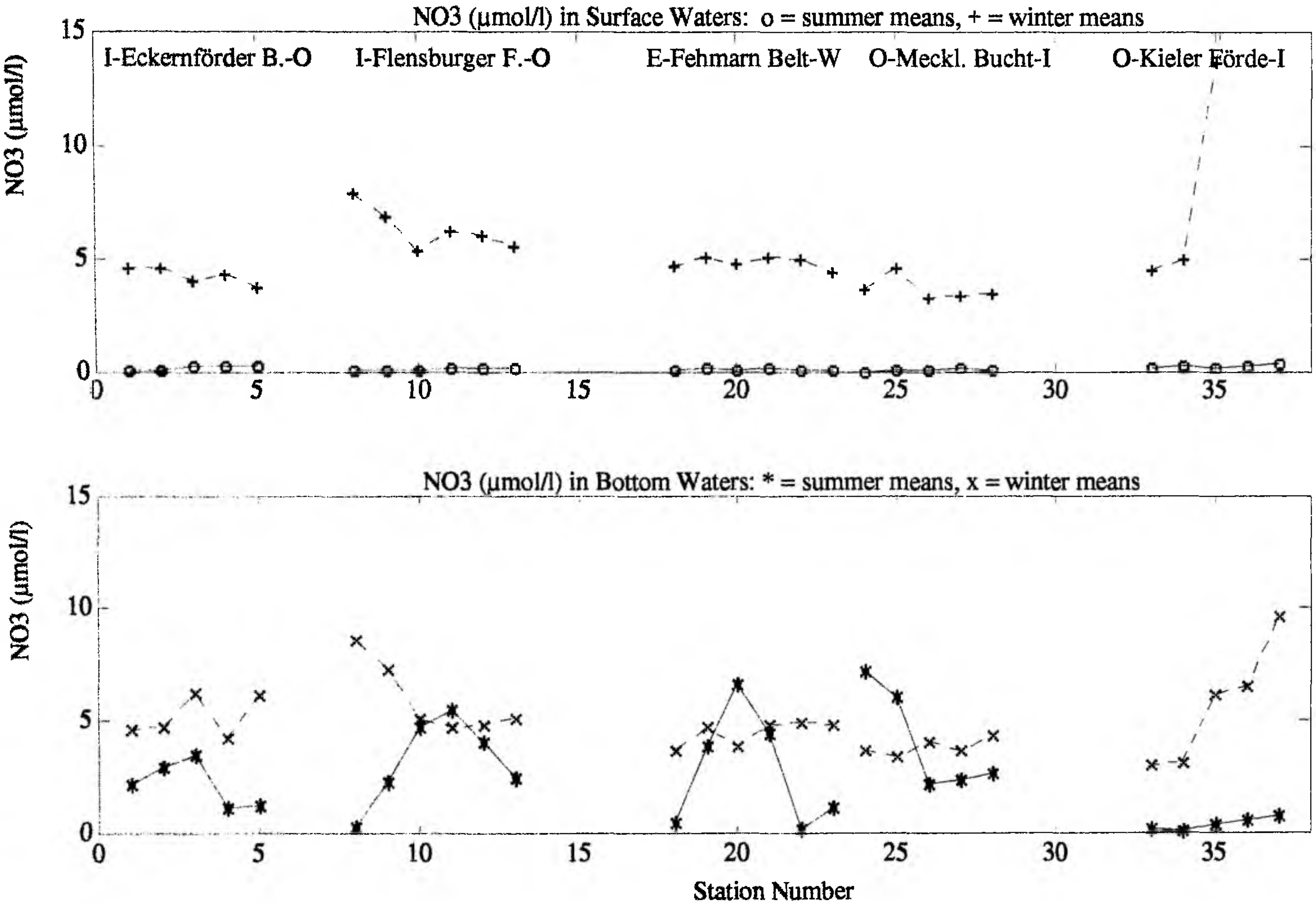


Figure 5. Ammonium versus station number in surface and bottom waters by season. I, O, E, and W in the area names indicate inner, outer, eastern, and western directions for orientation.

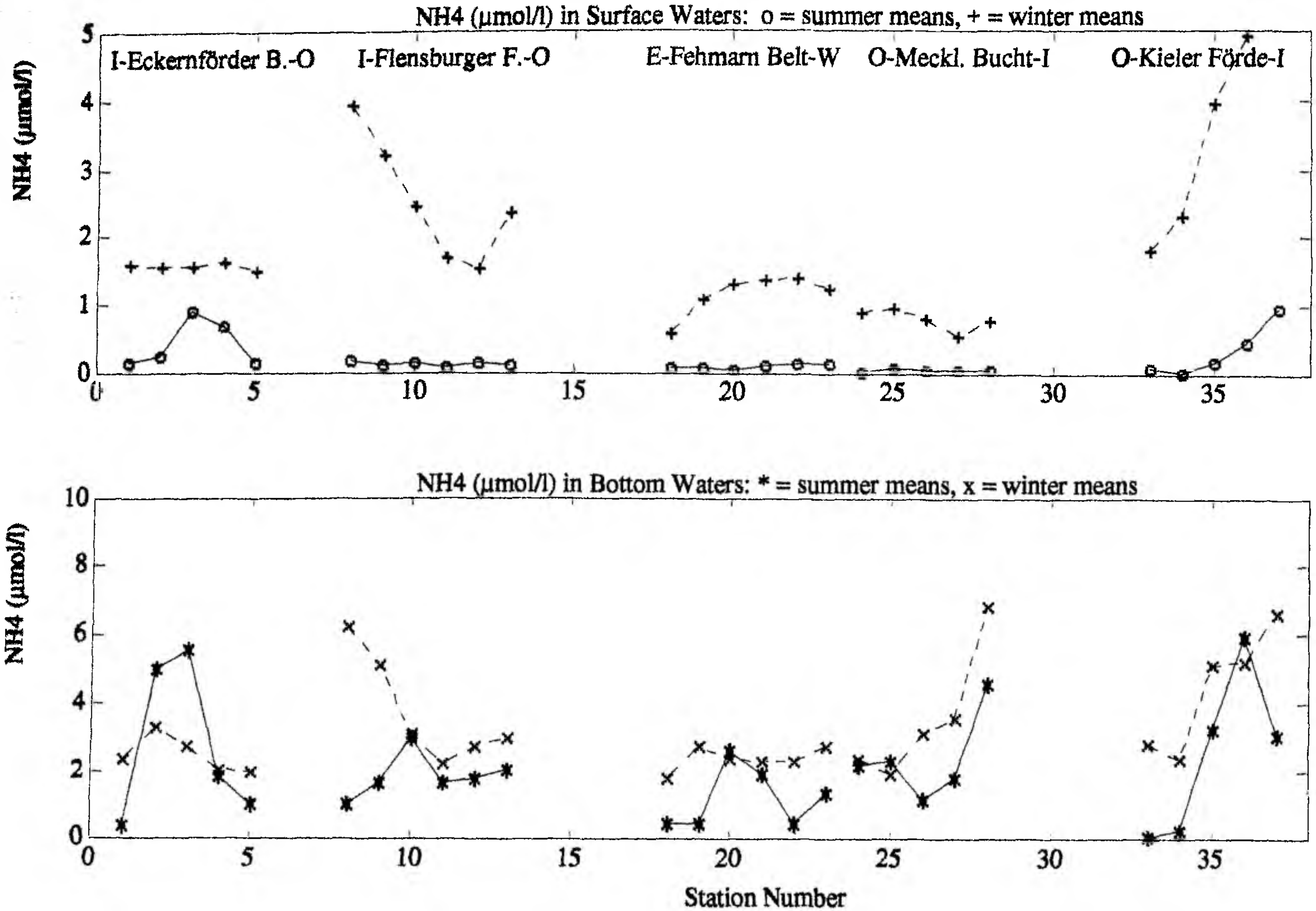


Figure 6. Silicate versus station number in surface and bottom waters by season. I, O, E, and W in the area names indicate inner, outer, eastern, and western directions for orientation.

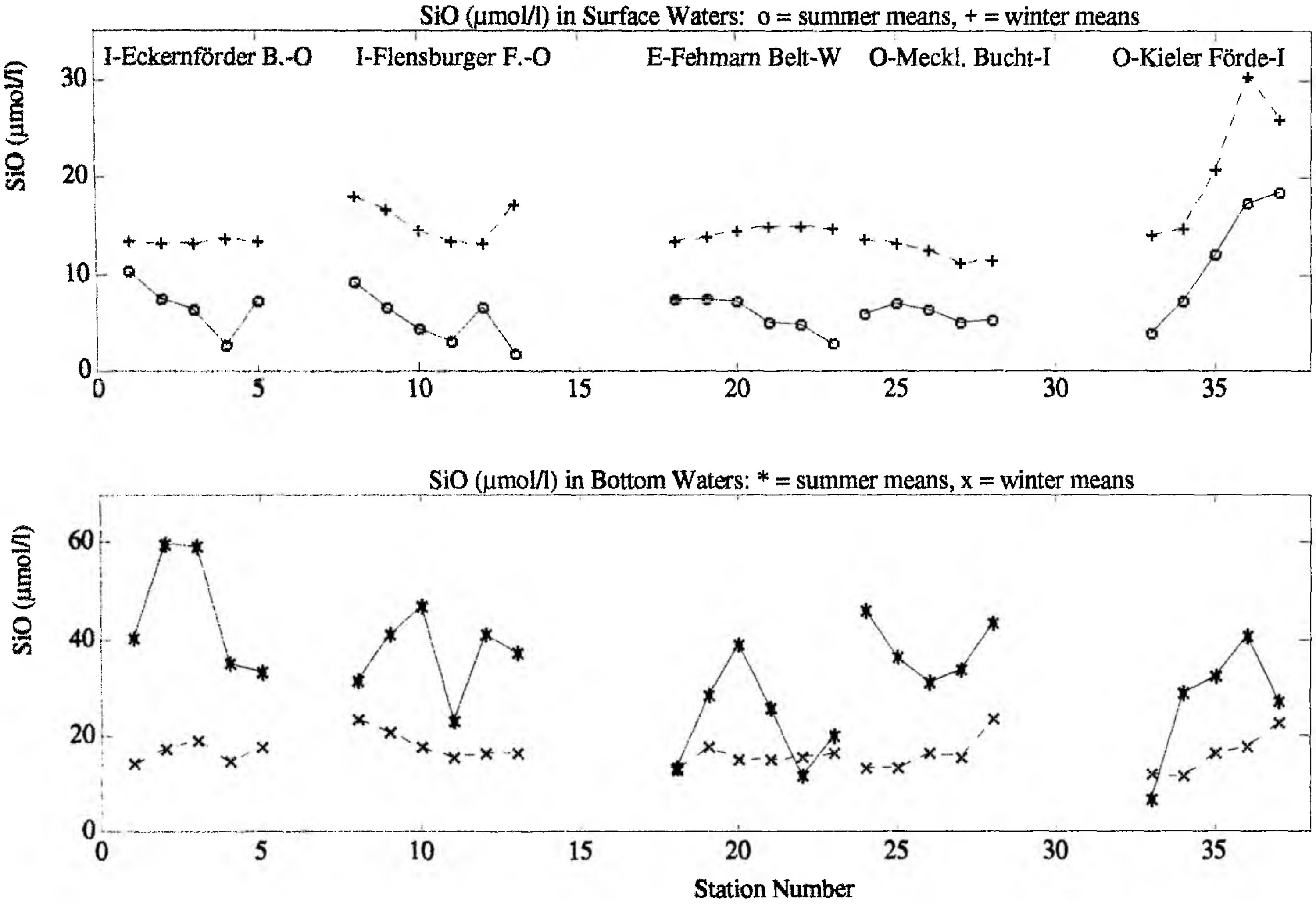


Figure 7. Phosphate versus station number in surface and bottom waters by season. I, O, E, and W in the area names indicate inner, outer, eastern, and western directions for orientation.

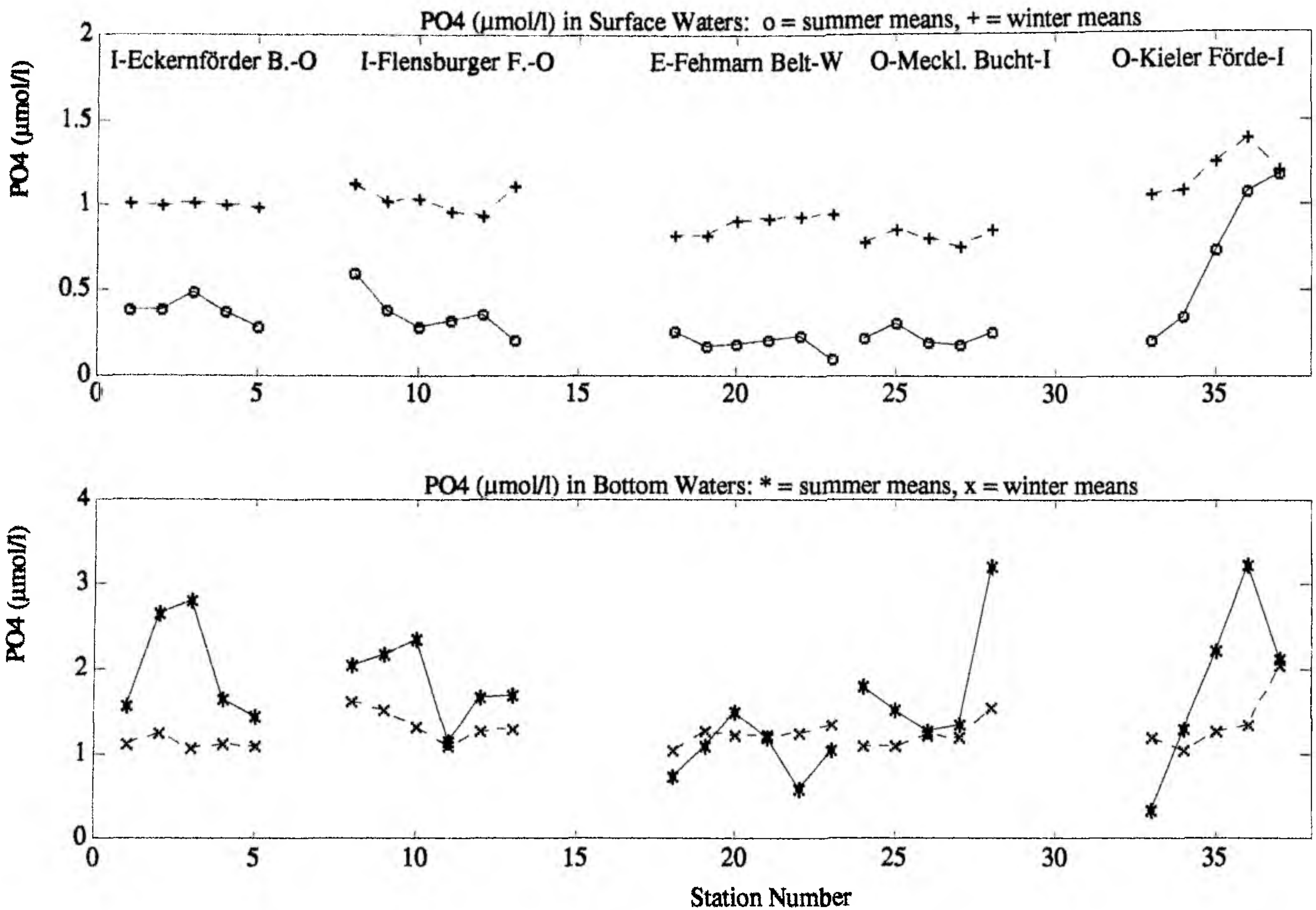


Figure 8. Percent oxygen saturation content versus station number in surface and bottom waters by season. I, O, E, and W in the area names indicate inner, outer, eastern, and western directions for orientation.

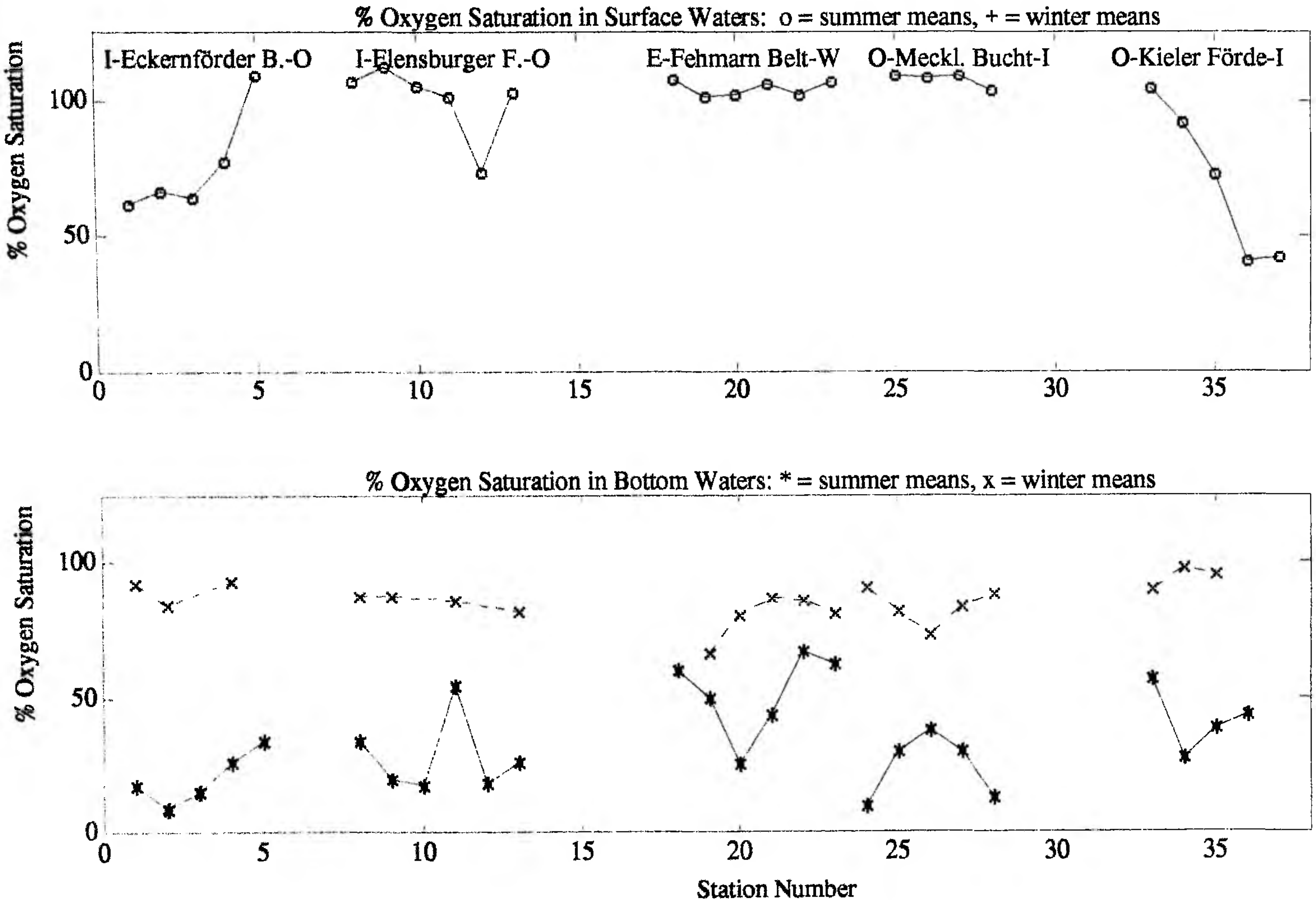


Figure 9. Particulate organic carbon versus station number in surface and bottom waters by season. I, O, E, and W in the area names indicate inner, outer, eastern, and western directions for orientation.

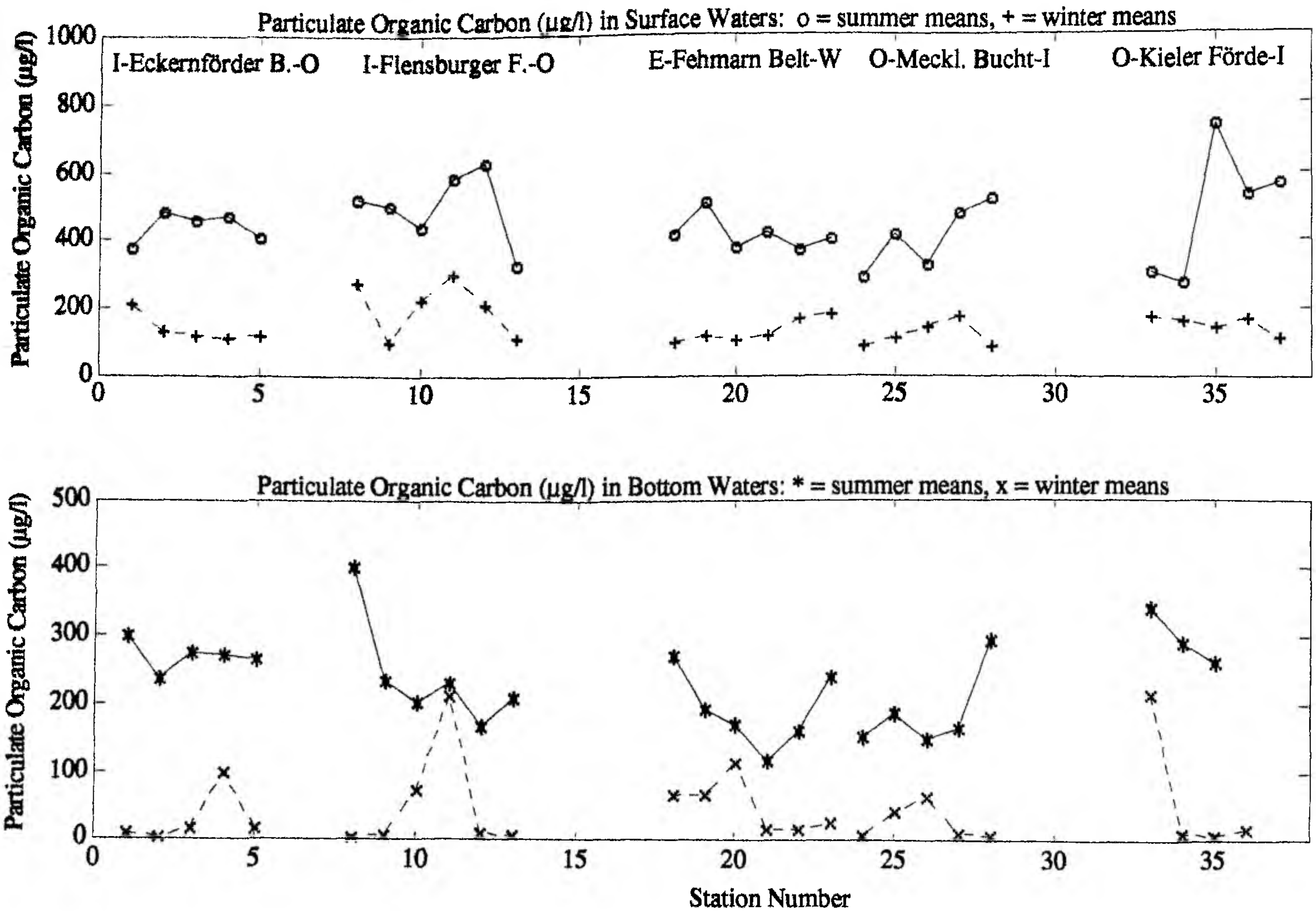


Figure 10. Particulate organic nitrogen versus station number in surface and bottom waters by season. I, O, E, and W in the area names indicate inner, outer, eastern, and western directions for orientation.

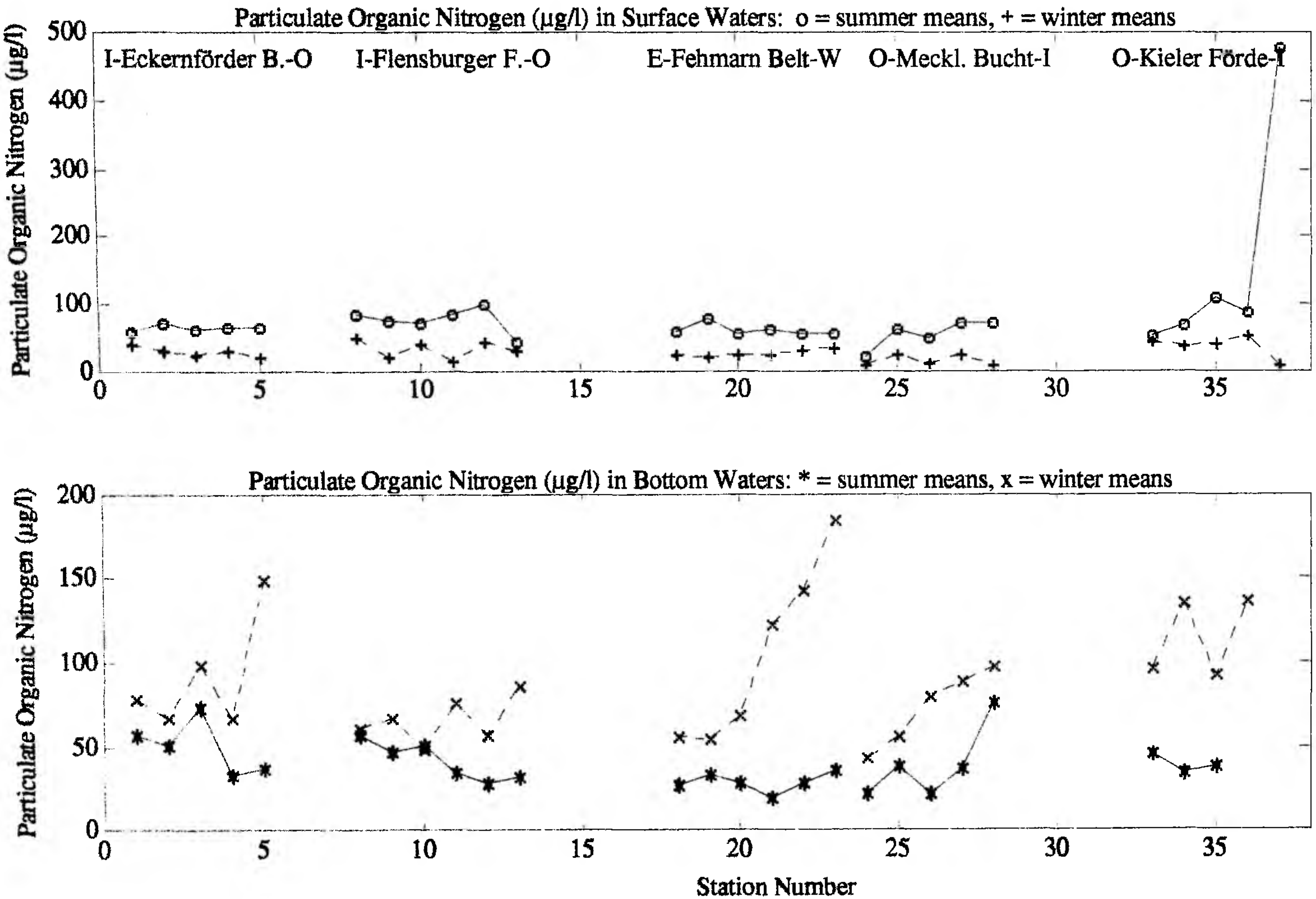


Figure 11. Chlorophyll-a versus station number in surface and bottom waters by season. I, O, E, and W in the area names indicate inner, outer, eastern, and western directions for orientation.

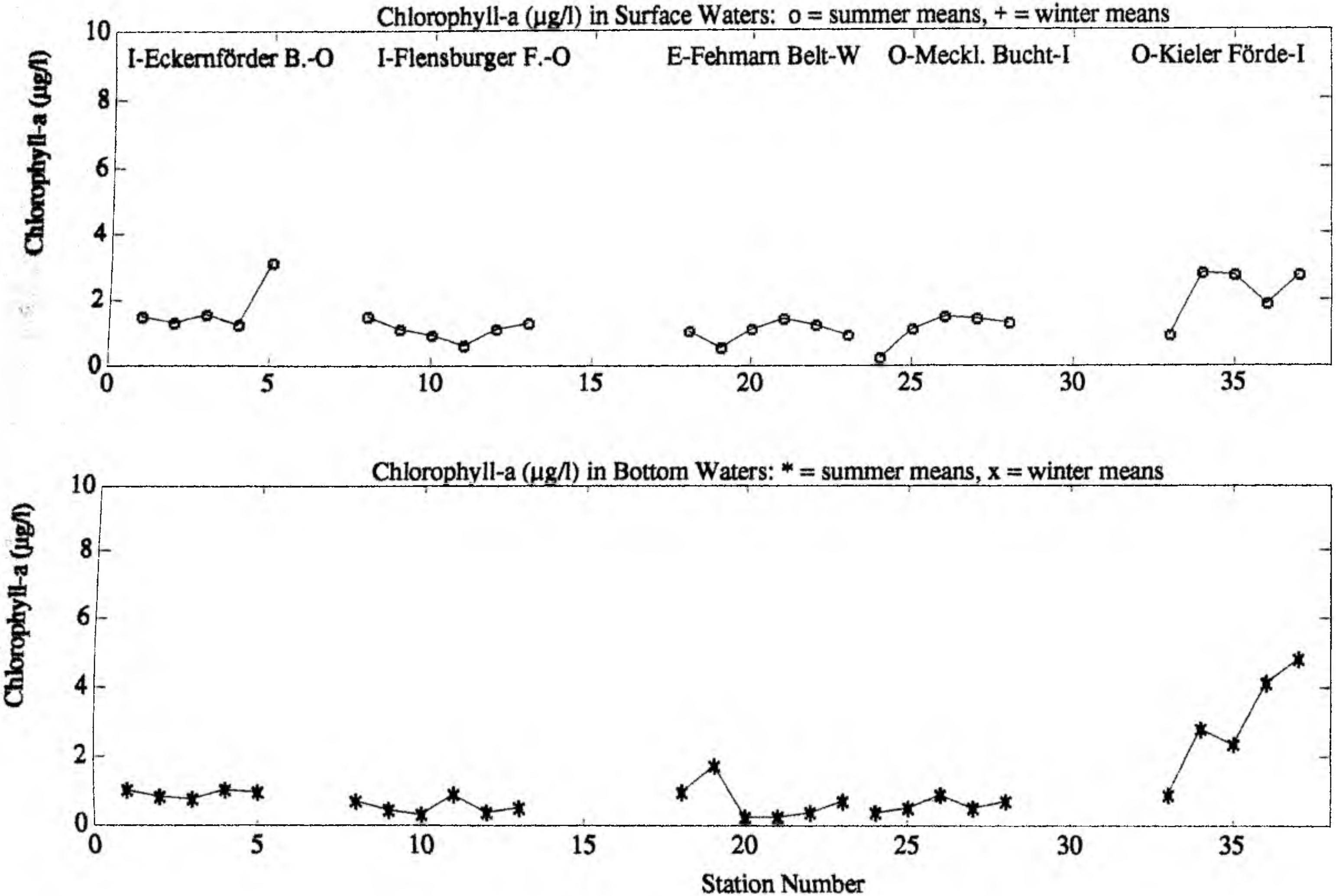


Figure 12. Dissolved (0.4 μm filtered) Co versus station number in surface and bottom waters by season. I, O, E, and W in the area names indicate inner, outer, eastern, and western directions for orientation.

