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Chesapeake Bay Atmospheric Deposition Study, Phase II Final Report July 1990 - December 1991

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Chesapeake Bay Atmospheric Deposition Study Phase II: Final Report July 1990 - December 1991

July 1994

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THE CHESAPEAKE BAY ATMOSPHERIC DEPOSITION STUDY

PHASE II: July 1990 - December 1991

Sponsor:

U.S. Environmental Protection Agency, Chesapeake Bay Program Office

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i. FORWARD

This report describes the second phase of the Chesapeake Bay Atmospheric Deposition Study (CBADS). Data resulting from the analysis of samples collected between July and December 1991 are presented and integrated with previously reported CBADS data (Baker *et al.*, 1992. Mr. Rich Batiuk of the Chesapeake Bay Program Office, U.S. Environmental Protection Agengy served as the project officer for CBADS Phase II. Results of this ongoing study are also described in several published papers (see Leister and Baker, 1994a; Scudlark *et al.*, 1994; Wu *et al.*, 1992; Quinn *et al.*, 1992).

The purpose of the study was to determine atmospheric loadings of selected trace elements and organic compounds directly to the surface waters of the Chesapeake Bay. The work in this report represents the first eighteen months of the Chesapeake Bay Atmospheric Deposition Study. Future reports will describe and integrate results from the CBADS network through September 1993.

ii. EXECUTIVE SUMMARY

a. Overview. An 18 month field study (6/90 - 12/91), conducted to estimate the deposition of atmospheric trace contaminants to the Chesapeake Bay, represents Phase II of the Chesapeake Bay Atmospheric Deposition Study (CBADS). Data from Phase I (6/90 - 7/91), which was previously presented (Baker *et al.*, 1992) is presented here in concert with data from 7/91 - 12/91. The trace elements (aluminum, arsenic, cadmium, chromium, copper, iron, manganese, nickel, lead, selenium, and zinc), polychlorinated biphenyl (PCBs) congeners, and polycyclic aromatic hydrocarbons (PAHs) were measured in the ambient atmosphere and in precipitation. In addition several major ions, (chloride, sulfate, nitrate, sodium) were measured in precipitation at the three sites, either by us this study or by others in co-located acid deposition networks. Weekly integrated samples of aerosol and precipitation were collected for elemental constituents at three field stations, one on the northeastern shore (Wye), one on the mid-bay western shore (Elms), and one on the southwestern shore (Haven Beach) of the Chesapeake Bay. Organic contaminants in precipitation samples were collected bi-weekly and organic contaminants in the ambient air were collected for twelve to twenty-four hours semi-weekly at the Elms and Haven Beach stations. Measurements of organic contaminants in precipitation and in the atmosphere at the Wye station commenced during the summer of 1992 and these data will be presented in our Phase III report (1/92 - 12/92). Phase IV will include data from sampling through September of 1993.

Dry aerosol deposition fluxes were estimated from the measured aerosol concentrations for crustal and noncrustal modes and literature-derived deposition velocities. As described in Section IV, these flux estimates contain considerable uncertainties. Wet deposition was calculated directly from contaminant concentrations in precipitation and the measured precipitation volume. The total atmospheric flux is reported as the sum of the wet and dry depositional fluxes. Atmospheric loadings of contaminants to the Chesapeake Bay were calculated as the total site-averaged atmospheric contaminant fluxes times the surface area of the mainstem Bay, including the tidal tributaies below the fall-line (1.15×10^{10} m^2). No attempts were made to extrapolate our measured fluxes to the entire watershed, both because the magnitude of deposition likely changes and because it is difficult to model the ultimate fate of atmospheric contamiannts deposited to the watershed.

b. Organic Contaminants. To estimate loadings of organic contaminants from the atmosphere to the Chesapeake Bay, ambient atmospheric concentrations and wet depositional fluxes of 14 polycyclic aromatic hydrocarbons (PAHs) and 74 polychlorinated biphenyls (PCBs) were measured at two shore based rural field stations (Elms and Haven Beach) between June 1990 and December 1991. Organic contaminant sampling at Haven Beach did not commence until Summer, 1992. Mean concentrations of individual PAHs in air ranged from 0.004 (dibenz[*ah*]anthracene) to 1.4 ng/m^3 (phenanthrene) at the mid-bay Elms station and ranged from 0.002 ng/m^3 (dibenz[*ah*]anthracene) to 3.5 ng/m^3 (phenanthrene) at the southern Haven Beach station. The observed temporal variability in PAH levels in the air ranged from

50% to almost 200% about the respective mean concentrations. The mean ambient atmospheric PCB concentration over the Chesapeake Bay during the study period was 0.21 ng/m^3 at the mid-bay station and 0.30 ng/m^3 at the southern bay station, with a relative standard deviation of about 60%. PCB concentrations in the air were slightly correlated with air temperature.

Volume weighted mean (VWM) concentrations of individual PAHs in precipitation measured at both field stations ranged from 0.33 ng/L (dibenz[*ah*]anthracene) to 17 ng/L (pyrene). Concentrations of PAHs in precipitation were slightly higher at the southern station than at Elms. The VWM *t*-PCB concentration was 1.6 ng/L at the mid-bay station and was 1.1 ng/L at the southern station. The temporal variability of hydrophobic organic contaminant (HOC) concentrations in rainfall was as large as one order of magnitude, with no apparent seasonal trend, suggesting highly variable HOC scavenging processes. Assuming a dry deposition velocity of 0.49 $\pm$ 0.23 cm/sec, dry particle fluxes of PAHs ranged from 1 $\pm$ 0.4 μg/m^2/year (anthracene) to 21 $\pm$ 10 (fluoranthene) μg/m^2/year. Wet fluxes of PAHs at the Elms and Haven Beach sites ranged from 1 (anthracene) to 20 (pyrene) μg/m^2/yr. Total (wet + dry) fluxes ranged from 2 $\pm$ 0.4 (anthracene) to 35 $\pm$ 7 (pyrene) μg/m^2/yr. The *t*-PCB wet flux was 1.8 μg/m^2/yr, with the estimated dry particle flux accounting for 49% of the total flux (3.5 $\pm$ 0.8 μg/m^2/year).

Combined wet and dry annual atmospheric loadings of individual PAHs to the surface waters of the Chesapeake Bay were calculated by extrapolating the total flux to the surface area of the Chesapeake Bay (1.15 x 10^{10} m^2). Individual PAH loadings (wet + dry) range from 19 $\pm$ 4 (anthracene) to 330 $\pm$ 86 (pyrene) kg/yr and the *t*-PCB annual atmospheric loading is 40 $\pm$ 9 kg/yr. These estimates of annual atmospheric deposition do not include gaseous exchange across the air-water interface, which has been shown to be considerable relative to wet deposition and dry aerosol deposition in recent studies in other water bodies (Achman *et al.*, 1993).

c. Aerosol Trace Elements. In addition to samples analyzed during the first full year of the study, more than 90 samples collected during June - December 1991 were analyzed for > 30 elements, including Al, As, Cr, Fe, Mn, S, Se, and Zn by instrumental neutron activation analysis (INAA); for Pb, Ni, and Cu by inductively-coupled plasma-atomic emission spectrometry; and for Cd and Ni by Zeeman/graphite furnace-atomic absorption spectrometry.

Concentrations of anthropogenic elements such as As, Cr, Se, V, and Zn exhibited similar seasonal trends, generally, increasing from summer to winter, in accordance with decreasing environmental temperatures. Superimposed on this trend are peaks, especially in late summer and winter months, which presumably reflect elevated emissions during peak air conditioning and heating, periods of low precipitation scavenging, transport dynamics, and conditions of atmospheric stagnation. Concentrations of elements associated with crustal material (*e.g.*, Al, Fe, and Mn) tended to be elevated in the spring and summer months, probably reflecting increased agricultural and construction activities. Concentrations of S are characteristically elevated during the summer months when more photochemical oxidants are available for the conversion of SO_2 to the particulate forms of S measured in this study. Overall, 18-month average concentrations determined for the Wye and Elms sites differed by $\leq$5% for As, Cr, Cu, Mn, Pb, and Zn; <10% for Br, Cd, Fe, S, and Se; and $\leq$27% for Al, Ni, and V. Average concentrations determined for the Wye and Haven Beach sites differed by <10% for As, Cd, Cu, Mn, Pb, Se, and Zn; <20% for Cr, Ni, and S; and approximatey 25% for Al, Fe, and V. Concentrations observed at Haven Beach were quite similar, however, fewer data are available and the averaging period is smaller due to the delayed start of sampling at this site.

Preliminary estimates of annual deposition fluxes to Bay waters were calculated for each element as the product of the annual average airborne concentration and a deposition velocity (V_d) for each element taken from the literature as described in the text (Section IV). Lower limits of V_d were taken

to be 0.26 $cm \cdot s^{-1}$ for noncrustal components and 1.4 $cm \cdot s^{-1}$ for crustal components. Upper limits of V_d are taken to be 0.72 $cm \cdot s^{-1}$ for noncrustal components and 4 $cm \cdot s^{-1}$ for crustal components. The average and ranges (in parentheses) of the high and low flux estimates for the three sites are as follows: Al, 120,000 (58,000 - 170,000); As, 100 (50 - 140); Cd, 20 (12 - 32); Cr, 200 (99 - 280); Cu, 420 (190 - 520); Fe, 64,000 (32,000 - 91,000); Mn, 1,300 (650 - 1800); Ni, 600 (256 - 710); Pb, 670 (300 - 820); Se, 250 (130 - 370); and Zn, 2,000 (1,100 - 2900) $\mu g \cdot m^{-2} \cdot y^{-1}$. A slight north-to-south gradient is evident in averages concentrations of a few of the noncrustally-associated elements (e.g., Cr, Cu, Nni, Pb, and Zn), however, too few data are available for the Haven Beach site to make a valid comparison at this time.

d. Precipitation Trace Elements. Eleven trace elements in precipitation were successfully collected and accurately determined in over two hundred weekly-integrated precipitation samples at the Wye, Elms, and Haven Beach sites. The annual wet flux ($\mu g \cdot m^{-2} \cdot y^{-1}$) averaged for the three sites were as follows: Al (14,000), As (50), Cd (80), Cr (100), Cu (530), Fe (10,400), Mn (1,100), Ni (260), Pb (580), Se (130), and Zn (1,600). For the majority of the elements, the average annual wet flux has not changed significantly from the CBADS Phase I estimates (Baker *et al.*, 1992), which did not include the Haven Beach site. However, the average flux for Cd and Cu increased two-fold due primarily to a few high concentrations found at the Haven Beach site, which may have resulted from contamination during sampling. In contrast, the Se flux decreased approximately 50% at all of the sites during Phase II.

Typically, the average monthly wet depositional flux of an element at a given site varies by a factor of 10-20, but can vary by as much as a factor of 90. On a decreasing time scale (*e.g.*, weekly), this temporal variability can be even greater. From an ecological perspective (*e.g.*, periods of fish spawning), such episodic inputs may be as significant as the cumulative annual loadings. A few spatial trends were noted, for example, a decreasing Pb signal from north to south and, conversely, increasing arsenic deposition from north to south. As indicated by these observations, the atmospheric wet deposition of trace metals thus appears to be a very heterogeneous process with respect to space and time. Consequently, an accurate assessment of bay-wide loading requires the employment of multiple sites over a long time frame.

Most of the elements examined in precipitation appear to have a dominant anthropogenic source. With the exception of Fe and Al (and, to a lesser extent, Cr and Mn), crustal sources do not provide an important source of trace elements deposited by wet deposition. While weekly concentrations vary spatially by as much as twenty times, the average monthly fluxes differ among the sites by a factor of five to ten times during the same months. Based on the concurrent estimates of dry deposition, the proportion of dry deposition for crustal elements (*e.g.*, Al and Fe) appears greater than that for wet deposition. For non-crustal elements (*e.g.*, Pb), the relative contribution of wet and dry deposition appear comparable. However, the inherent uncertainty in the dry deposition estimates, particularly for the noncrustal elements, currently prevents a more accurate and quantitative apportionment of wet *versus* dry atmospheric deposition.

e. Overall. Large variations in concentrations and fluxes for trace elements in precipitation and organic contaminants in the atmosphere and in precipitation are observed around Chesapeake Bay. Temporal variations in contaminant concentrations in both the air and in precipitation reflect the influence of the local micrometeorology and emission source strengths on atmospheric deposition. For example, greater concentrations of trace elements were observed in precipitation at the Wye and Haven Beach sites than at the Elms site but not in aerosol particles indicating that below-cloud scavenging processes are highly variable and driven by ambient meteorological conditions (*e.g.*, wind speed and direction).

In general, the wet fluxes are similar in magnitude to the corresponding dry aerosol fluxes for

trace elements of non-crustal origin and for organic contaminants. However, as described in the text, there is considerable uncertainty in the dry deposition velocity. Future research needs to consider the direct measurement of the dry deposition velocity, particularly over water. As micrometeorological conditions over water differ greatly from those over vegetative surfaces, the extrapolations of our land based measurements to water surfaces need to be further investigated over a fairly long time scale to accurately assess contaminant dry deposition to the Chesapeake Bay. In addition, dry depositional fluxes of gaseous organic compounds may be of considerable importantance to the overall flux of contaminants to the Bay

I. INTRODUCTION

I.1 Background

Atmospheric transport and deposition of anthropogenically-mobilized acids, trace elements, and organic chemicals may be a significant source of contaminants to coastal waters, including the Chesapeake Bay. Contaminants are released into the atmosphere from a variety of activities, including direct emissions from stationary sources (*e.g.*, combustion sources), mobile sources (*e.g.*, motor vehicles), and regional activities (*e.g.*, agrichemical applications, and soil erosion). Once in the atmosphere, contaminants may be chemically altered, partitioned between gaseous and particulate phases, and transported great distances. Contaminants are removed from the atmosphere and delivered to the Earth's surface by a variety of mechanisms, including scavenging during precipitation events (wet deposition) and by diffusive and turbulent transport during dry periods (dry deposition). Estimating the potential impact of atmospherically-deposited contaminants to surface waters requires not only an accurate quantitative measurement but also a thorough understanding of the processes which transport and scavenge these chemicals from the atmosphere.

I.1.1 Evidence of Atmospheric Deposition. The atmosphere is an important environmental pathway for the transport and deposition of contaminants to surface water systems. Numerous trace organic pollutants are dispersed worldwide predominantly due to atmospheric transport. Fish collected from Siskiwit Lake, a small lake on Lake Superior's Isle Royale, contain residues of polycyclic aromatic hydrocarbons (McVeety and Hites, 1988), polychlorinated biphenyls (Swackhamer and Hites, 1988), toxaphene and other airborne contaminants (Swain, 1978). As there are no local sources of these contaminants on Isle Royale, aerial transport and deposition is the source of contamination to this isolated location. Recent evidence suggests that the Arctic food chains have become contaminated with atmospherically-derived organochlorine contaminants (Bidleman *et al.*, 1989).

Duce *et al.* (1992) have recently synthesized the available data quantifying atmospheric deposition of trace elements, nutrients, and organic contaminants to the world's oceans. Atmospheric inputs can also be important for small bodies of water in the vicinity of major atmospheric sources. For example, both dry and wet deposition were found to be important sources of Pb to the 2 ha Skinface Pond located about 5.5 km from the coal-fired Savannah River Power Plant (Weiner, 1979). Atmospheric deposition is also an important source of Cu, Cr, Pb, Zn, and other metals to the Great Lakes (Sievering *et al.*, 1981) and other bodies of water characterized by low watershed area-to-water surface area ratios. Excess Cu, Pb, and Zn in surface sediments of the Chesapeake Bay have been attributed to atmospheric deposition (Helz *et al.*, 1985a; Helz *et al.*, 1985b), as well as salt-marsh sediments of Naraganesett Bay (Bricher, 1993).

I.1.2 Mechanisms of Atmospheric Deposition. Chemicals are removed from the atmosphere during precipitation events *via* various wet deposition processes. Particulate and gaseous contaminants are scavenged by hydrometeors, in-cloud processes such as diffusion, nucleation, coagulation, and coalescence, or below-cloud processes including impaction interception, and diffusion into hydrometeors. The efficiency of particle scavenging depends on the ambient suspended aerosol particle concentration and size, as well as the micrometeorology of the precipitation event. Gas phase species may be scavenged from the atmosphere *via* dissolution into rain drops. If the mass transfer of the gas into the drop is rapid, then gas scavenging by precipitation may be modelled as an equilibrium distribution following Henry's Law. Because precipitation scavenges organic particles much more efficiently than organic gases, the gas-particle distribution of many organic contaminants may control the magnitude of wet depositional fluxes (Leister and Baker, 1994a).

During dry periods, particle-associated chemicals are removed from the atmosphere as particles deposited on water, soil, and vegetation surfaces. The magnitude of particle transport and deposition depends in a complex way upon macro- and micrometeorological conditions, and has been modeled as a series of resistances to transfer in the bulk atmosphere and across the stagnant boundary layer. Combustion-derived contaminants are generally associated with submicrometer particles, which are not efficiently dry deposited, while many soil-derived (particles) components are attached to large particles which deposit rapidly. Gaseous contaminants actively exchange between the atmosphere and water and terrestrial surfaces at rates proportional to their instantaneous concentration gradients. Recent evidence suggests that the exchange of volatile organic contaminants is highly dynamic, with volatilization during warmer months offsetting efficient deposition during the winter season (Baker and Eisenreich, 1990; Hoff *et al.*, 1992; Achman *et al.*, 1993, Hornbuckle *et al.*, 1993; Baker et al., 1993).

I.1.3 Review of Previous Work. Atmospheric deposition may supply significant quantities of nutrients, organic carbon, and potentially-toxic trace metals and organic chemicals to the Chesapeake Bay. A 1988 report suggested that atmospheric deposition of inorganic nitrogen provides 25% of the total loading of this important nutrient to the Chesapeake Bay (Fisher *et al.*, 1988; Fisher and Oppenheimer, 1991). An independent evaluation concluded that as much as 35% of the nitrogen loading to the bay is derived from the atmosphere (Hinga *et al.*, 1991). Studies sponsored by the United States Environmental Protection Agency Chesapeake Bay Program Office during the early 1980's indicated that aerial loadings of organic carbon to the southern Chesapeake Bay are of the same order of magnitude as the estimated lower limit of organic carbon fixation by phytoplankton production (Velinsky *et al.*, 1986). Also, these studies determined that atmospheric deposition of hydrocarbons to Chesapeake Bay is comparable in magnitude to the inputs from wastewater treatment plants and accidental discharges (Webber, 1983). Anthropogenic hydrocarbons are estimated to account for approximately 50% of the hydrocarbons aerially deposited to the lower Chesapeake Bay (Webber, 1983). In the early 1980's, the EPA-sponsored Chesapeake Bay Aerial Precipitation Survey measured trace element wet fluxes in coordinated studies in the Maryland (Conkwright *et al.*, 1982) and Virginia (Wade and Wong, 1982) portions of the estuary. Data from this one year "pilot project" are discussed in Section IV of this report.

Bulk deposition (*i.e.*, wet and dry combined) of agrichemicals to the Chesapeake Bay region were measured by Williams (1986), Glotfelty *et al.* (1990), and Wu (1981). In these studies, open collectors were deployed for extended periods in locations adjacent to agricultural fields. While these studies provide some important first measurements of agrichemical deposition rates, the close proximity of sampling to agrichemical use areas likely result in overestimating the true, regional deposition fluxes. Church and Scudlark (1992) have measured wet depositional fluxes of trace elements at a coastal site adjacent to the Chesapeake Bay watershed (Lewes, Delaware) since 1982. This record of contaminant deposition reveals distinct seasonal and annual trends. For example, concentrations and fluxes of many trace elements peak in the summer months coincident with increased automobile and boat traffic. P levels in precipitation have decreased by more than a factor of 7 during the 10 years of sampling, presumably reflecting the phase-out of alkylated Pb in gasoline during this period.

I.2 Statement of the Problem

As tighter controls are exerted on conventional point source discharges, the relative contributions of non-point contaminant sources are increasing. As is the case for nutrients, the inventory of 'toxic' chemical sources includes several important non-point sources, including atmospheric deposition. The Chesapeake Bay Basinwide Toxics Reduction Strategy outlines a plan to determine both the absolute and relative contributions of a variety of sources of contaminants to the Chesapeake Bay, and specifically calls for quantification of atmospheric loadings (U.S. EPA, 1988). The 1990 Amendments to the Clean Air Act also recognize the importance of atmospheric deposition to coastal water quality, requiring that the

Federal Government establish and maintain monitoring networks around Chesapeake Bay and other coastal waters. The problem is simply stated: What quantity of inorganic and organic contaminants is entering the Chesapeake Bay *via* atmospheric deposition? Beginning in 1990, we initiated a field study to answer this question. Early results of this study are described in the CBADS Phase I report (Baker *et al.*, 1992) and in several peer reviewed publications (Leister and Baker, 1994a,b,c, Wu *et al.*, 1994; Scudlark *et al.*, 1994). This report describes the second phase of the study, in which the fluxes of atmospheric contaminants to the Chesapeake Bay were estimated for 18 months beginning in July, 1990.

I.3 Study Objectives

The overall objective of the Chesapeake Bay Atmospheric Deposition Study (CBADS) is to estimate the atmospheric fluxes of trace elements and organic contaminants to the surface of the Chesapeake Bay. To adequately address this question, we also focused on quantifying the spatial and temporal variability in atmospheric concentrations.

Our primary objectives for Phase 2 of the CBADS study were:

a) to accurately measure the concentration of selected trace elements and organic contaminants in precipitation and in the atmospheric aerosols,
b) to determine the temporal and spatial variability in precipitation concentrations and, where feasible, fluxes,
c) to evaluate the relative magnitude of atmospheric depositional processes (wet versus dry), and
d) to estimate the annual areal fluxes of the contaminants to the Chesapeake Bay surface waters.

I.4 Study Limitations

This report covers the second phase of CBADS, and does not explicitly address several related issues currently under investigation. Specifically, no attempt is made to model contaminant scavenging, to determine the sources of the deposited contaminants, or to quantify recycling of organic contaminants (*i.e.*, revolatilization) from the Chesapeake Bay. In addition, because of the large uncertainties in estimating the transport of chemicals through the watershed into the Chesapeake Bay and because our sampling locations may not be representative of the entire watershed, we have not calculated the magnitude of atmospheric deposition to the watershed. Finally, because highly heterogenous conditions were anticipated, sampling within the urban environment was consciously avoided. The loadings in this report are, therefore, only indirectly influenced by urban air masses and therefore, reflect conservative estimates of bay-wide loadings. The role of urban areas in supplying chemicals to coastal waters *via* the atmosphere remains unclear. In 1995, a field study, funded by U.S. EPA-AREAL, will be undertaken to document atmospheric deposition of contaminants to Chesapeake Bay that originate in Baltimore.

II. THE STUDY

II.1 Design

This field-based study was designed to estimate atmospheric depositional loadings of trace elements and organic contaminants to the Chesapeake Bay. As such, this work was constrained both by the limited understanding of depositional processes and by the available resources. Because little *a priori* information was available to anticipate the regional-scale variations in deposition rates, we chose initially

to establish two sampling stations in the Maryland portion of Chesapeake Bay in the summer of 1990. In a collaborative study sponsored by the U.S. EPA, Chesapeake Program Office, a third site in Mathews County, Virginia was established in December, 1990 (Dickhut *et al.*, 1992). Sampling for organic contaminants in the study has been conducted at the Elms and Haven Beach sites. To ensure that every precipitation event was collected, we employed automated wet-only precipitation samplers to collect integrated wet deposition samples over weekly (trace elements) or bi-weekly (organic contaminants) intervals. Continuous aerosol sampling provided weekly-integrated trace element concentrations at each site, while 12-16 hour integrated air samples were collected bi-weekly for organic contaminants (gas and aerosol).