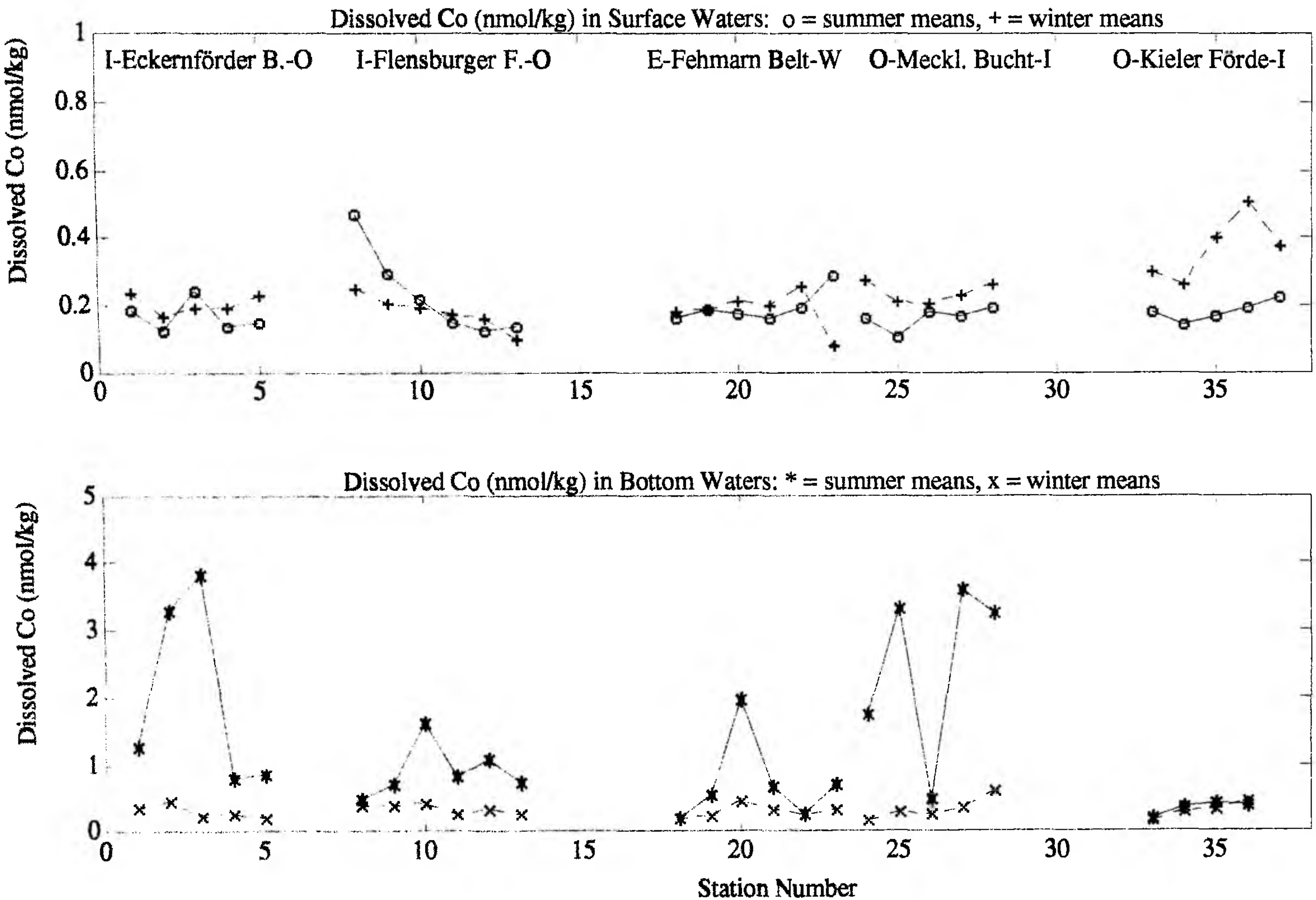


Figure 13. Dissolved (0.4 µm filtered) Co versus station number in Flensburger Förde, illustrating natural variability versus analytical precision of the measurements. Error bars indicate the total uncertainty (1 σ); the envelope bounded by the dashed and solid lines indicates the analytical precision of the measurements.

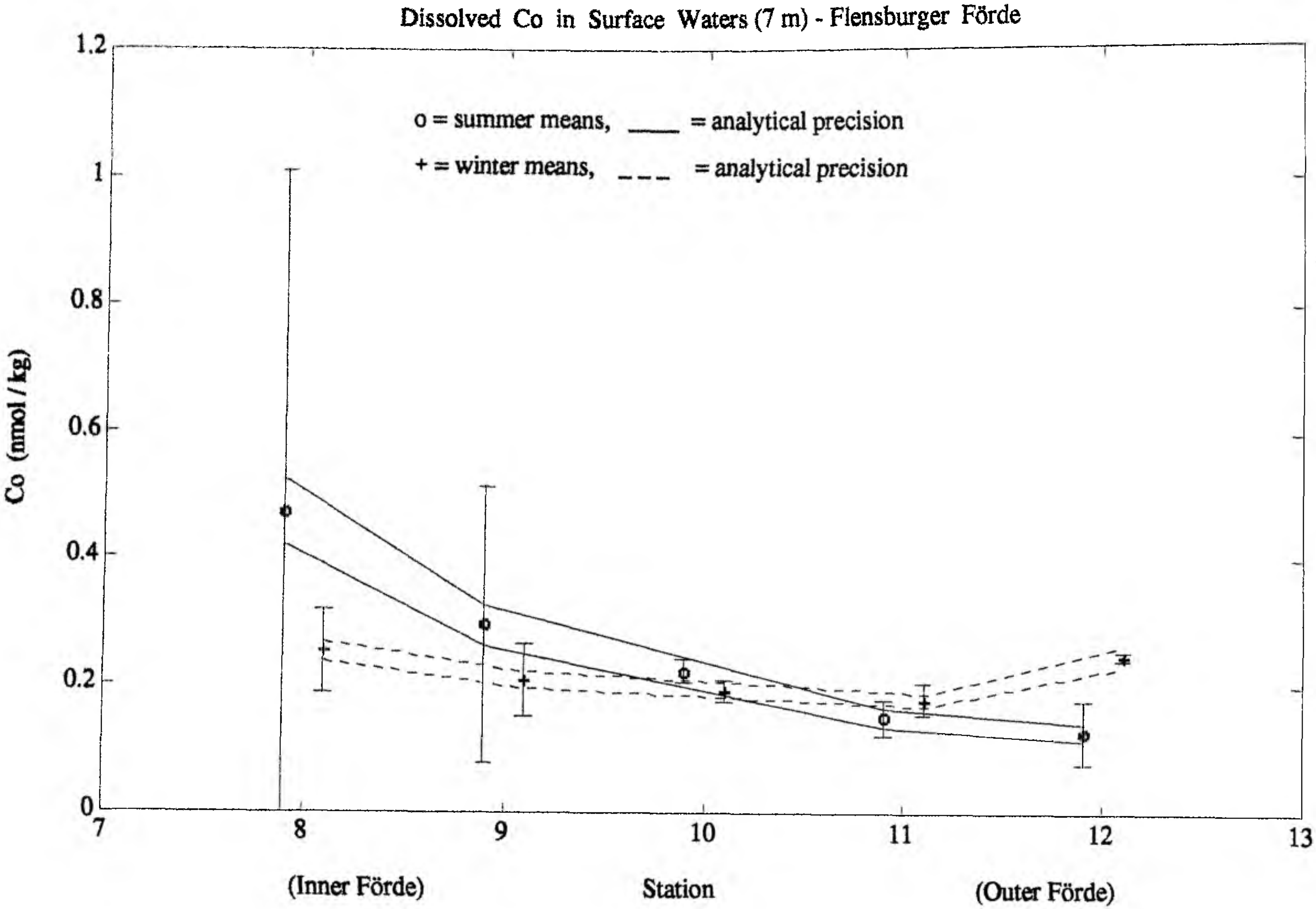


Figure 14. Dissolved (0.4 µm filtered) Pb versus station number in surface and bottom waters by season. I, O, E, and W in the area names indicate inner, outer, eastern, and western directions for orientation.

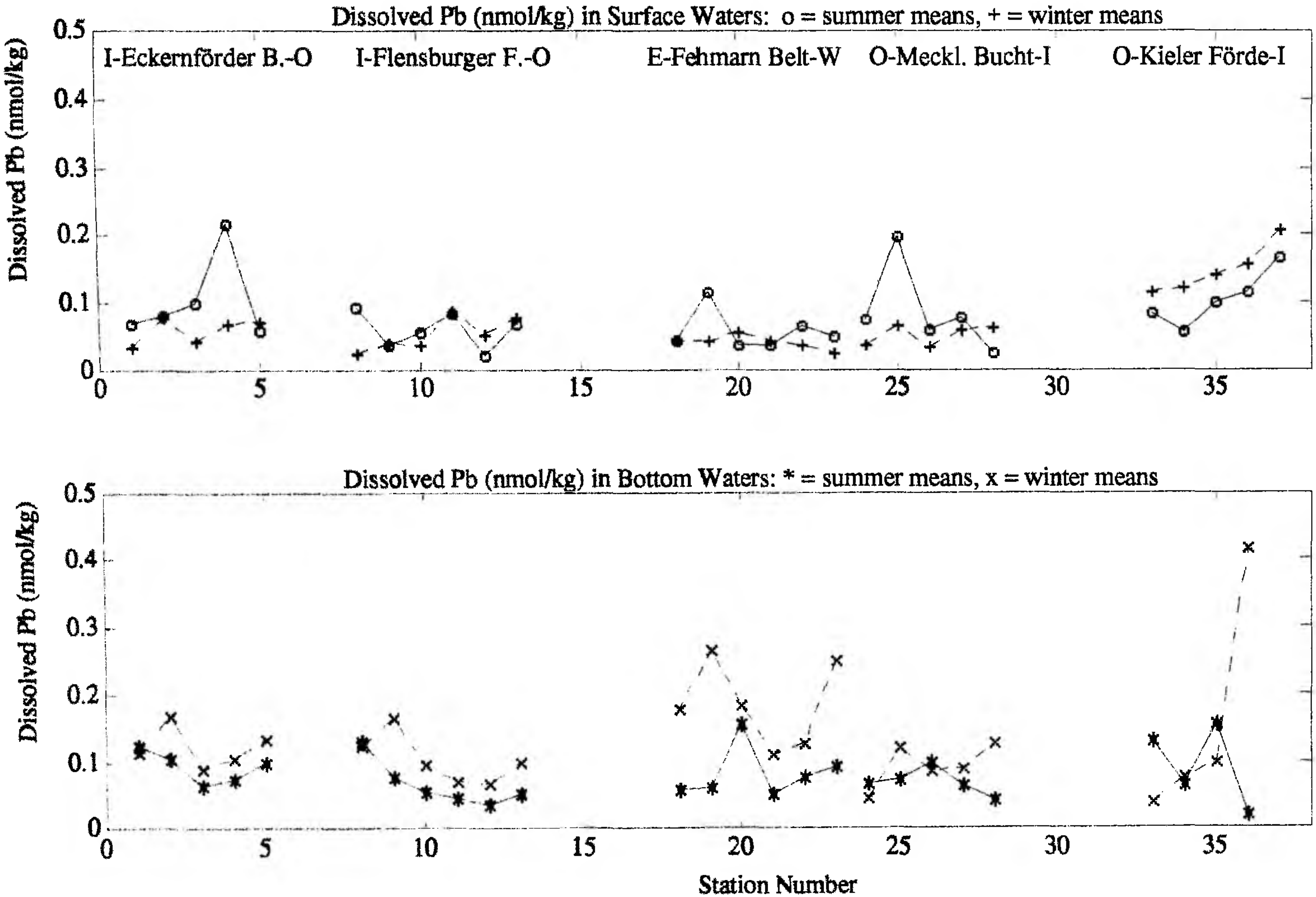


Figure 15. Dissolved (0.4 µm filtered) Cd versus station number in surface and bottom waters by season. I, O, E, and W in the area names indicate inner, outer, eastern, and western directions for orientation.

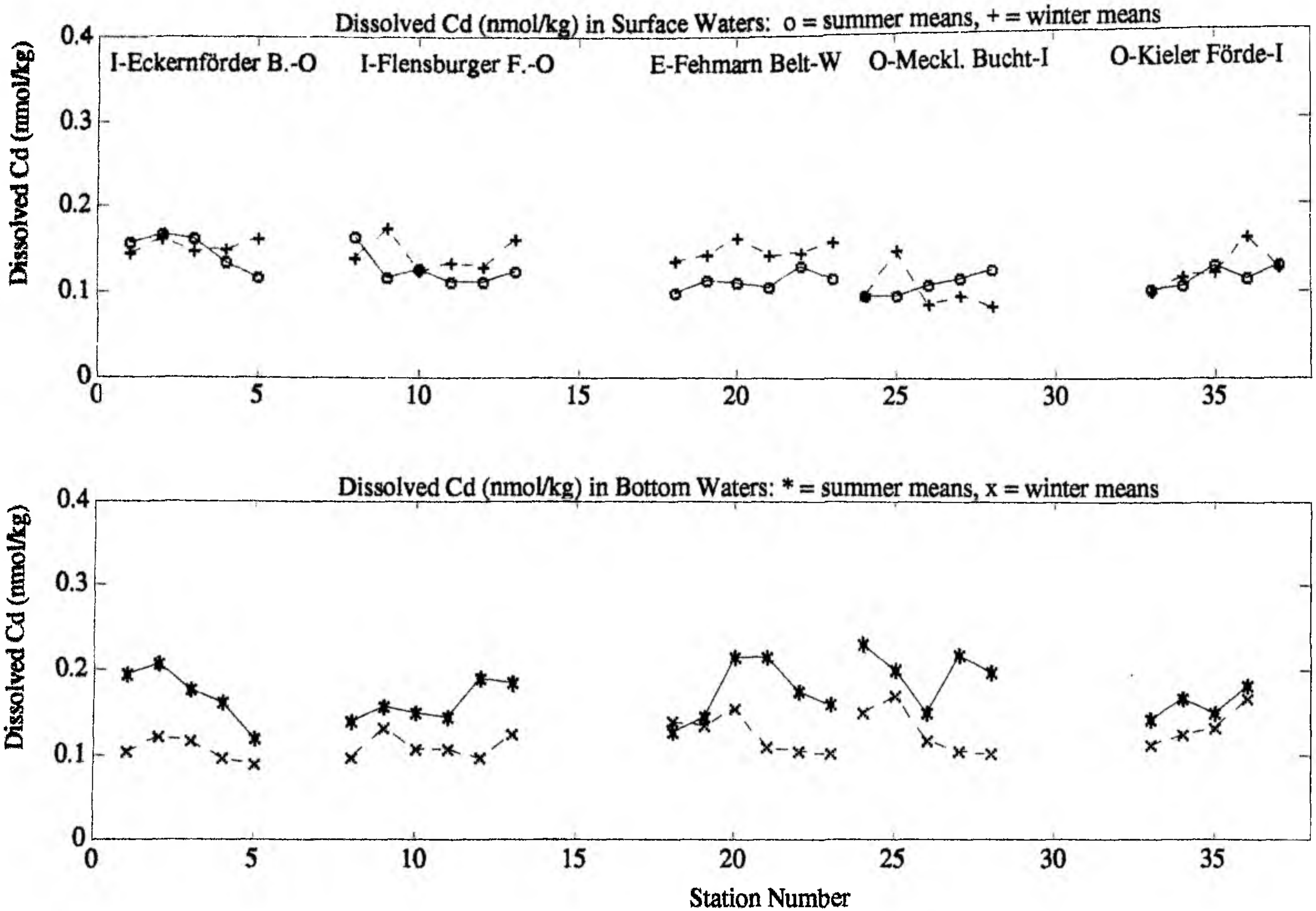


Figure 16. Dissolved (0.4 μm filtered) Cu versus station number in surface and bottom waters by season. I, O, E, and W in the area names indicate inner, outer, eastern, and western directions for orientation.

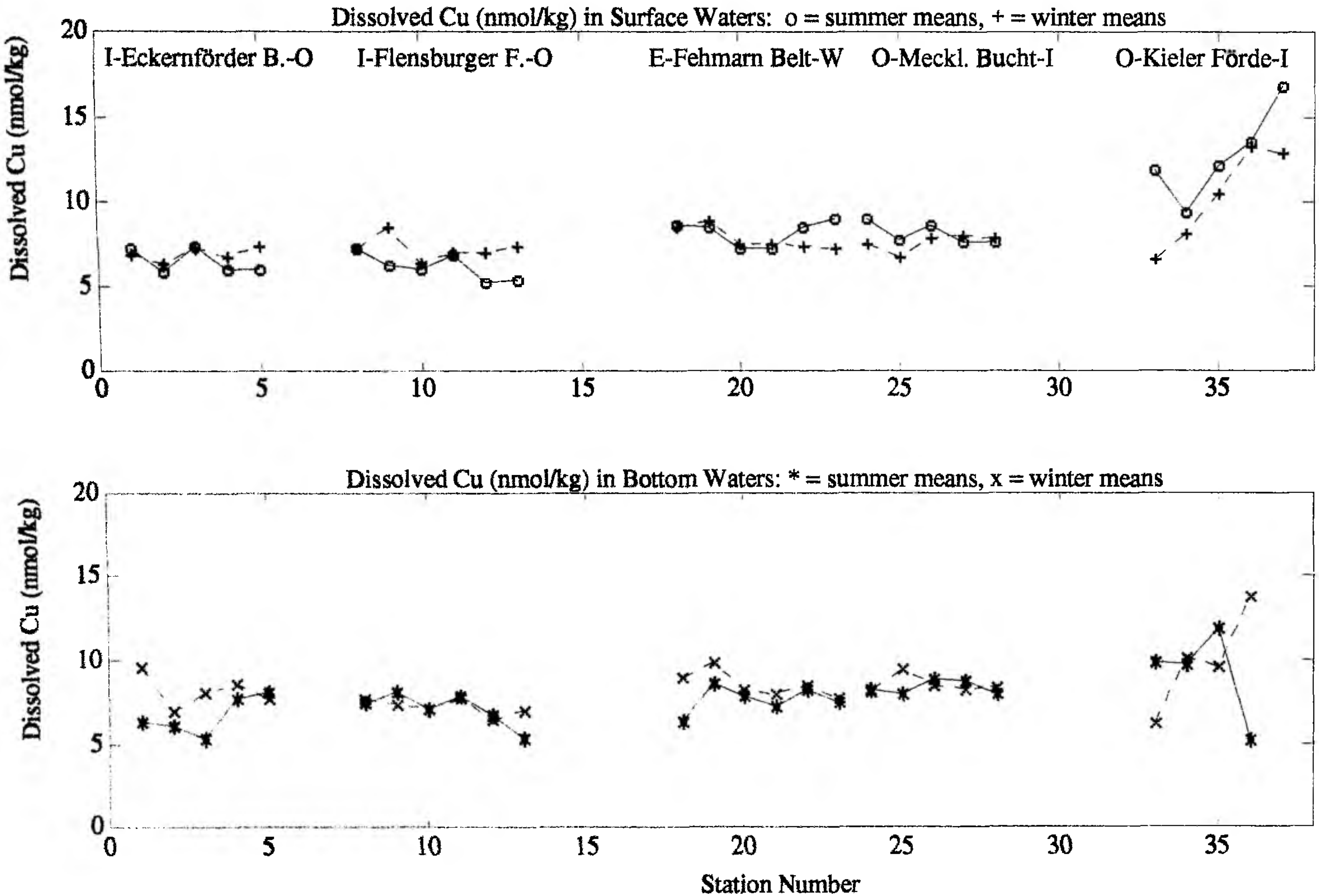


Figure 17. Dissolved (0.4 μm filtered) Ni versus station number in surface and bottom waters by season. I, O, E, and W in the area names indicate inner, outer, eastern, and western directions for orientation.

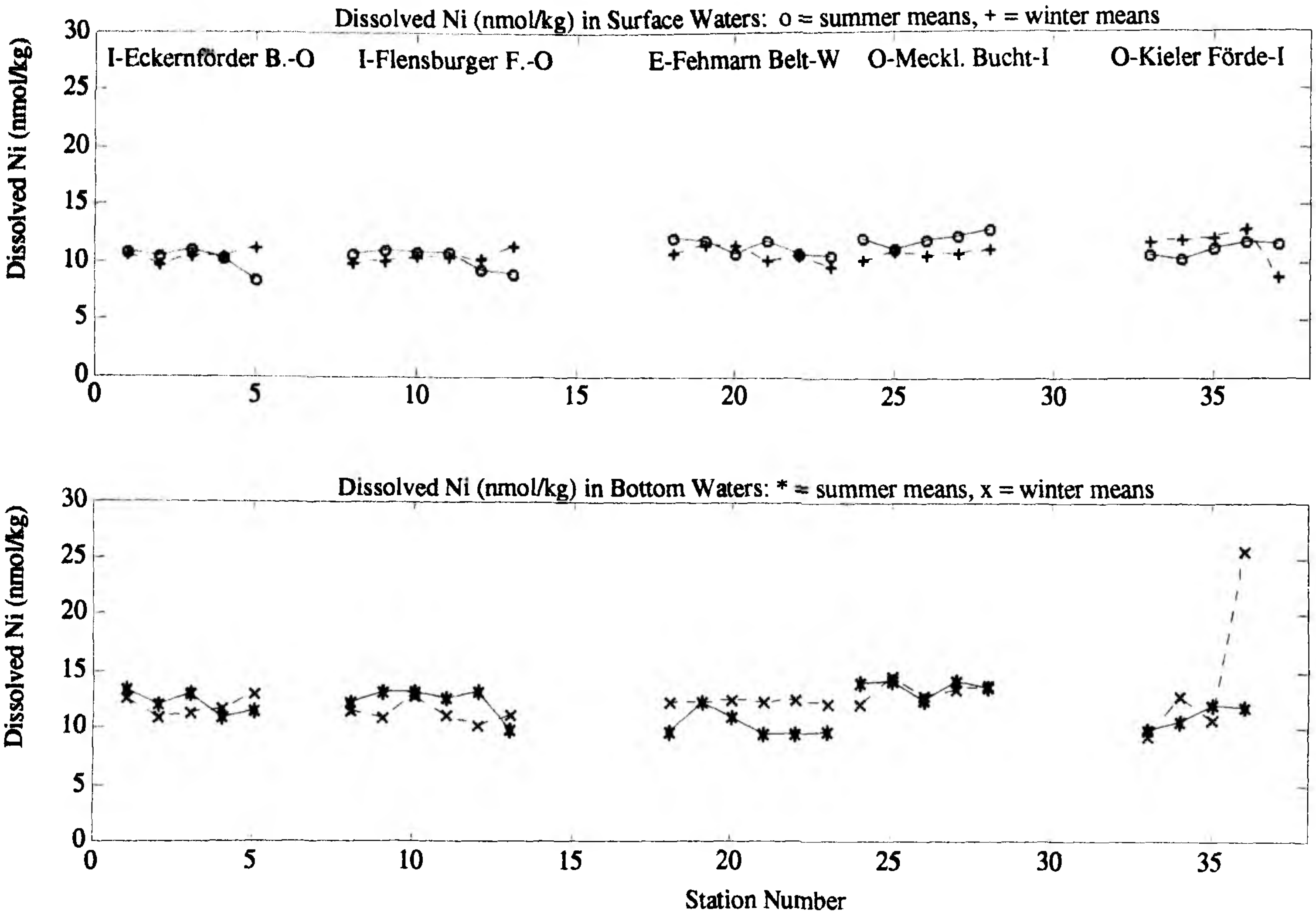


Figure 18. Dissolved (0.4 μm filtered) Fe versus station number in surface and bottom waters by season. I, O, E, and W in the area names indicate inner, outer, eastern, and western directions for orientation.

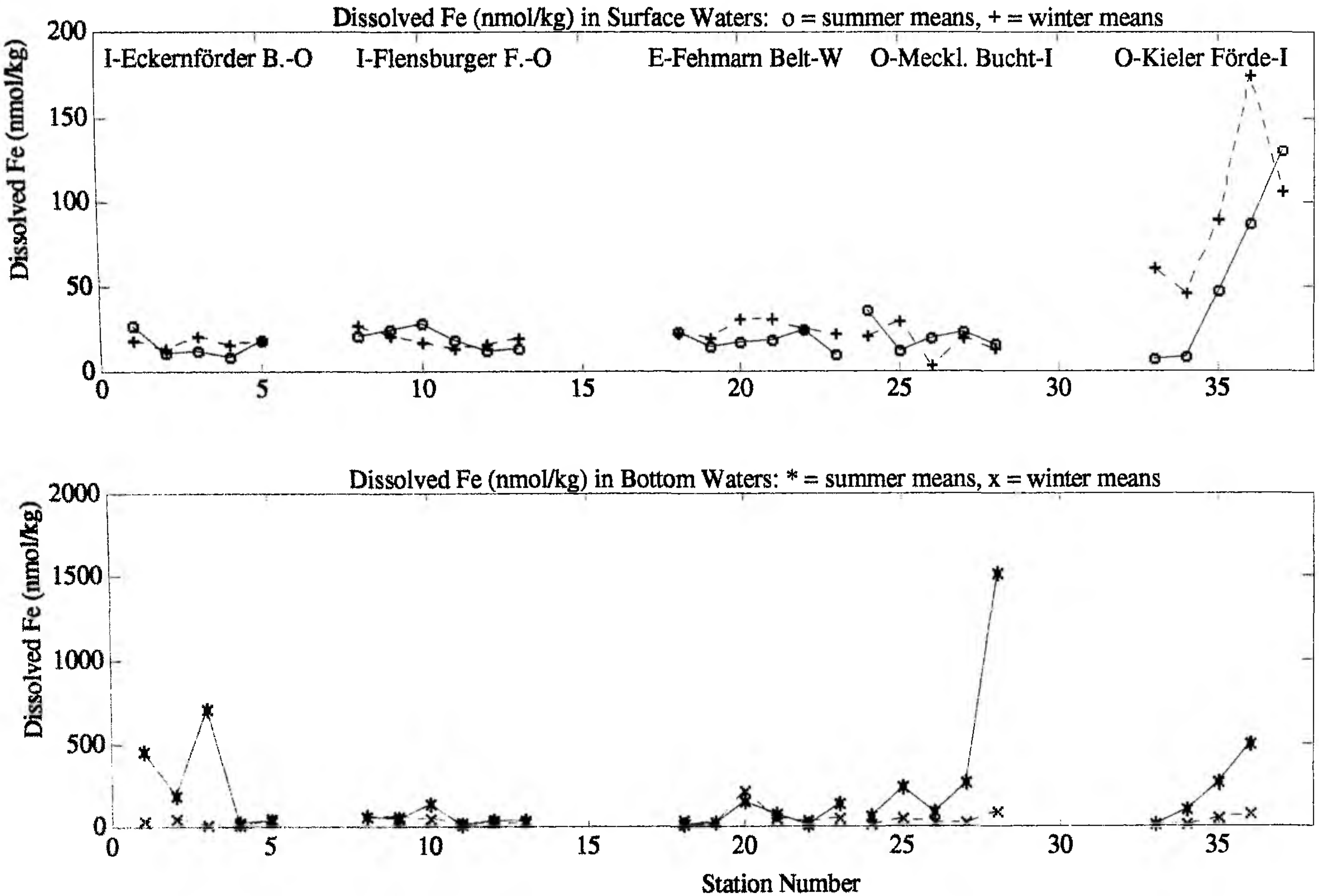
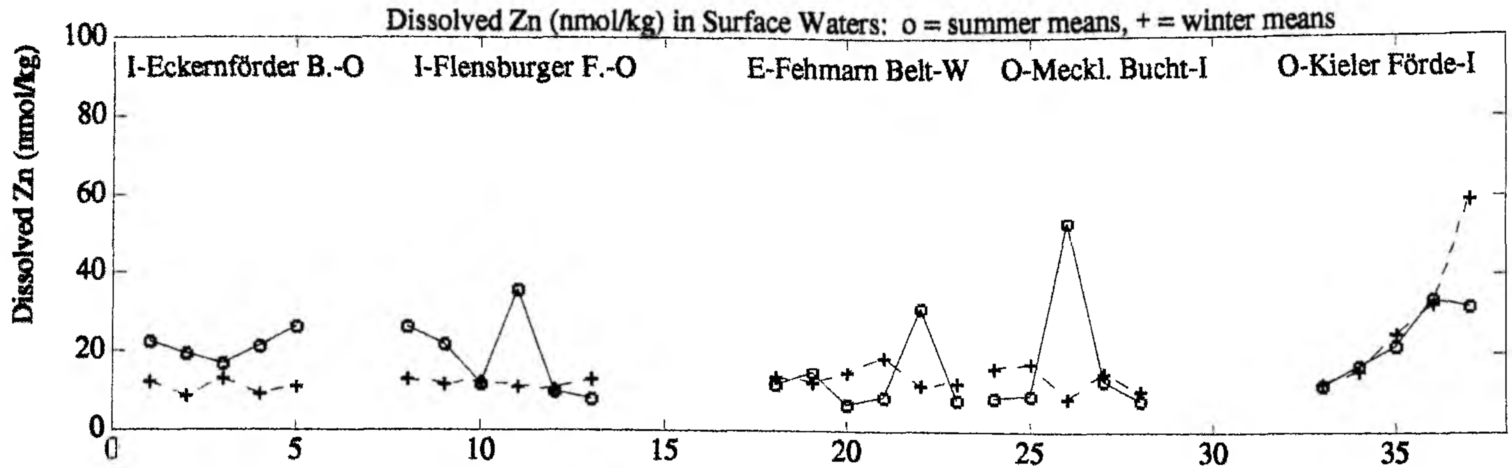


Figure 19. Dissolved (0.4 µm filtered) Zn versus station number in surface and bottom waters by season. I, O, E, and W in the area names indicate inner, outer, eastern, and western directions for orientation.



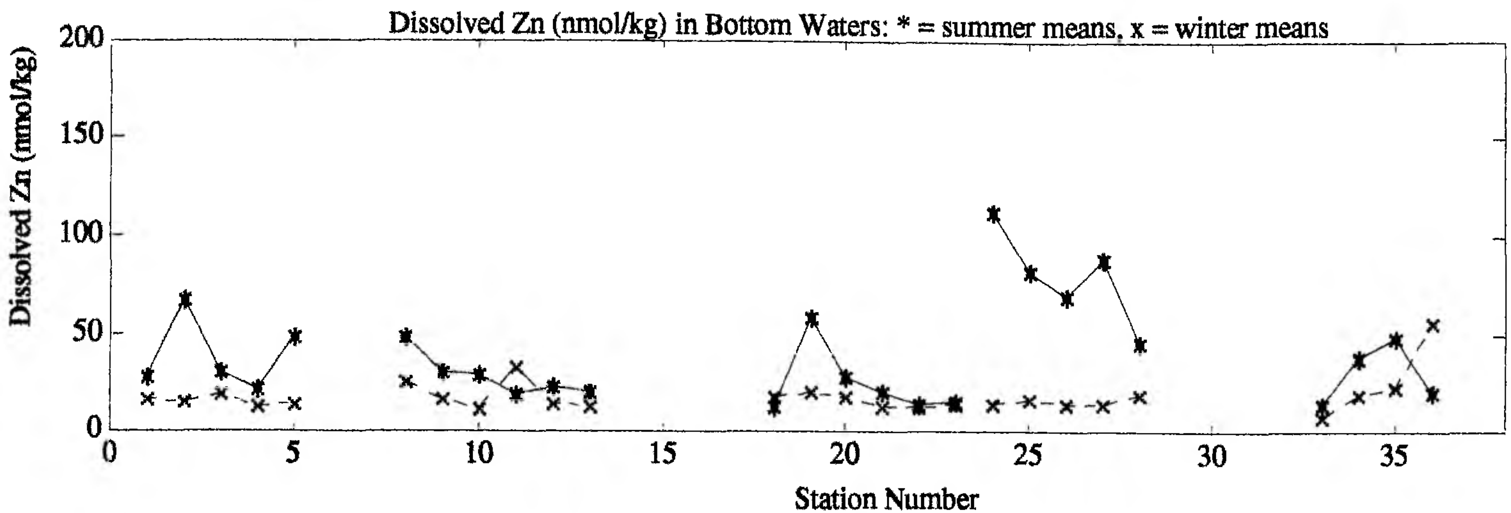


Figure 20. Dissolved (0.4 *μm filtered*) *Mn versus station number in* surface and bottom waters by season. I, O, E, and W in the area names indicate inner, outer, eastern, and western directions for orientation.

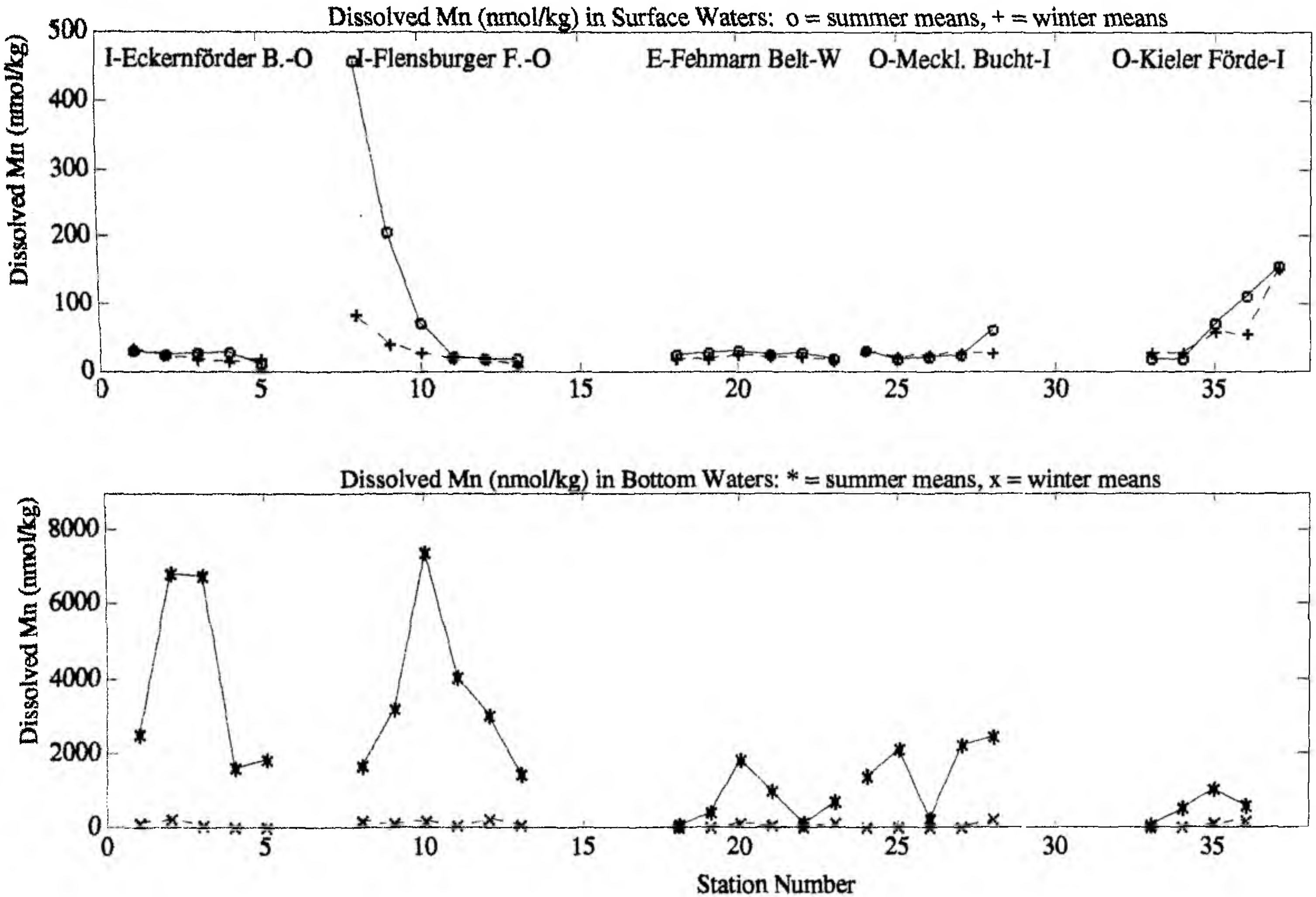


Figure 21. Dissolved (0.4 μm filtered) Co versus salinity in surface and bottom waters by season.

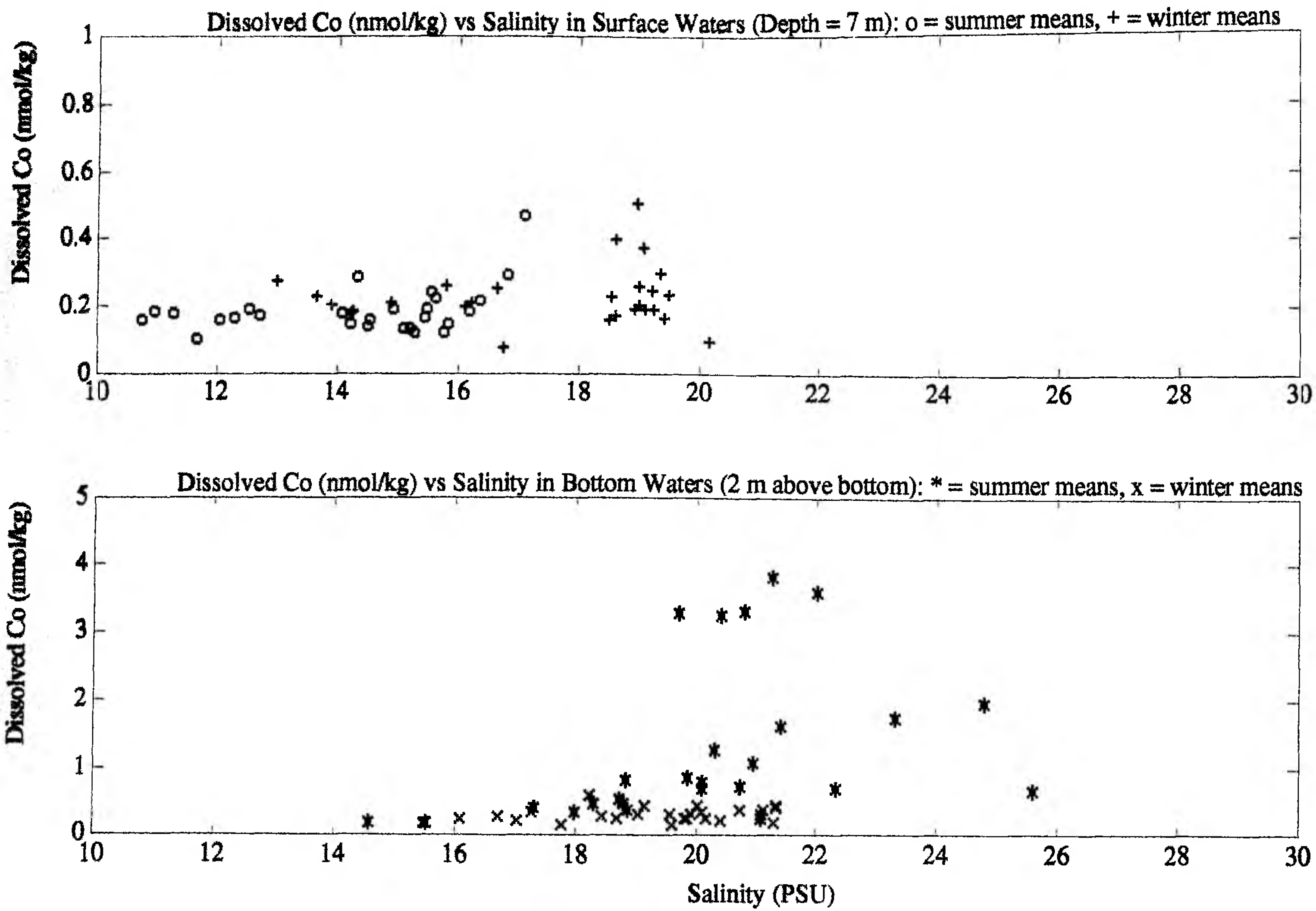


Figure 22. Dissolved (0.4 µm filtered) Pb versus salinity in surface and bottom waters by season.

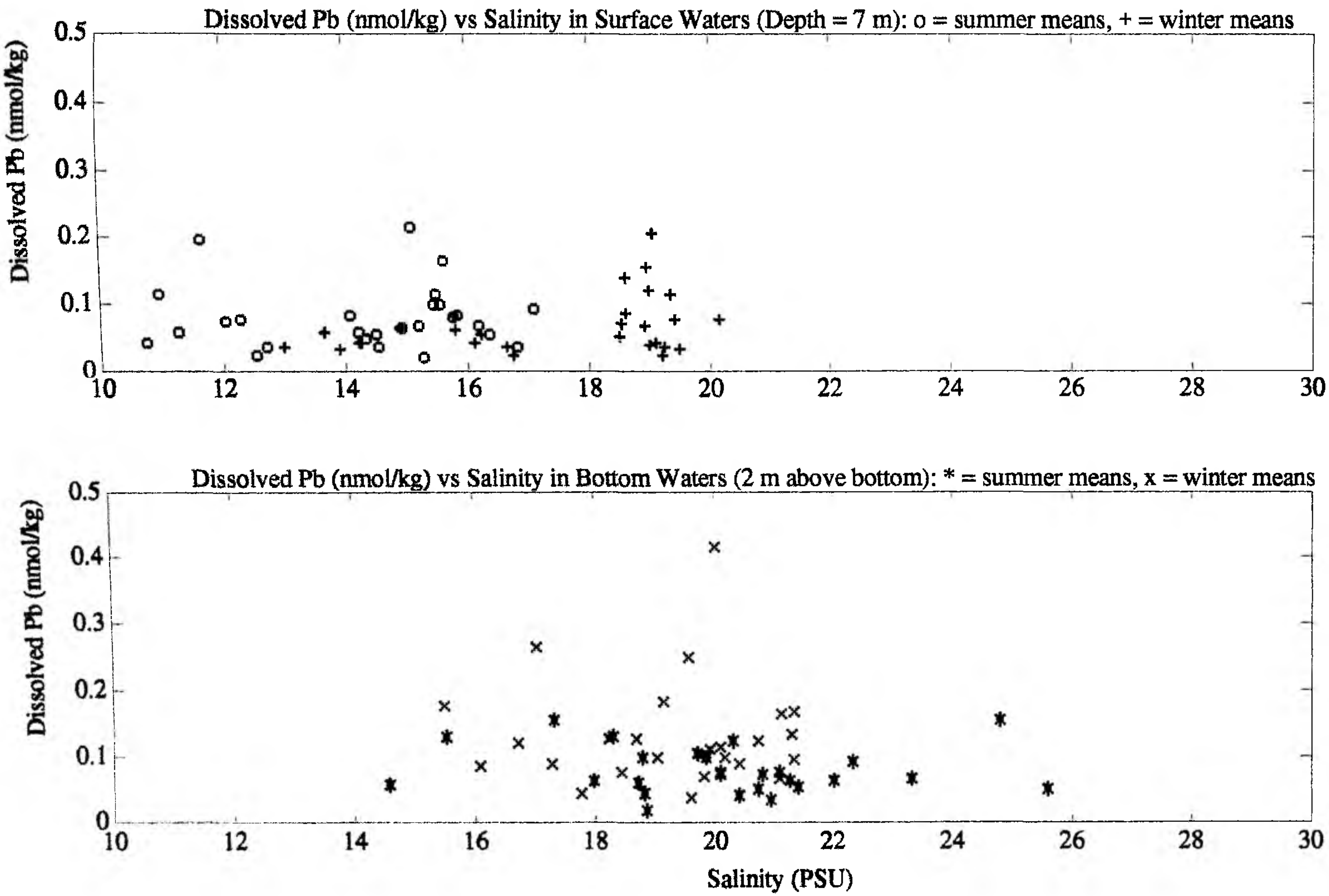


Figure 23. Dissolved (0.4 μm filtered) Cd versus salinity in surface and bottom waters by season.

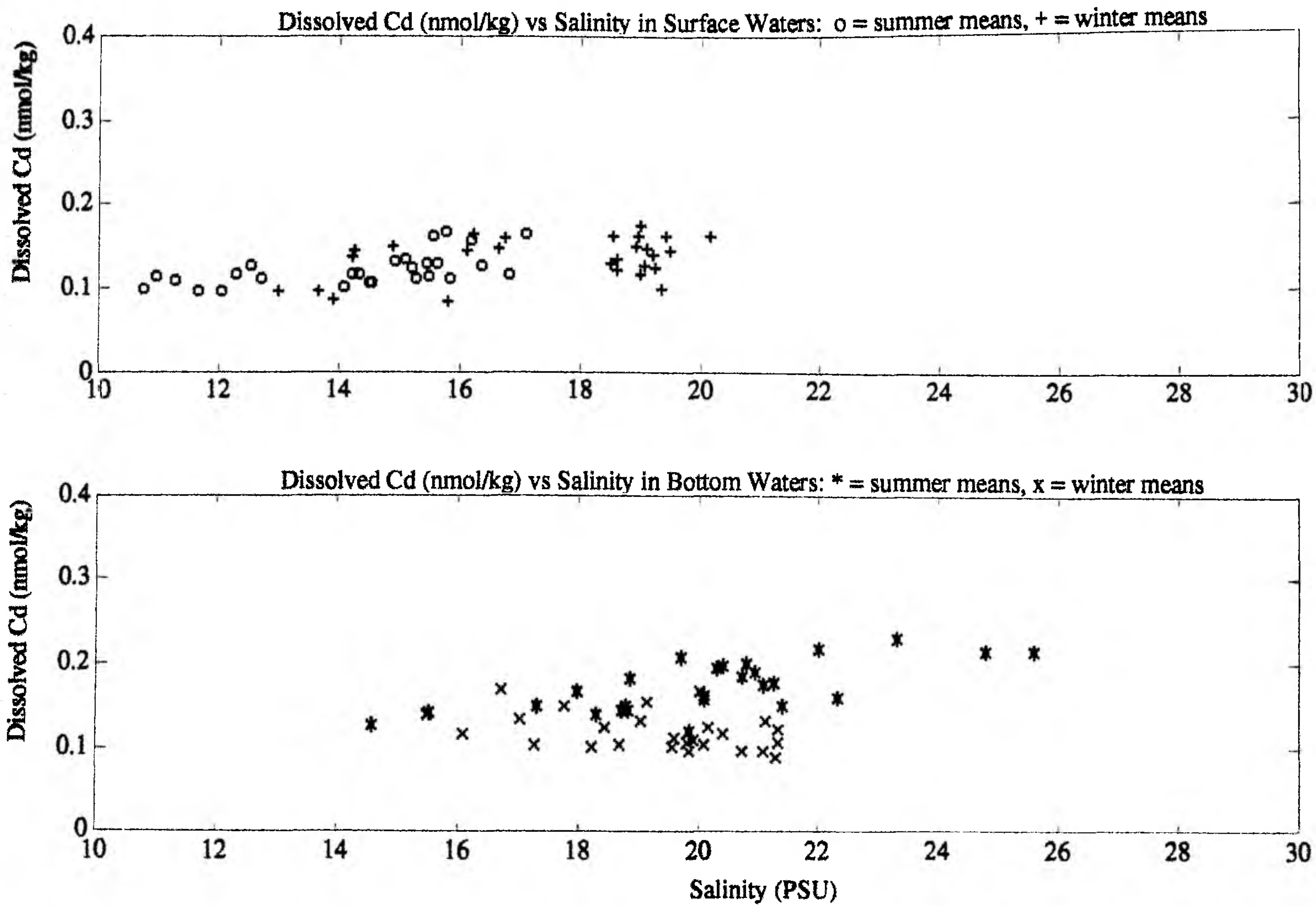


Figure 24. Dissolved (0.4 μm filtered) Cu versus salinity in surface and bottom waters by season.

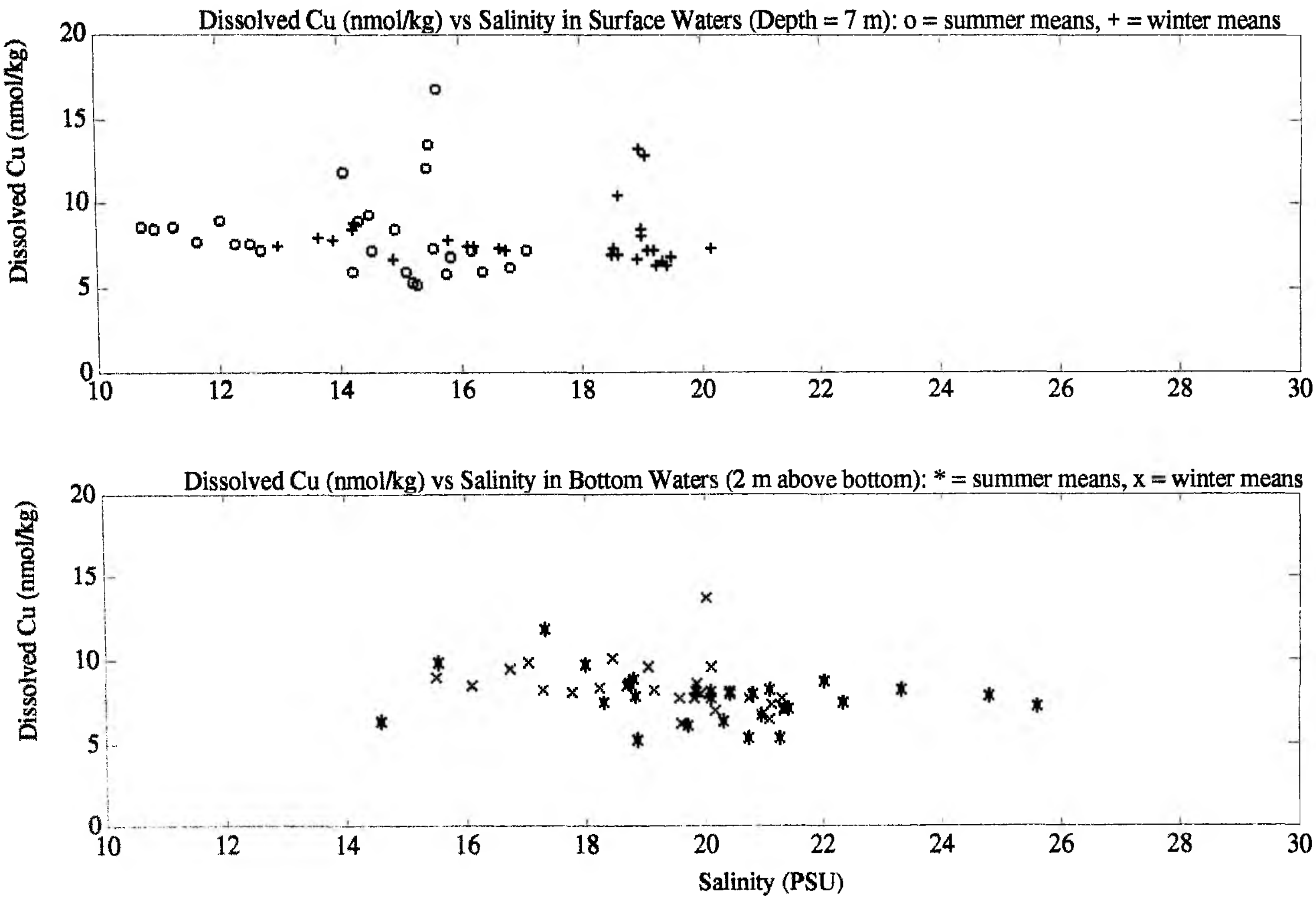


Figure 25. Dissolved (0.4 μm filtered) Ni versus salinity in surface and bottom waters by season.

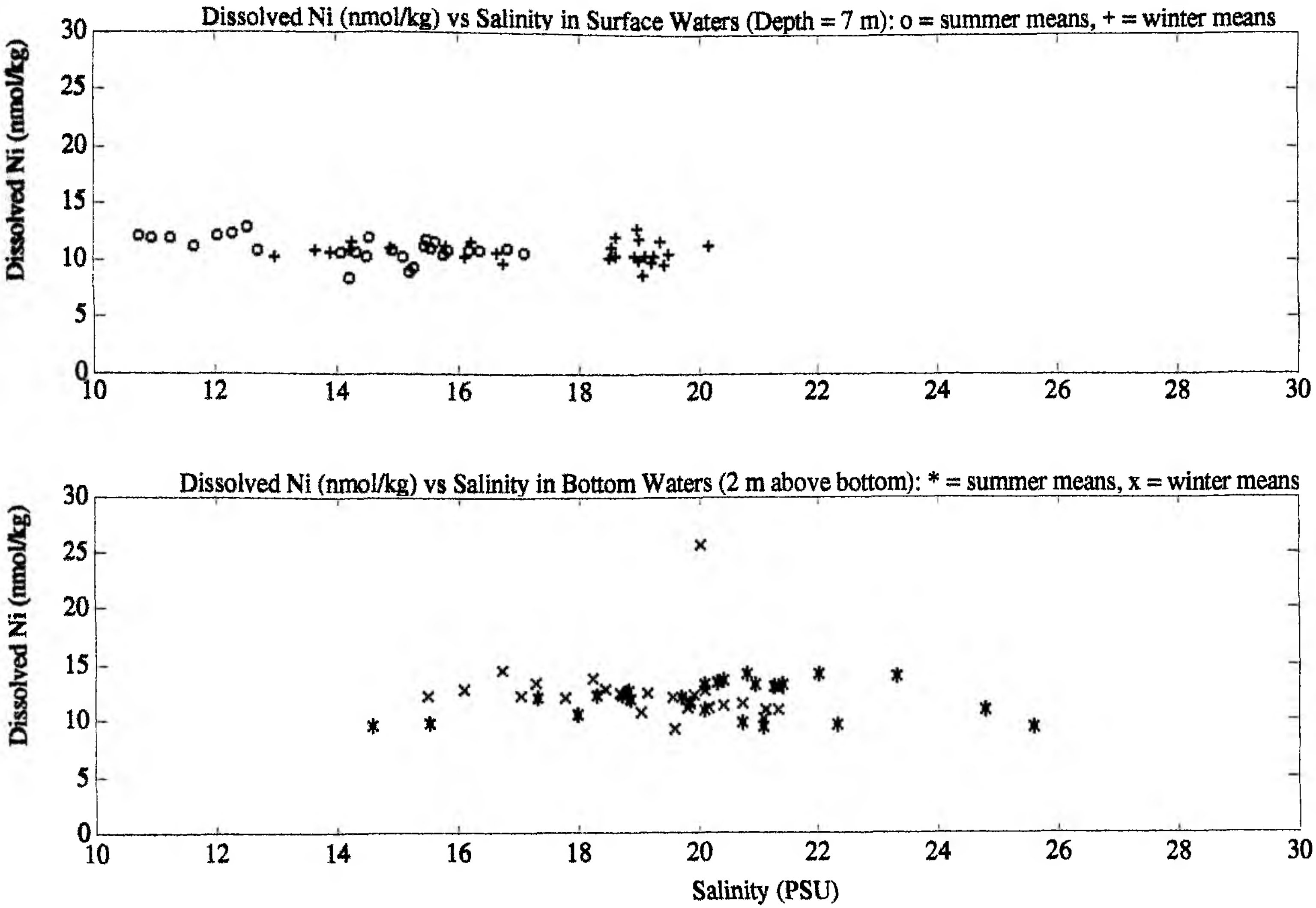


Figure 26. Dissolved (0.4 μm filtered) Fe versus salinity in surface and bottom waters by season.

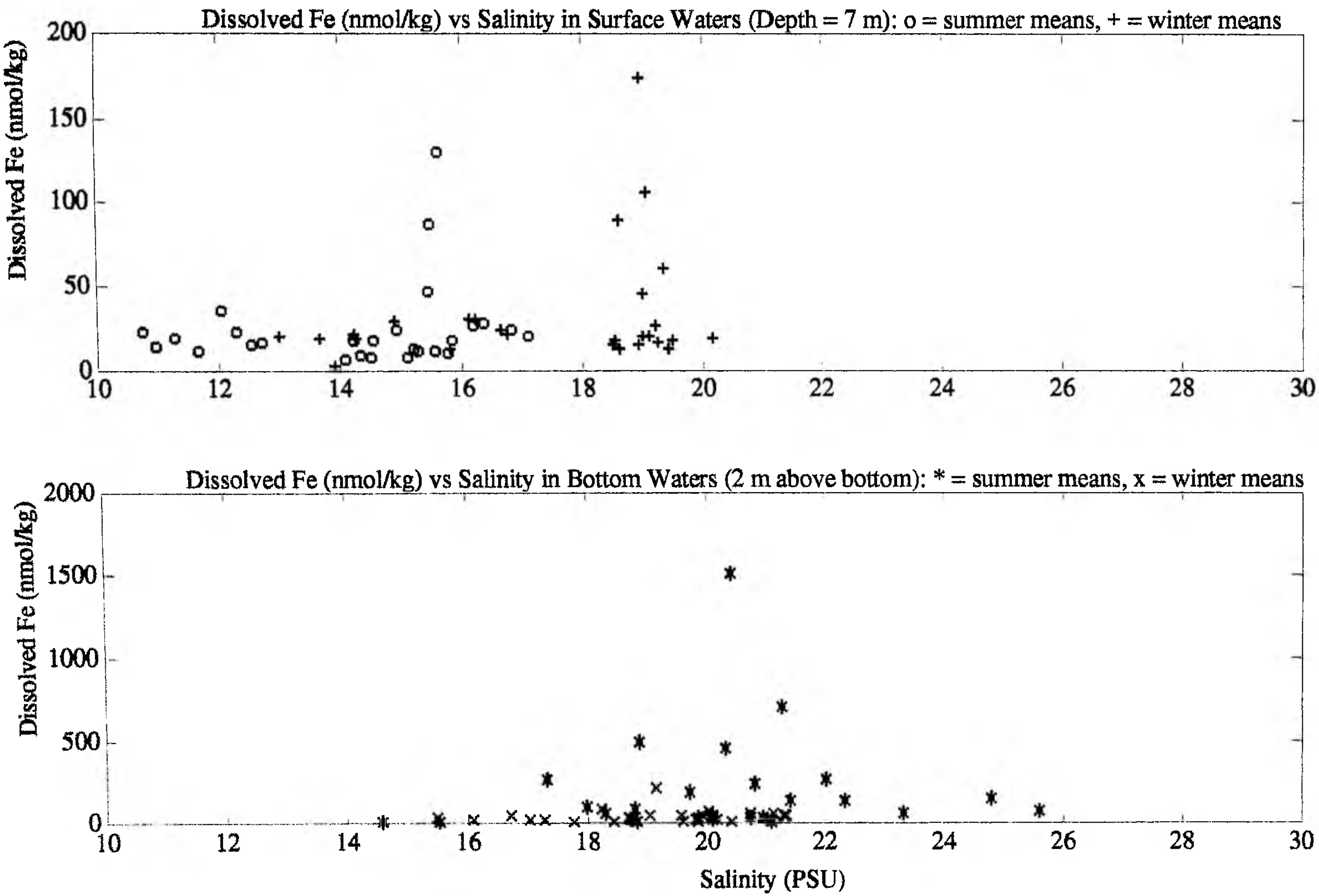


Figure 27. Dissolved (0.4 μm filtered) Zn versus salinity in surface and bottom waters by season.