A key characteristic of this study was the co-deployment of specialized, high quality samplers for trace elements and organic contaminants, with the subsequent analyses following stringent analytical protocols. As described below, the sampling and analytical procedures employed in this study resulted in reproducible data, with concentrations consistently well above our analytical detection limits with a minimum of contamination resulting from sample handling.

II.2 Sampling Site Locations and Descriptions

All CBADS precipitation and aerosol sampling described within this report was conducted at two sites in the Maryland portion of the Chesapeake Bay and one site in the Virginia portion of the southern Chesapeake Bay, subsequently referred to as the Wye, Elms, and Haven Beach sites (Fig II.2.1). Table II.2.1 summarizes the sampling activities at the sites.

II.2.1 Wye Site. The northern-most site is located on the grounds of the University of Maryland Agriculture Experiment Station, Wye Research and Education Center in Queenstown, MD (38°53'N, 76°08'W), on the eastern shore of Chesapeake Bay. This site is located <5 km from the shoreline of the Chesapeake Bay, in a primarily rural agricultural region. Under typical meteorological conditions, this site is downwind from the heavily populated Washington, D.C./Baltimore, MD corridor, approximately 65 km east of Washington and 45 km southeast of Baltimore. Trace elements in precipitation and aerosol particulates were sampled at this location. The sampling equipment was co-located at existing National Atmospheric Deposition Program (NADP)/acid rain station, in the middle of a large, flat, open, grassy field. The nearest buildings and roads are approximately 200 m away. The site operator, Mr. Mike Newell, was also responsible for the NADP site activities.

II.2.2 Elms Site. The mid-bay CBADS site is on the property of the State of Maryland Elms Environmental Education Center, near St. Mary's City, MD (38°13'N, 76°23'W). The land use in the vicinity of the site is generally a rural agricultural region, however, a local source of atmospheric pollutants is the Patuxent River Air Naval Station, 4.5 km to the north. In addition to the high aircraft traffic volume, the base operates a coal-fired power plant. The complete suite of organic contaminants and trace element aerosol/precipitation sampling were conducted at this site, which is co-located at the existing State of Maryland Department of the Environment acid rain monitoring network site. The sampling equipment was deployed on the eastern edge of a flat, grassy 75 x 75 m. clearing, flanked by woods to the north and west and a tidal marsh to the south. The Chesapeake shoreline is about 0.5 km to the west. The site operators, Ms. Dianne Leister and Ms. Cheryl Clark (University of Maryland, CEES/CBL), were responsible for all on-site sampling and processing activities.

II.2.3 Haven Beach Site. The southern-bay CBADS site is located at Haven Beach in Mathews County, Virginia (37°26'N 76°15'W). This site is south of the mouth of the Rappahanock River and approximately 100 km due east of Richmond, VA. The samplers are deployed on a wooden platform in a salt marsh directly adjacent to the western shoreline of the bay. Prior to CBADS, there were no

existing atmospheric monitoring stations in the southern Chesapeake Bay. Personnel from Old Dominion University and the Virginia Institute of Marine Sciences operated the samplers at this site.

III. METHODS

III.1 Organic Compounds in Air and Precipitation.

Atmospheric organic contaminants exist as vapors which adsorb to suspended particulate material. Because the washout efficiencies of these two phases differ, the partitioning behavior of the contaminants strongly influences their overall depositional fluxes. In an effort to assess the magnitude of these fluxes, we used samplers which collected vapor and particulate organic contaminants from the atmosphere and which isolated dissolved and particulate organic contaminants from precipitation. The sampling protocol will be discussed in the following section, along with a detailed description of sample extraction/fractionation methods, analyte analysis and quality assurance efforts made.

III.1.1 Sampling.

III.1.1.1 Air Sampling. A high-volume air sampler (General Metals Works, Cleves, OH) was deployed to collect bi-weekly ambient air samples. This sampler operationally isolates the vapor and aerosol phases of atmospheric contaminants by successively drawing air through a 20.3 x 25.4 cm glass fiber filter (Schleicher & Schuell #25) to collect aerosols and a polyurethane foam plug (8.5 cm x 10 cm) to collect vapors (Bidleman and Foreman, 1987 and references cited within). This type of sampler has been used extensively over the past decade for remote atmospheric sampling of organic contaminants (Atlas *et al.*, 1981, Eisenreich *et al.*, 1981, Bidleman *et al.*, 1988, McVeety and Hites, 1988, Baker and Eisenreich, 1990). The glass fiber filters utilized in this study are composed of 100% borosilicate glass fibers, arranged in layers that entrap particles. The mean pore diameter is 2.9 μm. The filters are ~ 95% free of organic material and offer low background levels of contaminants to samples (Grosjean, 1983). The filtration efficiencies of several brands of glass fiber filters have been measured to be > 99.1% (John and Reischl, 1978). Using a Berner low pressure impactor downstream of our glass fiber filter, we observed no breakthrough of particles >0.04 μm. The polyurethane foam is an efficient adsorbent of hydrophobic organic contaminants and has been used extensively in remote environments such as the Arctic (Bidleman *et al.*, 1989), the Great Lakes (Baker and Eisenreich, 1990), the western North Atlantic Ocean and the Adirondack Mountains (Knap and Binkley, 1991). The foam has a density of ~ 0.022 $g \cdot cm^{-3}$ and its open structure allows air to flow through easily, permitting large volumes of air to be sampled readily (Pankow, 1989).

Two potential sampling artifacts can occur with this type of air sampling. First, the measured particulate concentrations of hydrophobic organic contaminants may be overestimated due to the adsorption of low molecular weight vapor phase compounds onto the filter surface during sample collection (Cotham and Bidleman, 1992). Second, evaporative losses of adsorbed contaminants may lead to an underestimation of the filter-retained material. In effort to assess the extent of adsorption, a routine back-up filter was deployed with each sample (Ligocki, 1985b). In this study, low molecular weight polycyclic aromatic hydrocarbons (*e.g.*, phenanthrene, fluorene) were occasionally detected on back-up filters. In five air samples, average phenanthrene concentrations on the back-up filter were 19% of those measured on the front filter. Back-up filter concentrations for fluorene, anthracene and fluoranthene were similar. Because the back-up contaminant concentrations were low relative to the front filter concentrations for those preliminary samples, we did not correct the remaining front filter data for vapor adsorption. Evaporative losses occur due to the gas phase concentration differential between the surface of the filter cake and the ambient air at the sampler inlet. This concentration gradient may result from

a) changes in vapor phase organic contaminant concentrations during the collection period, b) the pressure drop associated with the air flow across the filter and c) increases in ambient temperature. However, Zhang and McMurry (1991) have published sampling efficiency curves for air samplers with pressure drops equal to 10 Pa which suggest evaporative losses due to pressure drops are $\leq$ 10%. To minimize losses resulting from temperature changes, samples in this study were generally collected begining in late afternoon and continuing through the night.

Air sampling times ranged from 12-16 hours with flow rates between 0.5-0.8 $m^3 \cdot min.^{-1}$ Some samples were collected for longer periods (16-24 hours), particularly those in the winter seasons. Flow rates were estimated for each sample from the measured pressure drop across the sampling train. The flow rate (m^3/min.) is proportional to the square root of the pressure drop as measured with a manometer (inches of water). The pressure drop was measured in the field at the beginning and end of each the sample period and an average flow rate was calculated using a factory-supplied calibration curve. A flow controller installed in the sampling train maintained a constant sampling rate independent of the amount of aerosols collected. The door of the sampler house was kept ajar during sampling to allow for venting of pump exhaust and a peaked lid above the sampler house repelled birds and prevented precipitation and very large (> 100 μm) particles from entering the sampler.

Ambient samples were collected bi-weekly, concurrently with the rain sampling strategy. An air sample was collected on the day the precipitation sampler was serviced (generally every other Tuesday). Prior to sampling, the glass fiber filters were individually wrapped in aluminum foil and ashed at 450°C for 24 hours. The polyurethane foam plugs were cleaned via 24-hour extractions with petroleum ether. The extracted plugs were dried in a vacuum desiccator to remove any remaining solvent, wrapped in aluminum foil and, along with the glass fiber filters, stored in the laboratory until used. The sampling train was loaded in the laboratory with two glass fiber filters and one foam plug, covered with aluminum foil and transported to the site. After sampling, the entire train was brought back to the laboratory, the filters and plug were removed with stainless steel forceps, and then wrapped in foil and stored at 4°C in the dark until analysis. Blank filters and foam plugs were routinely placed in the field to determine if either matrix accumulated analytes during the sampling period. Appendix A.1.8 lists the volume of air collected and other field notes for each sample.

III.1.1.2 Precipitation Sampling. For the assessment of low level organic contaminants in precipitation, a modified, wet-only collector was developed to a) collect large volumes of precipitation and b) to operationally isolate the particulate and dissolved fractions of the contaminants during a precipitation event. The collection area is a 1 m^2 stainless steel funnel which is kept closed during dry periods by a 1 m^2 aluminum lid tightly sealed over the top flange of the funnel. At the onset of a precipitation event, a moisture sensor activates a Campbell Scientific CR-10 data module, which in turn energizes a pressurized pneumatic system to open the lid. Collected precipitation is channeled down the funnel, filtered through a glass fiber filter (142 mm diameter, Schleicher & Schuell #25) and passed through a stainless steel column (2.5 cm x 30 cm) which contains a slurry (250 ml, ~ 80 g dry weight) of XAD-2 macroreticular resin (Amberlite, Rohm and Haas, Philadelphia, PA). The XAD-2 resin isolates dissolved organic contaminants from the precipitation. A peristaltic pump prevents rainwater from accumulating in the funnel and assures a constant flow rate through the resin column at 200 ml/min. Liquid level sensors control the pump to ensure that the filter and resin remain wet, minimizing any sampling artifacts caused by volatilization of contaminants from a dry filter or drying of the resin. Contamination of the sample could result if the resin beads cracked or split open as a result of drying.

Precipitation samples were integrated over 14 days and changed every other Tuesday. Resin columns were packed in the laboratory and transferred to the field capped with stainless steel fittings. The XAD-2 resin was precleaned in the laboratory by sequential 24-hour extractions with solvents in this

order: methanol, acetone, hexane, dichloromethane, hexane, acetone and methanol, then rinsed with deionized water and stored in a 4L amber glass bottle as an aqueous slurry. All solvents were pesticide residue grade (J. T. Baker Co.). The glass fiber filters were pre-cut and ashed at 450°C for 4 hours before sampling and were transported to the field wrapped in aluminum foil and sealed in a plastic bag.

Upon arrival at the site, an immediate check was made to ensure the sampler was functioning by wetting the moisture sensor with tap water. A portable computer was then connected to the CR-10 module to download the sensor data for the 14-day period. The resin column and the glass fiber filter were then removed from the sampler. The filter was removed from the filter plate with stainless steel forceps, folded in half and then wrapped in clean aluminum foil and labeled. The stainless steel funnel was then scrubbed with pre-cleaned (solvent extraction, 24 hours, acetone:hexane, 50:50) glass wool and deionized water in order to remove any adhering particles that were not effectively washed down the sampling train during the precipitation event. Because the funnel remains "sealed" during dry periods, particulate matter in the funnel originated from the atmosphere during precipitation events. The funnel rinse, consisting of the wetted glass wool, was wrapped in foil, labeled, put into a plastic bag and transported to the laboratory. The funnel rinse was analyzed as a separated sample to measure the contribution of the funnel-retained particles to the total measured contaminant concentrations.

After the glass wool cleaning, the funnel was thoroughly rinsed with deionized water, methanol, dichloromethane, and deionized water again to insure that the funnel surface and sampling train were clean. The lid was then closed and a new filter and resin column were put in place. A small volume of deionized water was then rinsed down the sampling train to make sure the water level was above the liquid level sensors. The volume of precipitation collected in the reservoir was measured, recorded and then discarded. The CR-10 data module was then reset and the system was ready for a new sampling period. Before leaving the site, the moisture sensor was activated again to insure the sampler was functioning and that the lid was closing properly. All samples were stored in the laboratory in the dark either in the refrigerator (resin samples) or freezer (rain filters, air filters and air vapor samples) until analyzed. The resin samples were removed from the stainless steel column and stored in glass jars with Teflon-lined lids. All filters and foam plugs were stored wrapped in aluminum foil.

III.1.2 Analytical Procedures

III.1.2.1 Sample Extraction. All samples were analyzed for 14 polycyclic aromatic hydrocarbons (PAHs) and 74 polychlorinated biphenyls (PCBs) (Table III.1.1). Target PAHs are listed as EPA priority pollutants. These compounds were chosen because their molecular weights, vapor pressures, and aqueous solubilities span a wide range and thus are expected to demonstrate variable atmospheric deposition patterns. Resin samples were extracted for 24 hours with 1:1 acetone:hexane. Filter samples were sequentially extracted for 24 hours in methanol followed by dichloromethane. Vapor samples were extracted for 24 hours in petroleum ether. Resulting fractions of each matrix extraction were combined and the more polar solvent was removed by liquid-liquid partitioning into deionized water. The remaining non-polar fractions were then dried over anhydrous Na_2SO_4 (J. T. Baker Co.) and concentrated to <10 ml in a Kuderna-Danish (KD) apparatus. The dichloromethane fractions were exchanged for hexane during the evaporation process. The extracts were further concentrated to ~ 4 ml under a stream of chromatographic grade nitrogen, transferred from the KD apparatus to weighed amber vials, and a 10-25% subsample was reserved for PAH analysis. The remaining extract was concentrated to ~ 1 ml under nitrogen and further purified by fractionation on a 13 g magnesium aluminum silicate column (Florisil, 60 - 100 mesh, J. T. Baker Co.). The Florisil, partially deactivated with 1.25% deionized water, acts as a polar stationary phase to remove any polar interferences present in the extract such as lipids, phthalates, and some of the more polar pesticides. The non-polar PCBs are eluted through the column with 80 ml hexane. A second elution with 80 ml of a 10% (v/v) solution of

diethyl ether/hexane removes the retained polar organic compounds such as lindane (γ-hexachlorocyclohexane), o,p' and p,p'- DDT and dieldrin. A small Na_2SO_4 layer was placed on the Florisil column prior to elution to remove any traces of water present in the extract and to prevent further deactivation of the Florisil. All Florisil was cleaned by extracting with a 1:1 acetone/hexane solution for 24 hours and was activated at 550°C for a minimum of 4 hours prior to use. Following the Florisil separation, the fractions were concentrated to ~ 8 ml in a KD apparatus and further to 1 ml under nitrogen. The concentrated extracts were then transferred to amber autosampler vials, sealed with a Teflon-faced cap and stored at 4°C in the dark until analysis.

III.1.2.2 Quantification of Analytes. Concentrations of PCBs were determined by capillary gas chromatography and electron capture detection using a Hewlett-Packard 5890 gas chromatograph. Congeners that were not commercially produced in the Aroclor mixtures and hence, are not present in the environment (2,4,6 trichloro- and 2,2',3,4,4',5,6,6' octochlorobiphenyl, Ultra Scientific, North Kingstown, RI) were used as internal standards to quantify the individual congeners in each sample. Five nanograms of each internal standard was added to each sample prior to injection. The use of the internal standard method eliminates errors propagated by inconsistent sample injections and it is independent of the final extract volume (Swackhamer, 1987). A single calibration standard was used to generate response factors for each congener relative to the internal standards. The standard solution was a mixture of three Aroclor commercial mixtures (1232, 1248 and 1262) which were obtained from the EPA Repository for Toxic and Hazardous Materials, Research Triangle Park, NC. Following the procedure of Mullin (1985), a 610 ng/ml PCB solution was made in a 25:18:18 ratio for the three mixtures, respectively. Congeners were identified based on retention times and relative response factors and were calculated from calibration standards. The congener masses in the samples were then calculated and the corresponding concentrations were then calculated by dividing the mass in the sample by the sample volume in liters for precipitation or cubic meters for air. In instances where congeners could not be separated completely, their combined concentrations are reported. Total PCB concentrations were calculated as the sum of the 74 congeners.

The PAH subfraction was quantified with a Hewlett Packard 5890A GC coupled to a 5970 mass spectrometer. Five deuterated PAH internal standards (MSD Isotopes, Cambridge, MA; Supelco Separation Technologies, Bellefonte, PA) were combined as a mixture and used to calculate relative response factors for individual PAHs. Identification of individual PAHs was based on appropriate retention times, and were confirmed by the abundance of a secondary ion relative to the molecular ion. All 14 target PAHs were chromatographically resolved.

III.1.2.3. Detection Limits. In this study the limit of detection was based on the signal to noise ratio of the baseline adjacent to expected analyte peaks. Individual sample analytical detection limits were estimated by assuming a minimum quantifiable peak area of 400 for a GC/MSD chromatographic peak and a minimum peak area of 100 for a GC/ECD chromatographic peak. In general, for both the GC/ECD and the GC/MSD, the peak to peak noise ratio was ≥ 2. A comparison of the mean vapor concentrations of several PAHs and total PCBs to the mean analytical detection limit is shown in Table III.1.2. PAHs that are generally absent from the vapor phase approach the analytical detection limit such that the signal to noise ratio is closer to 1.

Precipitation sampler detection limits were calculated based on an annual precipitation of 75 cm (2.88 cm/14 days), resulting in an estimated 28.8 L sample collected during a two-week period. Dividing the analytical detection limit by this estimated volume gives field detection limits in ng/L. A comparison of sample field detection limits to the measured concentrations in a precipitation sample from early August in 1990 is shown in Figure III.1.1 for several PCB congeners. Congeners are plotted in order of decreasing vapor pressure. With the exception of congener 200, all matrices are generally well

above the field detection limits. The detection limit of congener 136 is close to the dissolved concentration. Congener 48 was not detected in the funnel sample. Generally the less volatile PCBs are not present in the dissolved phase and as a result the sample concentrations are close to the field detection limits. Congener 180 is an exception, in all three matrices its sample concentration is 10 times larger then the field detection limit.

III.1.3 Quality Assurance. In this study, quality assurance procedures specified the use of surrogate spikes to all matrices, laboratory blanks and field blanks. These procedures help insure that the data obtained is of acceptable quality and that they represent the true environmental signal.

III.1.3.1 Extraction Efficiencies. In effort to evaluate the efficiency of the analytical procedures, recoveries of several perdeuterated PAHs and non-commercially produced PCBs which were added to all samples as surrogates prior to extraction were measured. Surrogate compounds are listed in Table III.1.3, along with average recoveries for each compound in each sample matrix for the organic contaminant analysis of air and rain samples collected at the Elms and Haven Beach site. Because the same surrogates were not used in all matrices, analyte concentrations were not corrected for sample recoveries. Resulting recovery data for individual samples are listed in Appendix A1.6.

In addition to analytical evaluations, we began using field surrogates in June of 1991 to assess the efficiency of the sampling procedures. The efficiency of the XAD-2 resin was evaluated by adding known amounts of deuterated PAHs to the column prior to deployment in the field. Average recoveries of surrogates spiked onto two columns were: d-10 anthracene, 64% and d-10 pyrene, 65%. Volumes of rain for these samples ranged from 0 (no precipitation) to 66 L. Junk *et al.* (1974), using similar extraction procedures, reported an average recovery of a wide variety of organic compounds in water at the 10 - 100 μg/L level from XAD-2 resin of 78% $\pm$6%. Again, because field surrogates were not routinely used in every sample, no attempt was made to correct existing data for field recoveries. The retaining ability of the polyurethane foam was evaluated with the use of d-12 fluoranthene. Prior to sampling, a foam plug was spiked with 371 ng of d-12 fluoranthene in hexane. The solvent was then allowed to evaporate and the spiked plug was placed into the sampling train. The recovery for this compound was 55% (N = 1). Based on the laboratory recovery of 56% for d-12 benzo[b]fluoranthene in this single sample, we conclude that the 45% loss of the field surrogate occurred in the extraction and concentration steps rather then in the field during sampling. The retention of several PCB congeners on polyurethane foam has been investigated by an elution chromatography system such that recoveries of the total quantity of isomer applied to the spike plug ranged from 76-95% (Simon and Bidleman, 1979) and similar results are reported for several chlorinated pesticides (Turner and Glotfelty, 1977) in a similar sampling apparatus. Thus, we are confident that the polyurethane foam is an efficient trap for hydrophobic organic contaminant vapors.

III.1.3.2 Procedural and Field Blanks. Accurate trace chemical determinations require accurate knowledge of the analyte blanks. Procedural matrix blanks were extracted with each set of samples to characterize any laboratory sources of contamination and to determine if the pre-cleaned filters, resin, and PUF plugs contributed significant interferences to the sample extracts. Listed in Table III.1.4 are the mean masses of PAHs and PCBs found in our laboratory and field matrix blanks. In cases where a field blank was extracted with a group of samples, the laboratory blank was not used for quantification purposes. Instead the field blank was used, as was the case with most of the air vapor samples. The largest laboratory and field blank analyte in the polyurethane foam was phenanthrene and these values were generally only 13% of the sample analyte. All other PAHs in the foam blanks were insignificant compared to the samples. Total PCBs in the laboratory foam blank were about 18% of the average vapor phase concentration, assuming an average sample volume of 800 m^3.

In general, individual compounds in laboratory blanks were less than 20 to 33% of the analyte in the sample, and often were less. In instances where the blank mass was larger then 33% of the analyte mass in the sample, the analyte was reported as being "non-quantifiable," or "NQ." In those cases where the blank contributed less than 33% of the sample analyte, the blanks were not subtracted because the blank data were generally not normally distributed. All matrix laboratory and field blank data are listed in Appendices A1.1-A1.4. Because concentrations of PCBs and lower molecular weight PAHs (< 202 amu) on air and rain filters were very low, the relatively low laboratory blanks provide a substantial contribution (> 33%) to the total analyte present. The blank value of PCB congeners 8/5 on the XAD-2 resin was extremely large, and precluded any dissolved phase quantification. If congeners 8/5 was included in the total mass of dissolved sample analyte, its mass value would be at least 50% that of the total PCB mass for that sample. A coeluting chromatographic peak for congeners 8/5 was present in most of resin samples and as a result it could not be determined if the peak present in the sample chromatogram were indeed congeners 8/5.

III.2 Trace Elements in Aerosol

III.2.1 Sampling. Samples at each site were collected continuously for 168 hours at a flow rate of 10 $L \cdot m^{-1}$,on 2-μm-pore, 47-mm, Gelman "Teflo" filters using dichotomous samplers each equipped with a single stage impactor to remove particles > 10 μm in diameter. Each sampler was also equipped with a "dry" gas meter with cumulative display to determine sample volume. As shown in Tables II.2.1, sampling was initiated at the Wye and Elms sites on 5 June, 1990, and at Haven Beach on 23 November, 1990. Between 5 June, 1990, and 31 December, 1991, 77 of 82 possible aerosol samples were collected at Wye and 76 were collected at Elms. Between 23 November, 1990, and 31 December, 1991, 27 of 59 possible samples were collected at Haven Beach. Field blanks, five each at Wye and Elms, and three at Haven Beach, were collected by installing a second loaded sampling head beside the regular sampling head and exposing it for the duration of the weekly sampling period.

III.2.2 Analyses. The 180 samples, 15 laboratory blanks, and 13 field blanks were divided into two equal parts. Half of each filter was analyzed for more than 30 elements, including Al, As, Cr, Fe, Mn, S, Se, and Zn, by instrumental neutron activation analysis (INAA). Particles on the other half of the filters were dissolved and analyzed for Cu, Ni, and Pb, simultaneously by inductively-coupled plasma-atomic emission spectrometry (ICP-AE), and for Cd by graphite furnace atomic absorption spectrometry with Zeeman background correction (GFAA-Z).

To determine activities from the decay of short-lived nuclides, each filter portion was individually heat-sealed in precleaned polyethylene film and irradiated along with 1-mg Ni monitors for 10 minutes at a flux of approximately 4.5×10^{13} $n \cdot cm^{-2} \cdot s^{-1}$ in the NBS research reactor located at the National Institute for Standards and Technology (NIST) in Gaithersburg, MD. Spectra of γ-rays emitted by the samples were collected after decay periods of 5 and 15 minutes with intrinsic Ge γ-ray detectors with photopeak efficiencies ranging from 20 to 40% at an energy of 1332 kev. At least one week after the first irradiation, the samples were repackaged and irradiated a second time for 4-6 hours at a flux of approximately 1×10^{14} $n \cdot cm^{-2} \cdot s^{-1}$, and γ-ray spectra were collected for 4 and 12 hours after respective cooling periods of 3 days and 3-5 weeks. Analytical sensitivities were determined by irradiating prepared elemental standards and checked for accuracy against NIST Standard Reference Material (SRM) 1633A (Eastern Coal; Table III.2.1). Spectral data were reduced on a personal computer with the Ortec Ominigam analysis package, which corrected count rates for pulse pileup, decay during spectral acquisition, and decay after irradiation. Multielement standards for INAA were prepared from NIST-certified standard solutions, except for elements determined from short-lived activation products. Standards for Al, Br, Ca, Cl, In, K, Mn, Na, and V were made from high-purity laboratory reagents. Calibrations for S and Ti were made by irradiating accurately-weighed aliquots of the these elements in

their elemental forms. Forty-four of the samples, 6 laboratory blanks, and 4 field blanks were analyzed for long-lived neutron activation products using similar procedures at the MIT reactor.

Prior to analyses by the atomic spectroscopy techniques, particles adhering to the filter portions were dissolved in ultra-high purity ("Suprapur") acids under a clean-air fume hood located in a laboratory Class-100 clean room. Each filter portion was placed in a 50-ml Teflon-covered Teflon beaker and leached overnight at room temperature in a mixture of 6 ml of concentrated nitric and 0.1 ml 40% hydrofluoric acids. After leaching, the Teflon covers were removed and the samples were allowed to dry on a hot plate under low heat. The residues were then dissolved in a mixture of 4 ml concentrated HNO_3 and 0.2 ml 70% $HClO_4$, and refluxed for 24 hours, after which the filter was removed and rinsed with a few drops of concentrated HNO_3. The resulting clear solutions were allowed to dry on the hot plate at high heat, and then reconstituted with 2 drops of concentrated HNO_3. These were transferred to 15-ml polyethylene bottles, dried with an infrared lamp, and stored in the UMCP clean room. Prior to analysis, the residues were gravimetrically reconstituted by dissolution and dilution to a volume of 3 ml with 2% HNO_3. Dissolutions were performed in batches of 24 samples along with two aliquots of the (NIST) SRM No. 1648, "Urban Particulate Material."

The ICP-AE analyses required approximately 2.5 ml of each of the solutions, and the remaining 0.5-ml aliquots were used to determine Cd by GFAA-Z. For both ICP-AE and GFAA-Z analyses, prepared standard solutions were aspirated into the instrument (ICP-AE, Jobin-Yvon, model JY70-Plus; AA, Perkin Elmer, model 5000) at the beginning and end of each analysis session and at 1.5-h intervals. At least two aliquots of SRM-1648 were analyzed during each analysis period. The ICP-AE instrument provided for three replicate measurements of each sample and five replicate measurements for prepared standards and SRMs. To prevent Cd vapor from escaping the graphite furnace tube during heating, a 0.8 μl aliquot of a 0.1 μg/μl solution of $Pd(NO_3)_2$ in 6% citric acid was added to the graphite tube and dried at 2450°C before injecting each sample. If two replicate determinations differed by more than 5%, a third 15 μl aliquot of the sample was analyzed.

III.2.3 Quality Assurance. Analytical integrity was maintained through the use of prepared single and multi-elemental standards for atomic and nuclear techniques, respectively, and by frequent analyses of NIST-certified SRMs. Sensitivities for INAA were derived from spectra for more than 25 multielement standards and checked by analyzing more than 30 aliquots of SRM 1633A. As shown in Table III.2.1, results of the SRM analyses are in excellent agreement with NIST certified and published results. Results for additional elements determined by INAA are listed in Table A.2.2 in Appendix A.2. Overall quality of the resultant data is evaluated from estimates of the net uncertainty for each reported value, through comparisons with other data sets, and through the analysis and evaluation of laboratory and field blanks.

III.2.3.1 Estimation of Uncertainties. For INAA, the uncertainty in the measurement depends mainly on counting statistics, imprecision in positioning the samples and flux monitors (geometry errors), spectral background, and the sometimes substantial concentrations of the various elements in the blank filter substrates. The maximum relative uncertainty associated with geometry, 1.7%, was estimated from the coefficient of variation of the corrected count rates of 8 Ni flux monitors. We assume that a similar uncertainty applies to both flux monitors and standards, so that the total uncertainty in geometry is $\sqrt{2} \cdot 1.7\%$. An additional uncertainty of approximately 1.5% arises for some elements from corrections for coincidence error, when samples are counted very close to the detector. Uncertainties in prepared standards and detector intercalibrations are approximately 5%. For ICP-AE and GFAA-Z analyses, analytical uncertainties are derived from the deviation of replicate measurements, uncertainties in the calibration data, and uncertainties in the analyses of filter and reagent blanks. All of these uncertainties are reflected in the net reported uncertainty (S_{net}).

III.2.3.2 Evaluation of Uncertainties in Blank Corrections. The overall quality of the resultant data may be strongly influenced by the magnitude of corrections for filter and, where applicable, reagent blanks. Uncertainty arising from variations in the substrate blank concentrations are minimized when sample-to-blank (S:B) ratios are sufficiently large. In the first year's data set, sample-to-blank ratios for Al, As, Fe, Mn, S, Se, Zn, V, and Br, were quite large, averaging 54, 660, 70, 90, 360, 180, 70, 1400, and 270, respectively. For these elements filter blank corrections contributed less than 10% for from 96% to 100% of the concentration values determined (see Tables A2.3a and A2.5b in Appendix A.2). Uncertainties in the filter blank correction (S_b) often contributed significantly to S_{net} for Cd, Cr, Cu, Ni, and Pb, for which the S:B ratios typically averaged 9, 7, 6, 23, and 11, for samples collected at all three sites. The effect of S:B on the measurement uncertainty depends on the analytical precision, S_a (derived from uncertainties in counting statistics, geometry, and preparation of standards), and the uncertainty in the concentration of the various elements in the blank filters, S_b, as shown below:

$$S_{net,rel} = (n + 1)/(N - 1) \cdot [S_a^2 + S_b^2/(n - 1)]^{1/2} \quad (5)$$

where, n is the S:B ratio. In this work, S_as were <10% for all elements except S, for which S_a was typically 10 to 20%. As shown in Table III.2.2, S_b was often quite large for Cd, Cr, Cu, Ni, and Pb, and S_b contributed significantly to $S_{rel,\ net}$, which generally resulted in net uncertainties that were substantially larger than those obtained for the other elements. For these elements, the percentages of values for which $S_{rel,\ net}$ was <20%, were approximately 79, 36, 80, 75, and 59-84%, respectively, in the first year's data.

As shown in Table III.2.2, the average concentrations of the elements in laboratory blanks from 7/91 - 12/91 fell in the range of those determined in the blanks from 6/90 - 7/91. For example, S:B ratios for Al, As, Fe, Mn, S, Se, Zn, V, Br, and in addition, Cd at all three sites were as good as or better than their values for 6/90 - 7/91, exceeding 39, in every case. In addition, average S:B ratios for Cr and Cd, were markedly improved, *i.e.*, ≥40 and ≥14, respectively, at all three sites; however, average S:B ratios for Cu, Ni, and Pb at the three sites, were as small as 6, 9, and 3. The latter is attributed to the somewhat lower sample volumes recorded at Haven Beach as a result of difficulties with sampling pumps. Sampling systems that operated almost flawlessly at the other sites were plagued with problems attributable to the moist, marsh environment at Haven Beach. At Wye, $S_{rel,\ net}$ was <20% in at least 85% of all cases for all elements. At Elms, this was true for all elements except Cd, Cu, and Ni, for which the percentage of values with $S_{rel,\ net}$ >20% ranged from 50 to 60%, and for Pb, 36%. At Haven Beach, where fewer numbers of samples were successfully collected and often with lower sample volumes, uncertainties for Cd, Cu, and Pb were typically about 25%. Those for Ni and S were <20% in 63 and 68% of the cases, respectively.

III.2.3.3 Evaluation of Field Blanks. Concentrations of elements in laboratory and field blanks are compared in Table III.2.2. Results for the four field blanks collected at Wye from 6/90 - 7/91 fell within the range of those for laboratory blanks, as did most of the results for Elms. However, the metal fitting above the filter holder was left open during field blank collections at Elms and evidently caused contamination of Cd, Zn, V, Ni, and possibly Fe in some field blanks, but not samples. For example, Cd was elevated in EFB2, for which the measured mass was approximately two-fold larger than the maximum laboratory blank; Zn in EFB1 and EFB2, (5- and 50-fold larger); and V in EFB3, (6-fold larger). Despite the possibility of sporadic contamination for Cd and Zn at Elms, the good agreement between their average concentrations and those at Wye suggests that the Elms data set was not widely affected.

Results for the two Haven Beach field blanks collected during 7/91 - 12/91 fell within the range of those for laboratory blanks for all elements except Cu and Zn in VFB1, for which the amounts observed exceeded their maximum laboratory blank concentrations by 3.5- and 8.5-fold (Table III.2.2).

The value for Zn in VFB1 is equivalent to an atmospheric concentration of 2.3 ng/m^3, which is at most about 20% of the average concentration observed for this element. The value for Cu corresponds to about 30% of its average atmospheric concentration at Haven Beach. As discussed below, plots of concentration vs. time for Haven Beach data occasionally show large excursions for Zn and Ni, that were not observed at the other sites. In addition, atmospheric concentrations for Zn, Ni, and Cu were substantially greater at Haven Beach than at Wye or Elms. Bay salinity is substantially elevated in the southern Bay, and the marsh location provided an especially wet and corrosive environment. The site is surrounded by a galvanized chain-link fence and the sampler is mounted on a galvanized metal tower. In addition, corrosion was observed inside one of the "quick disconnect" fittings installed at the top of the sampling head at Haven Beach. We conclude, therefore, that sporadic field contamination may have occurred at this site for Zn and, possibly, for Ni and Cu as well.

Concentrations of elements in field blanks collected from 7/91 - 12/91 were similar to their corresponding laboratory blanks, except for Cd, Zn, and Fe, for which the amounts observed exceeded their maximum laboratory blank concentrations by 4.9-, 2.9-, and 7.4-fold in at least one of the field blanks. Contamination by Fe at the worst field blank concentration is insignificant. Contamination by Zn at the indicated level would have generally resulted in a bias of about 15%; and by more than 30% at the lower values (5.05 ng/m^3) determined at Haven Beach. Contamination by Cd at the indicated level would amount to an average bias of about 30%. However, the effect of sporadic contamination is probably much less than this.

III.3 Trace Elements in Precipitation

III.3.1 Sampling. Weekly-integrated samples were collected every Tuesday, coincident with ongoing NADP (Wye), State of Maryland (Elms) and ODU CBADS (Haven Beach) acid rain/major ions precipitation sampling. Trace element "clean" protocols developed by Tramontano *et al.* (1987) and modified by Scudlark *et al.* (1992) were followed by the on-site operators (see Appendix A.3). At the Wye site, due to the lack of an available clean bench, only steps 1-6 of the collection procedure were conducted on site. The sample buckets with lids were sealed in plastic bags and frozen in a trace metals-dedicated freezer on site pending retrieval and processing at the University of Delaware laboratory. At the Elms site, all sample processing was conducted at the Chesapeake Biological Laboratory under a Class 100 clean bench. Site supplies (acid-cleaned collection buckets and bottles, ultra-high purity acid, disposable gloves, etc.) were provided to the site by the laboratory at the University of Delaware. At Haven Beach, the samples were retrieved by Old Dominion University personnel, sealed in plastic bags and transported to the laboratory in Norfolk, VA for processing (in a class 100 clean laboratory) and analyses. All supplies (trace metal and major ion) for the Haven Beach site were provided by the lab at Old Dominion.

Precipitation was sampled using a commercially available, automated, wet-only collector which was specially modified for trace metals sampling (Aerochem Metrics, Inc., Bushnell, FL). Details of collection, sample processing and analysis can be found in Tramontano *et al.* (1987) and Scudlark *et al.* (1992). Briefly, this involves collection in an acid-washed clear HDPE bucket, acidification with ultra-high purity HCl (to 0.4% v/v), followed by partitioning after a 24-hour desorption period into acid-washed LDPE (or HDPE at Haven Beach) sample bottles. Samples were stored frozen until analysis. Specific sample collection protocols employed by the CBADS operators are provided in Appendix A.3.

Sampling was initiated at the Wye site on 17 April 1990, and at the Elms site on 5 June 1990, and at Haven Beach on 20 November 1990 (Table II.2.1). However, due to a persistent sampler malfunction, for practical purposes the data record at the Wye site did not commence until 5 July 1990. The Haven Beach trace metal record begins on 4 December 1990 due to insufficient precipitation for

analysis. This report covers all sampling through 31 December 1991. At the Wye site, the 18 month record yielded 64 precipitation samples, 12 field blanks (weekly samples with no measurable precipitation) and 3 samples with insufficient volume to analyze. Collected during the 19 months of sampling at the Elms site were 65 precipitation samples, 13 field blanks and 4 samples not analyzed for various reasons (3 insufficient sample volume, 1 operator error). Sampling at Haven Beach for 13 months resulted in 40 precipitation samples, 8 field blanks, and 6 weeks insufficient volume for analysis.

The recorded precipitation amount averaged 7.7 cm/month at the Wye site (which equals 92 cm/year), 9.3 cm/month at the Elms site (112 cm/yr) and 9.4 cm/month at Haven Beach (113 cm/yr). The 12-month total precipitation at Elms was more than 10% higher than the long term annual average for this site, while the total at Wye was slightly below the average of the past 7 years [M. Newell, personal communication]. The yearly precipitation total at Haven Beach agrees well with the 50 year average of 109 $\pm$ 14 cm/yr for Virginia (Historical Climatological Series, 1983).

III.3.2 Analyses. To remove trace element contamination introduced *via* manufacture and/or prior use, all plasticware (collection buckets and sample bottles) were rigorously cleaned. This cleaning involved successive leaching in acids of varying composition and strength (see Appendix A.3). Ultra-pure ASTM Type I (18 megohm/cm) rinse water (Millipore Milli-Q) was used for all sample processing and cleaning (subsequently referred to as Q-H_2O). Ultra-pure double quartz-redistilled HC1 (Qz-HC1) was used for sample acidification, analysis and processing which included a final "polishing" leach in the cleaning procedure. Analytical standards were prepared gravimetrically from certified standards, which were prepared in turn from pure metal dissolution (SPEX Industries, Inc.). All other reagents were of at least ACS quality. Every sample was carefully processed under a class 100 clean bench, in a dedicated clean room.

At the University of Delaware, precipitation samples were analyzed for Al, Cd, Cu, Cr, Fe, Mn, Ni, Pb, and Zn using a Perkin Elmer 1100-B Atomic Absorption Spectrophotometer, equipped with a 700 HGA graphite furnace (GFAA). This instrument was also equipped with deuterium background correction, and a L'vov platform is utilized to minimize matrix (salt) suppression by delaying atomization. For Al analysis, due to acidification with HCl, the char/ash step is limited to 170°C to prevent volatilization of $AlCl_3$ (b.p. 185°C). Citric acid was used as a matrix modifier for Al and Fe to increase analytical sensitivity. The standard analyte injection was 60 μl for all elements except for Zn (10 μl). Multiple injections were used for Cd, Cr, Ni and Pb, increasing the volume of analyte to 120-180 μl and thus augmenting the sensitivity 2-3 times. GFAA calibration curves included an analytical blank and at least three standards. The accuracy of the calibration curve was confirmed by an EPA or NIST reference standard (refer to Section III.3.3., Quality Assurance). Replicate samples were run on separate days to verify true analytical reproducibility (which included but was not limited to instrument reproducibility). Reproducibility of less than 10% variation was deemed acceptable.

At Old Dominion University, precipitation samples from the Haven Beach site were analyzed for Al, Cd, Cu, Fe, Mn, Pb, and Zn using a Perkin Elmer 4000 Atomic Absorption Spectrometer equipped with a HGA 400 graphite furnace and AS 40 autosampler. A L'vov platform was used in the graphite atomizer to minimize matrix suppression and deuterium background correction was employed to correct for non-atomic absorption. For all elements except Al, an analyte volume of 20 μL was used. The determination of Al was modified to include the addition of citric acid as a matrix modifier to increase analytical sensitivity. However, this necessitated the reduction of the analyte volume to 10μL. The GFAAS system at ODU was calibrated using an analytical blank and at least three standards. Additionally, the standard additions method was used on one sample every 15 samples to verify the calibration curve. Accuracy was confirmed using the analysis of a standard reference solution (see Section III.3.3) for every 15 samples. Each sample was split into two aliquots, with triplicate analyses

of each.

The trace elements As and Se were present in precipitation at concentrations significantly lower than the detection limits of commercially available hydride/AA systems. Accurate quantification of these elements required the application of non-traditional analytical methods (Cutter, 1986; Cutter *et al.*, 1991). Methods for both As and Se involve hydride generation, preconcentration by cryogenic trapping and subsequent volatilization. The As hydride was determined using gas chromatography-photoionization detection, while the Se hydride was determined with an air/hydrogen quartz burner fitted to an atomic absorption spectrometer. Larger analytical volume requirements limit metalloid analysis to precipitation samples greater than 200 mls. (*ca.* 0.3 cm precipitation). Standard curves for the metalloid analyses included a blank and at least four standards. Large volume events (about 30% of all analyses) were analyzed by the method of standard additions. Samples were run at least in triplicate and 5-10% of the samples were replicated on a second day to establish reproducibility. The calibration curve was verified utilizing certified reference solutions (see Section III.3.3., Quality Assurance). At ODU the standard additions method was used for daily calibrations, and reagent blanks and samples were all analyzed in triplicate. In addition, 5% of the samples were re-analyzed on a second day to evaluate reproducibility. A standard reference solution was analyzed every 15 samples. Employing the above methodology, we conservatively estimate our analytical detection limits for all of the elements determined (D.L. =3X std. deviation of analytical blank) and are cited in Table III.3.1.

III.3.3 Quality Assurance Program. Recent reviews of the historical data on the concentration of trace elements in precipitation (Galloway *et al.*, 1982; Barrie *et al.*, 1987) cast considerable doubt on the reliability of previously reported values or the efficiency of the collection and analysis techniques utilized. In many of these studies, it was apparent that the authors failed to observe proper sampling and handling precautions, resulting in either gross contamination, or conversely, irreversible adsorptive losses of certain elements to container walls. Based on more than 15 years of experience in precipitation sampling and analysis, it was our conviction that strict adherence to a rigorous quality assurance program was essential to establish and maintain data accuracy.

Our QA program encompassed all components of this study, from the initial site selection to final data validation. Essential elements of our QA program were:

a) conducting and evaluating operational blanks on a regular basis,
b) use of externally-certified analytical reference solutions,
c) intra-laboratory analytical comparisons using redundant analytical methods (GFAA and ICP-AE),
d) inter-laboratory analytical comparisons,
e) cross-checks on collection efficiency.

III.3.3.1 Operational Blanks. Most contamination associated with accurately quantifying the trace elements in precipitation is associated with field deployment and sampling (see Figure III.3.3). Thus, conducting and evaluating operational blanks on a regular basis was the most critical component in our QA Program.

Three types of additive, diagnostic operative blanks were routinely conducted: a Field Blank, Laboratory Blank, and Process Blank. Data from these blanks were interpreted both quantitatively, to accurately determine the background trace element contribution from materials and methods, and qualitatively to identify and remedy any source of severe contamination.

The Process Blank was 500 mL of Q-H_2O in a sample storage bottle, to which was been added

2.0 mL of Qz-HCl (*i.e.*, 0.4% v/v, identical ratio as samples). The Process Blank was a measure of the trace element contribution from the water, acid, leaching from the storage bottle and analytical procedures. The Laboratory Blank was 500 mL of Q-H_2O poured into a clean bucket under a clean bench, acidified, and processed as a precipitation sample. The Laboratory Blank gauges trace element input from all sources included the Process Blank, as well as metal leached from the collector bucket or contributed from airborne dust during the additional steps. The Field Blank was conducted identically to the Laboratory Blank, except for use of a bucket which was previously deployed in the collector for a weekly interval without rain. In addition to the sources included in the Laboratory Blank, the Field Blank will indicate contamination in the field from the input of fugitive dust to the sample bucket during transport, deployment, and recovery. Usually, the entire suite of blanks were done with every Field Blank, however, the Laboratory Blank and Process Blank were run at least quarterly, or if there was a significant change in methods, reagents (*e.g.* new batch of acid) or personnel (new or substitute operator). Because the Wye samples were processed at Lewes, the Wye Laboratory Blank and Process Blank were conducted at Lewes as well.

The Field Blank provided the most comprehensive representation of contamination during actual sample collection and processing. As an assessment of site suitability and operator proficiency, we compared the absolute Field Blank contributions at the three CBADS sites with those measured at our Lewes, DE site using identical protocols (Figure III.3.1).

At Lewes, sampling with a more experienced operator and with access to clean room facilities for sample processing, the blank levels were consistently lower. The Field Blank levels at the three CBADS sites were comparable, and do not indicate any severe contamination problem (Figure II.3.2). Noteworthy were the somewhat lower blank levels of the crustal tracers Al and Fe at the Wye site. Initial concerns existed about the potential for high soil resuspension and potential contamination associated with farming practices on the grounds of the agricultural research station where the Wye site is located. The Field Blank concentrations for As and Se at both sites were consistently below our instrumental detection limits, and were not presented graphically.

A comparison of the Laboratory Blanks with Field Blanks at the Wye and Elms sites (Figure III.3.3) revealed that almost all of the blank contribution was associated with field deployment. This included the inadvertent capture of fugitive dust during bucket deployment/recovery, as well as aeolian input associated with high winds during non-precipitating periods. For the most part, materials and reagents provided a consistently minor contribution to the blank levels.

III.3.3.2 Reference Solutions. Externally-certified reference samples were regularly included in analytical sessions only to verify the accuracy of the calibration curve. The results of these quality assurance checks are included in Table III.3.2.