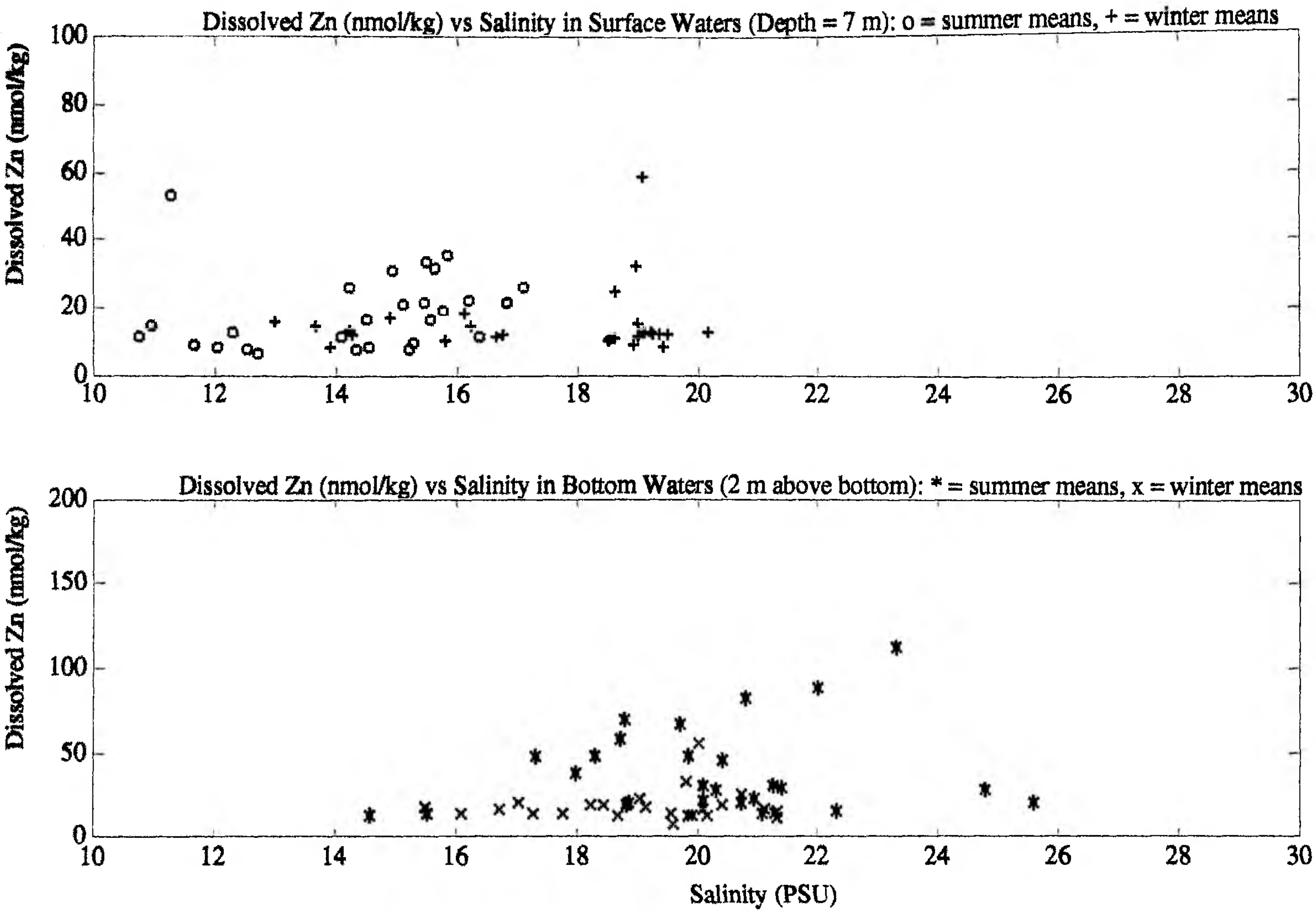


Figure 28. Dissolved (0.4 μm filtered) Mn versus salinity in surface and bottom waters by season.

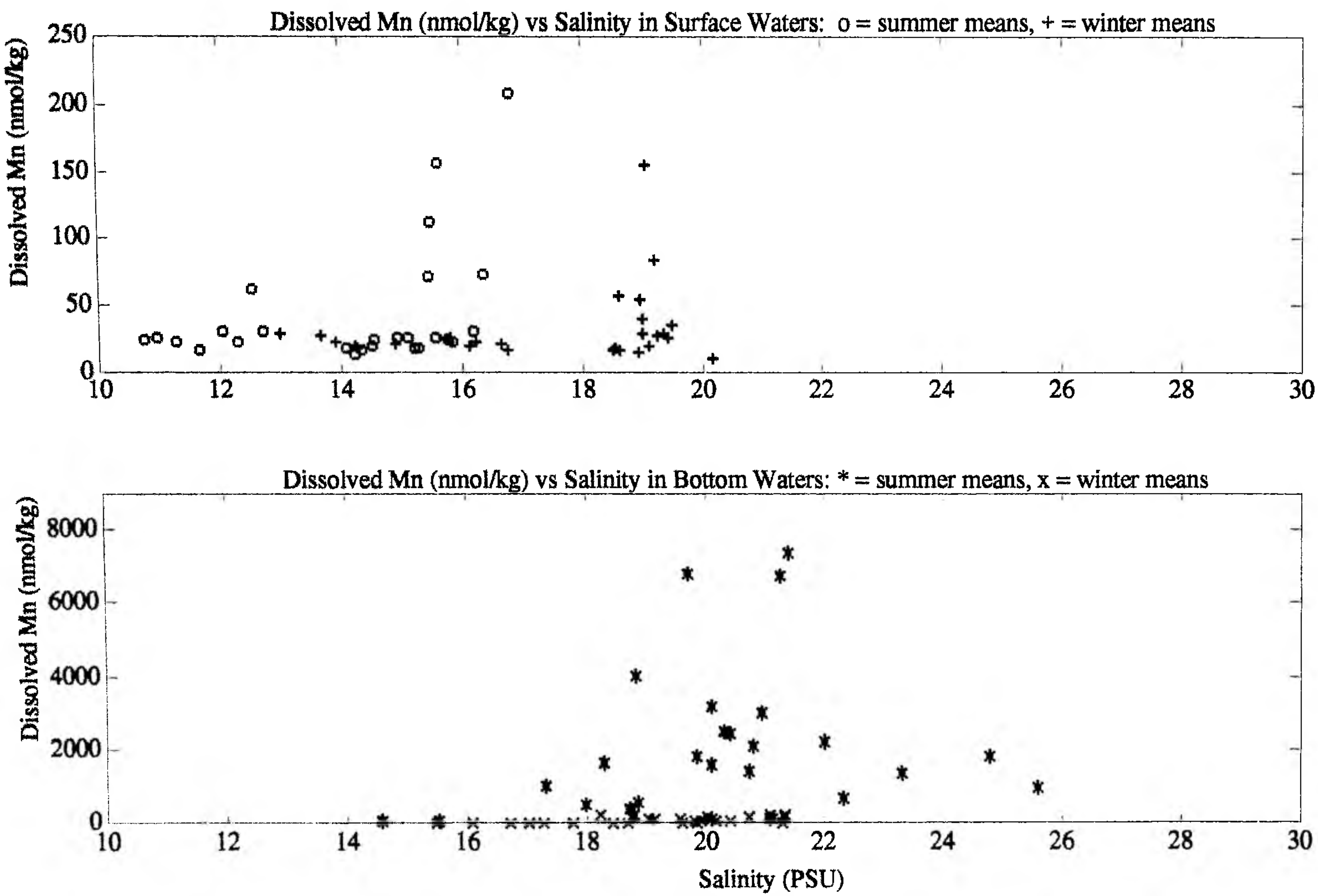


Figure 29. Dissolved (0.4 µm filtered) Co versus silicate concentration in surface and bottom waters by season.

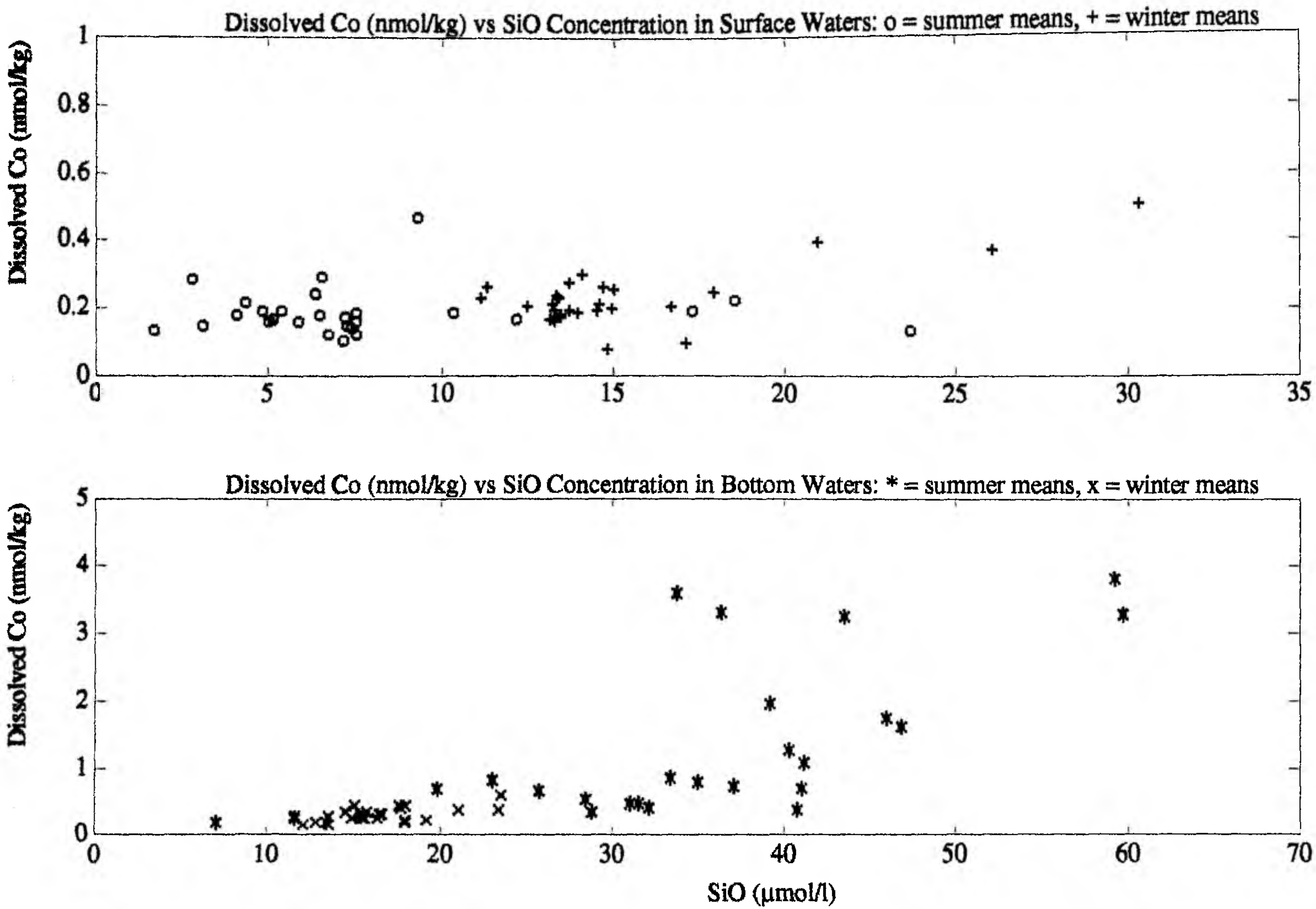


Figure 30. *Dissolved (0.4 μm filtered) Cd versus silicate concentration in surface and bottom waters by season.*

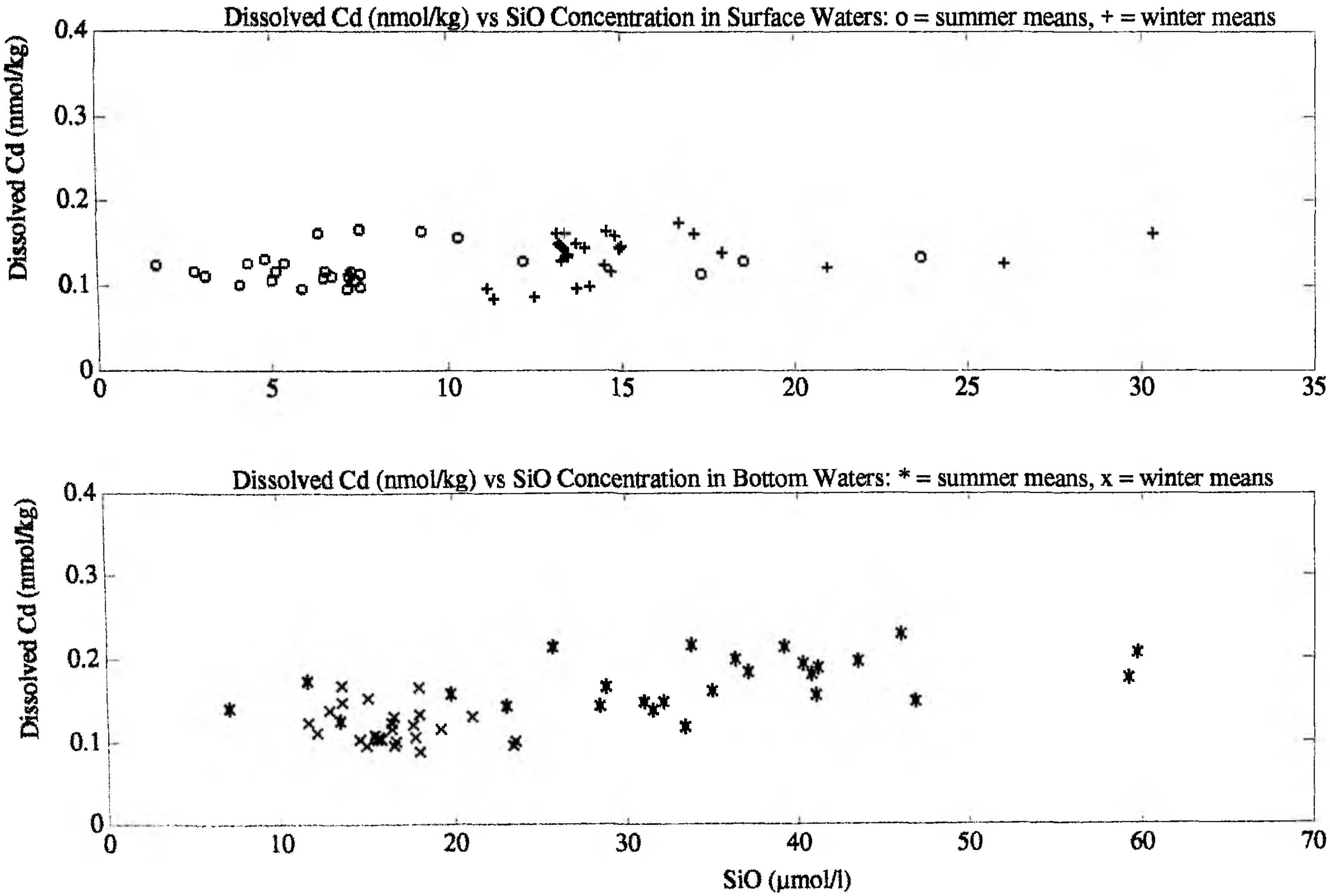


Figure 31. Dissolved (0.4 μm filtered) Cu versus silicate concentration in surface and bottom waters by season.

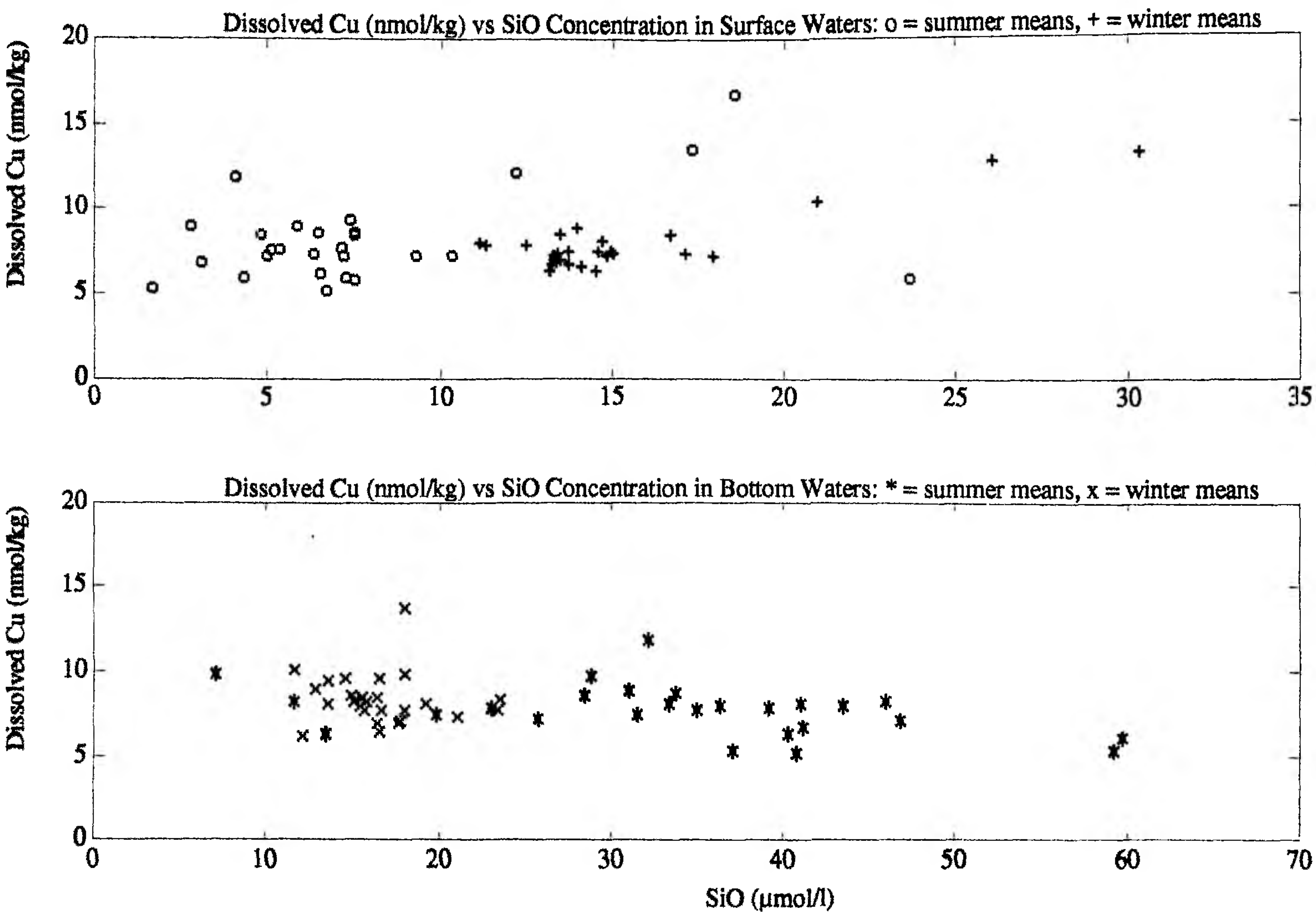


Figure 32. Dissolved (0.4 μm filtered) Ni versus silicate concentration in surface and bottom waters by season.

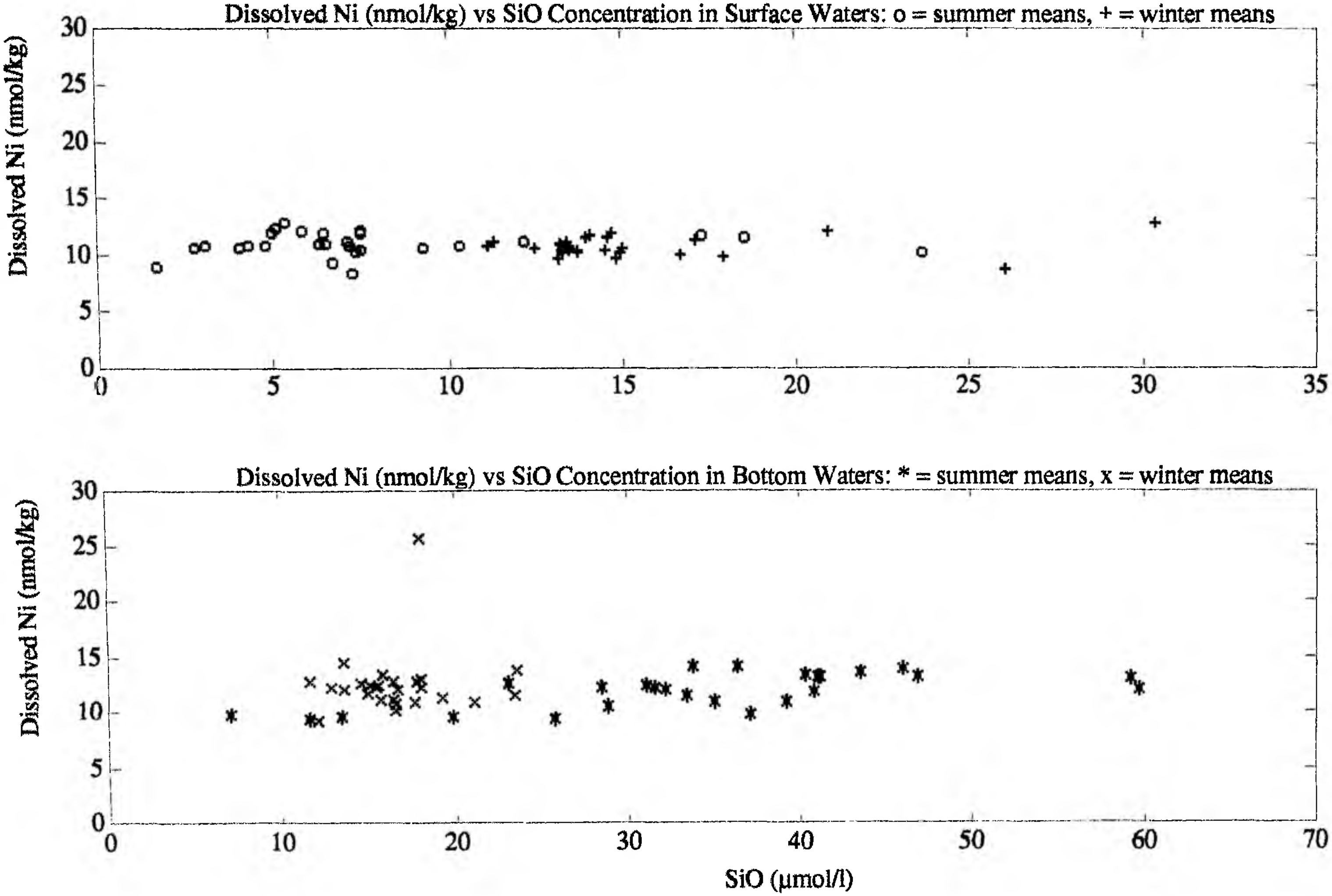


Figure 33. Dissolved (0.4 µm filtered) Zn versus silicate concentration in surface and bottom waters by season.

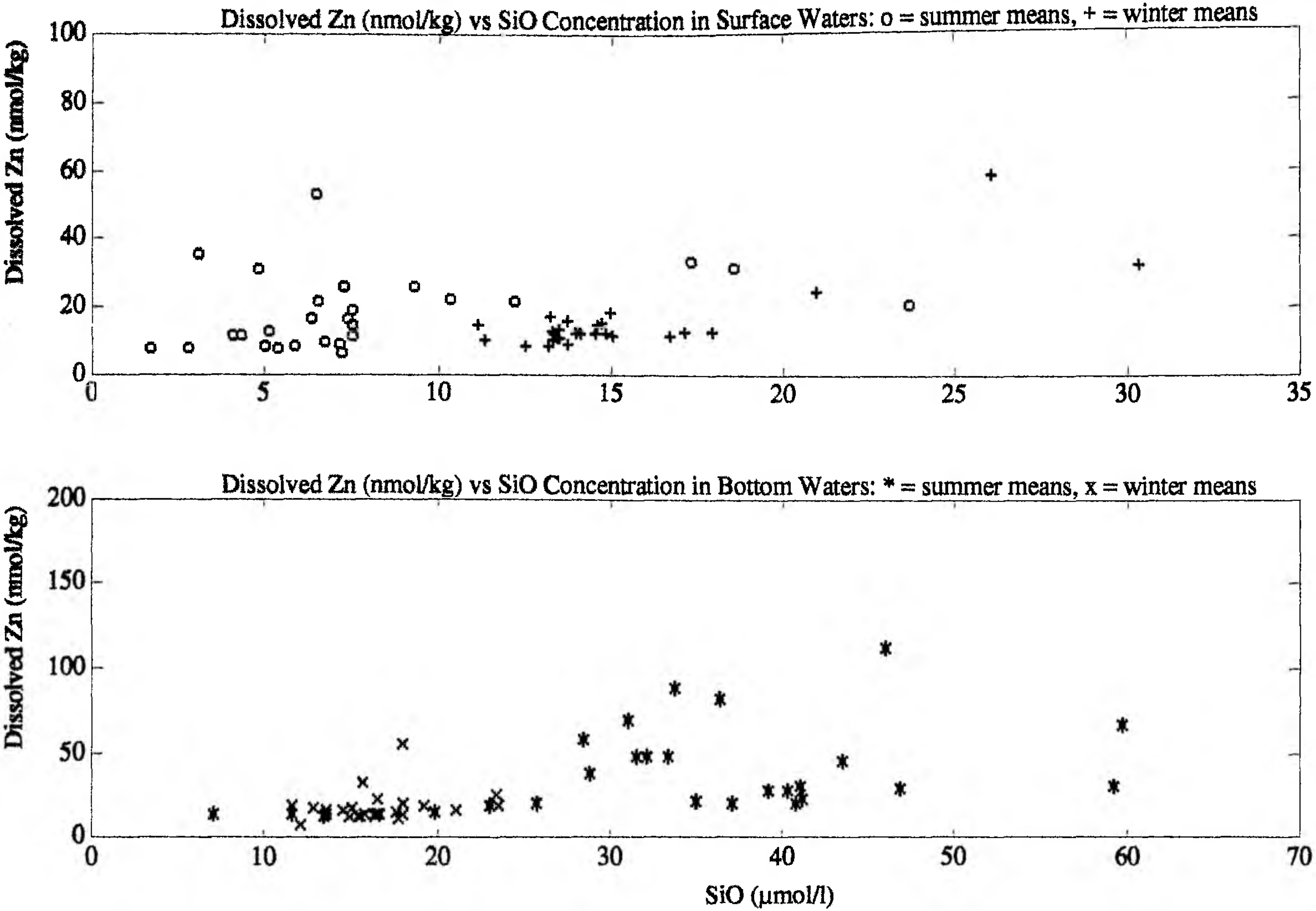


Figure 34. Dissolved (0.4 µm filtered) Mn versus silicate concentration in surface and bottom waters by season.

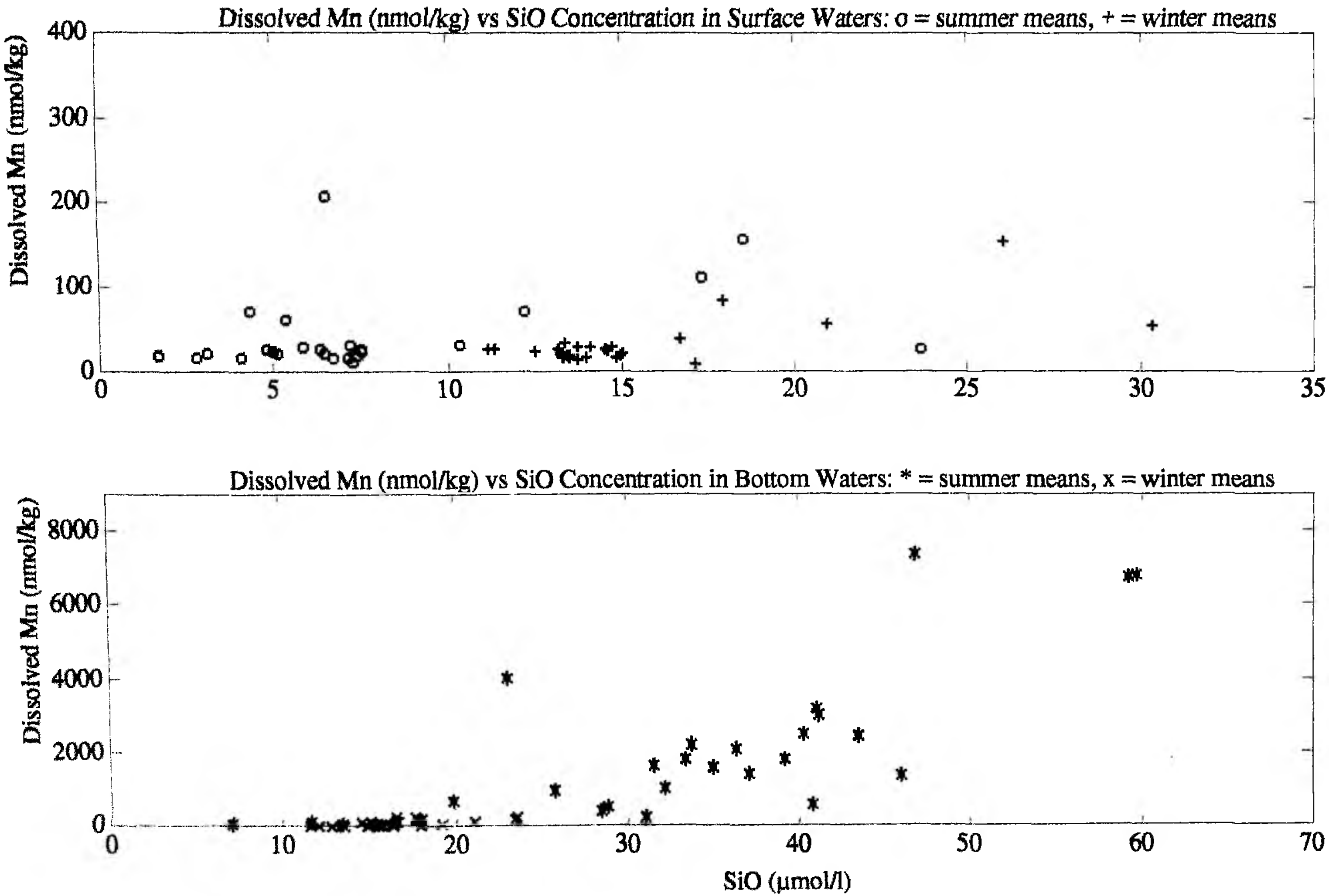


Figure 35. Dissolved (0.4 μm filtered) Cd versus PO_4 concentration in surface and bottom waters by season.