III.3.3.3 Intra-Laboratory Analytical Comparisons. To verify the accuracy of the GFAA analyses, selected samples were analyzed by Inductively-Coupled Plasma Atomic Emission Spectroscopy (ICP-AE) using an Instruments SA/Jobin-Yvon-70 Plus ICP. For Al, Fe, Mn and Zn, low instrumental detection limits coupled with comparatively high precipitation concentrations allowed for cross-checking determinations by both methods without preconcentration (Jickells *et al.*, 1992).

III.3.3.4 Precipitation Collection Efficiency. The accuracy of the wet deposition calculation depends equally on the accuracy of trace element concentrations as well as the corresponding precipitation amount. Precipitation amount at the Wye and Elms sites were determined gravimetrically using a Belfort continuously-recording rain gauge, with an approximate resolution of 0.01" precipitation. Because of repeated malfunction with the tipping bucket rain gauge at the Haven Beach site, the collected

precipitation volume was used as a measure of the incident precipitation for internal consistence. This aspect is examined further in the following discussion.

To verify the accuracy of the Belfort precipitation gauge and to establish the collection efficiency of the Aerochemetric collector, the gauge reading was compared to the precipitation volume collected (for each of the three sites). This comparison (Figure III.3.4) revealed generally good agreement between the predicted and actual precipitation amount. In about 10% of the cases, however, the precipitation gauge reading was found to be inconsistent with the sample volume collected. In these cases, the larger of the two values was employed for deposition calculations. Overall collection efficiency of the ACM collector was determined to be >95% at both sites, which included samples not analyzable due to insufficient volume, collector malfunction and operator error.

III.4 Major Ions in Precipitation. The major anions (Cl^-, NO^{-3}, and SO_4^{-2}) were determined in precipitation samples collected at the Haven Beach site by David Burdige at Old Dominion University in Norfolk, VA *via* ion chromatography and conductivity detection. The system was calibrated with analytical blanks and five standards. The calibration was verified via the analysis of NIST Simulated Rainwater (SRM 2694a). The major cations (Na^+, K^+, Ca^{+2}, and Mg^{+2}) were determined in precipitation samples collected the Haven Beach site at the University of Delaware utilizing an Inductively Coupled Plasma-Atomic Emission Spectrophotometer that was calibrated with analytical blanks an five standards. This calibration was also verified with NIST Simulated Rainwater. All major ion samples and blanks were analyzed in triplicate. Samples from Haven Beach were analyzed for pH immediately upon return to the Old Dominion University lab using a pH meter equipped with a liquid junction electrode. The pH meter was calibrated using NIST buffers and NIST Simulated Rainwater was analyzed to verify this calibration. For the Wye and Elms sites, data for major ions in precipitation (those listed above) were provided through other co-located studies (Wye: NADP; Elms, MD MDE).

IV. RESULTS

IV.1 Organic Contaminants

IV.1.1 Spatial and Temporal Variations in Atmospheric Concentrations. Concentrations of polycyclic aromatic hydrocarbons and polychlorinated biphenyl homologs in air samples collected at the Elms and Haven Beach sites are shown Figures VI.1.1 through V.1.22 and summarized in Table IV.1.1. Average total (vapor + aerosol-bound) PAH concentrations range from 34 (dibenz[*a,h*]anthracene) to 1780 (phenanthrene) ng/m^3 at Elms and from 19 (dibenz[*a,h*]anthracene) to 3507 (phenanthrene) ng/m^3 at Haven Beach. Not surprisingly, the more volatile PAHs are present in higher concentration in the atmosphere, with phenanthrene having the highest inventories at both sites. PAH concentrations in the air over the Chesapeake Bay are higher than those over other more remote water bodies (*e.g.*, Lake Superior, Mediterranean Sea), and are similar in magnitude to those over the Baltic Sea (Table IV.1.2). PAH levels measured in urban areas (*e.g.*, Baltimore, Portland, Denver, Stockholm) are ten to 100 times greater than those measured at the rural CBADS sites. This is generally due to washout and atmospheric mixing processes, which decrease contaminant concentrations in the atmosphere during transport from urban areas. In addition, decomposition of PAHs *via* photo-oxidation in the atmosphere is also suspected to reduce levels reaching non-urban areas (Korfmacher *et al.*, 1980).

Concentrations of PAHs in the atmosphere at both the Elms and Haven Beach sites varied considerably with time (Figures VI.1.1 through V.1.22), with relative standard deviations typically greater than 100% and ranges spanning 50-100 fold. Concentrations of higher molecular weight, less volatile PAHs such as indeno[*123-cd*]pyrene have the highest variability, perhaps due to their high affinity

for atmospheric particles. Such large variation in PAH concentrations is likely driven by several factors, including variations in local and regional emission strengths, variations in wind direction and local meteorology, and variations due to the cleansing of the atmosphere by precipitation immediately before some air samples were collected. Several of the higher molecular weight PAHs (*e.g.*, benzo[*g,h,i*]perylene, benzo[*a*]pyrene, benzo[*b*]fluroanthene) exhibit seasonal changes in air concentrations, with higher concentrations during the winter months. This may reflect the contribution of wood and fuel oil combustion for home heating in the local areas. Elevated atmospheric concentrations of many PAHs were measured during a six to eight-week span during summer of 1990 at the Elms site. This enrichment, which was also measured in the precipitation samples collected during that period, was not observed during the same months in 1991. The reason for this interannual variability is unclear, as there were no obvious changes in local land use or in meteorology.

The distribution of PAHs between the vapor and aerosol phases broadly follows the behavior predicted by the Junge-Pankow model (Junge 1977; Pankow 1987). PAHs more volatile than benz[*a*]anthracene exist predominately in the vapor phase while those less volatile than chrysene are aerosol-bound (Figures V.1.1 through V.1.22). Due to their intermediate vapor pressures, the vapor-aerosol distributions of chrysene and benz[*a*]anthracene are highly variable, often shifting from vapor- to aerosol-dominated between consecutive sampling periods (Figures V.1.6 and V.1.7). Although the vapor-aerosol distribution is predicted to vary with ambient temperature and the aerosol concentration and composition, the PAH distributions at Elms and Haven Beach show no distinct seasonal variations.

The mean annual PAH concentrations were compared between the Elms and Haven Beach sites to evaluate spatial variability. In order to make a direct comparison, mean values for calendar year 1991 were calculated for both sites (Table IV.1.1). Mean annual concentrations at Haven Beach are consistently higher than those determined at Elms for most PAHs, with the ratio of Haven Beach to Elms averages ranging from near one (anthracene, benz[*a*]anthracene, benzo[*b*]fluoranthene, benzo[*e*]pyrene) to as high as 2.5 for fluorene. The approximately double mean annual 1991 concentrations of fluorene and phenanthrene at Haven Beach may reflect local sources of these volatile PAHs in the southern Chesapeake Bay. Interestingly, when one uses the overall mean concentrations from Elms (including the elevated Summer, 1990 concentrations) to make the comparison, the PAH concentrations at the two sites are quite similar. This emphasizes the importance of obtaining consistent, long-term measurements in order to accurately assess possible spatial gradients in these highly time-variable parameters.

The concentration of total PCBs in the atmosphere averaged 214 and 298 pg/m^3 at the Elms and Haven Beach sites, respectively (Table IV.1.1). These concentrations are quite similar to those recently reported over southern Ontario (Hoff *et al.*, 1992), Lake Erie (McConnell, 1992) and Lake Baikal, Siberia (McConnell *et al.*, 1993), but are significantly lower than those over the northern Great Lakes (Swackhamer *et al.*, 1988; Baker and Eisenreich, 1990; Achman *et al.*, 1993; Hornbuckle *et al.*, 1993), the Adirondack Mountains and Bermuda (Knap and Binkley, 1991; Table IV.1.3). Total PCB concentrations are highly variable with time, ranging from 17 to 508 pg/m^3 at Elms and from 26 to 730 pg/m^3 at Haven Beach during the study period. PCB concentrations in the atmosphere are higher during the warmer summer months at both sites, consistent with the seasonal trends observed by Hoff *et al.* (1992) for many organochlorines in southern Ontario. These elevated concentrations in summer likely result from enhanced volatilization of PCBs from soils and surface waters, with subsequent reabsorption during colder seasons.

PCBs in the Chesapeake Bay atmosphere are dominated by the more volatile tri- and tetrachlorobiphenyl congeners. This distribution is remarkably close to that measured over southern Ontario (Hoff *et al.*, 1992), suggesting that PCBs have undergone significant geochemical transport and are fairly evenly distributed over continental scales (Leister and Baker, 1994a). Due to their relatively

high vapor pressures, PCB congeners exist predominately (*i.e.*, >99%) as vapors in the atmosphere over the Chesapeake Bay. Despite not being able to measure aerosol-bound PCBs directly, their concentrations can be estimated using the Junge-Pankow equation from the measured vapor concentration, the temperature-corrected subcooled liquid vapor pressures, the total particulate concentration in the atmosphere (Baker and Eisenreich, 1990; Leister and Baker, 1994a).

IV.1.2 Spatial and Temporal Variations in Precipitation Concentrations. Concentrations and speciation of polycyclic aromatic hydrocarbons in precipitation collected at the Elms and Haven Beach sites are shown in Figures IV.1.23 through IV.1.36 and summarized in Table IV.1.4. Volume-weighted mean concentrations (VWM = Σ[concentration x volume]/Σvolume) of PAHs range from 1.1 ng/L for dibenz[*a,h*]anthracene to 16.8 ng/L for pyrene at Elms and from 0.33 ng/L for dibenz[*a,h*]anthracene to 7.9 ng/L for phenanthrene at Haven Beach. Although the surrounding air was always enriched in the more volatile PAHs, precipitation contains relatively more of the less volatile, higher molecular weight PAHs, suggesting perhaps the role of particle scavenging in supplying HOCs to precipitation (Ligocki *et al.*, 1985b; Leister and Baker, 1994b,c). As with PAH levels in the air, concentration measured in precipitation varied greatly throughout the sampling period, with concentrations of individual PAHs ranging more than two orders of magnitude at both sites. In general, PAH concentrations in precipitation were greater during winter months relative to the summer, consistent with the observed seasonal trends in PAH inventories in the atmosphere. Higher PAH concentrations during winter months likely results both from increases in local emissions (*e.g.*, wood burning for residential heating) and from enhanced precipitation scavenging efficiencies at the lower ambient temperatures. Greatly elevated concentrations of PAHs in precipitation were observed in several samples collected during the Summer, 1990 at the Elms site, consistent with the higher concentrations measured in the atmosphere. As noted above, the cause of these elevated levels is uncertain.

PAHs in precipitation are distributed between the operationally-defined 'dissolved' and 'particulate' phases (Figures IV.1.23 through IV.1.36). As expected, the more soluble, lower molecular weight PAHs (*i.e.*, fluorene, phenanthrene, anthracene) are predominately dissolved while the more hydrophobic species are associated with particles in the precipitation. We observed considerable variability in PAH speciation, however, presumably reflecting differences in washout resulting from changes in meteorology and PAH speciation in the atmosphere. Leister and Baker (1994b,c) estimate that only less than five percent of PAHs in precipitation collected from the Elms site are thermodynamically dissolved, with approximately 30% associated with nonfilter-retained submicron particles.

Concentrations of total PCBs in precipitation averaged 1.6 ng/L at Elms (17 month volume weighted mean) and 1.12 ng/L at Haven Beach (Table IV.1.4, Figures IV.1.37 through IV.1.44). These concentrations are perhaps 50% lower than those measured during the mid-1980's in the Great Lakes region (Franz *et al.*, 1991; Murray and Andren, 1992), perhaps reflecting a general decline in PCB levels during the past decade. The observed temporal variability in total PCB concentrations in precipitation was less than that of PAHs, supporting the argument that PCBs are globally distributed and less influenced by local and regional sources. While there is some indication that PCB concentrations in precipitation increased during the summer months at Haven Beach (Figure IV.1.44), no such trend is apparent in the Elms data.

PCB congeners exist predominately in the 'dissolved' phase in precipitation collected at Elms and Haven Beach, as expected from their extremely high vapor/aerosol distributions in the atmosphere. Nonetheless, a significant portion of PCBs in precipitation are associated with particles that are retainable by a glass fiber filter, indicating that although only a very small fraction of atmospheric PCBs are associated with particles, the washout of those particles contributes to the wet depositional fluxes of PCBs. By comparing the measured dissolved and vapor-phase PCB concentrations, Leister and Baker

(1994b,c) determined that the precipitation is apparently supersaturated with PCB congeners relative to the surrounding atmosphere (*i.e.*, PCB concentrations in precipitation are higher than those supported by equilibrium partitioning of vapor-phase PCBs). They hypothesize that these enriched precipitation concentrations are due to PCBs associated with submicron colloidal particles in the precipitation which pass through the filter, resulting in an overestimation of the truly dissolved PCB concentration.

IV.1.3 Depositional Fluxes of Hydrophobic Organic Contaminants. Monthly wet depositional fluxes for each PAH and for total PCB and homolog groups were calculated as follows. Monthly volume-weighted mean concentrations were calculated by dividing the sum of the total mass of each chemical in all precipitation which fell during the month by the total volume of precipitation. In cases where the sampling period spanned a month's end, the precipitation gauge record was examined to partition the contaminant mass into each month. When calculating the monthly volume weighted mean concentrations, concentrations of compounds which were not detected were conservatively estimated to be equal to the analytical detection limit. The total volume of precipitation which fell during each month was determined using a Belfort gauge at Elms and from the weight of the trace metal precipitation sample at Haven Beach. Resulting monthly fluxes (ng/m^2-month) measured at the Elms and Haven Beach-sites are shown in Figure IV.1.45 through Figure IV.1.66. Annual wet depositional fluxes at each site were calculated as the sum of the twelve monthly fluxes (Table IV.1.5).

Not surprisingly, monthly wet fluxes of PAHs and PCBs are less variable than the concentrations measured in the semi-weekly precipitation samples. Interestingly, the higher PAH concentrations observed during the winter months do not necessarily result in higher wet fluxes during the winter, as the elevated concentrations are offset by lower amounts of precipitation during the winter. Total PCB wet fluxes are approximately twice as high during April and June than in the other months, due primarily to increased fluxes of tri- and tetrachlorobiphenyls. A similar increase was not seen at Elms, suggesting either localized sources of volatile PCBs or enhanced depositional processes in the southern bay during those months.

Dry aerosol depositional fluxes of PAHs and PCBs were calculated as follows. Due to the large uncertainty in dry aerosol deposition velocities, we only present average annual dry aerosol deposition fluxes for PAHs and PCBs. Arithmetic mean annual concentrations of aerosol-bound PAHs (ng/m^3) were multiplied by the non-crustal dry deposition velocity (0.49 cm/sec; 1.5 x 10^5 m/year) to estimate the annual dry aerosol flux at each site. These fluxes are only order of magnitude estimates and further refinements require a better understanding of the temporal variability in both the dry aerosol deposition velocity and the vapor-aerosol partitioning of the PAHs. Because PCB congeners were not consistently present in our aerosol samples above the analytical detection limit, their dry deposition fluxes were estimated by modeling the aerosol-bound concentrations. Using the empirical relationship between vapor-aerosol partitioning and ambient temperature determined by Foreman and Bidleman (1990) for PCBs in Denver, we estimated the aerosol-bound PCB concentration at our sites under typical winter and summer conditions. These t-PCB aerosol concentration estimates were then multiplied by the non-crustal dry aerosol deposition velocity in order to estimate winter and summer PCB dry fluxes, which were then added to generate an annual flux (μg/m^2/yr). This estimate of PCB dry aerosol deposition is highly uncertain.

It must be emphasized that CBADS did not address the issue of vapor exchange across the air-water interface. This exchange, including volatilization and gaseous absorption, has been shown to be quite substantial and temporally dynamic in other water bodies, including Lake Superior (Baker and Eisenreich, 1990), Green Bay, Lake Michigan (Achman *et al.*, 1993), and the lower Great Lakes (McConnell *et al.*, 1993). The overall direction and magnitude of volatilization and gaseous absorption of organic contaminants is a function of several parameters, namely the season (as driven by water

temperature) and the variability in the ambient air and water contaminant concentrations, which has been found to be quite large in the air in this study. Estimates of vapor exchange require coupled air and surface water sampling, which is beyond the scope of this study. Current efforts are underway to assess the magnitude and seasonality of gaseous exchange of organic contaminants in the Chesapeake Bay.

IV.1.4 Annual Loadings of Hydrophobic Organic Contaminants. Atmospheric loadings of HOCs to Chesapeake Bay are listed in Table IV.1.6. The loads were calculated by extrapolating the average measured wet fluxes and estimated dry fluxes from the Elms and Haven Beach data to the surface area of the Chesapeake Bay (1.15×10^{10} m^2). Since sampling at the Elms site began about six months eariler than at the Haven Beach site, a cumulative average and a calendar year 1991 average loading is calculated. Because of large uncertainties in estimating the transport of chemicals through the watershed into Chesapeake Bay and because our sampling locations may not be representative of the entire watershed, the magnitude of atmospheric deposition to the watershed is not estimated. Also, samples were consciously not collected within the urban environment. Therefore, the loadings presented in Table IV.1.6 reflect conservative values. The uncertainty of the annual loading is the extrapolated uncertainty in the dry flux to the total surface area of the Chesapeake Bay.

Individual PAH annual loadings to the surface of the Chesapeake Bay range from 19 $\pm$ 4 (anthracene) to 330 $\pm$ 86 (pyrene) kg/yr. Total PCB loadings are estimated to be 40 $\pm$ 9 kg/yr. It is interesting to compare the HOC loadings to point source loadings of similar compounds. Consider one 23 million gallons per day (MGD) wastewater treatment plant delivering total hydrocarbons to the bay at a concentration of 100 μg/L, resulting in a total loading of about 3200 kg/yr (Webber, 1983). PAHs are estimated to be 35% that of the total hydrocarbon detectable in wastewater (Webber, 1983), giving a PAH loading of 1120 kg/yr. The measured atmospheric loading of all 14 PAHs in this study comes to be 2100 kg/yr. This loading is about two times larger then that from the small, but significant, wastewater treatment facility. Another interesting comparison is to calculate the loading of an individual PAH from a major tributary such as the Susquehanna River, which has an average flow rate of 1100 m^3/sec. The VWM concentration of fluorene in precipitation was measured to be 2 ng/L, which is very close to the mean dissolved concentration of fluorene in Chesapeake Bay (1.5 ng/L; Baker and Ko, 1993). An annual loading of fluorene from the Susquehanna River tributary at 1.5 ng/L would be 52 kg/yr. From this study, the atmospheric loading is estimated to be 43 kg/yr. Hence, over a one year period, the atmosphere delivers fluorene to the Chesapeake Bay at the same rate as the Susquehanna River! Warner *et al.* (1992) estimated that fluorene is delivered from industrial discharges to the mid-section of the Baltimore Harbor at a rate of 3 kg/yr, a factor 20 times lower then what is delivered to the Chesapeake Bay *via* atmospheric deposition or from the Susquehanna River. These estimated comparisons demonstrate that the role the atmosphere plays in delivering contaminants to the Chesapeake Bay may be quite significant. Estimated dry loadings of HOCs from the atmosphere are about half of the total HOC loading, indicating that dry deposition of contaminant laden particles is a significant source of these compounds to the Chesapeake Bay. This is consistent with recent evidence. Measured dry fluxes of chlorinated dioxins and furans to Indianapolis, IN contribute at least 60% to the total depositional flux (Koester and Hites, 1992b).

Interestingly, although there were differences in the air and rain HOC concentrations between those measured at the mid-bay station and those measured at the Haven Beach site, the annual fluxes (wet and dry) for most HOCs are very close (Table IV.1.7). This indicates that the integrated atmospheric HOC fluxes measured at both sites are representative of the Chesapeake Bay (Maryland and Virginia) despite the spatial differences observed in the precipitation concentrations between samples. The relative homogeneity of the measured flux at both sites suggests that surface air above the bay is influenced by regional sources dispersed throughout the bay area and that the washout processes that remove contaminants from the atmosphere are very similar in air masses influencing the region.

IV.2 Aerosol Trace Elements

IV.2.1 Spatial and Temporal Variations in Atmospheric Concentrations. In this section, we present data on the spatial and temporal concentrations of selected elemental constituents (Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, S, Se, Zn) of aerosol particles and give preliminary estimates of their dry deposition fluxes to the Bay's surface waters. Concentrations of the various elements are plotted against Julian week in Figures IV.2.1 through IV.2.14 for all valid samples collected from 6/90 - 12/91. In general, concentrations rise and fall with source activity, precipitation, and meteorological and surface conditions. For elements carried on particles from anthropogenic sources, concentrations rise during periods of low winds and temperature inversions, wherein pollutants are trapped, and fall during windy periods and during periods of precipitation. The concentrations of elements associated with crustal material rise during dry windy periods and during earth disturbing activities, such as plowing and landscaping, and construction work. Based on Turekian and Wedepohl's compilation of average concentrations of elements in the earth's crust (Turekian and Wedepohl, 1961), more than 99% of the As, Cd, Pb, S, and Se, and >95% of the Cu, Ni, and Zn observed in aerosol particles in this study were of noncrustal, origin. Aluminum, Fe, and Mn have large (Al, 100%; Fe and Mn, each near 50%) crustal components and, on average, nearly 20% of the Cr is associated with crustal material. Some of the crustal material may be associated with coal, which cannot be distinguished from crustal material by elemental ratios.

As indicated in Figures IV.2.1-IV.2.14, concentration vs. time profiles of many of the anthropogenic elements are similar, especially those for Cr, Se, V, and Zn. Concentrations for nearly all of the elements of anthropogenic origin are elevated in August, September, and November, 1990 and in January and February, 1991. This behavior probably reflects a combination of increased emissions corresponding to peak air conditioning and heating periods, low precipitation scavenging and transport dynamics. Low concentrations observed in June, July, October, and April are consistent with elevated precipitation, as shown, for example, by Mn in Figure IV.2.8. Concentrations of particulate S are characteristically elevated during the summer months when more photochemical oxidants are available for the conversion of gaseous sulfur. Concentrations of crustal elements, Al, Fe, and Mn are elevated in the spring and summer months, which probably reflects agricultural and construction activities. This behavior is consistent with data reported for College Park, MD, in which average summertime concentrations for Al, Fe, and Mn reported by Kitto (1987) substantially exceeded those reported by McCarthy (1988) for winter months (see Table IV.2.2).

In the latter part of 1991, *i.e.,* in October, November, and December, there is a weak trend in the profiles of anthropogenic elements towards larger concentrations. This trend is most evident in the profiles of As, V, Br, and Se, and to a lessor extent, Zn, Ni, and possibly Cu, possibly reflecting increased fossil fuel use in the fall months. Concentrations of crustal elements, *e.g.*, Al, Fe, and Mn show the opposite trend, *i.e.*, their concentrations tend to decrease between summer and winter, presumably, for the reasons discussed above. Sulfur concentrations decrease markedly in the fall months. Profiles for elements with substantial crustal and noncrustal components show weaker trends. Various discrete events appear to be superimposed on the data for both crustal and noncrustal elements.