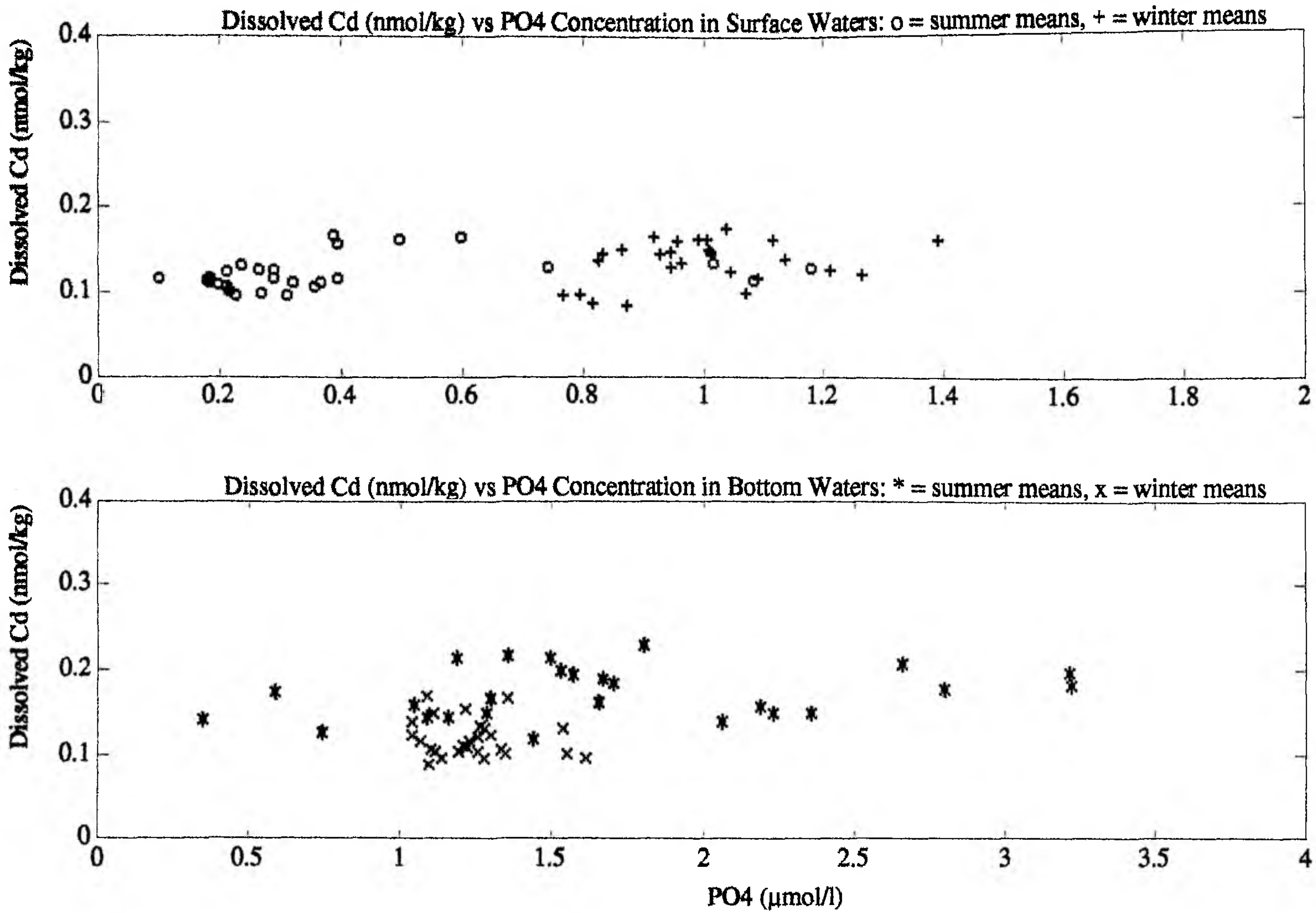


Figure 36. Dissolved (0.4 µm filtered) Cu versus PO_4 concentration in surface and bottom waters by season.

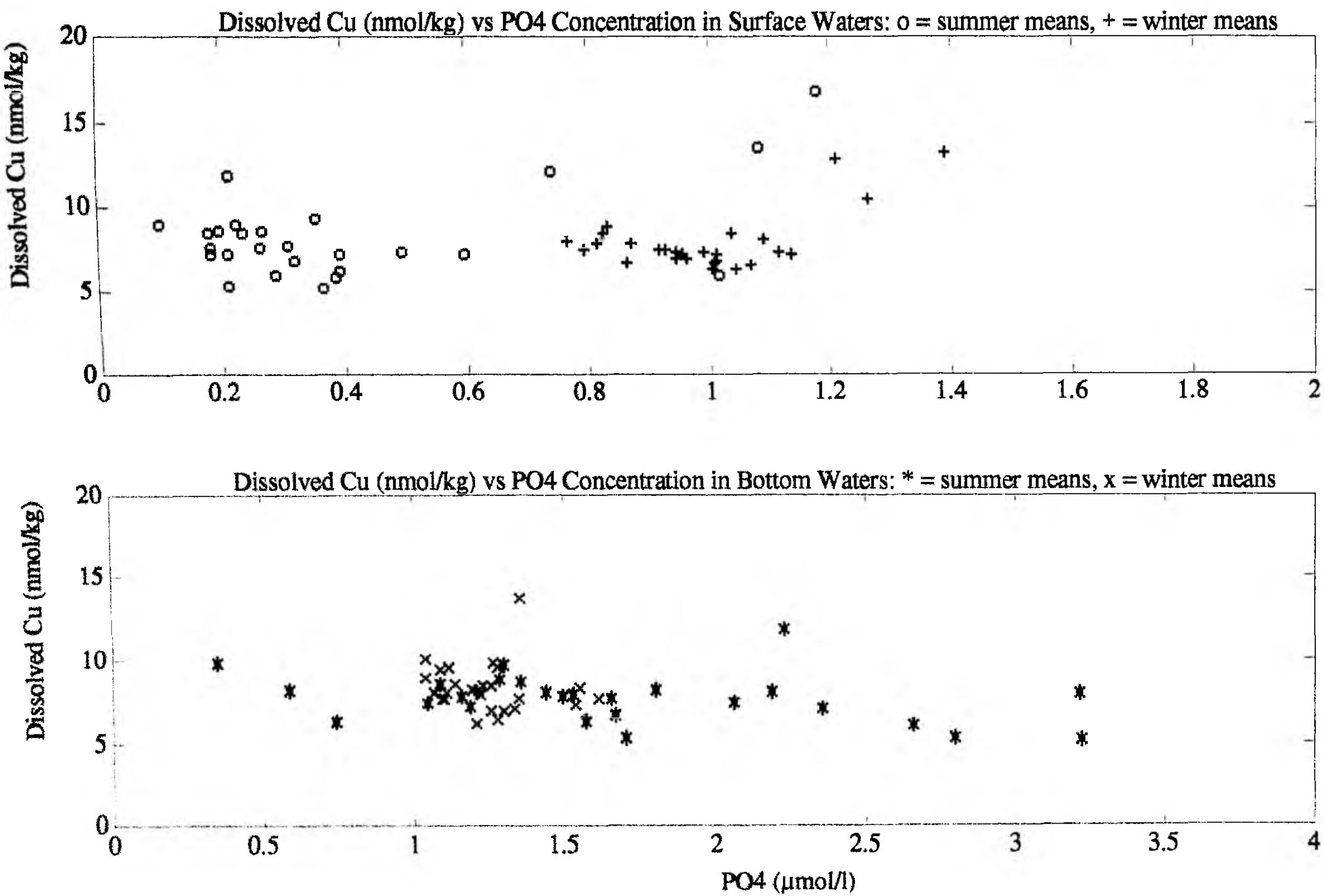


Figure 37. Dissolved (0.4 µm filtered) Ni versus PO_4 concentration in surface and bottom waters by season.

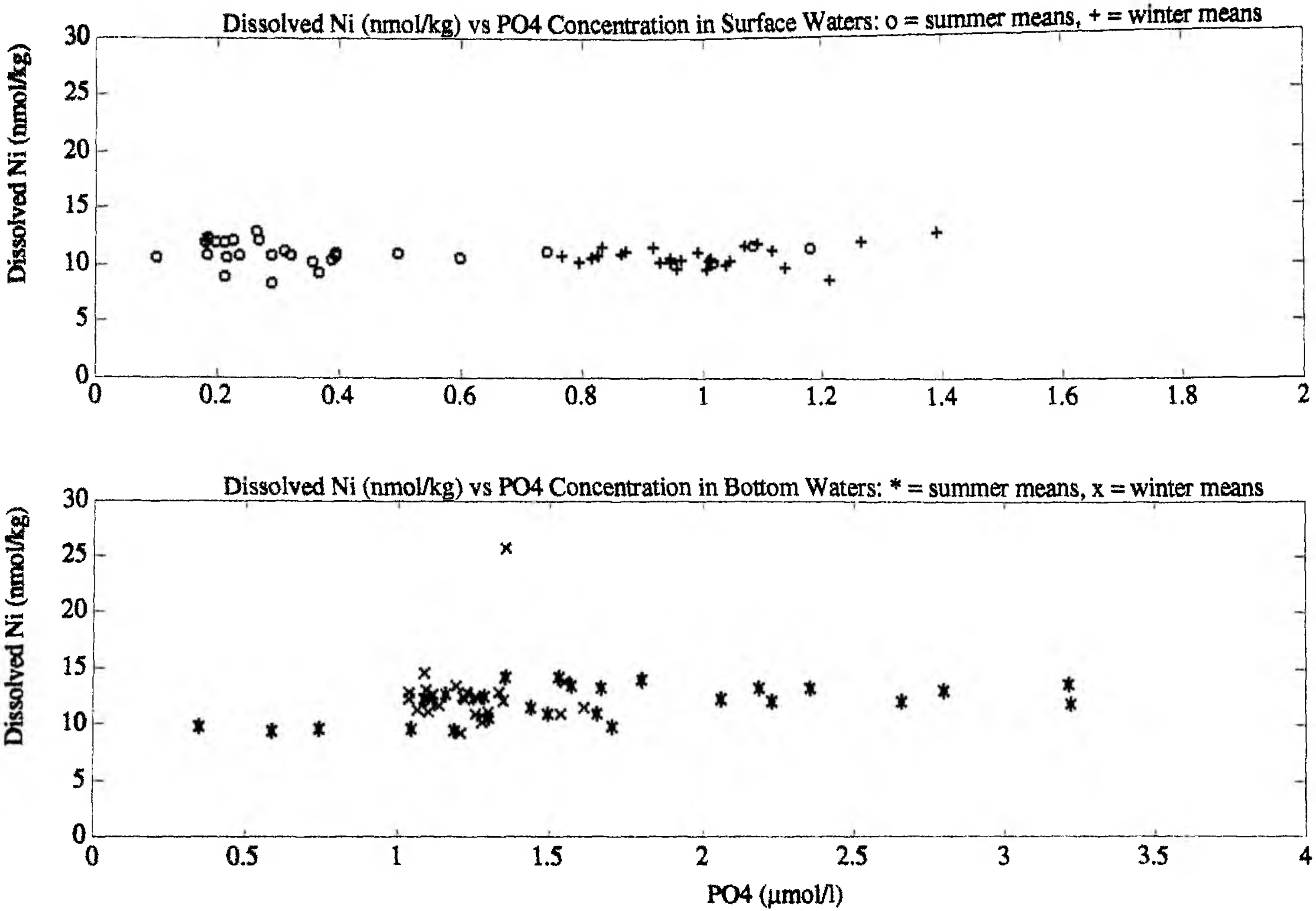


Figure 38. Dissolved (0.4 μm filtered) Fe versus PO_4 concentration in surface and bottom waters by season.

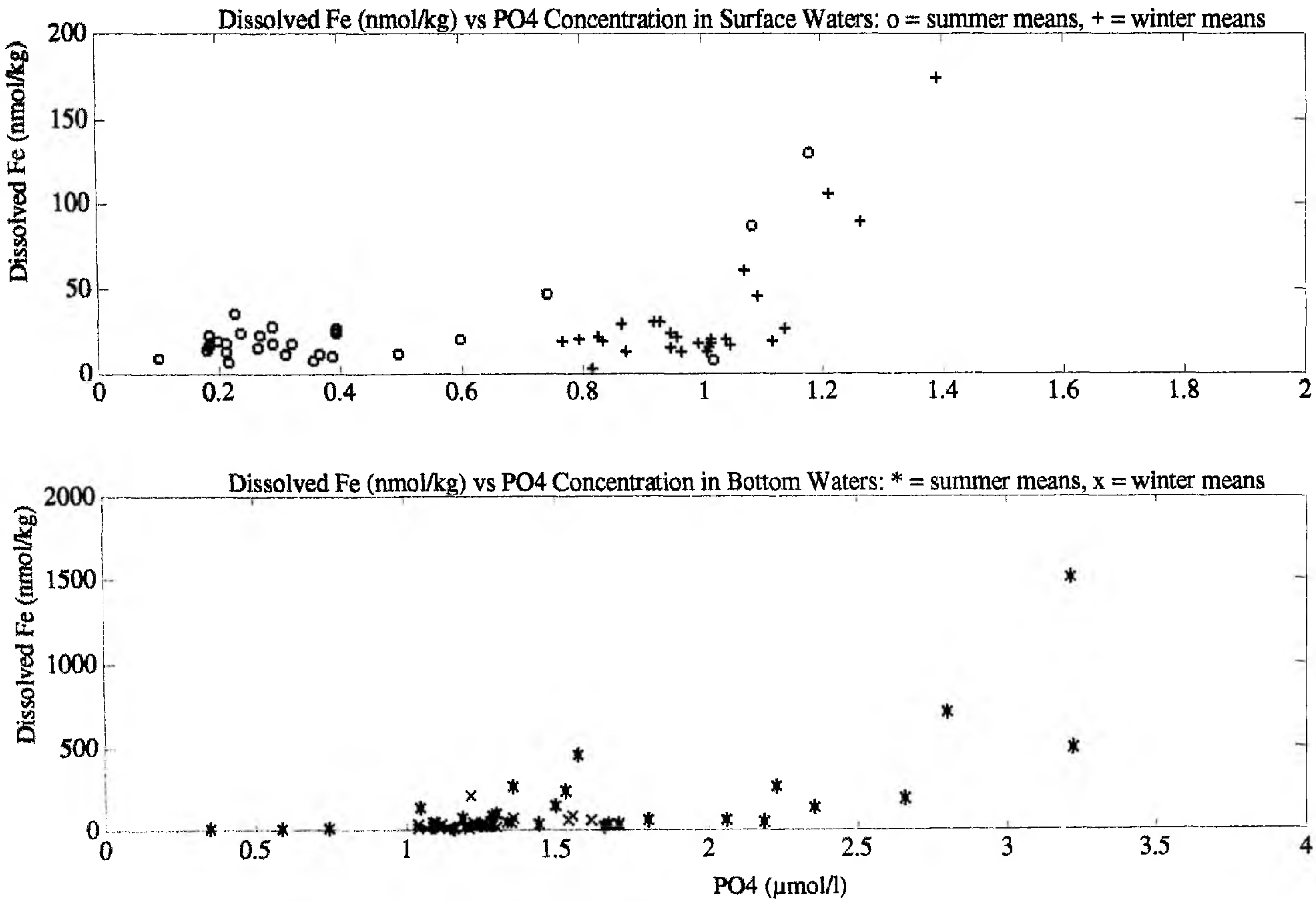


Figure 39. Dissolved (0.4 µm filtered) Mn versus PO_4 concentration in surface and bottom waters by season.

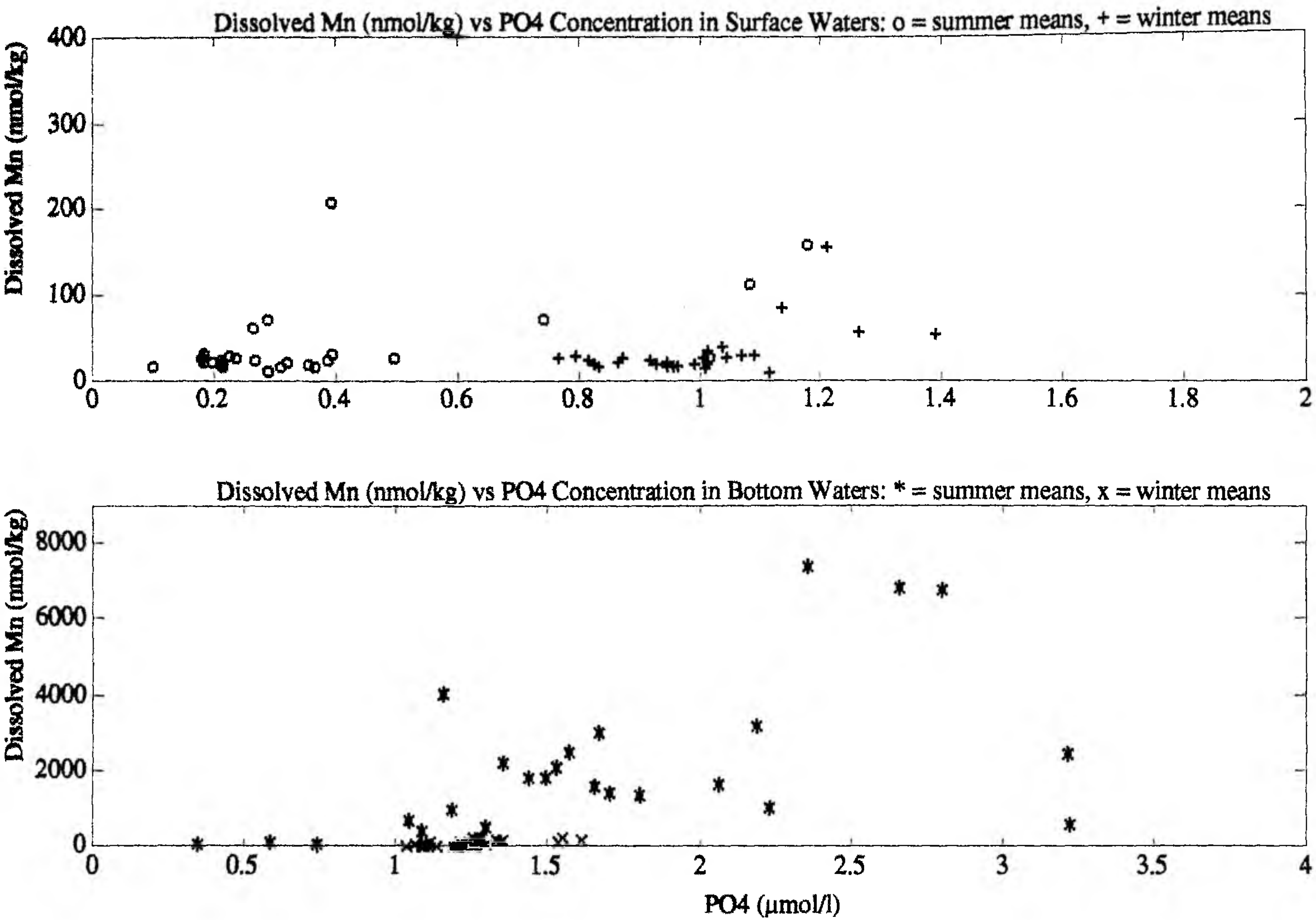
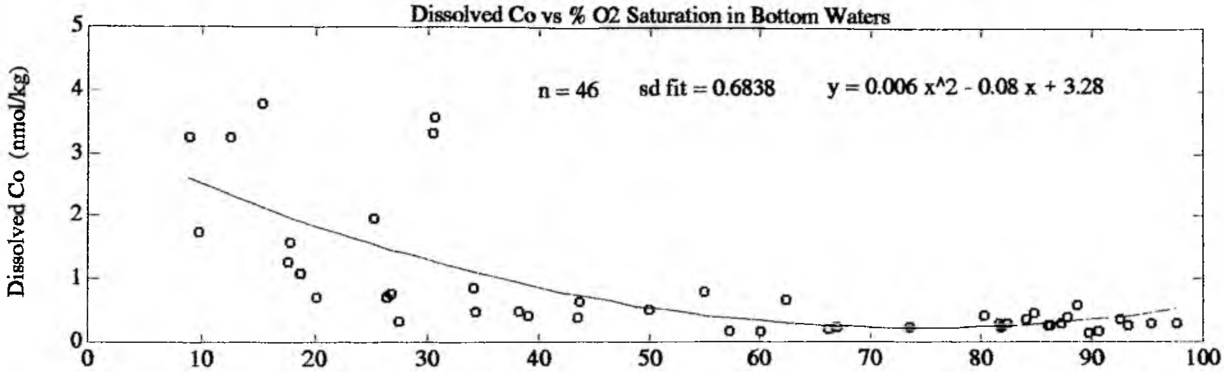
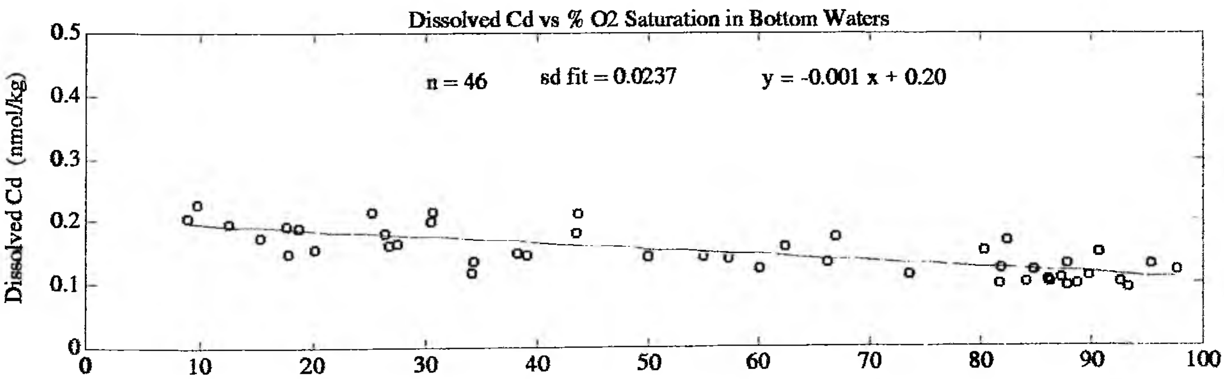


Figure 40. Variation of dissolved Co, Cd, and Fe concentrations versus percent oxygen saturation concentration.

A. Co



B. Cd



C. Fe

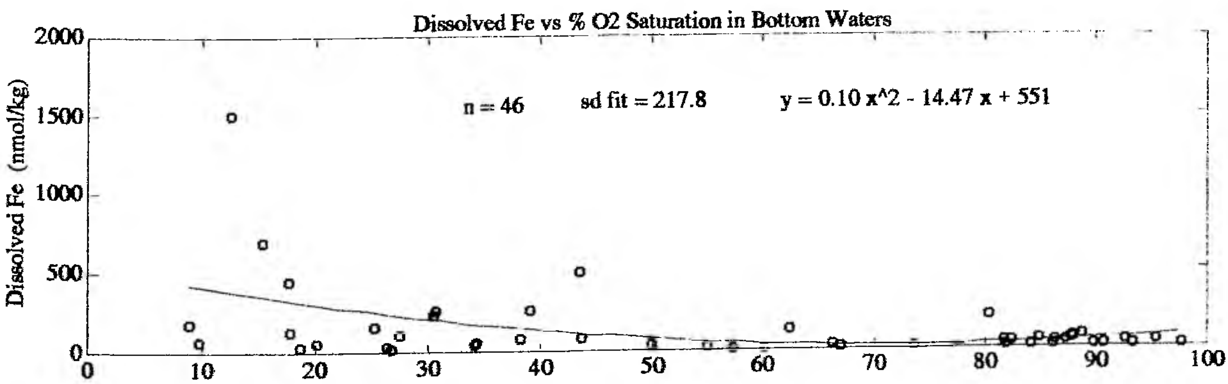
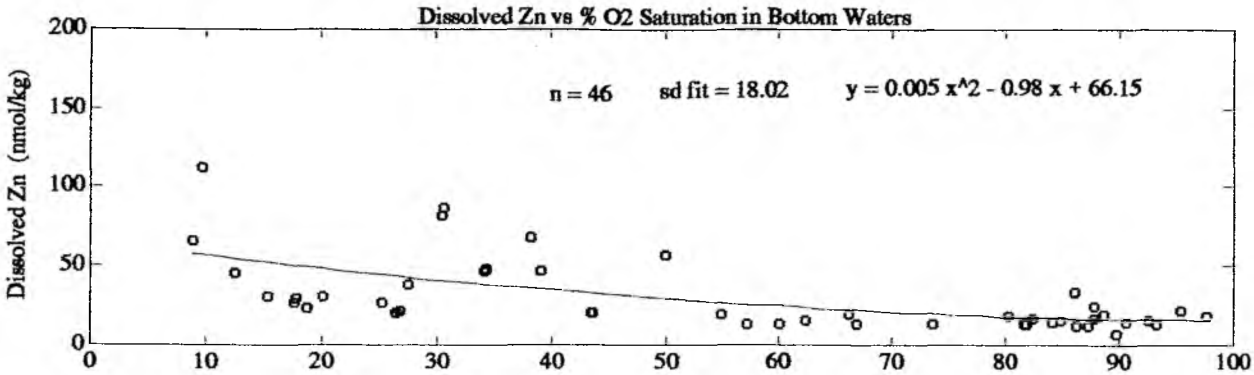


Figure 40 (Cont.). Variation of dissolved Zn and Mn concentrations versus percent oxygen saturation concentration.

D. Zn



E. Mn

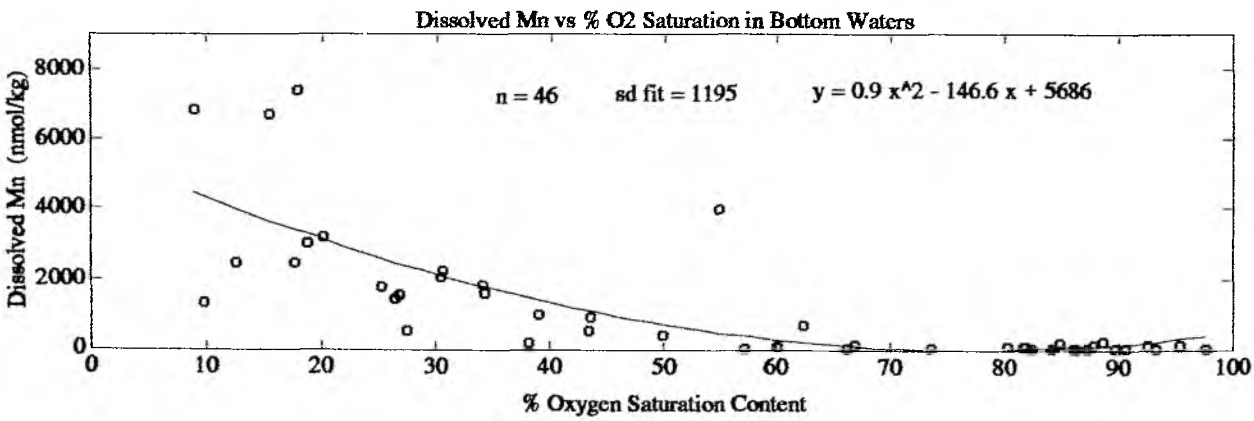


Figure 41. Mean suspended particulate matter concentration on 0.4 µm filters in surface and bottom waters by season. I, O, E, and W in the area names indicate inner, outer, eastern, and western directions for orientation.

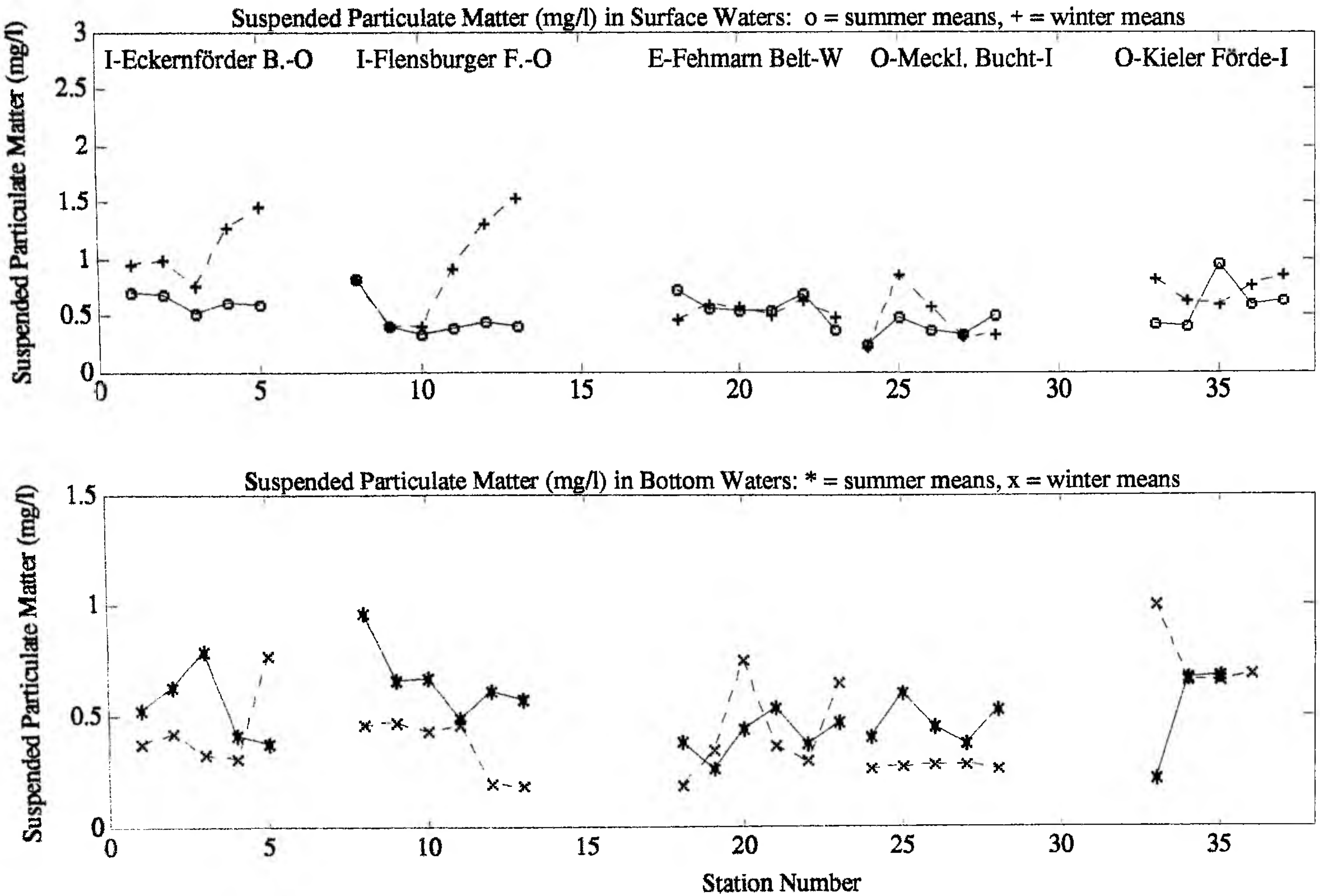


Figure 42. Mean particulate Co content on 0.4 μm filters in surface and bottom waters by season. I, O, E, and W in the area names indicate inner, outer, eastern, and western directions for orientation.