Cumulative and calendar year 1991 average concentrations of Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, S, Se, and Zn for samples collected at the three sites are listed in Table IV.2.1, along with their standard deviations, average uncertainties, numbers of values determined, and their minimum, and maximum values. The complete set of individual results are listed in Tables A2.6a through A2.8b, given in Appendix A.2. In cases where the measured concentration was near the instrumental detection limit (*i.e.*, from 6/90 - 7/91: 4 for Cr at Wye; and 4 for Cd, 3 for Cr, 7 for Cu, 2 for Ni, and 1 for Pb at Elms; 1 for Cd, Cr, and Ni, 2 for Cu and Pb, at Haven Beach; and, from 7/91 - 12/91: 1 for Cu, Pb,

and Zn, and 3 for S at Wye; 1 for Pb, 2 for Cu, and 3 for Ni at Elms; and 1 for As and Cu, 2 for Ni, 3 for Cd, 4 for Pb, and 6 for S at Haven Beach) the data were divided by two and included in the summary statistics in an attempt to minimize positive bias that would result from excluding small values. Relative uncertainties in the upper-limit-values transformed for this purpose were taken to be 100%. Air volumes determined for samples V4, V12, V16, and V27 are suspect, therefore, concentrations are not reported for these samples. We attribute abnormally high concentrations of Al, S, and V in W9 (6400 ± 380, $13{,}600 \pm 2000$, and 26.5 ± 2.2 $ng \cdot m^{-3}$,respectively) to local activities at Wye, and exclude these values from averages and flux calculations. Aluminum in sample W9 is 50-fold greater than the mean Al concentration computed without this value; including this value would nearly double the first year mean.

The data were screened for potentially contamnated samples as follows: A concentration value was considered to be an outlier if the following criteria were met: i) the ratio, r, of its concentration at Wye or Haven Beach to its corresponding concentration at Elms was:

$$r > (X + 3\sigma) \tag{7}$$

where X and σ were the average and standard deviation of the ratios for the full data set; and ii) its concentration, C, exceeded the average of concentrations for the full data set by 3-fold. Note, however, that the exclusion of valid data is possible. For example, the minimum Al concentration observed at Elms, 11.8 $ng \cdot m^{-3}$,was eliminated by the criteria even though airborne Al concentrations as low as 12 $ng \cdot m^{-3}$were observed by Han (1992) in Beltsville. Thus, there may be no valid reason to remove these data. Only a few outliers were identified by the first criterion, and except for Ni at Elms, and Ni and Zn at Haven Beach, the differences in averages for the full and reduced data set were less than approximately 10%. One value for Ni at Elms; all of the values for sample W12, and values for Al, Cd, and V in W9 at Wye, were identified as outliers by the criteria described above. Three to five outliers were identified by Wye/Elms ratios for Pb, S, V, Fe, and Mn; and, based on the first criterion, the remaining elements had fewer than 3. Five outliers were identified in the Haven Beach data for Cd; 4 for S; 3 for Fe, Se, and Mn; 2 for Zn, Cu, Ni, Pb, and As; and ≤ 1 for the remaining elements. In general, the Haven Beach data suffered from lower sample volumes resulting from pump failures and, possibly, from contamination by corrosion products.

As shown in Table IV.2.1, average concentrations determined at Wye and Elms are quite similar for most of the elements. Notable exceptions were average concentrations for Al, Fe, Cr, and Ni, which were from 17 to 26% larger at Wye; and V, for which the concentration at Elms was 24% greater than at Wye. Overall, 18-month average concentrations determined for the Wye and Elms sites differed by $\leq 5\%$ for As, Cr, Cu, Mn, Pb, and Zn; $< 10\%$ for Br, Cd, Fe, S, and Se; and $\leq 27\%$ for Al, Ni, and V. Average concentrations determined for the Wye and Haven Beach sites differed by $< 10\%$ for As, Cd, Cu, Mn, Pb, Se, and Zn; $< 20\%$ for Cr, Ni, and S; and approximatey 25% for Al, Fe, and V. Concentrations observed at Haven Beach were quite similar, however, fewer data are available and the averaging period is smaller due to the delayed start of sampling at this site.

The fact that the S concentrations at Wye often exceeded those at Elms, might reflect its proximity to urban plumes from Baltimore and Washington, DC, and local sources. The large spikes in Al at Elms might be attributable to traffic on the unpaved road at this site. Sulfur and V spikes suggest the influence of fuel-oil combustion sources, such as oil-fired power plants, or perhaps ship traffic. The relatively small differences in the median concentrations observed for the majority of the elements at the three sites suggest that these atmospheric pollutants have a strong regional contribution, or that their major sources, such as the Baltimore and Washington plumes, ubiquitous motor vehicle emissions, and

regionally dispersed sources tended to influence the two sites similarly during most of the week-long sampling periods.

Concentrations of airborne elements determined at the Bay sites may be compared with average concentrations determined at Beltsville and College Park, MD, and Lewes, DE, listed in Table IV.2.2. The Beltsville samples were collected in a large open grass-covered field surrounded by trees, several km from the nearest road or urban area in the Fall of 1990. The College Park samples were collected in an urban environment, during Summer months (1983 - 1985; Kitto, 1987) and in Winter months (1985 - 1986; McCarthy, 1988). The Lewes samples were collected in Cape Henlopen Park, a semi-remote rural coastal environment, during July, August, and September of 1989 (Han, 1992). Concentrations averages reported for Al, Cr, Cu, Fe, Mn, and Se are remarkably similar for the Beltsville and Lewes sites. Those for As, Br, S, and V are about 2-fold greater at Lewes than at Beltsville, possible reflecting the influence of ship traffic. Concentrations measured at the more urban College Park site are uniformly greater (generally by a factor of 2) than those reported for Beltsville. Average concentrations for As, Br, and Se in the Bay aerosol are similar to those measured in the more limited Beltsville data set. However, Bay values are about 2.5-fold less than the Beltsville averages for Al, Cr, Cu, Fe, Mn, and Zn. The Bay average concentration for S is nearly equal to the average of Summer and Winter concentrations reported for College Park.

IV.2.2 Estimation of Dry Deposition. The dry deposition fluxes of particulate-borne elements may be calculated for each sampling period as the product of the atmospheric concentration of each element and a deposition velocity (V_d) appropriate to water surfaces. In general, dry deposition rates over water are expected to be smaller than over land, where turbulence-inducing vegetation, terrain, and surface structures promote pollutant transport to the surface. Despite this, turbulence and deposition may be enhanced at the land-water boundary, where temperature differences create updrafts. Deposition velocities depend strongly on both particle diameter (D_p) and atmospheric stability. However, experimental measurements of V_d are few, contain large uncertainties, and are often reported without supporting meteorological data. Although various methods may be used to extrapolate limited V_d measurements to other meteorological conditions (for example, Dolske and Sievering, 1979), herein, we attempt to provide preliminary estimates of the annual fluxes using only the average annual concentrations.

Aerosol particles may be conveniently classified into crustal components, which comprise wind blown dust from natural and anthropogenic dust-making activities, and noncrustal components, which are typically derived from high-temperature combustion sources. Crustal components of the aerosol reside in larger particles, with mass median aerodynamic diameters (MMAD) typically <1 μm, whereas anthropogenic components reside in aerosol with MMADs typically ranging from 0.1 to >0.5 μm, depending on the proximity of major sources and the degree of atmospheric processing. At Deep Creek Lake, a rural recreational area in western Maryland, most of the mass for anthropogenic elements most often occurred in aerosol with modal aerodynamic diameters between 0.3 to 0.6 μm (Dodd *et al.* 1991). Mass median aerodynamic diameters often ranged from 2 to 3 μm for aged crustal aerosol and are typically 12-15 μm for urban crustal aerosol (Holsen *et al.*, 1992). As indicated by the work of Sievering *et al.* (1981) reported in Table IV.2.3, V_d s measured for elements with 50% crustal source (Fe and Mn) may be five or six fold greater than those measured for an element with predominately noncrustal source (Pb). In general, V_d is minimal for small particles (0.02 to 0.1 μm) and increases for larger particles, becoming equal to the gravitational settling velocity for particles with diameters ≥ 40 μm (4.8 cm/s for D_p of 40 μm).

The rate of pollutant transport to the Earth's surface increases inversely with atmospheric stability. Stable conditions exist when the air is warmer than the water and the wind speed, U, is low.

The atmosphere becomes more unstable as the temperature difference, ($dT = (T_{air} - T_{water})$), between the air and water decreases and as wind speed increases. The most unstable conditions exist when the water is warmer than the air and wind speeds are high. Under extremely stable conditions (dT, +8.5°C; and U, 3.8 ± 0.8 $m \cdot s^{-1}$), Sievering *et al.* (1981) reported V_ds of 0.13 $cm \cdot s^{-1}$ for Pb (noncrustal residence) and 0.55 to 0.65 $cm \cdot s^{-1}$ for Fe and Mn (elements with large crustal components). Larger V_ds are estimated from these data by Dolske and Sievering (1979) for less stable conditions. Monthly average wind speeds and temperature differentials derived for the Chesapeake Bay area from climatological compilations (see Table A.2.9) range from -3.3 to +0.83°C and 3.7 to 5.0 $m \cdot s^{-1}$, respectively, suggesting that Bay air is usually much less stable. For these conditions of average U and dT, Dolske and Sievering (1979) estimated V_ds of 0.47 and 0.72 $cm \cdot s^{-1}$.

Deposition velocity estimates from "box-model" calculations for phosphorous containing particles depositing on Lake Huron over a 6-month period (Delumyea and Petel, 1979) ranged from 0.01 to 1.8 $cm \cdot s^{-1}$ and averaged 0.57 ± 0.16 $cm \cdot s^{-1}$. The size distributions for phosphorous-containing particles were often bimodal, with concentrations peaking in particles with diameters between 0.3 and 0.5 μm, and 2.9 and >4.6 μm; suggesting "fine" and coarse components, as is the case for Fe and Mn, which have nearly equal noncrustal and crustal components. The fact that the average V_d reported for the Lake Huron study, (*i.e.*, 0.56 $cm \cdot s^{-1}$), was nearly identical to the values reported by Sievering *et al.* (1981) for Fe and Mn (0.65 and 0.55 $cm \cdot s^{-1}$), is problematical, as the latter should be minimum values, in accordance with the extremely stable conditions accompanying the Lake Michigan study. This demonstrates the difficulties in using these data for the Chesapeake Bay. Excluding Cd, for which V_ds appear to be inconsistently low, V_ds determined from a 12-day study in the North Sea using vaseline-coated plates (Dedeurwaerder *et al.*, 1983) averaged 0.26 ± 0.16 $cm \cdot s^{-1}$ for noncrustal elements in aerosol with MMAD ≤ 0.75 μm and, 1.18 ± 0.08 $cm \cdot s^{-1}$ for elements with both crustal and noncrustal components in aerosol with an MMAD of 1.2 μm. The data of Dedeurwaerder *et al.* (1983) are in logical agreement with those of Sievering *et al.* (1981) in that the mean V_d for their noncrustal elements, (0.26 $cm \cdot s^{-1}$), for a variety of stability conditions, is two-fold larger than the latter's value for Pb (*i.e.*, 0.13 $cm \cdot s^{-1}$) which was determined under extremely stable conditions.

Herein, we take the V_d of 0.26 $cm \cdot s^{-1}$ derived from the data of Dedeurwaerder *et al.* (1983) to apply to noncrustal components of the Chesapeake Bay aerosol, noting that the value applied by Dolske and Sievering (1979) to Lake Michigan during conditions appropriate to the Bay was substantially larger, *i.e.*, 0.72 $cm \cdot s^{-1}$. Combining the data of Dedeurwaerder *et al.* (1983) and Delumyea and Petel (1979) for elements with roughly equal crustal and noncrustal components we obtain an average of 0.84 $cm \cdot s^{-1}$, from which we infer a value of 1.4 $cm \cdot s^{-1}$ for totally crustal elements. To estimate atmospheric fluxes to the Chesapeake Bay, we determine the fraction of each element associated with crustal and noncrustal components and derive a weighted deposition velocity, V_d, accordingly. Annual fluxes, F_i (kg/yr), for each element, i, are calculated from

$$F_i = C_i \cdot V_{d'} \cdot 315 \qquad (9)$$

where, C_i is the annual average concentrations of element i ($ng \cdot m^{-3}$), F_i is in $\mu g \cdot m^{-2} \cdot yr$, and $V_{d'}$ in $cm \cdot s^{-1}$.

Results of the calculation are reported in Table IV.2.4, wherein we list both low and high estimates of the atmospheric fluxes. Low estimates are based on noncrustal and crustal V_ds of 0.26 and 1.4 $cm \cdot s^{-1}$, respectively and high estimates are based on respective V_d s of 0.72 and 4 $cm \cdot s^{-1}$. The former is that of Dolske and Sievering (1979), the latter is the limiting value for hygroscopic particles of diameters near 2 μm under conditions of turbulence-limited transfer (Slinn and Slinn, 1980).

Dry deposition estimates, however, remain uncertain. Keeler *et al.* (1992) observed that concentrations of particulate-borne elements were typically greater in air over Lake Michigan than in air over adjacent land site. If this were true for the Chesapeake Bay, then our land-based measurements may underestimate Bay air loadings and deposition fluxes. Furthermore, recent evidence (Holsen *et al.*, 1992) suggest that large particles (*i.e.*, aerodynamic diameter >10 to 100 μm) may control the deposition of anthropogenic and crustal elements. In our study, we considered only particles <10 μm. If the large particle hypothesis is true, then dry deposition to water might be severely underestimated. Finally, the underlying physics suggests that dry deposition to water surfaces occurs episodically, *i.e.*, during periods of high turbulence and great atmospheric instability. The disparity between deposition velocities for different wind speeds is so great that the deposition associated with a wind speed of 20 $m \cdot s^{-1}$ for 10 minutes a day would be equivalent to the deposition associated with an entire week at an average wind speed of 5 $m \cdot s^{-1}$. Thus, a small fraction of periods of high turbulence could lead to substantially enhance deposition relative to the estimates made herein.

IV.3 Trace Elements in Precipitation.

IV.3.1 Concentrations. The weekly measured trace element concentrations in precipitation collected at three sites are summarized in Figures IV.3.1-IV.3.11. The atmospheric deposition of a number of anthropogenically influenced elements (*e.g.*, As, Cd, Cr) exhibited a seasonality whereby maximum fluxes were observed during the summer, consistent with results nearby at Lewes, De (Church and Scudlark, 1992). This seasonality parallels trends in the acid components (H^+, SO^{-2}_4, NO^-_3) in the northeast U.S., although the acid seasonality has been attributed primarily to photochemically enhanced rates of acid precursor oxidation during summer (Lindberg, 1981). For trace elements in precipitation, other meteorological and physical processes are probably more important than chemical reactivity in contributing to the observed seasonality. These processes would include seasonal differences in: a) storm trajectory, favoring atmospheric transport from concentrated mid-west U.S. emission regions during summer (Church and Scudlark, 1992), b) micrometeorology, whereby summer convective precipitation events effectively scavenge a larger portion of the boundary layer (often 50-60,000 ft.), compared with typical winter frontal storms, and c) precipitation amount, often lower in summer storms, which usually yields samples with higher concentration (Lim et al, 1991). In fact, all of the "spikes" which appear in the weekly concentration record correspond to low volume precipitation events. However, within the scope of this study it is not possible to distinguish the degree to which of the above three factors is responsible for the observed intra-annual trends.

In calculating bay-wide fluxes, we assume that the precipitation concentrations and wet fluxes measured at the land-based sites are representative of those over the Bay surface. As previously discussed in Section IV.2.2, atmospheric aerosol concentrations and fluxes (and presumably precipitation by which they are scavenged) over water can be significantly different that those measured over land. Despite this caveat for practical and logistical purposes it was not possible to conduct our routine sampling at stations over the water. However, during this phase of the CBADS program we were afforded an opportunity to sample a precipitation event (23 October 1990) on board ship in the Chesapeake Bay at a station off the Potomac River (37°39.65'N, 76°17.58'W) coincidentally with several land-based sites, using similar sampling and analysis protocols (Table IV.3.1). To our knowledge this simultaneous sampling of trace elements in precipitation at five closely spaced sites, including over-water sampling, represents a unique data set. While any conclusions based on this comparison of only one isolated set of samples would be tenuous at best, an interesting pattern is evident:

(a) Crustally-derived elements (Al, Fe, and to some extent Mn and Cr) exhibited higher concentrations over land than water. This seems reasonable for crustal elements which are typically associated with ground-based, locally dominant emissions of large

($>2.5\mu m$) particles that tend to dry deposit close to their source.

(b) The precipitation concentrations of some (Cd, Ni, Pb), but not all anthropogenically dominated elements were higher over water than land. This may indicate more effective scavenging/convective meteorology over water for fine (submicron) particles enriched in these elements.

More extensive sampling is obviously required to test the hypothesis that the deposition of some trace elements over water differs from that which is observed over land.

IV.3.2 Wet Deposition. Monthly-integrated atmospheric wet fluxes, which appear in Figures IV.3.11-IV.3.22, were directly calculated for each site based on the total measured precipitation amount (gauge) and the monthly volume-weighted average trace element concentration. The total monthly precipitation amount is utilized to calculate wet deposition whether or not the volume was sufficient for analysis (*i.e.*, insufficient volume occurs for less than 2% of all samples). Thus, this calculation inherently assumes that the trace element concentrations in the events not analyzed (predominantly low precipitation events) are equal to the monthly average concentration. In reality, this assumption probably results in a somewhat conservative estimate for atmospheric wet flux, since low volume events typically exhibited higher than average concentrations (Lim *et al.*, 1991), as previously discussed.

On a monthly time scale, the inter-site variability can be as much as a factor of 10, and is even larger on a weekly or event basis. The atmospheric fluxes for crustal elements (Al, Fe, and Mn) at all three sites show dramatic peaks in wet deposition during spring (Mar/Apr) and summer (Jul/Aug), although these peaks were not necessarily associated with the same events or weekly samples. The differences in the timing of the "peak months" between the three sites could be caused by variations in the local meteorological conditions. However, meteorological trajectories would be necessary to confirm this speculation.

It is also interesting to note that the peaks evident in wet deposition do not parallel corresponding peaks in aerosol concentrations. This inconsistency suggests that the aerosol and precipitation composition may reflect different sources in that they tend to sample the lower and upper troposphere, respectively. It is also possible that peaks in transport and deposition revealed by episodic precipitation events are better resolved than weekly-integrated aerosol measurements. Furthermore, the Al/Fe ratios at Wye (1.31), Elms (1.29) and Haven Beach (1.43) were somewhat less than would be predicted from a shale source (1.69) (Turekian and Whedepohl, 1961). If this difference is significant within the uncertainties of average verses global crustal abundances, this may indicate a secondary source.

Using Al as a crustal normalizer, we can factor out the crustal component of the observed fluxes based on reported soil elemental ratios (Turekian and Wedepohl, 1961). As indicated in Table IV.3.2, it is apparent that except for Al, Fe, Mn, and Cr, the crustal contribution is relatively minor at all three sites. The crustal component for each element is rather consistent between sites.

For five elements examined (Al, As, Cd, Cu, and Zn), the wet depositional flux was higher at the Haven Beach site than at the Wye or Elms site (Table IV.3.2). However, for the remainder of elements (Cr, Fe, Mn, Ni, Pb and Se) the deposition was the highest at Wye, despite lower precipitation amounts (92 cm at Wye vs 112 cm at Elms and 113 cm at Haven Beach). This trend may reflect the influence of the Baltimore-Washington urban plume at the Wye site. At Elms the precipitation fluxes were consistently the lowest on both a monthly and yearly time scale.

The spatial variability in annual wet fluxes, expressed at the Wye:Elms:Haven Beach ratio varies

from 1.0:0.9:1.0 for Se, suggesting a fairly uniform deposition to 0.3:0.9:1.0 for As, which indicates a possible "southern-source" [Table IV.3.2]. The Pb ratio (1.3:1.3:1.0) as well as a comparison of the spatial trends of the monthly fluxes indicates a slight decrease in Pb concentrations at the most southern site. This is probably due to a strong Pb source from the Baltimore/Washington emission plume. Although alkyl-Pb additions to automobile fuel are in the process of being phased-out, there seems to be a slight residual signal from other sources (*e.g.*, coal burning).

Wet deposition is controlled by two factors: the amount of rainfall and the concentration of elements in the rainfall. Individual "peak" events can account for much of the annual flux for certain elements. Anthropogenic elements (*i.e.*, As, Cd, Pb) seem to be especially sensitive to high episodic deposition. The highest 10% of the events with the highest concentrations (which account for less than 2% of the total rainfall) are responsible for as much as 15% of the total flux. Obviously, calculating only an annual (or even monthly) flux into the Bay cannot truly indicate the actual environmental impact of anthropogenic elements in the Bay.

The average monthly wet depositional flux for a given element at each site was also highly variable, deviating by as much as a factor of 90 during the data record. Even the most consistent element (Zn) exhibits a range in the monthly flux by as much as a factor of 10. The temporal variability of all of the elements increased with a decreasing time scale (weekly or event). The average annual flux for the three sites is in general agreement with the yearly deposition that was reported in Phase I (6/90 - 7/91) of this study. With the data set covering a longer time period and with the addition of a third site, the average Se flux is 50% less than the original phase I estimate. The atmospheric wet flux of elements to Chesapeake Bay appears to be a very heterogeneous process with respect to space and time, requiring employment of multiple sites over a long time frame for accurate assessment of the source and magnitude of atmospheric trace element inputs.

IV.3.3 Interpretation of Trace Elements in Precipitation. Due to the paucity of other reliable measurements, it is difficult to put the CBADS fluxes in perspective either spatially or with respect to long-term trends. However, the following precipitation trace element data have been reported both nearby and in other regional water bodies which can be used as a basis of comparison (Figure IV.3.23):

a) Lewes, DE (Church and Scudlark, 1992) - The average wet fluxes for the period 1982-89 were reported at the mid-Atlantic coast, based on identical collection, processing and analysis methods as the CBADS Network. This probably represents the only long-term continual record of trace elements in precipitation in the U.S.

b) Chesapeake Bay (Wade and Wong, 1982 + Conkwright et al, 1982) - In two similar studies sponsored by the U.S. EPA precipitation collections were conducted at four sites in the lower Bay (Virginia), and six from the Maryland portion of the Bay (April 1981 - April 1982). Several of the sites were in close proximity to the CBADS sites. Wet fluxes were calculated from the arithmetic average concentrations of the sites, assuming an average precipitation amount of 100 cm/yr.

c) GLADS; Great Lakes Atmospheric Deposition Study, (Klappenbach, personal communication) - Wet fluxes were calculated from the arithmetically averaged precipitation concentrations reported at 13 "rural" sites (no population center > 15,000 within 40 km) for the period 1982-1989 and assuming an average annual precipitation of 100 cm/yr.

d) Puget Sound - (EPA, 1991). Fluxes were calculated from the arithmetic average of the

total (wet + dry) deposition from the two sites (Brown's Point and Riverside School) identified as "background." Sampling was conducted using a custom designed bulk (wet + dry) collector.

These wet fluxes are summarized in Figure IV.3.23 (it should be noted that not all elements were analyzed in all the studies). For most of the anthropogenically derived elements (notably Pb, Ni, Zn, Cd, and Cu), the long-term average fluxes measured at Lewes were somewhat higher than those measured in the CBADS Network. For Pb, this is not an unanticipated result, due to the phasing out of alkyl-Pb additives in gasoline over this period. In fact, the eight-fold decrease in the precipitation Pb concentration observed over the past decade at Lewes (Church and Scudlark, 1992) closely parallels the estimated decrease in the atmospheric Pb burden over this period (Shen, 1991).

For the other elements of interest, it is not possible to discern if the discrepancies between the Lewes and CBADS wet fluxes represented a spatial or temporal trend due to the different periods of determining atmospheric trace element deposition. This inconsistency can only be resolved by comparison of the CBADS data to Lewes data for an identical time period, of which analysis is currently underway. However, it is possible that enhanced deposition at Lewes results from unique chemical climatology in the marine coastal regime, which would be consistent with the hypothesis suggested by the shipboard sample comparison previously discussed (Table IV.3.2).

Except for Al, Fe, and Mn, wet fluxes calculated from the ChesBay 1982 studies were 1-2 order of magnitude higher than the CBADS data. If these differences are real, it would suggest that precipitation trace element concentrations have decreased dramatically over the past decade. However, this hypothesis is not supported by our own trace element record for this period at Lewes, which does not indicate a decrease (except for Pb).

The GLADS fluxes (rural measurements only) are comparable to the Lewes, DE measurements for the same time period. The Cu, Mn, and Ni fluxes also compare well to CBADS, even though the GLADS sampling (1982-1989) was not contemporaneous with CBADS. However, the Pb and Zn fluxes were about a factor of 3-4 times higher that what is found in the Chesapeake Bay area. The Puget Sound fluxes that have been reported are total deposition which include wet + dry measurements. Even including the highest estimates of the CBADS wet + dry deposition, the fluxes reported for Puget Sound are higher than would be expected for clean "background" sites (Nriagu, 1992). It is possible that the sites reported were not truly "background" or that the elevated depositions reflect sampling/analysis contamination.

The total atmospheric loading (Table V.1) of trace elements to Chesapeake Bay can be apportioned into wet and dry components using the data collected in this study. The data indicate that with the exception of the crustally-derived elements, wet deposition is the major atmospheric input of trace elements to Chesapeake Bay. Qualitatively, the proportion of dry deposition for crustal elements (Al, Fe) appears greater than for wet deposition, while the wet deposition proportion for some noncrustal elements (Pb, Cd) appears greater than dry. However, the range of dry deposition estimated, particularly for noncrustal elements, is considerable which currently prevents accurate or quantitative apportionment of wet versus dry atmospheric fluxes.

IV.3.3.1 Estimation of Uncertainty. There are two primary sources of uncertainty in estimating trace metal wet deposition: the sample collection efficiency which include the analytical error, and the spatial variability. The analytical error is conservatively estimated at $\pm 10\%$. This error takes into account the collection efficiency of the rain sampler, the analytical reproducibility of the instruments and any possible contamination that is seen in the Field Blanks. It must also be noted that samples with

insufficient volume for analysis will underestimate (conservatively) by approximately 5% due to higher concentrations that are typically in small volumes (Lim *et al.*, 1991).

The spatial variability is more difficult to estimate. The three CBADS sites were chosen to be regionally representative. As such, urban areas were intentionally avoided. However, the localized impact of urban plumes (*e.g.*, Baltimore/Washington or Norfolk) would have much higher concentrations. Accessing the input of urban deposition on the Chesapeake Bay and Lake Michigan is a current focus of the U.S. EPA Great Waters Program.

IV.4 Major Ions. The major ion data from the Haven Beach site are listed in Appendix A 3.3 and summarized in Figures IV.4.1.1-4. In addition to our normal QA/QC procedures, an ion balance was carried out with these data. The difference between the cation and anion equivalents in weekly samples ranged form 0.07% to 16.3% with the average for the 1991 data being 3.4±2.9%. This excellent agreement suggests that other possible "major" anions (*e.g.*, formate) are not likely major constituents in the precipitation at this site.

For brevity we have chosen here to discuss only a sub-set of the major ion data. Sodium has been chosen as an indicator of sea salt contribution, nitrate as an indicator of (local) internal combustion sources, and pH (or H^+) as an indicator of general acidity. Concentrations from weekly samples are shown in Figure IV.4.1.1 while monthly volume weighted average concentrations are shown in Figure IV.4.1.2. In this data set, nitrate and non-seasalt (nss) sulfate appear to be highly correlated ($r=0.8$ for the weekly concentration data) while both nss sulfate and nitrate appear to be highly correlated with H^+ ($r = 0.8$ and 0.7 for the weekly concentration data). This suggests that the major contributors to acidity in precipitation at Haven Beach are nitric and sulfuric acid. In contrast sodium appears not to be strongly correlated with nitrate, H^+ and nss sulfate ($r = 0.2$, 0.4, and 0.5, respectively). The behavior of sodium is likely due to strong wind events (storms) that increase the formation of sea salt aerosols.

Monthly fluxes for these ions are shown in Figure IV.4.1.3. No strong trends are immediately apparent although H^+, nitrate and nss sulfate fluxes may be slightly higher in the summer months (June through August). Sodium fluxes are high in the late summer/early fall (August through October), although high monthly fluxes are also observed in individual monthly fluxes throughout the year (*e.g.*, January, April, and June).

A comparison of the monthly fluxes of these ions from all three sites is shown in Figure IV.4.1.4. For any given month, fluxes of H^+, nss sulfate and nitrate are generally similar (±50%) at all three sites, although clear departures form this trend can be seen. At one level, these observations suggest that there may be a certain level of similarity in the sources of these anthropogenic components to the Bay region. However, spatial heterogeneity in the fluxes of these anthropogenic ions to the Bay is also clearly evident within this data set. Sodium fluxes clearly indicate the decreasing influence of marine sources to precipitation as one moves up the Bay. In general, the Wye site has the smallest sodium flux, with the Elms and Haven Beach site showing larger sodium fluxes. This observation is consistent with the proximity of the sites of the Bay (Haven Beach is the closest) and the average salinity of the Bay waters adjacent to each site (Haven Beach > Elms > Wye).

IV.4.1 Covariance with major ion data. Sources of the major ions in precipitation are well known, and this fact can be employed to examine the behavior of the trace elements. For this exercise, concentrations of the trace elements at each site were regressed against the concentrations of three major ions: non-sea salt sulfate (nss SO_4^{2-}), sodium, and nitrate. Sodium was selected as a tracer of sea salt aerosols, nitrate is largely derived from internal combustion (*e.g.*, automobile exhaust) and is transported over relatively short distances, and nss SO_4^{2-} in the eastern U.S. is primarily from fossil

fuel combustion and can be transported over long distances (*i.e.*, the oxidation of SO_2 is slow, allowing it to be transported far from its sources before removal.

Correlations (expressed as r, the correlation coefficient) between the trace elements and sodium at all three sites did not exceed 0.4, indicating that the generation of sea salt aerosols did not appreciably introduce or scavenge trace elements to precipitation over the Chesapeake Bay. In contrast, the concentrations of many of the trace metals were well correlated with that of nitrate. Arsenic (r = 0.8), copper (r = 0.6), manganese (r = 0.7), and selenium (r = 0.6) showed reasonable correlations with nitrate, suggesting input from local combustion sources. Wye and Elms displayed similar correlations, with the additions of cadmium (r = 0.5-0.8), iron (r = 0.5-0.7), Pb (r = 0.7-0.8), manganese (r = 0.5-0.7), nickel (r = 0.6-0.7), and zinc (r = 0.7-0.9). The inclusion of iron and manganese in the correlations with nitrate are likely due to the removal of nitrate onto mineral aerosols rather than these parameters sharing similar sources (*i.e.*, the correlation is due to similar removal processes, not similar sources).

In general, correlations between the trace elements and non-sea salt sulfate at the three sites were not as strong (*i.e.*, $r<0.5$) as those with nitrate. The notable exceptions were arsenic at Elms ($r=0.8$), copper at Wye and Elms ($r=0.6$), nickel at Wye ($r=0.6$), and zinc at Elms and Wye ($r=0.6$-0.7). Assuming that non-sea salt sulfate is largely due to fossil fuel emissions transported over long distances, these emissions do not appear to be a dominant source of trace elements to precipitation over the Chesapeake Bay. Instead, more local sources may have a larger effect (as manifested in the nitrate correlations). Interestingly, the correlations between major ions and trace elements are relatively uniform for three sites, even though their wet depositional fluxes are more variable. This observation suggests that the composition of precipitation at the three sites are effected by the same processes (*i.e.*, sources and removal mechanisms), but that the fluxes are driven by meteorological processes. Nevertheless, considerably more data covering a longer time period will be needed to thoroughly investigate the sources and fluxes of trace elements in precipitation over the Chesapeake Bay.

V. CONCLUSIONS

VI.1 Common Trends and Interpretations. As observed during the first phase of this study (6/90 - 7/91), great temporal variability was observed in the concentrations of organic contaminants and elemental concentrations of aerosol particles and rain. Spatial differences were also observed for trace elements in rain but not for elemental constituents in aerosol particles, suggesting that regional sources of trace elements are fairly ubiquitous in the ambient air throughout the bay area and that local meteorology strongly influences the overall washout and scavenging of contaminants from the atmosphere. Similar observations were made for organic contaminants in the atmosphere and in precipitation.

Annual temporal variations in inorganic pollutants in both aerosol particles and rain reflect seasonal fossil fuel usage, peaking in the winter heating and summer cooling seasons (*i.e.,* As, Se, and V). In addition peak photochemical activity in the summer months for sulfur was observed and peak agricultural and construction activities in the spring and summer months was evident as shown by the higher atmospheric inventories of Al, Fe, and Mn. A slight seasonal atmospheric signal was observed for the polychlorinated biphenyls, indicating volatilization from the Earth's surface. Elevated PAH concentrations were also observed in the winter time, reflecting the increased home heating and industrial fossil fuel usage. Concentrations of organic contaminants in precipitation did not exhibit strong seasonal trends, demonstrating the inherent influence of air masses on the region throughout the year (*e.g.* the fairly ubiquitous nature of contaminants in the atmosphere as a function of air mass source) and the relative driving of precipitation scavenging mechanisms by local meteorology (*e.g.,* temperature, wind speed and direction), air mass source, and emission strengths.

VI.2 Atmospheric Deposition of Contaminants to Chesapeake Bay. The annual atmospheric deposition of contaminants to the Chesapeake Bay is summarized in Tables IV.1.6 and V.1 from the data provided in this report. These data are updated from the Phase I (6/90 - 7/91) evaluation given previously (Baker *et al.,* 1992). The dry depositional fluxes should be reviewed with caution as there is substantial uncertainty in the excised data, which results from the estimated dry deposition velocities of particles to the surface of Chesapeake Bay (see Section IV.3). Dry deposition depends on the size distribution of aerosol particles and the structure of atmospheric turbulence as driven by the stability of the surrounding air column. In addition, the importance of large particle deposition cannot be accurately assessed from data collected in this study. Mathematical models suggest that dry deposition occurs episodically during highly unstable periods as determined by the ambient wind speed. Dry deposition velocities are expected to increase nearly 200 fold as the wind speed increases by a factor of 4. Fluctuations in ambient particle-associated contaminant concentrations with wind speed need to be measured over very short time scales to address these uncertainties.

The proportion of dry deposition for crustal elements (Al and Fe) appears greater than that for wet deposition (Table V.1), while the wet deposition proportion for some non-crustal elements (Pb and Cd) appears greater than the dry. This is likely due to the large differences in the size distribution of crustal and non-crustal elements. Soil derived elements are generally associated with larger particles and have higher dry deposition velocities which are strongly influenced by gravitational settling. Organic contaminant annual estimates of atmospheric deposition are given in Table V.1. In general, the dry loadings of particle-associated contaminants are substantially larger for compounds with vapor pressures less than 17 Pa. Compounds that are extremely volatile (*e.g.* fluorene, and many of the PCB congeners) exist primarily as gases in the atmosphere, resulting in minimal dry aerosol depositional rates relateve to precipitation scavenging. However, the dry depositional fluxes are highly uncertain due to the estimation of the dry deposition velocity. Without having an accurate description of organic contaminants as a function of particle size, it is highly uncertain to utilize a constant deposition velocity for all organic compounds. Many of the less volatile particle-associated compounds are likely on very small particles

with deposition velocities substantially lower than 0.49 cm/sec. Also, how the particle-size distribution of insoluble particulate matter changes as air masses travel from the shore to over the water surface of the Chesapeake Bay will strongly influence the dry deposition velocity of particles to the water.

VI.3 Future Research Initiatives. Recommendations for future research priorities for the Chesapeake Bay Atmospheric Deposition Study Program are offered below. As mentioned above, there needs to be a much better assessment of the dry fluxes. Reducing the uncertainty in the overall flux estimates will come about by 1) measuring the dry deposition velocity directly in the field, over land and water and 2) measuring the aerosol size distribution of particle-associated contaminants. In addition, the resolution of the data needs to be greater, *i.e.*, the affects of local meteorology on the flux need to be evaluated. Sampling at a higher frequency (*e.g.* precipitation event) with a higher frequency will allow us to describe contaminant removal mechanisms in greater detail. Atmospheric aerosol sampling on a daily basis will enable us to do air mass trajectory analysis and chemical source assessments of the trace elements. Unfortunately, due to the paucity of data for organic contaminant source signatures and profiles, source assessments for organics in the atmosphere is highly unlikely at this point. In addition, sampling atmospheric contaminants as a function of altitude should be considered since much of the variation observed in atmospheric concentrations of contaminants results from differential transport and scavenging regimes being altered as air masses traverse the lower stratospheric and upper tropospheric atmospheric layers. These types of studies are beyond the pollutant concentration and flux assessments described in this document and should be considered as in-depth atmospheric process studies.

Specific objectives for future atmospheric process studies could be to:

a) investigate atmospheric scavenging mechanisms and their relationship to local meteorology (*i.e.*, a modeling-based intensive sampling strategy),

b) identify atmospheric sources by geographic region and emission type, including documenting organic contaminant source profiles and the influence of localized urban atmospheric contaminant emissions on bay-wide deposition,

c) determine if atmospheric fluxes at land-based sites are truly representative of fluxes observed over bay waters and waters within the watershed,

d) determine if atmospheric concentrations measured on the ground are representative of those at cloud height

e) determine if scavenging mechanisms within clouds are similar to those operating below the cloud layer,

f) improve estimates of dry deposition, including documenting deposition velocities, the role of large particles and episodic atmospheric instability, and the size distribution of particle-associated contaminants,

f) estimate the atmospheric fluxes of contaminants to other geochemical inputs such as groundwater, fluvial, and watershed inputs that currently use data of limited quality and quantity,

g) estimate the indirect atmospheric loading *via* watershed runoff from the drainage basin to Chesapeake Bay, which requires the derivation of "transmission/retention factors" for

each contaminant under different land use regimes (*e.g.* agricultural, commercially developed, rural).

Objective (a), which focuses on intensive sampling strategies, is addressed in Year 3 of this study (1/92 - 12/92). Achieving the remaining objectives will require ancillary studies of atmospheric deposition to coastal and inland waters, which are presently being considered under funding from U.S. EPA/AREAL under the Great Waters Program. The utility of the data presented in this report will really only be essential for the mitigation of contaminant inputs to the Chesapeake Bay when contaminant assays of equal quality to those determined herein are obtained from other routes of contaminant entry (objectives (f) and (g)). These, along with the other objectives, will provide accurate quantification of atmospheric inputs of trace atmospheric contaminants to the Chesapeake Bay, which will provide the necessary background required for the investigation of environmental effects of contaminants to the Bay ecosystem.

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VIII. LITERATURE CITED

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Table II.2.1. Sampling Schedule, CBADS 1990 - 1991

	Date		Sampling	
	Start	End	Frequency	Interval
Wye				
Trace Elements-Precipitation	5 July 1990	31 December 1991	7 Days	7 Days
Trace Elements-Aerosols	5 June 1990	31 December 1991	6 Days	7 Days
Organics-Precipitation	14 July 1992		14 Days	14 Days
Organics-Air	14 July 1992		14 Days	0.5-1 Day
Elms				
Trace Elements-Precipitation	5 June 1990	31 December 1991	7 Days	7 Days
Trace Elements-Aerosols	5 June 1990	31 December 1991	7 Days	7 Days
Organics-Precipitation	26 June 1990	31 December 1991	14 Days	14 Days
Organics-Air	12 June 1990	31 December 1991	14 Days	0.5-1 Day
Haven				
Trace Elements-Precipitation	4 December 1990	31 December 1991	7 Days	7 Days
Trace Elements-Aerosols	23 November 1990	31 December 1991	7 Days	7 Days
Organics-Precipitation	18 December 1990	31 December 1991	14 Days	14 Days
Organics-Air	18 December 1990	31 December 1991	14 Days	0.5-1 Day

Table III.1.1. Organic Contaminants and Elements Analyzed in CBAD Study.

Organic Contaminants - Polycyclic Aromatic Hydrocarbons	**Polychlorinated Biphenyls**
Fluorene	74 Congeners listed in Appendix A1.2 and A1.4
Phenanthrene	
Anthracene	**Chlorinated Agrichemicals**
Fluroanthene	Hexachlorobenzene
Pyrene	α-hexachlorocyclohexane
Benzo[a]anthracene	ß-hexachlorohexane
Chrysene	G-hexachlorohexane
Benzo[b]fluoranthene	Heptachlor
Benzo[k]fluoranthene	Heptachlor epoxide
Benzo[e]pyrene	Aldrin
Benzo[a]pyrene	Endrin
Indeno[123-cd]pyrene	p,p'-DDE
Benzo[ghi]perylene	p,p'-DDD; o,p'-DDD
Dibenzo[ah]anthracene	p,p'-DDT; o,p'-DDT
Elements*	**Major Ions**
Aluminum	Calcium
Arsenic	Potassium
Cadmium	Magnesium
Chromium	Chloride
Copper	Nitrate
Iron	Sulfate
Manganese	Sodium
Nickle	Ammonium
Lead	
Selenium	
Zinc	

*An additional 20+ elements were quantified on aerosol samples by neutron activation analysis (Appendix A2).

Table III.1.2. Mean field measured vapor concentrations, pg/m^3, and mean analytical detection limits for PAHs and PCBs, Chesapeake Bay, 1990-1991.

Polycyclic Aromatic Hydrocarbon	Mean Vapor Concentration Elms	Mean Analytical Detection Limit Elms	Mean Vapor Concentration Haven	Mean Analytical Detection Limit Elms
Fluorene	686	0.5	1626	0.3
Phenanthrene	2011	0.3	3424	0.3
Anthracene	52	0.3	69	0.3
Fluoranthene	337	0.3	425	0.6
Pyrene	413	0.3	509	0.6
Benzo[a]anthracene	9	0.8	9	0.6
Chrysene	24	1.2	50	0.6
Benzo[b]fluoranthene	10	1.0	7	0.6
Benzo[k]fluoranthene	6	0.8	5	0.6
Benzo[e]pyrene	7	1.1	7	0.6
Benzo[a]pyrene	4	1.0	5	0.6
Indeno[123-cd]pyrene	2	2.0	26	2.7
Dibenz[ah]anthracene	2	2.2	13	2.7
Benzo[ghi]anthracene	2	1.5	28	1.1
Total Polychlorinated Biphenyls	330	1.1	273	1.2

Table III.1.3. Summary of Laboratory Surrogate Compounds for Chesapeake Bay Atmospheric Deposition Samples, Elms Site, 1990-1991.

Deuterated PAH	Sample Matrix	Mean% Recovery	Relative* STD Dev (%)	N**	70% < N N < 130%
d-10 Anthracene	Funnel Wash	53.6	68	10	2
d-12 Benzo(b)Fluoranthane		82.1	13	12	10
d-10 Anthracene	Rain Filter	59.1	48	19	7
d-10 Pyrene		52.6	22	13	3
d-10 Fluoranthene		67.9	51	23	11
d-12 Benzo(b)Fluoranthane		72.6	35	30	15
d-10 Anthracene	Rain Dissolved	75.5	30	24	16
d-10 Pyrene		73.5	50	19	10
d-10 Fluoranthene		63.8	57	15	6
d-12 Benzo(b)Fluoranthane		84.9	37	33	21
d-10 Anthracene	Air Filter	55.8	46	9	4
d-10 Pyrene		108.2	16	6	1
d-10 Fluoranthene		61.2	41	28	8
d-12 Benzo(b)Fluoranthane		111.7	24	22	14
d-10 Anthracene	Air Vapor	59.6	46	14	5
d-10 Fluoranthene		79.0	60	16	6
d-12 Benzo(b)Fluoranthane		118.7	35	22	10
Non-Commercial (PCB)	**Sample Matrix**	**Mean % Recovery**	**Relative* STD Dev (%)**	**N****	**70-% < N N < 130%**
3,5-dichlorobiphenyl	Funnel Wash	88.2	38	11	8
2,3,5,6-tetrachlorobiphenyl		87.8	18	11	10
3,5-dichlorobiphenyl	Rain Filter	70.1	39	46	22
2,3,5,6-tetrachlorobiphenyl		90.3	34	12	8
3,5-dichlorobiphenyl	Rain Dissolved	75.4	35	39	23
2,3,5,6-tetrachlorobiphenyl		69.1	36	7	1
3,5-dichlorobiphenyl	Air Filter	62.4	52	15	6
2,3,5,6-tetrachlorobiphenyl		86.7	67	15	5
3,5-dichlorobiphenyl	Air Vapor	98.5	41	33	20
2,3,5,6-tetrachlorobiphenyl		83.3	30	10	5

*Relative STD DEV = STD DEV * 100/[Mean].
**Number of Samples.
^70% < % Rec < 130%

Table III.1.3 (Cont'd). Summary of Laboratory Surrogate Compounds for Chesapeake Bay Atmospheric Deposition Samples, Haven Beach Site, 1990-1991.

Deuterated PAH	Sample Matrix	Mean% Recovery	Relative* STD Dev (%)	N**	70% < N N < 130%
d-10 Anthracene	Funnel Wash	77.7	12.5	33	30
d-12 Benzo(a)Anthracene		107.0	12.6	32	29
d-12 Benzo(a)Pyrene		102.0	16.0	28	26
d-10 Anthracene	Rain Filter	81.7	12.0	32	30
d-12 Benzo(a)Anthracene		102.8	10.7	31	30
d-12 Benzo(a)Pyrene		97.3	5.3	31	31
d-10 Anthracene	Rain Dissolved	81.0	19.5	32	27
d-12 Benzo(a)Anthracene	(XAD-2)	102.0	16.3	32	29
d-12 Benzo(a)Pyrene		100.5	13.8	31	30
d-10 Anthracene	Air Filter	87.0	10.0	46	45
d-12 Benzo(a)Anthracene		110.5	15.1	45	42
d-12 Benzo(a)Pyrene		99.7	10.5	45	44
d-10 Anthracene	Air Vapor	81.9	13.2	49	41
d-12 Benzo(a)Anthracene	(PUF Plugs)	105.4	12.4	49	47
d-12 Benzo(a)Pyrene		101.1	11.6	49	48
Non-Commercial (PCB)	**Sample Matrix**	**Mean % Recovery**	**Relative* STD Dev (%)**	**N****	**70-% < N N < 130%**
3,5-dichlorobiphenyl	Funnel Wash	41.4	27.1	28	1
2,3,5,6-tetrachlorobiphenyl		51.2	47.7	27	3
2,3,4,4',5,6-hexachlorobiphenyl		82.6	28.2	33	22
3,5-dichlorobiphenyl	Rain Filter	42.2	26.4	29	0
2,3,5,6-tetrachlorobiphenyl		40.8	42.7	27	2
2,3,4,4',5,6-hexachlorobiphenyl		77.2	18.6	31	22
3,5-dichlorobiphenyl	Rain Dissolved	57.4	53.8	30	3
2,3,5,6-tetrachlorobiphenyl	(XAD-2)	50.1	38.5	28	4
2,3,4,4',5,6-hexachlorobiphenyl		88.0	19.2	31	29
3,5-dichlorobiphenyl	Air Filter	46.9	30.1	46	2
2,3,5,6-tetrachlorobiphenyl		48.4	51.6	44	3
2,3,4,4',5,6-hexachlorobiphenyl		85.8	20.9	46	35
3,5-dichlorobiphenyl	Air Vapor	-	-	-	-
2,3,5,6-tetrachlorobiphenyl	(PUF Plugs)	48.4	64.4	41	4
2,3,4,4',5,6-hexachlorobiphenyl		76.3	18.6	48	32

*Relative STD DEV = STD DEV * 100/[Mean].
**Number of Samples.