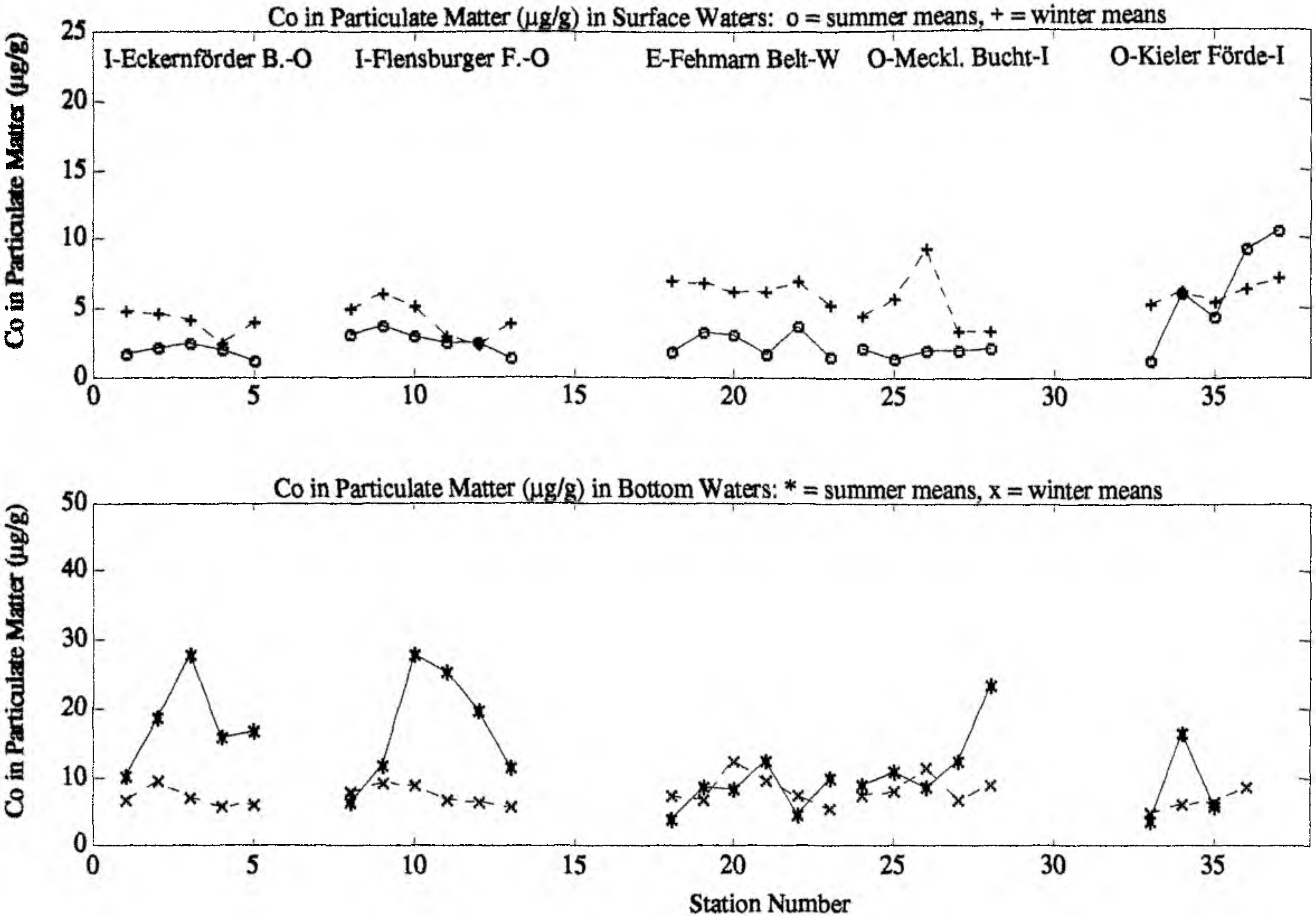


Figure 43. Mean particulate Pb content on 0.4 µm filters in surface and bottom waters by season. I, O, E, and W in the area names indicate inner, outer, eastern, and western directions for orientation.

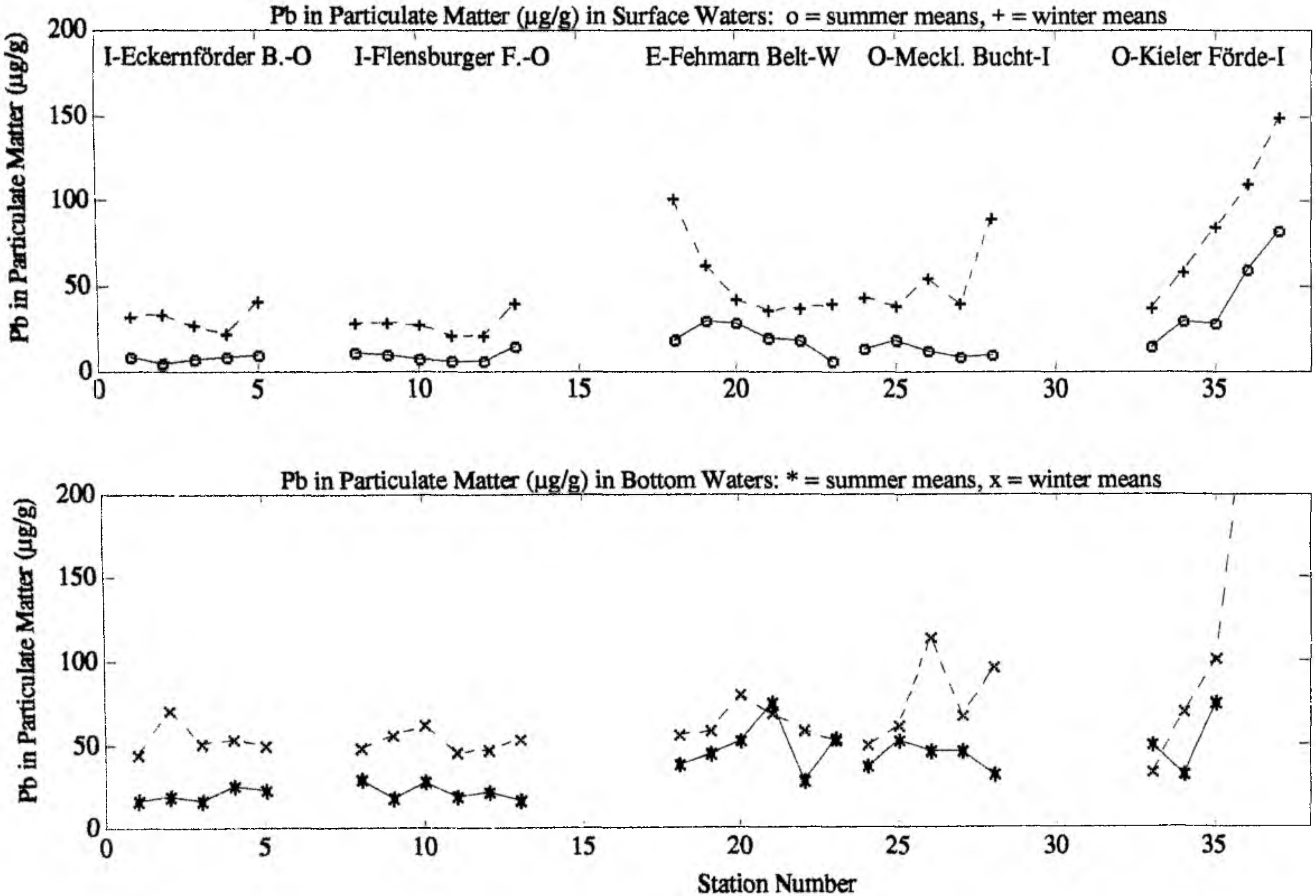


Figure 44. Mean particulate Cd content on 0.4 μm filters in surface and bottom waters by season. I, O, E, and W in the area names indicate inner, outer, eastern, and western directions for orientation.

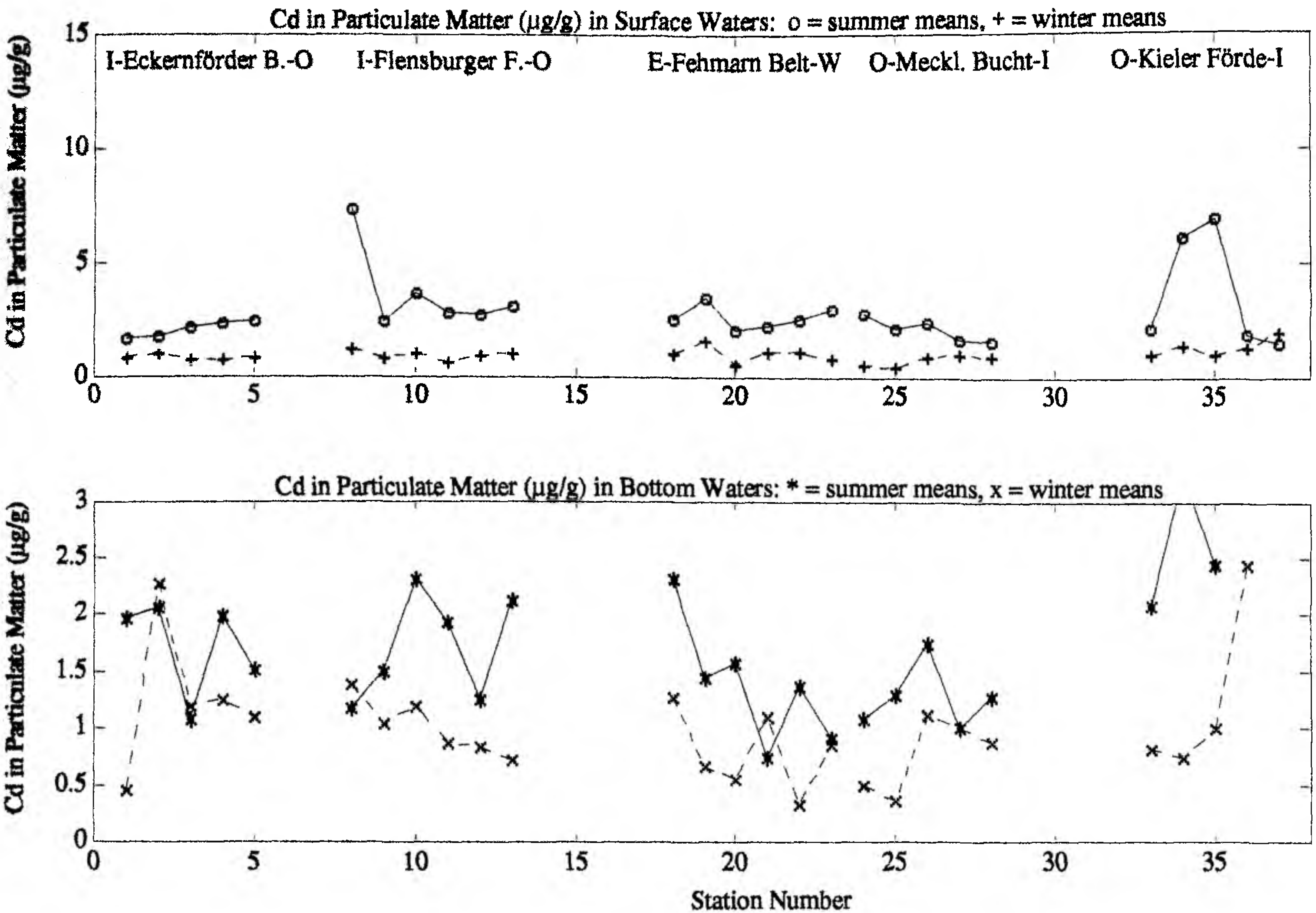


Figure 45. Mean particulate Cu content on 0.4 μm filters in surface and bottom waters by season. I, O, E, and W in the area names indicate inner, outer, eastern, and western directions for orientation.

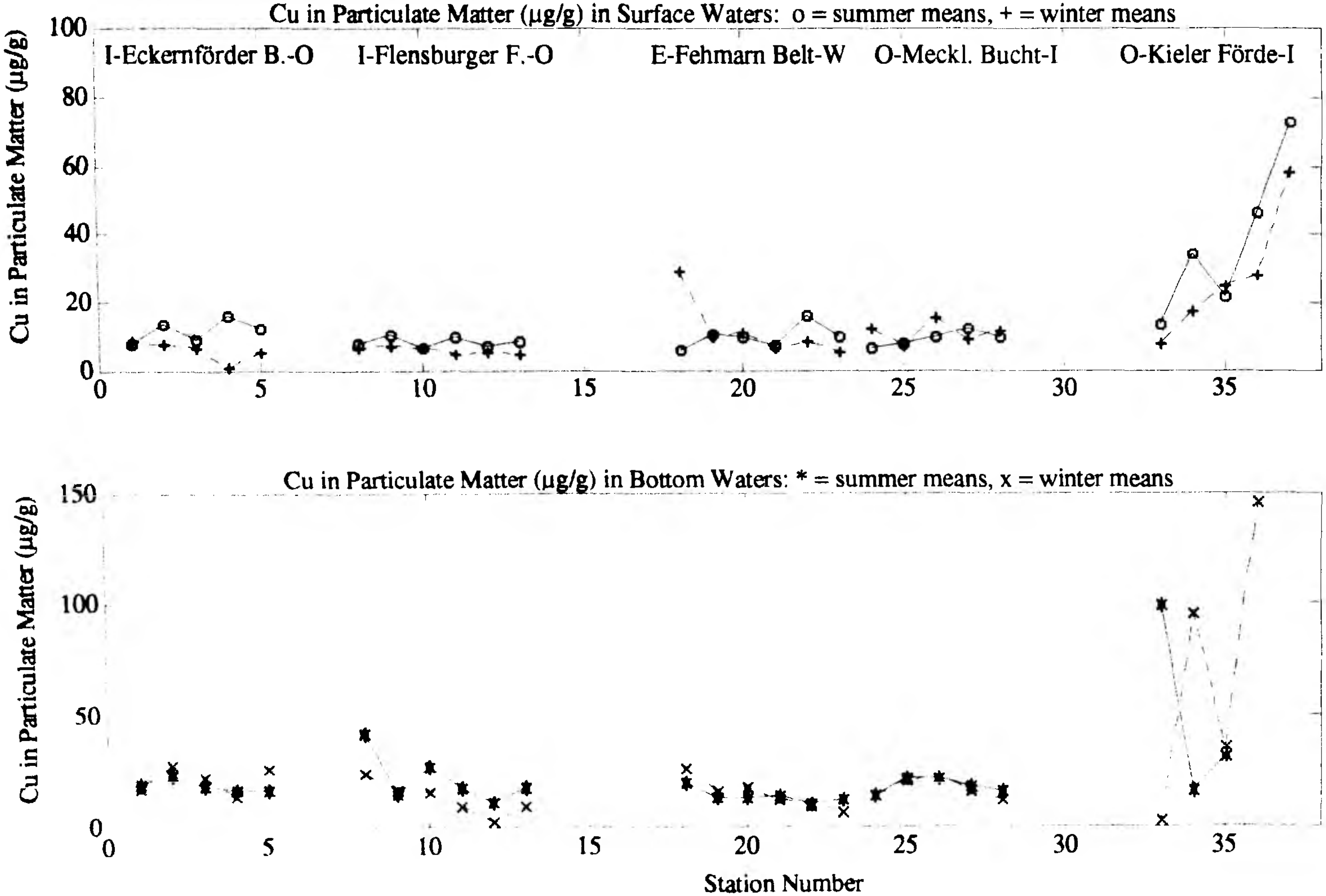


Figure 45. Mean particulate Cu content on 0.4 μm filters in surface and bottom waters by season. I, O, E, and W in the area names indicate inner, outer, eastern, and western directions for orientation.

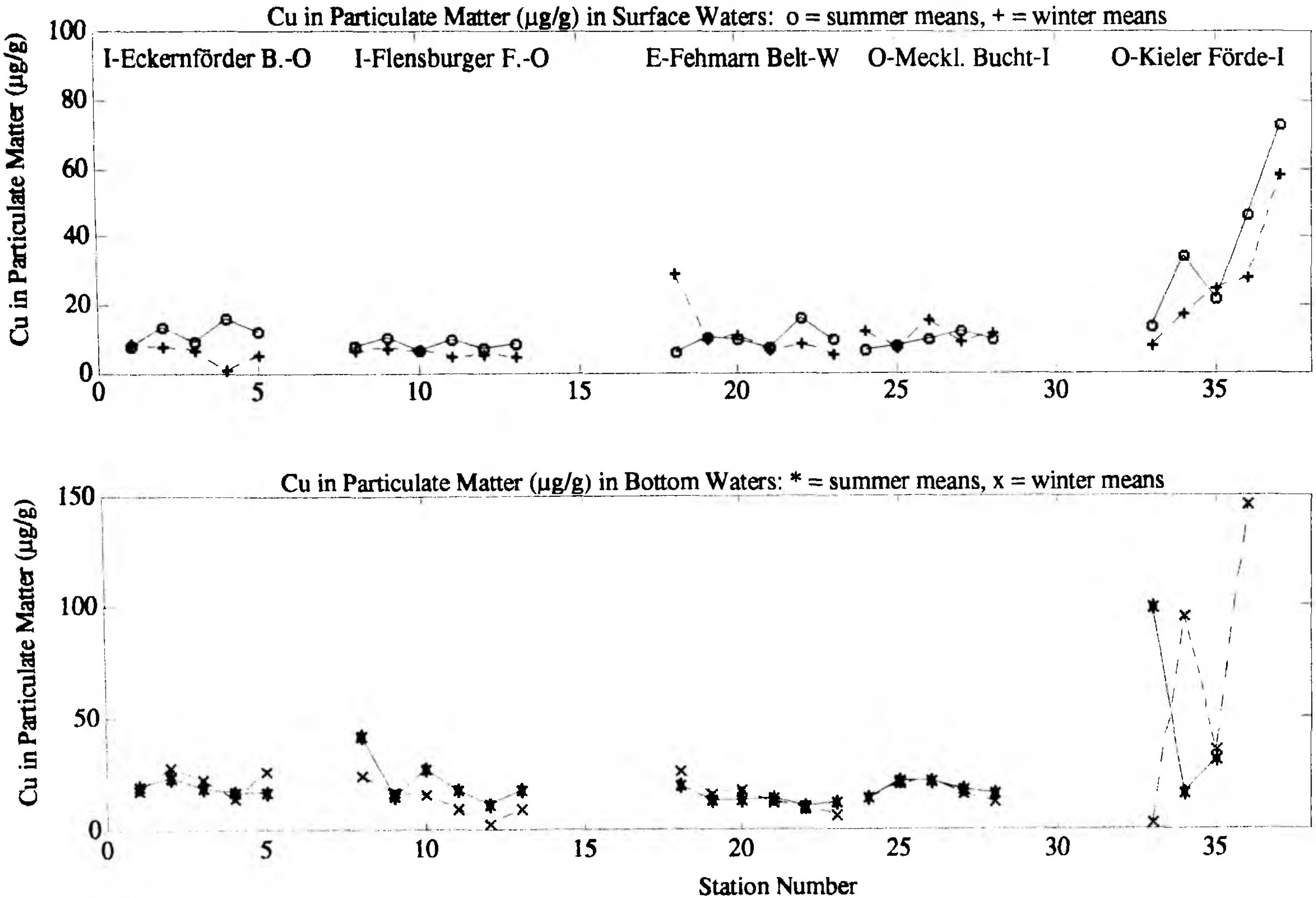


Figure 45. Mean particulate Cu content on 0.4 µm filters in surface and bottom waters by season. I, O, E, and W in the area names indicate inner, outer, eastern, and western directions for orientation.

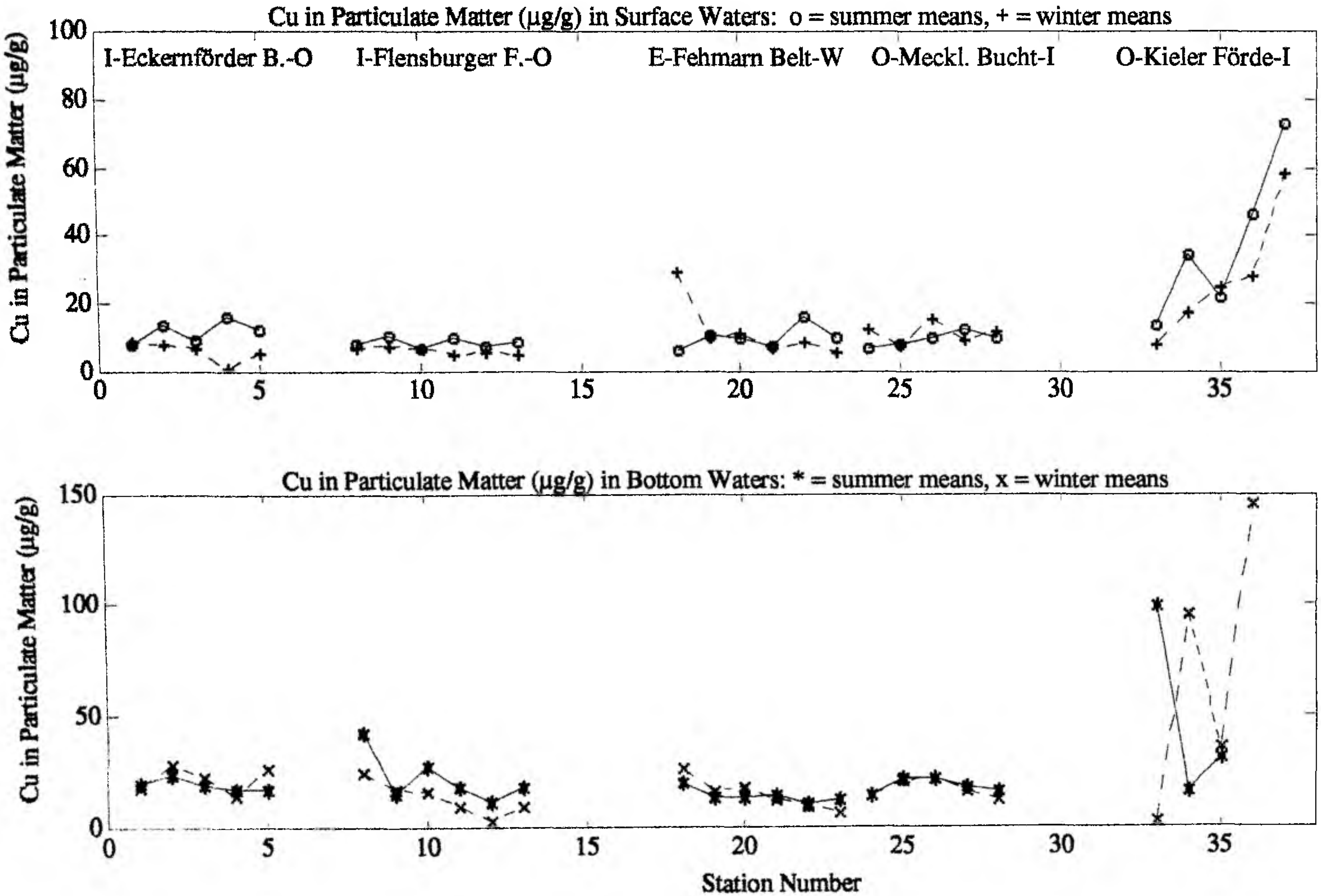


Figure 46. Mean particulate Ni content on 0.4 µm filters in surface and bottom waters by season. I, O, E, and W in the area names indicate inner, outer, eastern, and western directions for orientation.

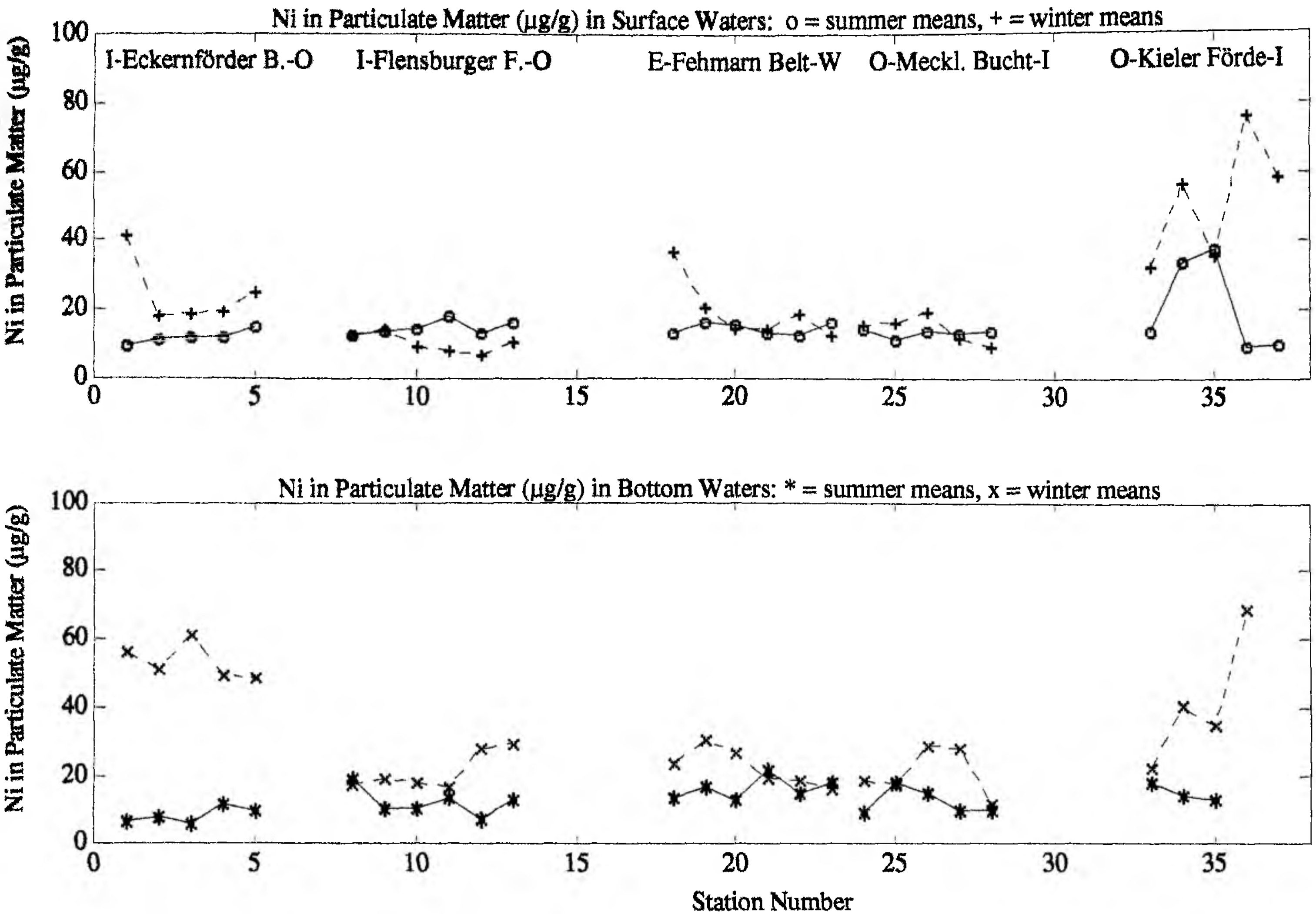


Figure 47. Mean particulate Fe content on 0.4 µm filters in surface and bottom waters by season. I, O, E, and W in the area names indicate inner, outer, eastern, and western directions for orientation.

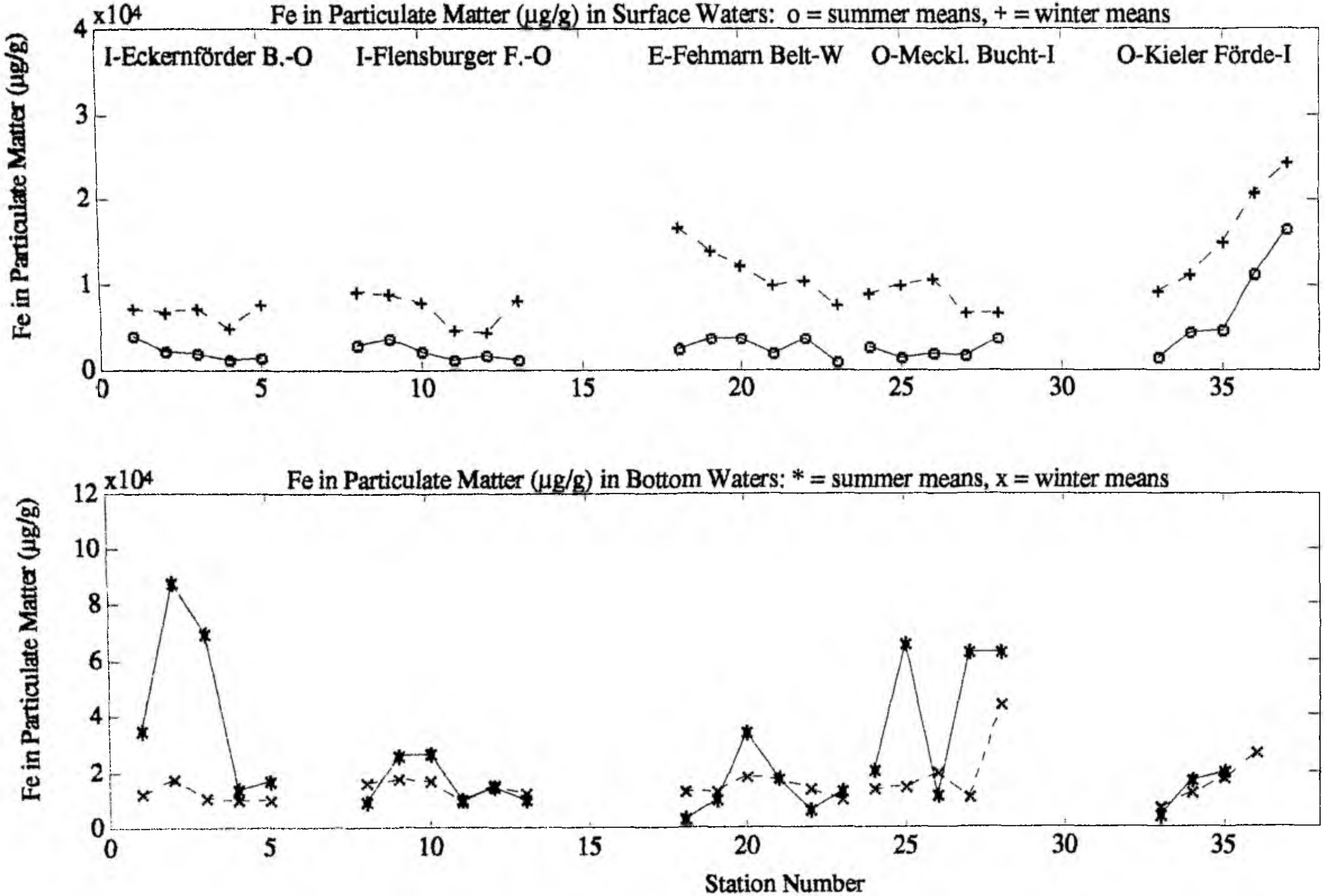


Figure 48. Mean particulate Zn content on 0.4 µm filters in surface and bottom waters by season. I, O, E, and W in the area names indicate inner, outer, eastern, and western directions for orientation.

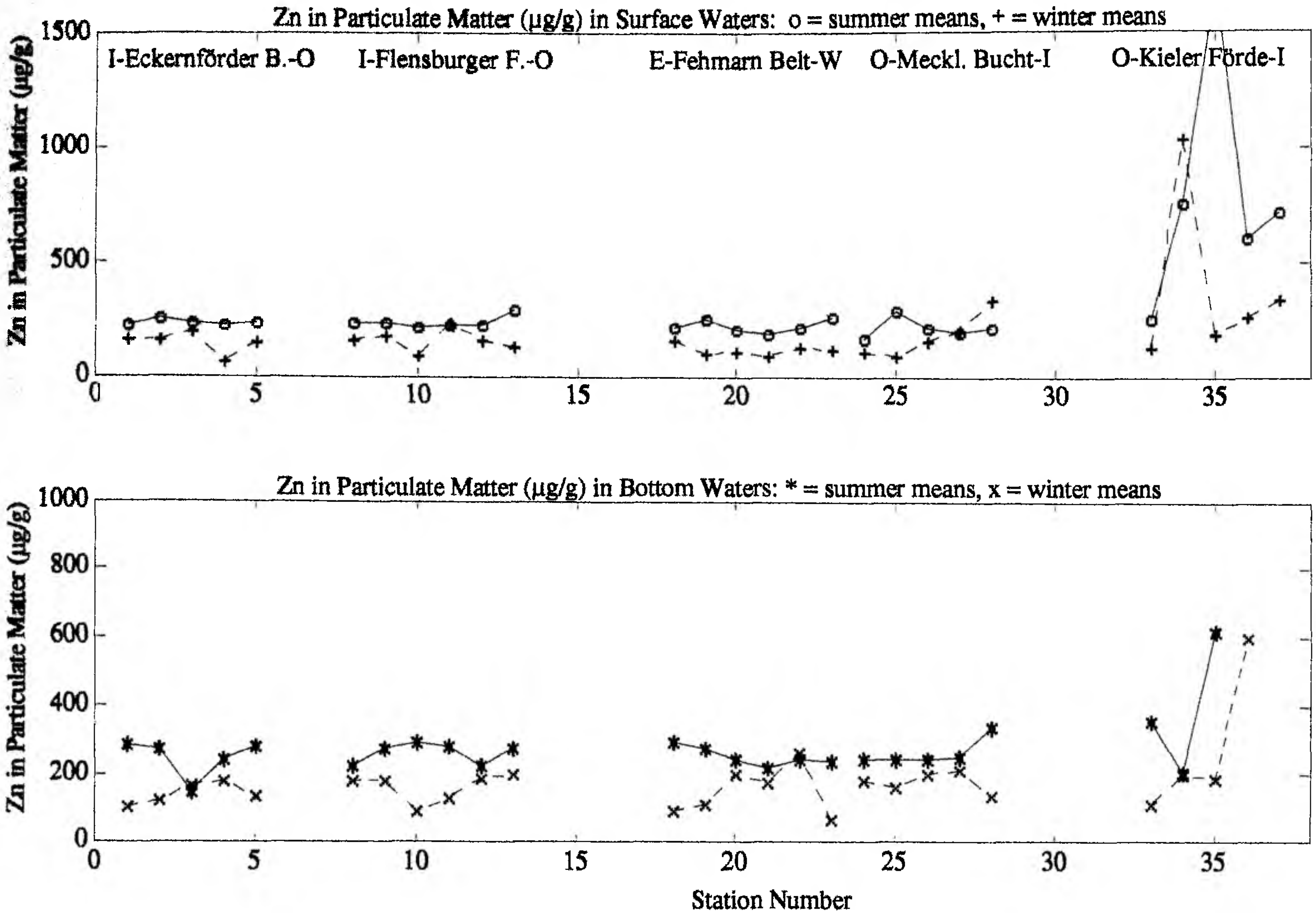


Figure 49. Mean particulate Mn content on 0.4 µm filters in surface and bottom waters by season. I, O, E, and W in the area names indicate inner, outer, eastern, and western directions for orientation.

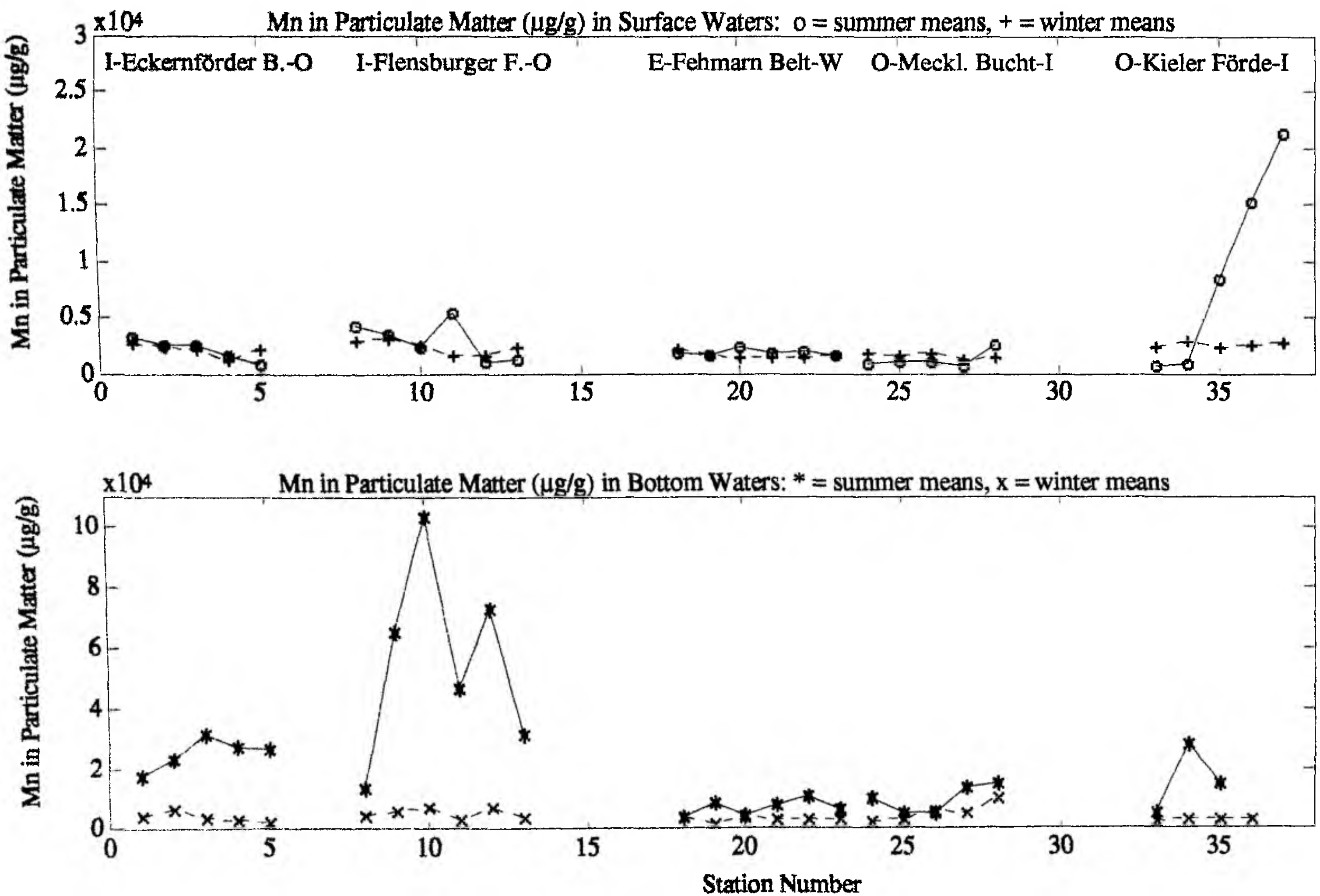


Figure 50. Mean particulate Al content on 0.4 μm filters in surface and bottom waters by season. I, O, E, and W in the area names indicate inner, outer, eastern, and western directions for orientation.

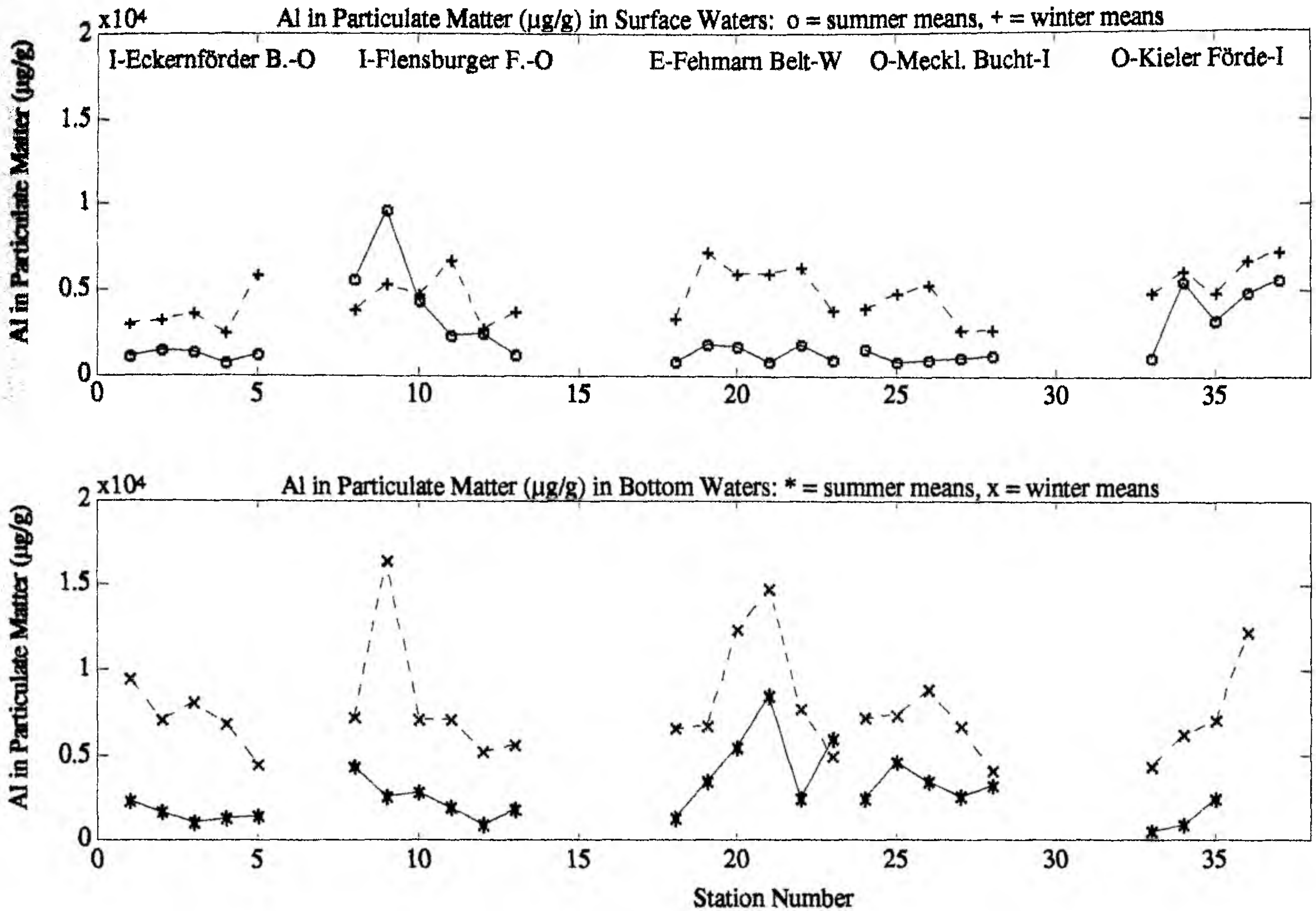


Figure 51. Total Hg concentration versus station number in surface and bottom waters by season. I, O, E, and W in the area names indicate inner, outer, eastern, and western directions for orientation.

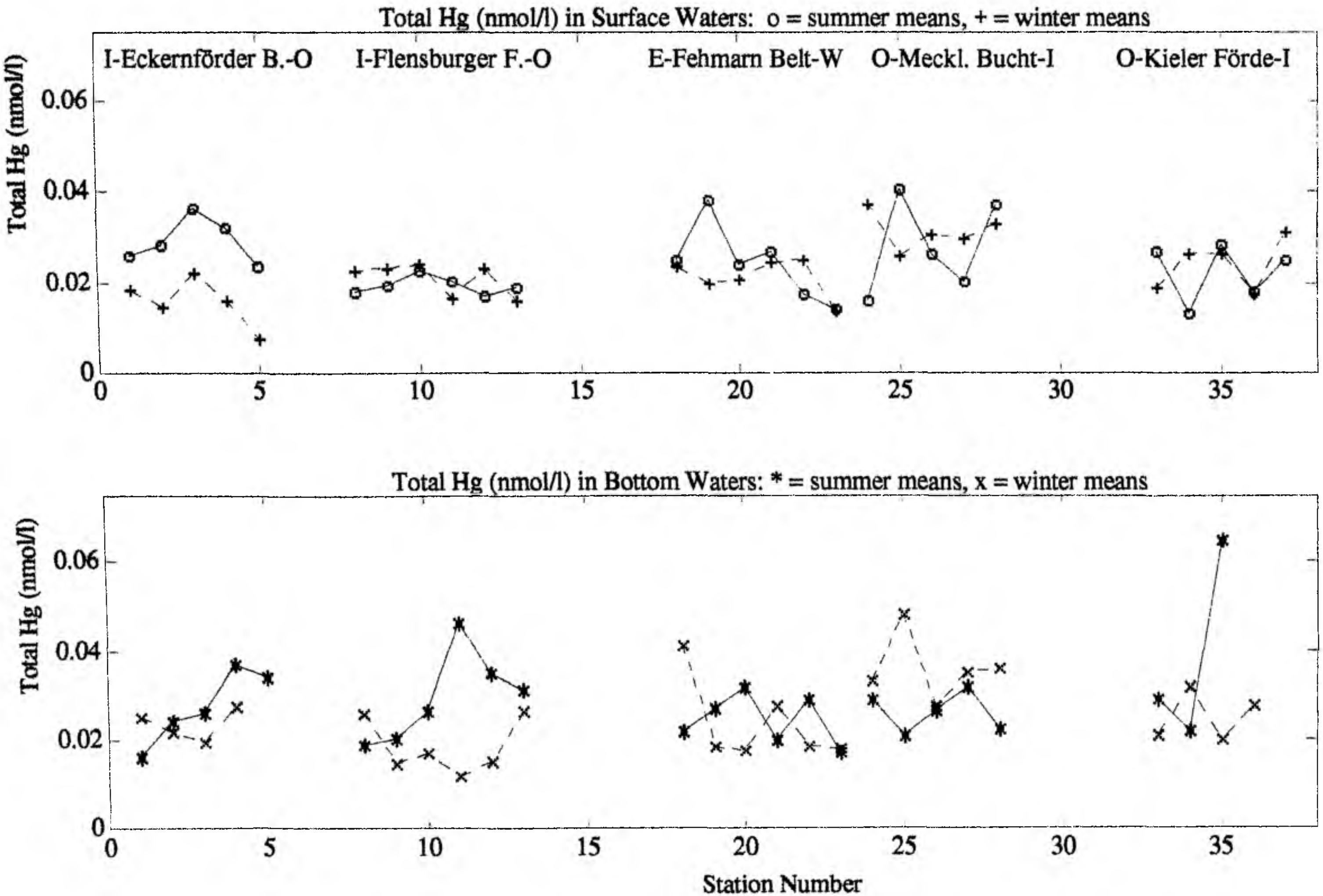


Figure 52. Mean particulate Cd concentrations vs mean particulate organic carbon on 0.4 μm filters in surface and bottom waters by season.

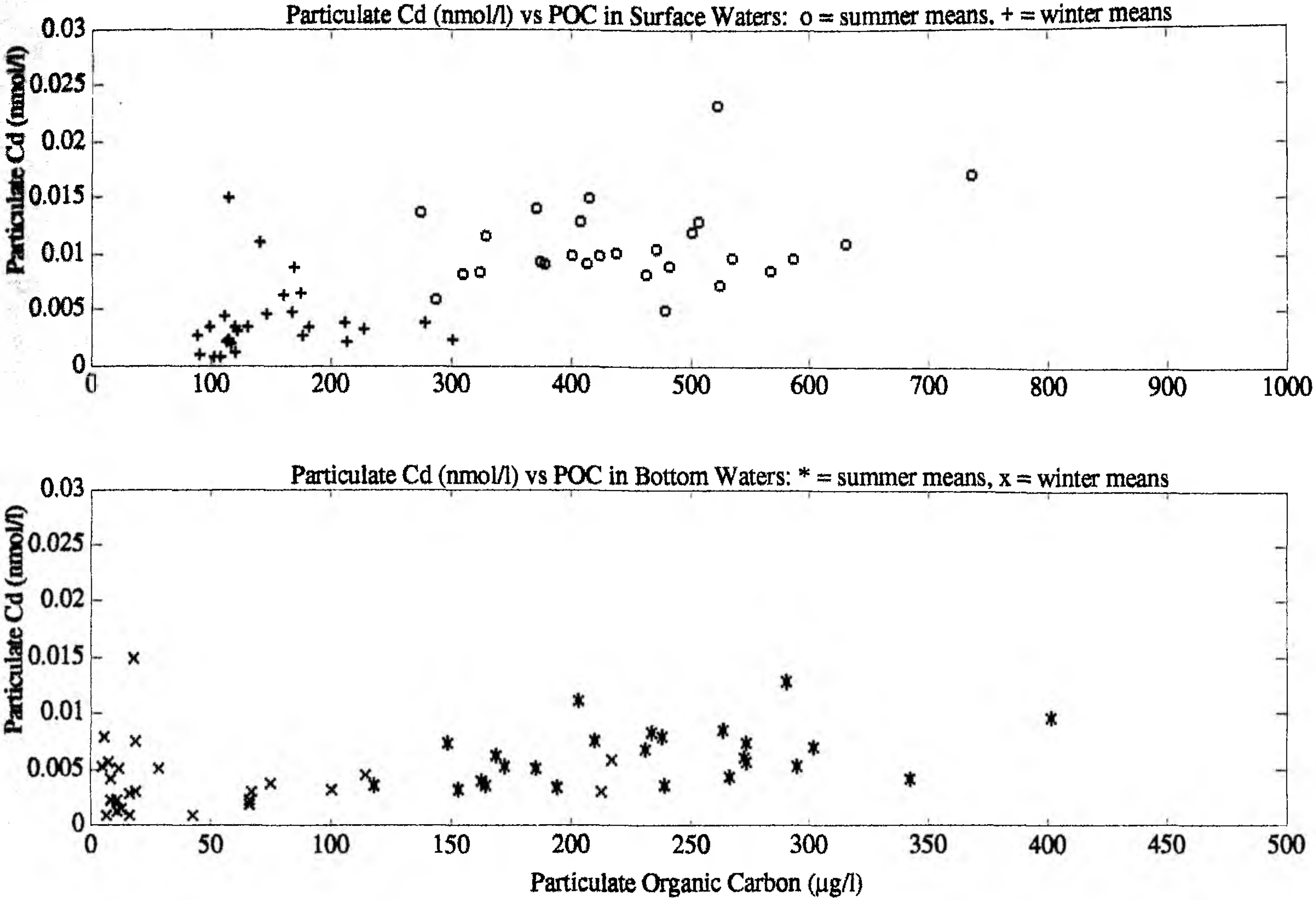


Figure 53. Mean particulate Zn concentrations vs mean particulate organic carbon on 0.4 μm filters in surface and bottom waters by season.

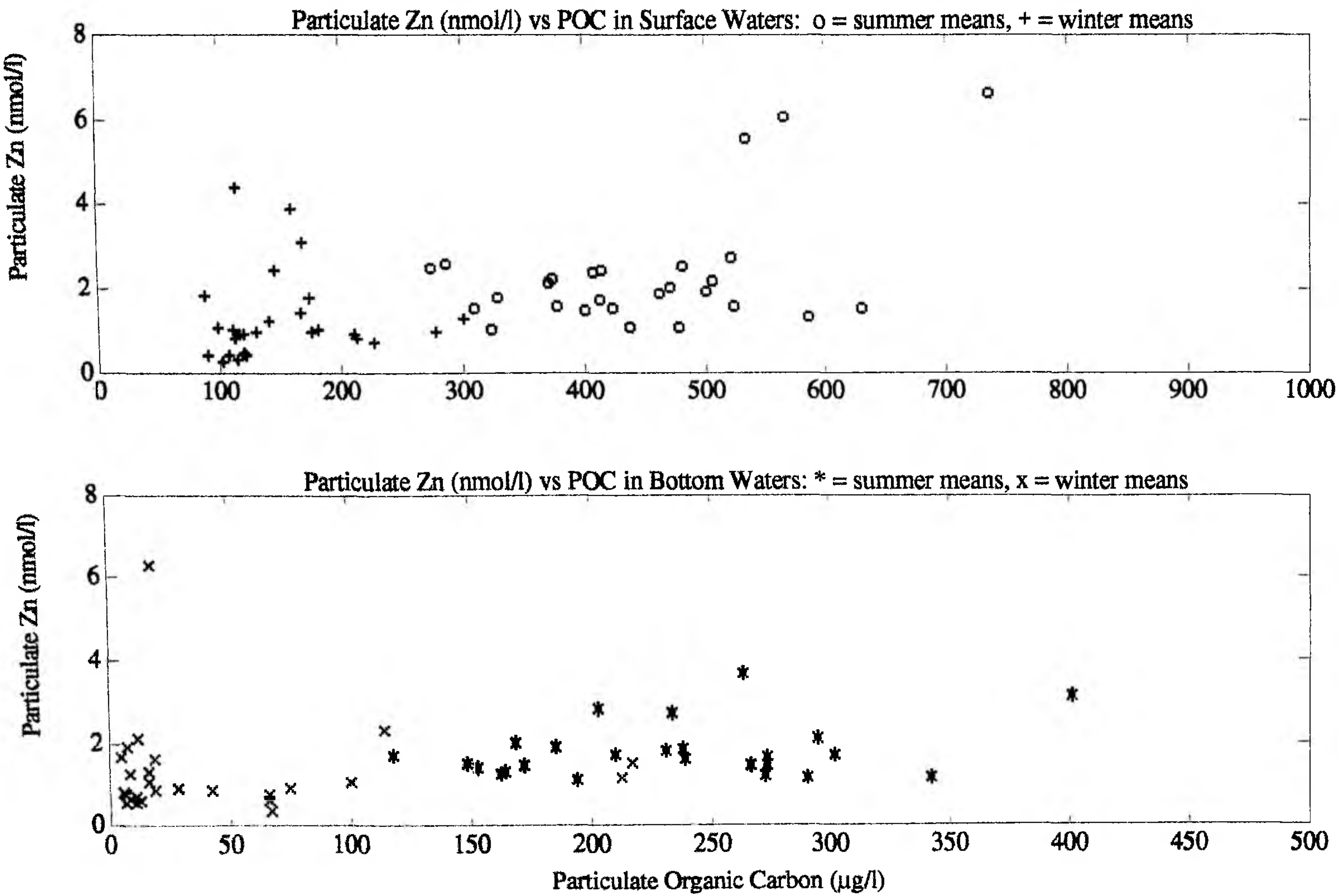


Figure 54. Particulate Co fraction (%) in surface and bottom waters by season. I, O, E, and W in the area names indicate inner, outer, eastern, and western directions for orientation.

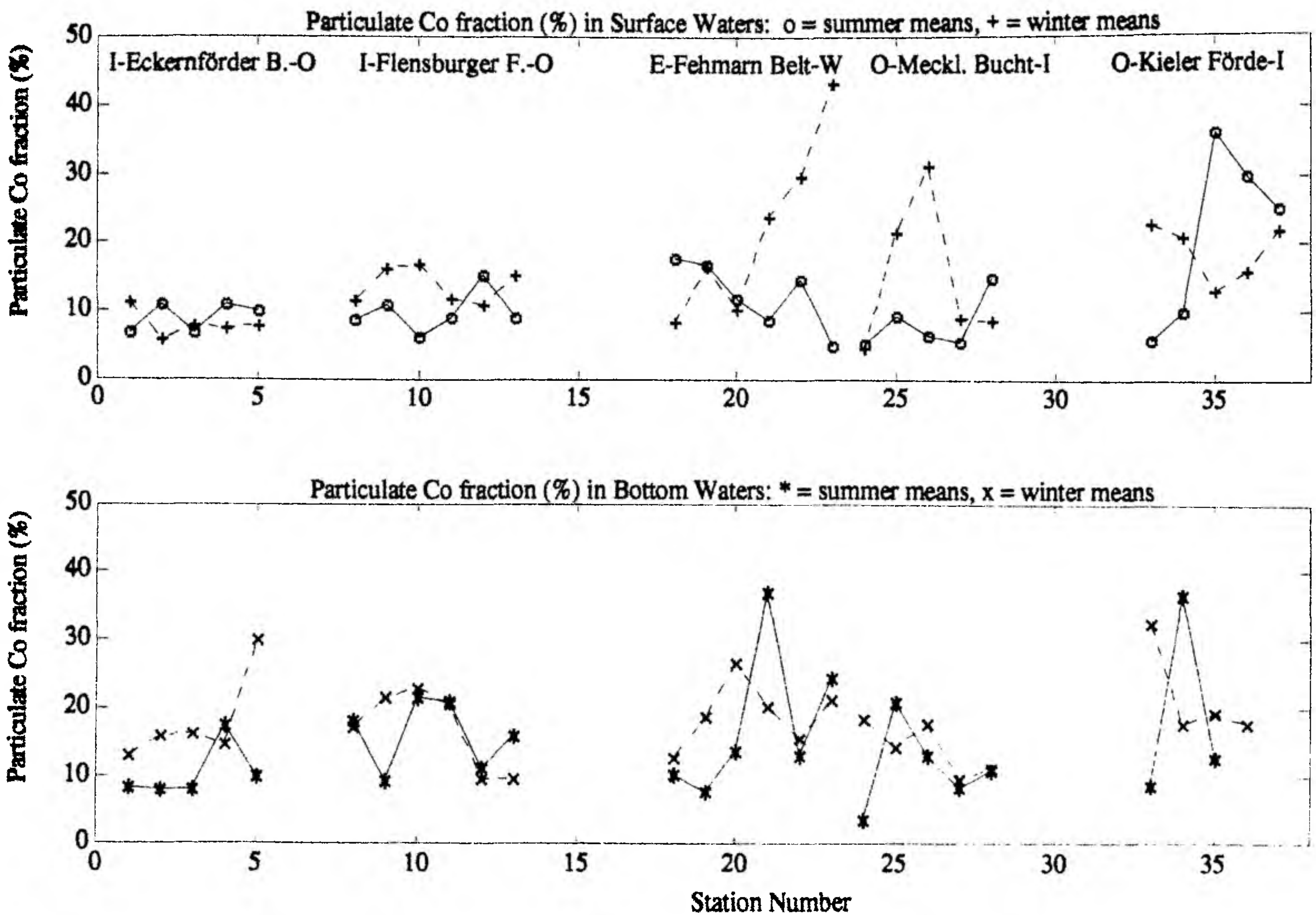


Figure 55. Particulate Pb fraction (%) in surface and bottom waters by season. I, O, E, and W in the area names indicate inner, outer, eastern, and western directions for orientation.