Table III.1.4. Mean Mass (ng) Summary of Polycyclic Aromatic Hydrocarbons and Polychlorinated Biphenyls in Laboratory and Field Blank Matrices, Chesapeake Bay Atmospheric Deposition Project, Elms, 1990 - 1991.

	Laboratory						Field					
Polycyclic Aromatic Hydrocarbon	Mean Resin (N=9)	%Rel STD^	Mean Filter (N=11)	%Rel STD	Mean Foam (N=3)	%Rel STD	Mean Resin (N=2)	%Rel STD	Mean Filter (N=3)	%Rel STD	Mean Foam (N=2)	%Rel STD
Fluorene	14.3	171	7.2	267	ND	--	1.7	141	0.5	134	48.6	126
Phenantharene	70.4	156	16.7	211	13.8	21	10.0	1	3.7	161	212.6	130
Anthracene	85.5	249	8.7	253	1.6	100	2.1	105	2.6	62	12.4	129
Fluroanthene	24.3	116	16.3	237	1.5	173	2.0	70	0.3	90	23.0	134
Pyrene	172.4	191	126.2	318	5.7	103	2.4	49	10.6	168	8.5	123
Benzo[a]Anthracene	17.1	167	6.3	137	ND	--	0.4	141	2.2	143	0.8	141
Chrysene	16.4	109	7.7	154	ND	--	5.8	52	2.8	124	0.7	141
Benzo[b]Fluoranthene	20.1	122	8.5	156	ND	00	ND	--	4.2	153	0.9	141
Benzo[k]Fluoranthene	20.4	100	7.7	146	ND	--	ND	--	4.3	153	0.8	141
Benzo[e]Pyrene	4.3	139	0.1	225			12.0	126	0.2	141	ND	--
Benzo[a]Pyrene	22.4	163	6.9	136	ND	--	24.9	141	0.3	173	0.6	141
Indeno[123]Pyrene	21.9	300	8.3	188	ND	--	ND	--	ND	--	ND	--
Dibenzo[a]Anthracene	12.3	252	4.4	332	ND	--	2.7	141	0.3	173	ND	--
Benzo[ghi]Perylene	21.3	173	10.7	152	ND	--	ND	--	0.3	173	0.9	141
TOTAL PCB* **	19.3	52	19.7	90	48.3	64	32.2	55	5.8	74	27.5	30

*Number of samples.
^Relative STD DEV = STD DEV * 100/[mean].
~74 congeners, N = 7 for lab resins.

Table III.1.4 (Cont'd). Mean Mass (ng) Summary of Polycyclic Aromatic Hydrocarbons and Polychlorinated Biphenyls in Laboratory and Field Blank Matrices, Chesapeake Bay Atmospheric Deposition Project, Haven Beach, 1991.

	Laboratory										Field					
Polycyclic Aromatic Hydrocarbon	Resin (N=5) Mean	%Rel Std	Mean PPT Filter % Rel (N=5)	STD	Mean FW % Rel (N=6)	STD	Mean Air Filter % Rel (N=6)	STD	Mean Foam % Rel (N=8)	STD	Mean Resin % Rel (N=2)	STD	Mean PPT Filter % Rel (N = 2)	STD	Mean FW % Rel (N=2)	STD
Fluorene	1.9	150	0.5	6.2	0.8	80	0.9	54	1.5	21	4.5	100	2.9	61	0.9	19
Phenantharene	9.4	87	4.6	67	4.0	75	3.1	43	6.1	26	51.4	56	2.4	29	7.6	54
Anthracene	0.1	200	N.D.	-	N.D	-	0.2	224	N.D	-	0.7	100	2.3	100	0.4	100
Fluroanthene	1.8	76	0.3	54	0.4	24	1.6	117	1.1	31	26.2	81	1.7	33	4.6	81
Pyrene	0.9	91	0.3	54	0.5	37	1.1	97	1.7	99	11.1	10	1.6	26	3.9	78
Benzo[a]Anthracene	0.4	114	0.1	123	0.2	72	0.2	102	0.3	108	1.8	68	0.5	36	1 3	85
Chrysene	0.8	114	0.2	97	0.3	72	0.3	90	0.4	76	1.7	19	1.2	36	3.2	83
Benzo[b]Fluoranthene	0.4	105	0.1	159	0.4	124	0.1	142	1 1	112	0.5	100	0.9	40	2.7	85
Benzo[k]Fluoranthene	0.1	200	<0.1	200	0.2	129	<0.1	224	0.5	112	0.2	100	0.6	56	1.8	81
Benzo[e]Pyrene	0.5	113	<0.1	200	0.2	102	<0.1	224	0.1	182	N.D.	-	0.7	35	2.1	85
Benzo[a]Pyrene	3.6	59	0.1	200	0.2	127	<0.1	224	0.5	112	7.2	20	0.6	34	1.2	79
Indeno[123]Pyrene	N.D.	-	N.D	-	0.2	224	N.D.	-	0.5	152	N.D.	-	0.8	100	3.1	100
Dibenzo[a]Anthracene	0.1	200	0.1	200	0.2	224	0.1	224	1.4	116	0.4	100	0.3	100	0.4	100
Benzo[ghi]Perylene	0.5	94	0.5	82	0.5	127	0.4	128	1.5	88	0.3	100	0.8	100	3.6	84
TOTAL PCB***	12.0	84	16.1	103	16.4	69.5	12.9	103	23.6	43	2 6	-	1.6	8	1.9	50

*Relative STD DEV * 100/[mean].
**Number of samples.
***86 Congeners, N= for lab filters, N = 2 for lab foam; N = 1 for field filters; N= 2 for field foam.

Table III.2.1 Concentrations of Elements Determined in NIST Standard Reference Materials

Element	Unit	SRM	Method	Literature Conc. Sigma	This Work Avg Sigma	N
Al	%	1632A	INAA	2.95 ± 0.1	2.93 ± 1.80	7
As	μg/g	1632A	INAA	9.3 ± 1[1]	7.6 ± 0.8	23
Br	μg/g	1632A	INAA	41 ± 2	39 ± 4	23
Cd	μg/g	1648	Zeeman -- AA	75 ± 7[1]	73 ± 3	7
Cr	μg/g	1632A	INAA	34.3 ± 1.5[1]	37 ± 2	23
Cu	μg/g	1648	ICP-AE	609 ± 27[1]	586 ± 10	6
Fe	%	1632A	INAA	1.11 ± 0.02[1]	1.16 ± 0.06	23
Mn	μg/g	1632A	INAA	28 ± 2	31 ± 7	7
Ni	μg/g	1648	ICP-AE	82 ± 3[1]	88 ± 6	6
Pb	μg/g	1648	ICP-AE	6550 ± 80[1]	6397 ± 65	6
S	%	1632A	INAA	1.55 ± 0.1	ND[2]	
Se	μg/g	1632A	INAA	2.6 ± 0.7[1]	2.6 ± 0.5	23
V	μg/g	1632A	INAA	44 ± 3[1]	43 ± 3	7
Zn	μg/g	1632A	INAA	28 ± 2[1]	29 ± 6	23

[1]Nist certified value.
[2]ND = not detected.

Table III.2.2 Comparison of Laboratory and Field Blanks, ng/filter

	Laboratory Blanks				WFB1 6/26-7/3/90	WFB2 10/9-16/90	WFB3 1/1-8/91	WFB4 4/2-9/91	EFB1 6/20-26/90	EFB2 10/16-23/90	EFB3 1/22-29/91	EFB4 4/9-16/91	VFB1 11/13-20/90
	JUNE 1990 - JULY 1991												
	Ave. + Sigma	N	Min	Max	Mass+Sigma	Mass+Sigma	Mass+Sigma	Mass+Sigma	Mass+Sigma	Mass+Sigma	Mass+Sigma	Mass+Sigma	Mass+Sigma
Al	282+180	10	7.2	598	445+27	636+39	240+15	25.4+1.8	470+29	589+36	342+21	153+10	268+17
As	0.088+0.055	4	<0.01	0.088	0.48+0.04	0.52+0.06	0.08+0.02	0.86+0.12	0.54+0.06	0.7+0.1	0.047+4.6	0.009+0.94	0.01+0.85
Br	0.942±1.1	4	0.16	2.73	0.6±0.5	1±0.6	2.2±0.1	5.8±0.3	1.56±0.42	0.84±0.7	1.71±0.16	0.200 ±0.049	0.4±0.0
Cd	1.46±1.1	7	<1.0	3.8	2.02±0.17	1.53±0.10	2.11±0.23		1.39±0.11	6.79±0.73	0.77 ±	0.96±0.02	
Cr	10+13	4	1.62	23.3	8.4+1.8	5.8+2.2	6.9+0.4	1.29+0.44		7.2+2	27.8+1.1	2.1+0.5	6.43+0.47
Cu	46.7+18.1	10	18.2	76.5	56.4+4.0	67.0+4.0	63.1+2.5	5.20+4.5	61.6+1.2	52.3+1.8	46.8+1.5	40.8+2.0	118.3+0.5
Fe	169+2	2	145	193	<40	<40	114+19				552+115	121+33	
Mn	2.72+1.3	8	<1.2	4.4	2.3+0.1	3.7+0.15	1.12+0.06	1.8	1.58+0.07	5.94+0.2	3.52+0.2	2.9	
Ni	18.5+10.1	10	6	47.2	70	31.9+12	130	160	415+71	170	150	190	100
Pb	43.4+24.7	7	21	87	27	5.54	13.1	22.0	8.01+7.05	30.9	52.2	26	5.69
S	668+727	3	<320	3050				490+327					
Se	0.8+0.5	1	0.83	0.83				0.79+0.49					0.45+0.28
V	0.249+0.17	4	0.08	1.6	1.55+0.11	1.79+0.13	0.93+0.1	NA	1.59+0.12	1.39+0.1	10.0+0.6	0.65+0.07	0.26+0.08
Zn	16+10	4	3.1	22.9	28+8	34+8	13.9+2	2.28+1.15	120+16	1140+120	16.1+3.5	14.6+2	197+14

Table III.2.2 (Cont'd) Comparison of Laboratory and Field Blanks, ng/filter

	Laboratory Blanks					WFB5 11/26-13/3/91	EFB5 11/5-12/91	VFB2 6/4-11/91	VFB3 12/3-10/91
JULY 1991 - DECEMBER 1991									
	Ave. ± Sigma		N	Min	Max	Mass±Sigma	Mass±Sigma	Mass±Sigma	Mass±Sigma
Al	204	94	5	9.7	362	173±11	198±14	203±13	104±7
As	0.034	0.012	4	0.02	0.050	0.01±0.77	0.003±0.001	0.05±0.02	NA
Cd	0.26	0.25	2	0.01	0.52	2.54±0.41	0.17±0.14	0.4±0.03	0.35±0.31
Cr	4.3	1.1	4	2.79	5.75	3.29±1.00	4.79±0.55		16.0±0.72
Cu	22	15	5	7.94	40.9	41±1	26±2.2	23.7±0.7	10±1.4
Ni	27	18	4	<13	45.9	63.4±3.2	39.6±20	67.1±1.5	17.3±21
Pb	50	12	5	37.42	73.0	46.5±30	20.1±2.0	66±16	30.3±10
S	31	16	5	12.7	51.2	<13	<49		<51
Se	1.0	0.4	1			0.95±0.49	0.46±0.24	110	0.49±0.26
Zn	28	8.5	5	20	43.5	21.8±3.4	117±8.3	4.28	127±9.0
Br	0.26	0.22	5	0.079	0.65	<0.045	0.283±0.68	600±270	0.674±0.29
V	0.086	0.031	5	0.012	0.125	0.103 ±0.038	<0.015		0.063±0 021
Fe	123	75	2	49	198	NA	1473±52	0.22±0.04	1354±51
Mn	4.73	1.0	5	3.34	5.74	4.31±0.17	9.79±0.24	18.1±1.7	5.84±0.23
Dates						11/26-13/3/91	11/5-12/91	6/4-11/91	12/3-10/91

Values without uncertainties are upper limits

Table III.3.1 Analytical Detection Limits (μg/L) for the Determination of Trace Elements in Precipitation

	UDE	ODU		UDE	ODU
Al	0.12	0.29	Fe	0.05	0.64
As	0.007	0.008	Mn	0.10	0.10
Cd	0.006	0.02	Ni	0.12	4.0
Cr	0.10	NA	Pb	0.12	0.12
Cu	0.12	0.12	Se	0.009	0.002
			Zn	0.14	0.06

Table III.3.2 Results of Quality Control Check Solutions for Trace Element Wet Deposition

	SRM 1643c (Trace Elements in Water)		EPA WP 386 (Trace Metals I)		EPA TMA989 (Trace Metals I)	
	Certified	Experimental	Certified	Experimental	Certified	Experimental
	Value ± STD	Value ± STD	Value ± STD	Value ± STD	Value ± STD	Value ± STD
Al	114.6 ± 5.1	116.0 ± 3.0	500 ± 50	503.4 ± 13.6		
As					50.0 ± 5.34	49.3 ± 10.4
Cd	12.2 ± 1.0	11.7 ± 0.6	25 ± 1.97	22.5 ± 1.3		
Cr			100 ± 10.20	84.5 ± 5.73		
Cu	22.3 ± 2.8	22.8 ± 1.1	100 ± 6.20	102.4 ± 17.2		
Fe	106.9 ± 3.0	108.3 ± 1.0	100 ± 8.78	109.1 ± 22.4		
Mn	35.1 ± 2.2	37.3 ± 1.2	100 ± 5.79	98.0 ± 6.11		
Ni			100 ± 7.89	81.8 ± 13.0		
Pb			100 ± 8.40	98.2 ± 6.59		
Se					50.0 ± 4.86	50.8 ± 11.78
Zn	73.9 ± 0.9	73.8 ± 0.5	100 ± 7.36	100.9 ± 11.13		

Table III.3.3 Trace Element Wet Deposition Intercomparison

	Al	As	Cd	Cu	Fe	Mn	Pb	Se	Zn
Corr(r)	0.993	0.852	0.838	0.870	0.979	0.999	0.888	0.824	0.956
Slope(b)	1.10	1.02	0.45	1.31	0.34	0.97	0.68	0.33	1.28

Table IV.1.1 Mean Total (Vapor + Particulate) Air Concentrations ^^ of Polycyclic Aromatic Hydrocarbons and Total Polychlorinated Biphenyls, Elms Site, 1990 - 1991

Polycyclic Aromatic Hydrocarbon	18 Month Mean Conc	% REL STD DEV	1991 Mean Conc	Minimum^	Maximum	% Particulate Minimum	% Particulate Maximum	N**
Fluorene	573.2	121	664.0	56.0	2724.5	0.0	23	35
Phenantharene	1779.3	66	1771.9	357.0	5692.2	0.3	23	35
Anthracene	50.4	78	47.1	0.9	181.3	0.0	100	35
Fluoranthene	404.7	94	330.1	46.9	2274.9	1.0	100	35
Pyrene	482	79	426.1	34.4	1502.6	0.8	100	35
Benzo[a]anthracene	40.0	102	27.6	1.9	152.8	0.0	100	35
Chrysene	96.9	103	85.0	13.9	537.5	0.0	100	35
Benzo[b]fluoranthene	100.5	117	74.2	2.4	463.8	0.0	100	35
Benzo[k]fluoranthene	58.3	114	47.3	3.1	214.1	12.2	100	35
Benzo[e]pyrene	64.8	128	50.5	3.2	325.5	0.0	100	35
Benzo[a]pyrene	33.9	125	24.0	3.3	162.1	0.0	100	35
Indeno[123-cd]pyrene	58.0	141	62.6	6.8	304.5	7.3	100	35
Dibenz[ah]anthracene	33.9	175	9.2	7.3	58.9	6.0	100	35
Benzo[ghi]perylene	63.8	118	60.7	5.6	242.7	12.4	100	35
TOTAL PCBs***	213.9	56	185.6	17.4	507.8	n/a	n/a	38

^^Air concentrations in pg/m3.
**Number of samples.
***74 congeners.
^for non-detectables, the detection limit is given, range over all data

Table IV.1.1 (Cont'd). Mean Total (Vapor + Particulate) Air Concentrations ^^ of Polycyclic Aromatic Hydrocarbons and Total Polychlorinated Biphenyls, Haven Beach, 1991.

Polycyclic Aromatic Hydrocarbon	1991 Mean Conc	Range		% Particulate Minimum	% Particulate Maximum	N**
Fluorene	1635.8	298.7	3671.8	0.2	1.4	27
Phenanthrene	3506.7	1218.4	8285.6	0.4	10.0	27
Anthracene	48.9	1.1	140.0	1.4	100.0	25
Fluroanthene	558.0	202.3	1591.5	2.7	67.3	27
Pyrene	622.1	177.4	1302.4	2.2	74.1	27
Benzo[a]Anthracene	31.7	3.2	213.6	14.9	100.0	24
Chrysene	122.2	13.7	548.5	9.7	97.1	27
Benzo[b]Fluoranthene	83.9	1.9	601.8	56.8	100.0	26
Benzo[k]Fluoranthene	67.0	1.5	416.1	56.8	100.0	24
Benzo[e]Pyrene	53.6	2.7	375.3	29.1	100.0	27
Benzo[a]Pyrene	36.9	1.7	262.4	66.8	100.0	25
Indeno[123]Pyrene	92.1	7.1	443.4	27.8	100.0	22
Dibenzo[a]Anthracene	19.4	8.8	51.0	38.5	100.0	9
Benzo[ghi]Perylene	71.9	3.7	369.1	50.7	100.0	23
TOTAL PCBs* **	298.3	26	730	-	-	27

^^Air concentrations in pg/m3.
**Number of samples.
***76 congeners.

Table IV.1.2 Polycyclic Aromatic Hydrocarbons Concentrations in Air, pg/m^3.

Polycyclic Aromatic Hydrocarbon	Lake Superior ~	Lake Superior ~^	Denver Colorado^^	Niagara River*	Portland Oregon**	Baltimore Maryland*^	Stockholm Sweden ~*	Baltic Sea ~*	Mediterranean Sea ~ ~	Chesapeake Bay"
Fluorene	110	450	na	na	6100	na	na	na	na	570
Phenantherene	92	2600	38000	13800	2700[2]	1800	2560	740	26	1780
Anthracene	5.6	na	3200	1000	2800[2]	2900	120	20	3.7	50
Fluoranthene	na	180	12600	5100	8300	20000	1700	340	30	405
Pyrene	8	340	21200	4200	7500	27000	1370	180	24	480
Benzo[a]anthracene	22	130	na	2800[2]	1500	7600	160	30	4 8	40
Chrysene	67[1]	6.3[1]	na	3900[2]	1800	12000[1]	780[1]	110[1]	35[1]	97
Benzo[b]fluoranthene	na	23	na	na	3500	10600	na	na	na	101
Benzo[k]fluoranthene	na	20	830	1100	na	10600	480	110	na	58
Benzo[e]pyrene	44	6.3	na	420[2]	1200	5000	420	70	22	65
Benzo[a]pyrene	22	5	1700	230[2]	1200[2]	5800	160	140	6.2	34
Indeno[123-cd]pyrene	50	18	3600	na	na	4600	410	110	6	58
Dibenz[ah]anthracene	na	nd	4200	na	na	na	na	na	na	9
Benzo[ghi]perylene	41	13	4200	530[2]	2000[2]	8000	640	70	9.1	64

~McVeety, B.D. and Hites, R.A., 1988
~^Baker, J.E. and Eisenreich, S.J., 1990
^^Foreman, W.T. and Bidleman, T.F., 1990
*Hoff, R.M. and Chan, K., 1987
**Ligocki, M.B. et al., 1985a, b
*^Benner, B.A. et al., 1989
~*Broman, D. et al., 1991
~ ~Simo, R. et al., 1991
"This study (from the mid-bay Elms station)
[1] = Chrysene and triphenylene
[2] = Aerosol phase only

Table IV.1.3 Total Polychlorinated Biphenyls in Air, pg/m^3

Location	Total PCBs	Reference
Arctic	17	Bidleman, et al., 1988
Siskiwit Lake	2700	Swackhamer et al., 1988
Lake Superior	1200	Baker and Eisenreich, 1990
Adirondacks	950	Knap and Binkley, 1991
Bermuda	600	Knap and Binkley, 1991
Chicago	13500	Holson, et al., 1991
S. Ontario	200	Hoff, et al., 1992
Green Bay, MI	250 - 2300	Achman, et al., 1992; McConnell, 1992; Hornbuckle, et al. 1993
Lake Erie	370	McConnell, 1992
Lake Baikal	200	McConnell, et al., 1992
Chesapeake Bay	210	This study; Elms Site

Table IV.1.4. Mean Total (Particulate (Filter + Funnel) and Dissolved) Rain Concentrations ^^ of Polycyclic Aromatic Hydrocarbons and Total Polychlorinated Biphenyls, Elms Site, 1990 - 1991.

Polycyclic Aromatic Hydrocarbon	Jun 90 - Dec 91 17 Months VWM~ ~	1991 VWM	Minimum^ Conc	Maximum Conc	% Particulate Minimum	% Particulate Maximum
Fluorene	1.8	1.4	0.1	48	0.8	76.0
Phenanthrene	6.7	5.3	1.3	89	2.8	76.8
Anthracene	1.2	0.7	0.1	30	19.0	99.8
Fluroanthene	9.0	4.9	0.6	20.8	10.4	97.1
Pyrene	16.8	2.6	0.5	912	16.4	98.4
Benzo[a]Anthracene	1.3	0.9	0.2	14	12.0	94.7
Chrysene	3.4	2.7	0.6	25	10.5	91.9
Benzo[b]Fluoranthene	5.7	3.1	0.9	265	16.8	92.6
Benzo[k]Fluoranthene	3.1	1.5	0.0	34	6.1	98.2
Benzo[e]Pyrene	2.4	2.1	0.3	30	0.8	96.8
Benzo[a]Pyrene	1.9	1.2	0.0	185	11.2	95.9
Indeno[123]Pyrene	2.1	2.4	0.2	9	19.0	99.0
Dibenzo[a]Anthracene	1.1	0.8	0.1	29	5.1	97.3
Benzo[ghi]Perylene	2.3	2.4	0.6	11	36.2	99.0
TOTAL PCBs* **	1.6	1.2	0.1	34	7.1	95.0

^^Rain concentrations in ng/L.
~ ~ Volume weighted mean concentration.
Total volume ppt, PAH samples, 17 months = 1.51 m^3, 1991 = 0.960 m^3.
Total volume ppt, PCB samples, 17 months = 1.29 m^3, 1991 = 1.00 m^3.
Number of samples, 17 months = 32; 1991 = 26
^Ranges given for 17 months data.
**74 Congeners.

Table IV.1.4 (Cont'd). Mean Total (Particulate (Filter + Funnel) and Dissolved) Rain Concentrations ^^ of Polycyclic Aromatic Hydrocarbons and Total Polychlorinated Biphenyls, Haven Beach, 1991.