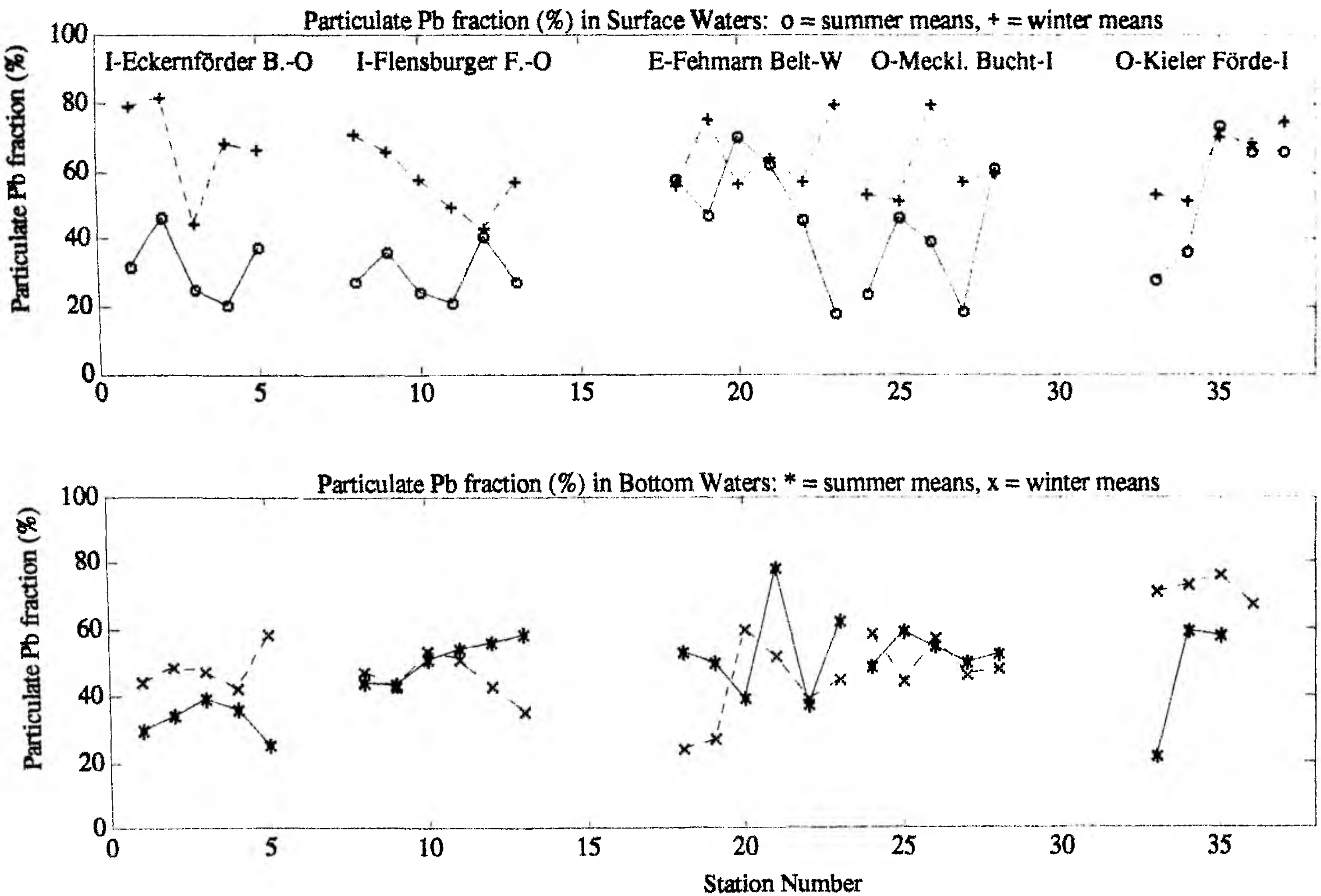


Figure 56. Particulate Cd fraction (%) in surface and bottom waters by season. I, O, E, and W in the area names indicate inner, outer, eastern, and western directions for orientation.

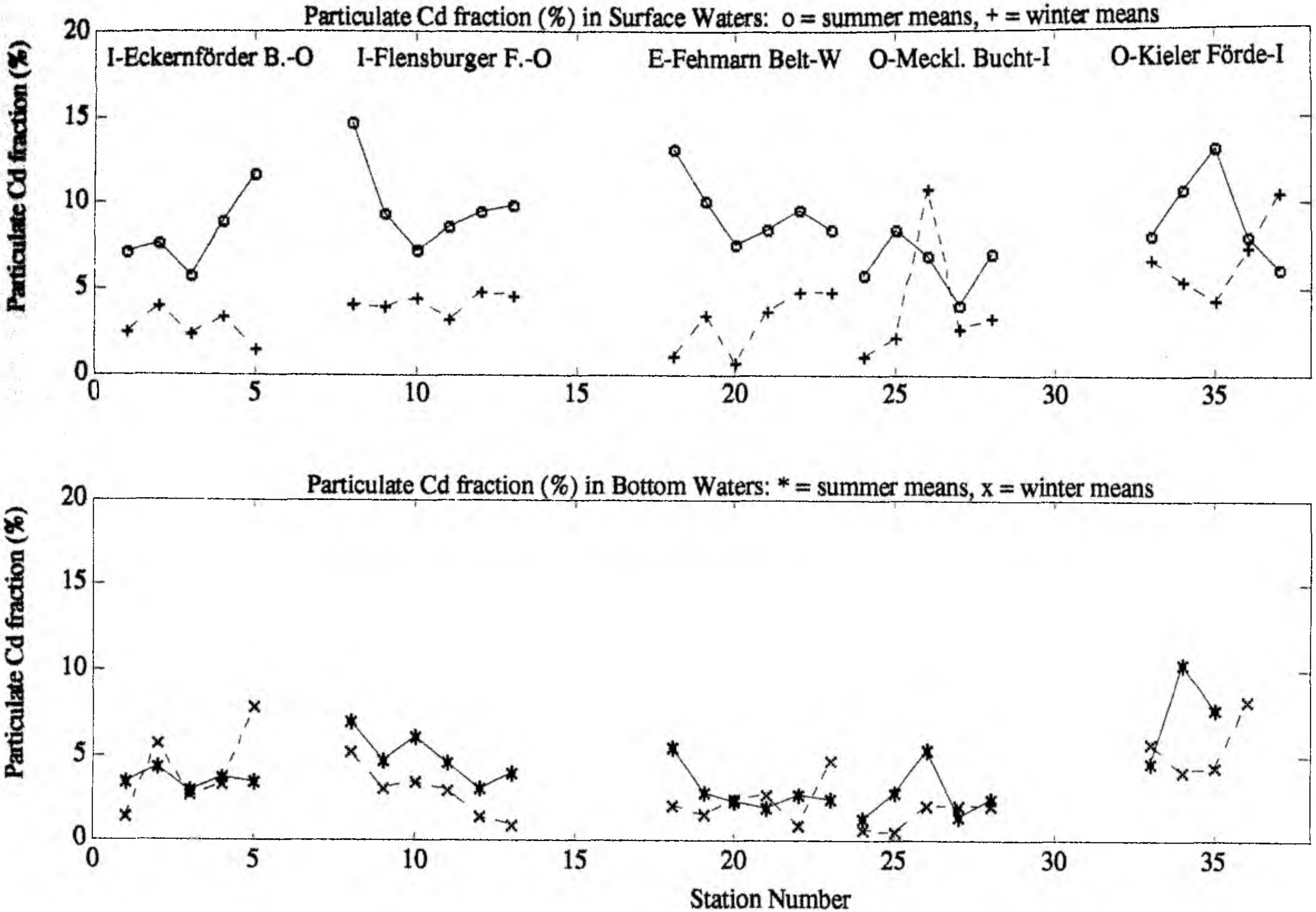


Figure 57. Particulate Cu fraction (%) in surface and bottom waters by season. I, O, E, and W in the area names indicate inner, outer, eastern, and western directions for orientation.

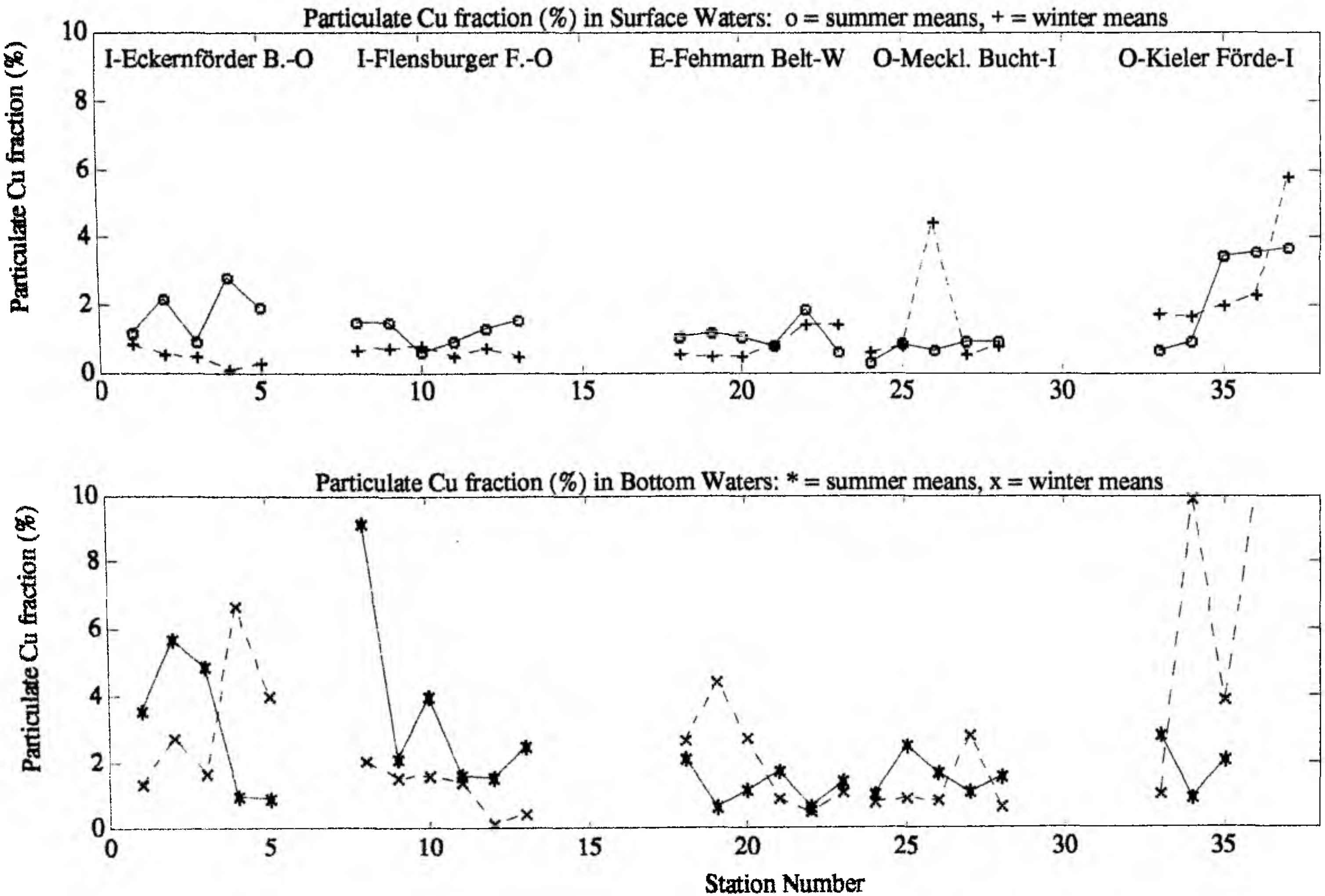


Figure 58. Particulate Ni fraction (%) in surface and bottom waters by season. I, O, E, and W in the area names indicate inner, outer, eastern, and western directions for orientation.

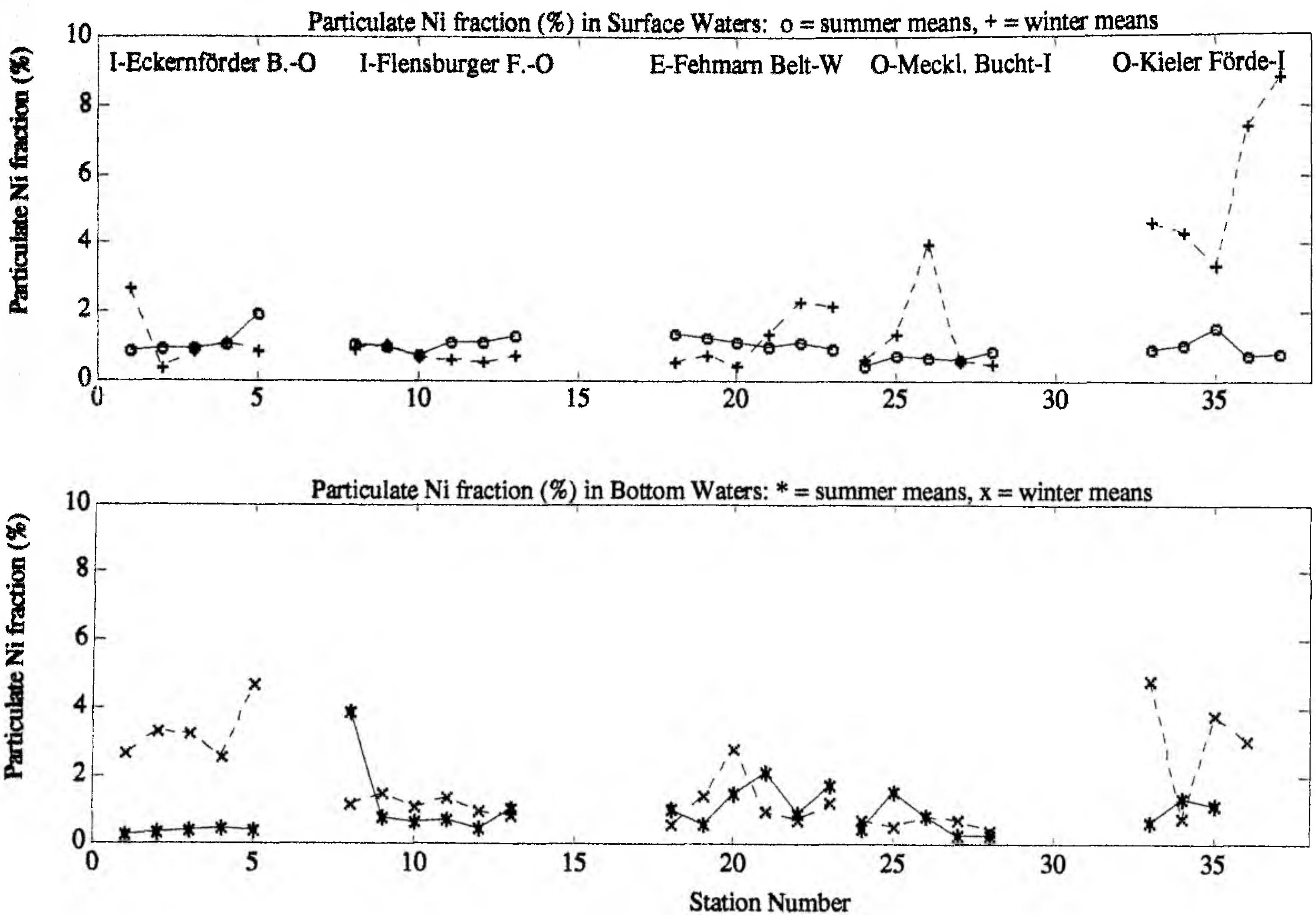


Figure 59. Particulate Fe fraction (%) in surface and bottom waters by season. I, O, E, and W in the area names indicate inner, outer, eastern, and western directions for orientation.

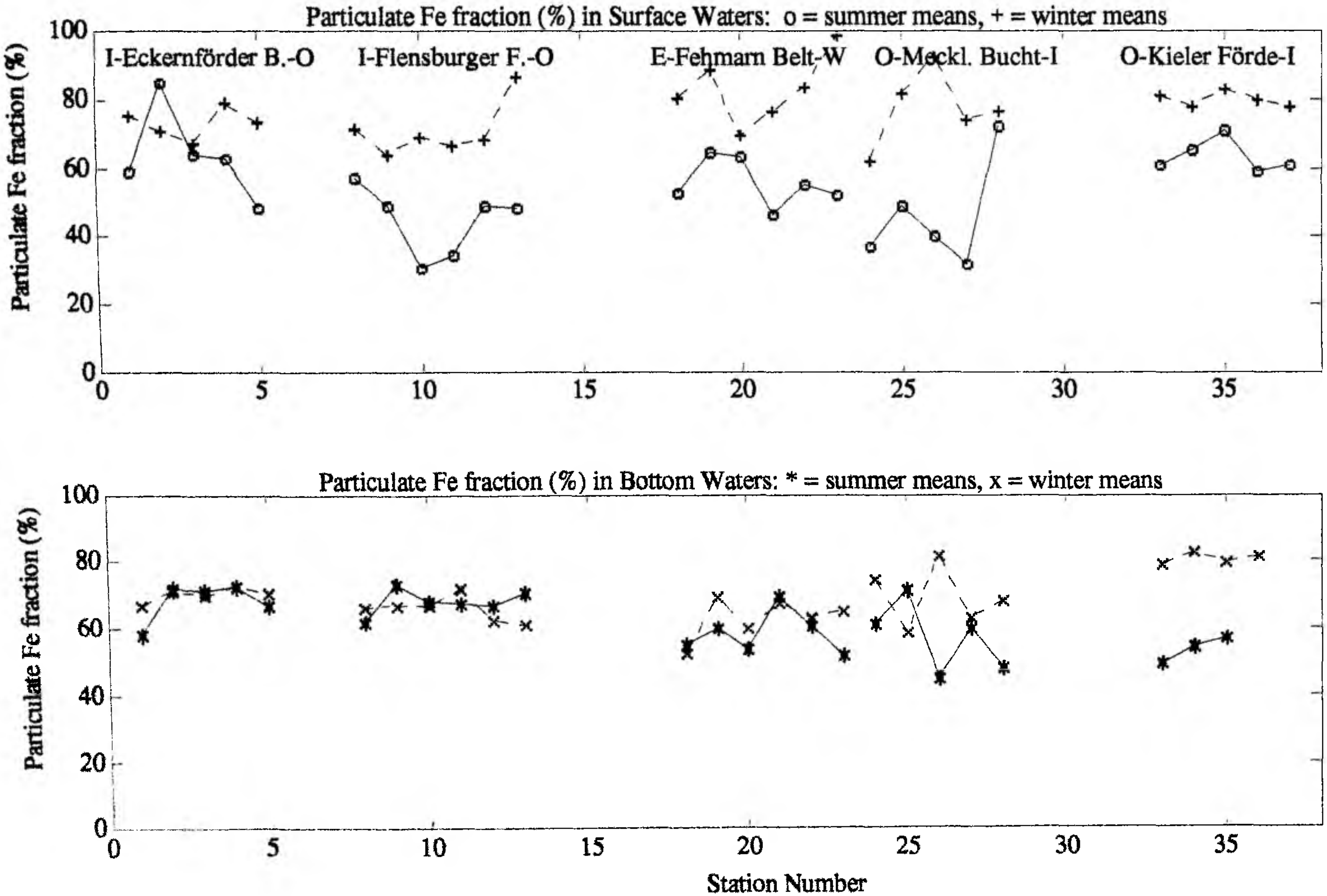


Figure 60. Particulate Zn fraction (%) in surface and bottom waters by season. I, O, E, and W in the area names indicate inner, outer, eastern, and western directions for orientation.

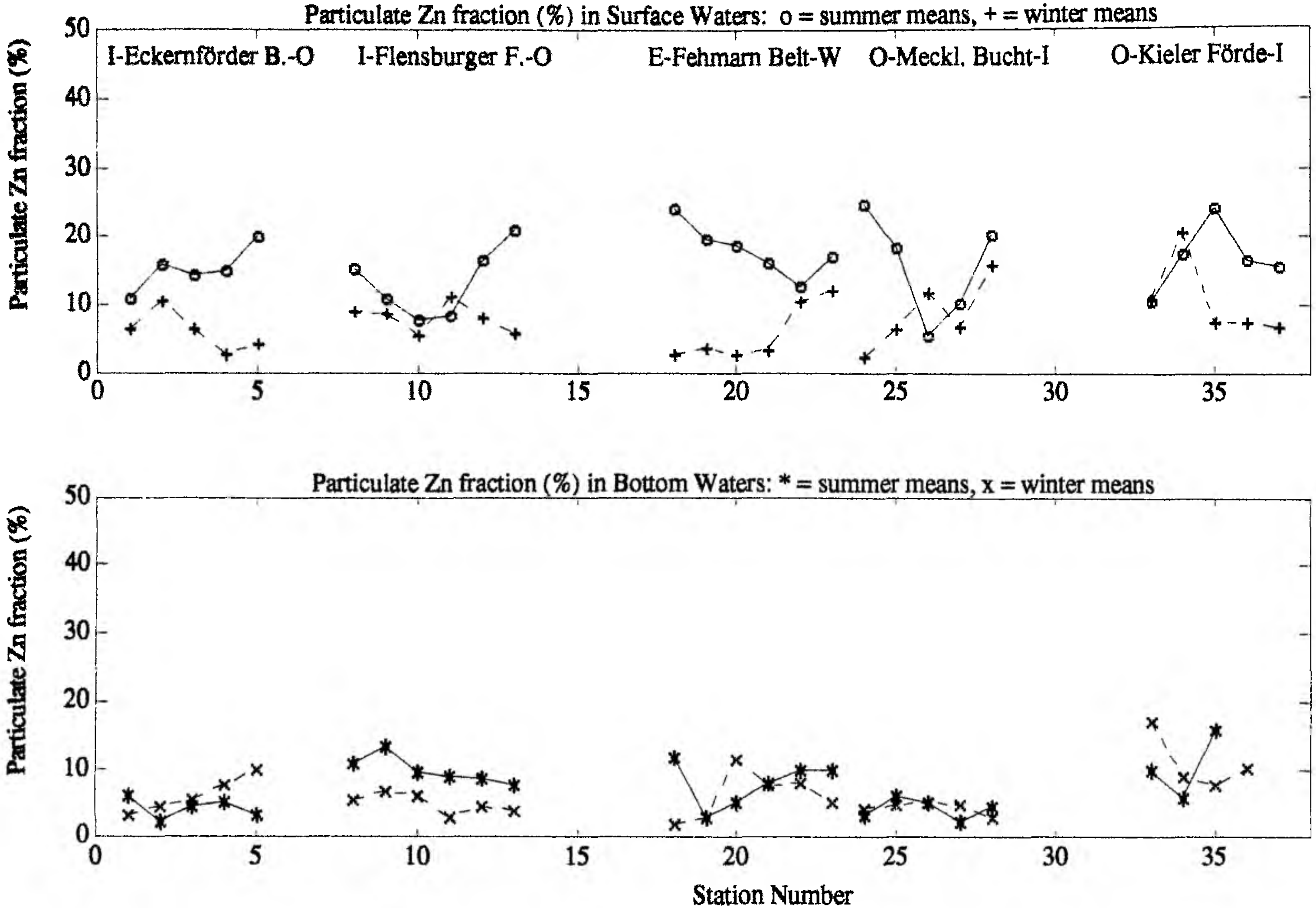


Figure 61. Particulate Mn fraction (%) in surface and bottom waters by season. I, O, E, and W in the area names indicate inner, outer, eastern, and western directions for orientation.

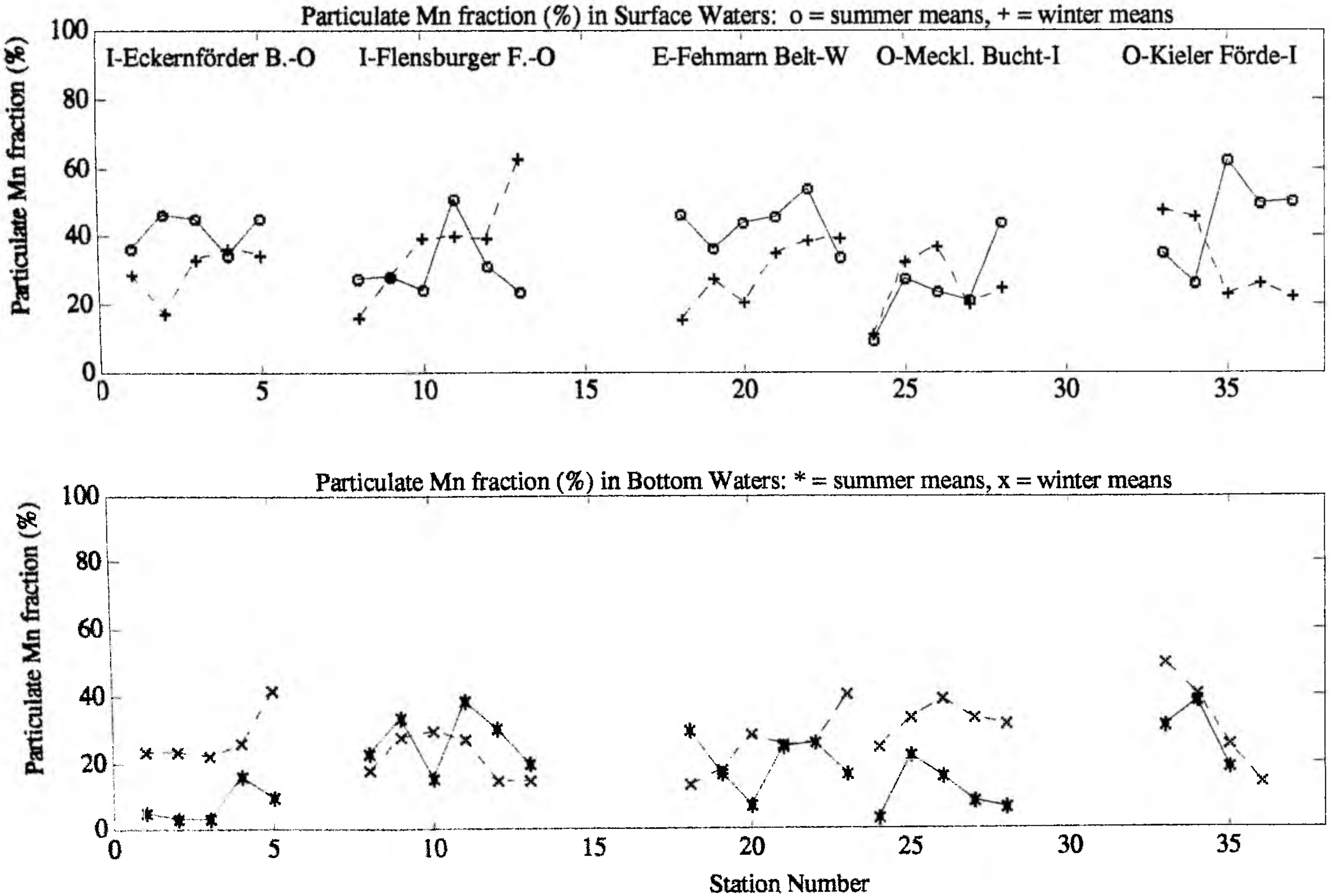
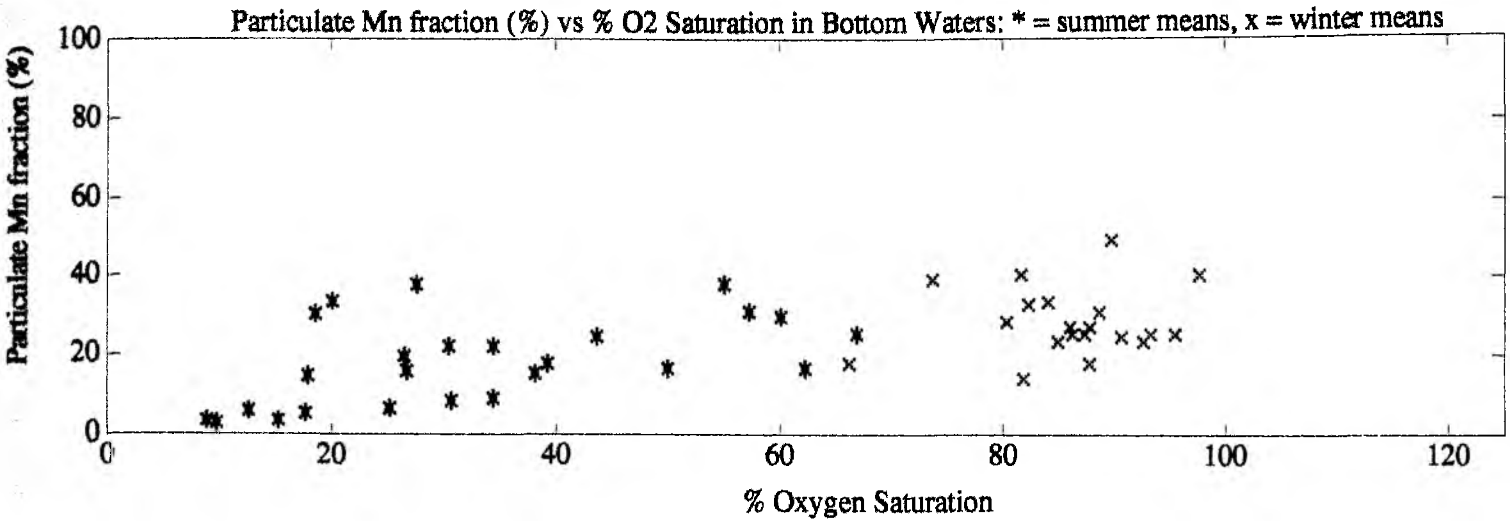


Figure 62. Particulate Mn fraction (%) and particulate Co fraction (%) vs percent oxygen saturation in bottom waters by season.



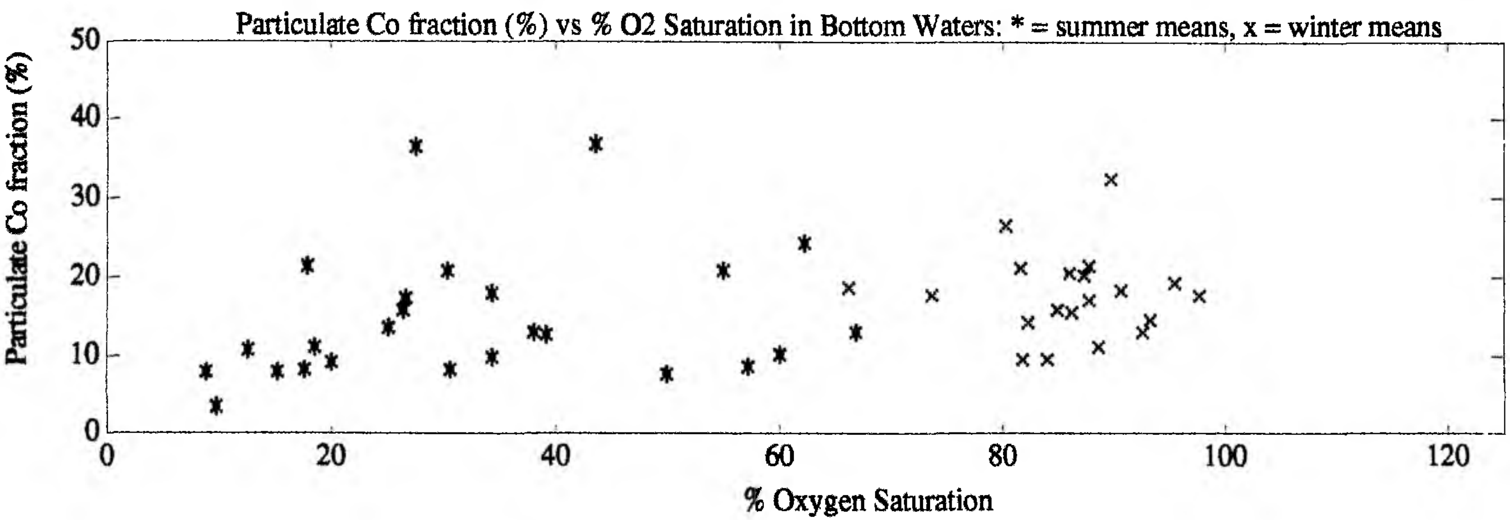


Figure 63. Particulate Fe fraction (%) and particulate Zn fraction (%) versus percent oxygen saturation in bottom waters by season.