Polycyclic Aromatic Hydrocarbon	1991 VWM ~ ~ Conc	Minimum Conc	Maximum Conc	% Particulate Minimum	% Particulate Maximum	N**
Fluorene	1.78	0.18	15.99	1.12	100.00	26
Phenanthrene	7.91	2.40	78.95	1.55	100.00	26
Anthracene	0.42	0.09	6.66	4.56	100.00	26
Fluroanthene	4.67	1.72	29.35	11.77	85.59	26
Pyrene	3.57	1.44	21.92	14.04	90.49	26
Benzo[a]Anthracene	0.68	0.23	5.70	43.70	100.00	26
Chrysene	2.07	0.61	14.00	28.55	95.13	26
Benzo[b]Fluoranthene	1.77	0.35	15.80	45.23	97.71	26
Benzo[k]Fluoranthene	1.28	0.32	10.68	37.13	100.00	26
Benzo[e]Pyrene	1.29	0.30	10.40	45.00	97.31	26
Benzo[a]Pyrene	1.14	0.22	9.56	11.12	100.00	26
Indeno[123]Pyrene	1.90	0.42	16.29	39.47	98.26	26
Dibenzo[a]Anthracene	0.33	0.05	3.25	14.45	100.00	26
Benzo[ghi]Perylene	1.80	0.41	12.40	41.90	100.00	26
TOTAL PCBs* **	1.12	0.34	5.84	0.51	72.58	26

^^Rain concentrations in ng/L.
~ ~Volume weighted mean concentration; total vol = 1011.2L.
**Number of samples.
***74 congeners.

Table IV.1.5 Mean Dry and Wet Fluxes ^^ of Polycyclic Aromatic Hydrocarbons and Total Polychlorinated Biphenyls, Elms and Haven Beach, 1990 - 1991

Polycyclic Aromatic Hydrocarbon	Elms Dry Flux		Elms Wet Flux		Total Flux ~ Elms				Haven Beach Dry Flux	Haven Beach Wet Flux	Haven Beach Total Flux ~
	Jun 1990-Dec 1991	Jan 1991-Dec 1991	June 1990-Dec 1991	Jan 1991-Dec 1991	Jun 1990-Dec 1991	±*	Jan 1991-Dec 1991	±	Jan 1991-Dec 1991	Jan 1991-Dec 1991	Jan 1991-Dec 1991
Fluorene	1.6	1.3	2.6	2.1	4.2	1	3.4	1	1.5	1.8	3.3
Phenantharene	12	10	8.9	6.7	21	6	17	5	12	8.0	20
Anthracene	0.90	0.80	1.3	0.8	2.2	0.4	1.6	0.6	0.74	0.4	1.2
Fluroanthene	16	9.6	15	5.2	31	7	15	4	21	5.4	26
Pyrene	15	7.6	20	3.1	35	7	11	4	18	4.3	22
Benzo[a]Anthracene	5.6	4.0	1.7	1.0	7.3	3	5.0	2	4.2	0.8	5.0
Chrysene	12	9.1	5.3	3.0	17	5	12	4	11	2.3	13
Benzo[b]Fluoranthene	15	11	7.6	3.4	23	7	14	5	13	2.0	15
Benzo[k]Fluoranthene	8.2	7.3	5.0	1.6	13	4	8.9	3	10	1.5	11
Benzo[e]Pyrene	9.0	7.6	2.3	2.2	11	4	9.8	4	8	1.5	9.5
Benzo[a]Pyrene	4.3	3.5	2.4	1.8	6.7	2	5.3	2	5.5	1.3	6.8
Indeno[123]Pyrene	9.6	11	2.1	2.5	12	5	13	5	14	2.2	16
Dibenzo[a]Anthracene	1.8	1.7	1.1	0.8	2.9	1	2.5	1	3	0.4	3.4
Benzo[ghi]Perylene	11	9.7	2.4	2.6		5	12	5	10	2.2	12
Total PCBs**	1.4	1.3	1.9	1.4	3.3	0.6	2.7	1	2.1	1.6	3.7

^^Fluxes are in $\mu g/m^2$/year and include dissolved, particulate and funnel matrices dry fluxes are aerosol only.
~Total flux = dry + wet.
**74 Congeners.
*Error represented by the largest assumed dry deposition velocity of 0.72 cm/s (to one significant figure).

Table IV.1.6 Mean Dry and Wet Loadings[1] of PAHs and Total PCBs, Chesapeake Bay, 1990 – 1991

Polycyclic Aromatic Hydrocarbon	Dry Loading		Wet Loading		Total Loading[2]			
	June 1990 – Dec 1991	Jan 1991 – Dec 1991	June 1990 – Dec 1991	Jan 1991 – Dec 1991	June 1990 – Dec 1991	±*	Jan 1991 – Dec 1991	±
Fluorene	18	16	25	23	43	10	39	10
Phenantharene	138	127	97	85	235	69	211	63
Anthracene	9.4	8.9	10	7.0	19	4	16	5
Fluroanthene	213	176	114	61	327	98	237	81
Pyrene	190	147	140	43	330	86	190	69
Benzo [a] Anthracene	56	47	14	10	71	29	57	23
Chrysene	132	116	44	31	176	58	146	52
Benzo [b] Fluoranthene	161	138	55	31	216	75	169	63
Benzo [k] Fluoranthene	105	99	37	18	142	52	117	46
Benzo [e] Pyrene	98	90	22	21	120	46	111	46
Benzo [a] Pyrene	56	52	22	18	78	29	70	29
Indeno [123] Pyrene	136	141	25	27	161	63	168	63
Dibenzo [a] Anthracene	28	27	8.4	6.7	36	12	34	12
Benzo [ghi] Perylene	121	113	26	27	147	58	141	58
Total PCBs[3]	20	20	20	17	40	9	37	9

[1] Kg/yr
[2] total loading = dry + wet
[3] 74 congeners
*error represented by the largest assumed dry deposition velocity of 0.72 cm/s to one significant figure

Table IV.1.7. 1991 annual loadings[1] of PAHs and Total PCBs, Chesapeake Bay, for Maryland and Virginia areas

	Annual Loading Kg/yr					
PAH	MD[1]	±	VA[1]	±	Baywide	±
Fluorene	18	5	21	4	39	10
Phenantharene	90	27	127	37	217	64
Benzo[a]pyrene	28	11	42	19	70	29
Indeno[123–cd]pyrene	69	27	98	43	166	70
Dibenz[ah]anthracene	13	6	20	6	34	12
Benzo[ghi]perylene	65	27	78	31	143	58

[1] area is 0.53 x 10e10 m^2 for MD portion of the Bay; 0.62 x 10e10 m^2 for VA
[2] baywide = sum of Maryland and Virginia loading
* error represented by the largest assumed dry deposition velocity of 0.72 cm/s

Table IV.2.1. Summary of Concentrations[1] of Trace Elements on Aerosols Determined at Wye, Elms, and Haven Beach

	Cummulative Average ng/m³	Sigma	Avg Error	N	Minimum	Maximum	1991 Average ng/m³	Sigma	Avg Error
Elms	6/5/90 - 12/31/91								
Al	155	114	12	76	12	570	150	120	11
As	0.62	0 27	0.05	76	0.11	1.6	0 56	0.20	0.03
Br	3 2	1.2	0 28	76	0.70	6.2	3.3	1.1	0.29
Cd	0.14	0.08	0.03	74	0.0025	0.4	0.13	0.08	0 03
Cr	0.66	0.33	0.17	75	0.0710	1.40	0 65	0 34	0.17
Cu	1 9	1.5	0.22	73	0.080	8 3	1.5	1 1	0.20
Fe	150	106	6.0	76	14 0	507	150	109	4.5
Mn	2.7	1.5	0.09	74	0.55	13	2.7	1.7	0.09
Ni	2.6	2.2	0.25	64	0.1100	9 1	2.4	2.1	0.24
Pb	3.6	2.4	0 48	71	0.35	12	2 7	1.8	0 43
S	3000	1500	470	69	736.00	6638	3000	1500	450
Se	1.72	0.72	0.15	76	0 31	3.80	1.8	0.71	0.13
V	4.40	2.1	0.56	76	1 1	13	4 7	2 2	0.68
Zn	13 0	6.7	0.9	76	3.20	36	12	5.4	0.65
Wye	6/5/90- 12/31/91								
Al	114	60	10	75	25	300	109	56	8.3
As	0.64	0.33	0.05	76	0.11	2.0	0.61	0.30	0 028
Br	2 9	1.3	0.21	75	0 06	8.4	3.0	1.1	0.20
Cd	0.14	0.07	0 02	75	0 01	0 43	0.13	0.05	0 017
Cr	0.77	0 45	0 19	75	0 04	2.3	0.75	0 43	0 19
Cu	2.1	1.6	0.24	74	0.31	9.2	1.8	1.2	0.22
Fe	114	48	4.9	76	33	283	107	42	3 7
Mn	2.9	1 3	0 13	76	0 05	8.2	2 7	0.91	0.084
Ni	3.0	2.5	0.29	76	0.16	11.4	2.7	2.0	0 29
Pb	3 9	2.3	0.48	76	0.11	13.6	3.4	1.8	0.42
S	2600	1600	380	70	27	7400	2600	1600	340
Se	1.6	0.62	0.14	76	0.42	3 5	1.7	0.56	0.13
V	3.3	1.3	0 24	75	0 56	7 0	3.4	1.1	0.24
Zn	14	7.4	1 4	76	4.7	48	14	5 9	1.2
Haven Beach	11/23/90- 12/31/91								
Al	129	103	11	34	11	540	130	109	11
As	0.52	0 34	0.031	34	0.0001	1.4	0.47	0.28	0.03
Br	3.7	1.8	0.27	34	0.26	8.4	3 6	1.9	0 25
Cd	0.14	0.09	0.037	31	0 002	0.424	0.13	0.076	0.04
Cr	0 63	0.46	0 34	32	0.04	1.9	0.52	0.36	0.30
Cu	2.2	1.2	0.40	24	0.3	5	2.1	1.2	0.39
Fe	116	65	4	33	6.3	300	120	67	4.4
Mn	2.8	1.4	0 15	31	0.2	6.9	2.9	1.5	0.2
Ni	2.8	2	0.45	22	0.5	6.20	2.9	1.5	0 45
Pb	3.0	2.3	0.71	29	0.2	11	2.4	1.6	0.68
S	2100	1300	390	24	35	4700	2100	1500	370
Se	1.6	0.88	0.12	33	0.18	3.9	1.5	0.86	0.11
V	4.7	1.9	0.34	34	0.42	10	4 8	2.0	0.33
Zn	11	7	1.1	23	1.5	28	11	7.0	1.1

[1] concentrations reported to two significant figures

Table IV.2.2 Concentrations of Airborne Elements Determined in Beltsville, College Park, MD, and Lewes, DE, ng/m³.

	Beltsville				College Park								Lewes	
	9/22 - 12/1990[1]				Summer Months, 1983 - 1985[2]				Winter Months, 1985 - 1986[3]				7/24 - 9/8/89	
	Ave. ± Sigma	Min	Max	N	Ave. ± Sigma	Min	Max	N	Ave. ± Sigma	Min	Max	N	Ave. ± Sigma	N
Al	230 ± 222	12.4	868	(23)	1230 ± 810	420	4140	(31)	420 ± 280	90	1400	(24)	272 ± 265	(91)
S	1690 ± 1425	384	4863	(24)	4000 ± 2380	900	11000	(30)	2100 ± 1100	910	5600	(24)	3771 ± 3225	(92)
Cd					0.53 ± 0.22	0.29	0 86	(5)	0.52 ± 0.39	0.069	1.5	(18)		
Cr	2.01 ± 1.60	0.150	7.77	(24)	5 ± 2.8	1.5	13.2	(29)	3 9 ± 2.2	1.7	9.6	(24)	2.08 ± 1.54	(92)
Cu	5.90 ± 3.19	1.52	10 7	(9)	12 ± 5	4	18	(8)				(24)	6 21 ± 5.06	(56)
Fe	238 ± 175	33.4	733	(24)	830 ± 430	280	2200	(30)	440 ± 310	41	1600	(24)	203 ± 197	(92)
Mn	5.07 ± 5.55	1.07	28.4	(23)	20 ± 8	6	43	(31)	14 ± 7	6	36	(24)	5.32 ± 4.66	(89)
Se	1.55 ± 1.12	0.183	4.75	(24)	2.1 ± 1	0.37	4.4	(30)	2.4 ± 1	1 2	5.7	(24)	1.99 ± 1.78	(92)
V	3.47 ± 3.74	0.513	13.7	(20)	10 ± 10	1	56	(31)	9.1 ± 4.6	3.2	21	(24)	7 44 ± 5.06	(90)
Zn	25.9 ± 24.2	2.41	96.24	(24)	43 ± 17	18	100	(30)	41 ± 17	18	94	(24)	17 4 ± 13.2	(92)
As	0.518 ± 0.536	0.0993	2.38	(19)	1.01 ± 0 59	0.25	2.56	(30)	0 87 ± 0 4	0.39	1.7	(24)	1 11 ± 1.16	(83)
Br	4.00 ± 2 49	0.957	10.8	(24)	41 ± 26	11	140	(31)	28 ± 23	9 2	120	(24)	10.7 ± 12 2	(91)

[1]Han, 1992.
[2]Kitto, 1987
[3]McCarthy, 1988.

Table IV 2.3 Deposition Velocities Determined for Aerosol Particles Over Water

Investigator	Stability	Species	V_d cm/s	MMAD μm
Sievering et al., 1979 Aerometric mass balance over Lake Michigan May 18-20, 1979	extremely stable Tair 15.8° Twater 7.3° ü 3.8 ± 0.8 m/s	S04 Pb Fe Mn	0.2 ± 0.16 0.13 0.65 0.55	88% < 1 μm 82% < 1 μm 47% < 1 μm 49% < 1 μm
Dolske and Sievering, 1979 estimated from diabatic drag coef. Vd = Cdd* üair - üwater) over Lake Michigan May - Sept., 1977	3.6 to 5.2 m/s <0.9 to +0.9 unstable dT = + 1.0 to + 2.7 +2.8 to +8.2 stable	Aerosol	0.47 ± 3x 0.72 ± 3x 0.51 ± 3x 0.39 ± 3x	0.1 to 2 μm 0.1 to 2 μm 0.1 to 2 μm 0.1 to 2 μm
Delumyea and Patel, 1979 mixing box model April - October, 1977 over Lake Huron	variable[1]	aerosol P	0.57 ± 0.16 (0.79 to 1.22) (6 month ave.)	1 μm (28% < 1 μm)
Dedeurwaerder et al., 1983 vasaline - coated plates 12 days, 1980 - 1981 Souther Bight, North Sea	not reported	Cu Zn Pb Cd Fe Mn	0.19 (5) 1.0 (2) 0.20 (7) 0.23 (2) 0.42 ± 0.01 (9) 0.04 (7) 0.10 (2) 1.35 ± 0.05 (9) 0.49 (7) 0.77 (2)	0.38 μm 1.2 μm 0.20 μm 0.66 μm 0.68 to 0.75 μm 0.52 μm 1.1 μm 1.25 ± 0.05 μm 0.84 μm 0.98 μm

[1]Air and surface temperatures and wind speed not reported

Table IV.2.4. Data Summary and Atmospheric Dry Flux Estimates for Trace Elements to Chesapeake Bay

	Cummulative Average[1], ng/m³			Crustal Component %			Cummulative Deposition flux, µg/m²/yr (Low estimates)			Cummulative Deposition flux, µg/m²/yr (High estimates)		
	Elms	Wye	Haven Beach	Elms	Wye	Haven Beach	Elms	Wye	Haven Beach	Elms	Wye	Haven Beach
Al	155	114	129	100%	100%	100%	68197	50274	56889	194848	143640	162540
As	0.62	0 65	0 52	0 55%	0.38%	0 54%	52	54	44	143	150	121
Br	3.2	2 90	3.66	0 18%	0.15%	0 13%	262	239	301	724	662	835
Cd	0 14	0.14	0.14	0 14%	0.10%	0 12%	11	12	12	32	32	32
Cr	0.66	0.77	0 63	20.88%	13 24%	18 31%	104	100	93	293	280	262
Cu	1 90	2.10	2.2	3 12%	2 08%	2 25%	177	188	198	492	521	550
Fe	150	114	116	46.61%	45 21%	50 28%	37391	27845	30444	106256	79107	86567
Mn	2.7	2.9	2 8	49.58%	34 64%	40.60%	714	598	638	2031	1696	1810
Ni	2.60	3	2 8	3.33%	2.13%	2 58%	244	269	255	679	746	710
Pb	3.60	3 9	3	0 82%	0.56%	0.82%	305	327	255	847	907	706
S[1]	2983	2600	2100	0.02%	0 02%	0 02%	244509	213102	172173	677126	590146	476808
Se	1.72	1.6	1.6	0.01%	0 01%	0 01%	141	131	131	391	363	363
V	4.36	3.3	4 7	4 30%	4.19%	3 33%	424	320	441	1183	891	1228
Zn	12.65	13.5	11	0 94%	0 65%	0.90%	1079	1137	936	2992	3152	2597

	1991 Average Concentration ng/m³			Crustal Component %			Low Flux Estimates 1991			High Flux Estimates 1991		
	Elms	Wye	Haven Beach	Elms	Wye	Haven Beach	Elms	Wye	Haven Beach	Elms	Wye	Haven Beach
Al	150	109	130	100%	100%	100%	66150	48083	57330	189000	137379	163800
As	0 56	0.61	0 47	0 52%	0 37%	0 53%	47	51	39	129	140	108
Br	3.3	3 0	3.6	0 17%	0 14%	0 15%	273	249	293	756	690	811
Cd	0 13	0 13	0.13	0 15%	0 11%	0 13%	11	11	10	29	30	29
Cr	0 65	0 75	0 52	20 38%	13 24%	18 24%	101	97	77	284	272	217
Cu	1 5	1 8	2 1	2 69%	2.00%	2.02%	134	162	185	371	450	513
Fe	150	107	120	51 53%	46.37%	58.62%	40040	26580	35138	113876	75529	100037
Mn	2 7	2.7	2 9	48 78%	33 05%	44.94%	705	545	700	2004	1543	1989
Ni	2 4	2.7	2.9	3.47%	2 24%	1 82%	230	246	255	640	682	709
Pb	2 7	3 4	2 4	0 67%	0.54%	0.71%	231	283	205	641	785	569
S[1]	3000	2600	2100	0 02%	0.02%	0.02%	245928	213117	172159	681056	590191	476767
Se	1.8	1.7	1.5	0 01%	0.01%	0 01%	150	143	120	415	395	331
V	4 7	3.4	4 8	4.82%	4.55%	4 04%	462	338	463	1288	942	1290
Zn	12	14	11	0 95%	0.66%	1.07%	1066	1173	982	2957	3252	2724

aerosol particle data only, Elms and Wye 6/5/90 - 12/31/91, Haven Beach 11/23/90 - 12/31/91

Table IV.3.1 Comparative Precipitation Concentrations (μg/L) for a Single Rain Event (23 October 1990) at Five Mid-Atlantic Sites (Volume weighted averages)

	Al	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
	μg/L								
Chesapeake Bay (Shipboard)	1.9	0.013	0.025	0.09	1.4	0.07	0.66	0.27	0.16
Wye CBADS	3.8	0.007	0.199	0.18	2.7	2.65	0.29	0.17	0.77
Elms CBADS	2.5	0.001	0.081	0.10	3.2	0.34	0.14	0.13	0.23
Beltsville, MD[a]	1.9	0.007	0.140	0.13	3.6	0.14	0.05	0.09	0.56
Lewes, DE	1.3	0.067	0.032	0.17	0.8	0.10	0.10	0.13	0.19

[a]USDA Experimental Station, collection and analysis methods identical to CBADS (Scudlark *et al.*, 1994).

Table IV.3.2 Spatial Variability in Trace Element Wet Deposition at Three CBADS Sites for 1991 [$\mu g/m^2/year$].

Element	WYE Total (% Crustal)[a]		ELMS Total (% Crustal)[a]		HAVEN BEACH Total (% Crustal)[a]		Flux Ratio (Wye: Elms: Haven)
Al	16,042	(100)	8,411	(100)	17,524	(100)	0.9:0.5:1.0
As	37	(7)	54	(3)	60	(5)	0.6:0.9:1.0
Cd	46	(*)	55	(*)	151	(*)	0.3:0.4:1.0
Cr	104	(17)	87	(11)	NA		1.2:1.0:--
Cu	210	(4)	216	(2)	1,176	(1)	0.2:0.2:1.0
Fe	12,290	(77)	6,498	(76)	12,277	(84)	1.0:0.5:1.0
Mn	1,230	(14)	891	(10)	1,236	(15)	1.0:0.7:1.0
Ni	271	(5)	240	(3)	NA		1.1:1.0:--
Pb	633	(*)	623	(*)	480	(1)	1.3:1.3:1.0
Se	133	(*)	115	(*)	128	(*)	1.0:0.9:1.0
Zn	1,358	(1)	1,377	(1)	2,030	(1)	0.7:0.7:1.0

(*) = less than 1%
[a Al normalized]

Table V.1 Summary[1] of Atmospheric Fluxes and Loadings of Trace Contaminants to Chesapeake Bay, 1991

Organic Contaminant	Fluxes µg/m²/yr			Loadings (Kg/yr)**			
	Dry	Wet	Total	Dry	Wet	Total	±[3]
Fluorene	1.4	2.0	3.4	16	23	39	10
Phenantharene	11	7.4	18	127	85	211	63
Anthracene	0 8	0.6	1 4	9	7	16	5
Fluroanthene	15	5.3	21	176	61	237	81
Pyrene	13	3.7	17	147	43	190	69
Benz[a]anthracene	4.1	0.9	5.0	47	10	57	23
Chrysene	10	2 7	13	116	31	146	52
Benzo[b]fluoranthene	12	2.7	15	138	31	169	63
Benzo[k]fluoranthene	8.7	1.5	10	99	18	117	46
Benzo [e] Pyrene	7 8	1 9	10	90	21	111	46
Benzo[a]pyrene	4.5	1 6	6.1	52	18	70	29
Indeno[123]pyrene	12	2.4	15	141	27	168	63
Dibenz[ah]anthracene	2.4	0 6	2.9	27	7	34	12
Benzo[ghi]perylene	9.9	2 4	12	113	27	141	58
Total PCBs[2]	1.7	1.5	3.2	20	17	37	9
Trace Element	**Dry Flux**	**Wet Flux**	**Total Flux**	**Dry Loading**	**Wet Loading**	**Total Loading**	**±**
Al	110290	14000	124290	1300000	160000	1460000	680000
As	86	50	136	1000	580	1800	630
Cd	20	80	100	130	920	1200	130
Cr	175	100	275	2000	1100	3100	1300
Cu	302	530	832	3500	6100	11000	2600
Fe	65200	10000	75200	750000	120000	870000	450000
Mn	1247	1100	2347	15000	12700	30000	8600
Ni	460	260	720	5300	3000	10000	3800
Pb	452	580	1032	5200	6700	12000	3000
Se	259	130	389	3000	1500	4500	1600
Zn	2026	1600	3626	23000	18000	41000	14000

[1] average of the bay sites (Elms and Haven Beach for organics; Wye, Elms, and Haven Beach for trace elements)
[2] sum of 74 congeners
[3] represents the uncertainity represented by the largest assumed dry deposition velocity (to one significant figure)
**loadings calculated by extrapolating the average flux to the surface area of the Chesapeake Bay below the fall line (1.15E10 m²)

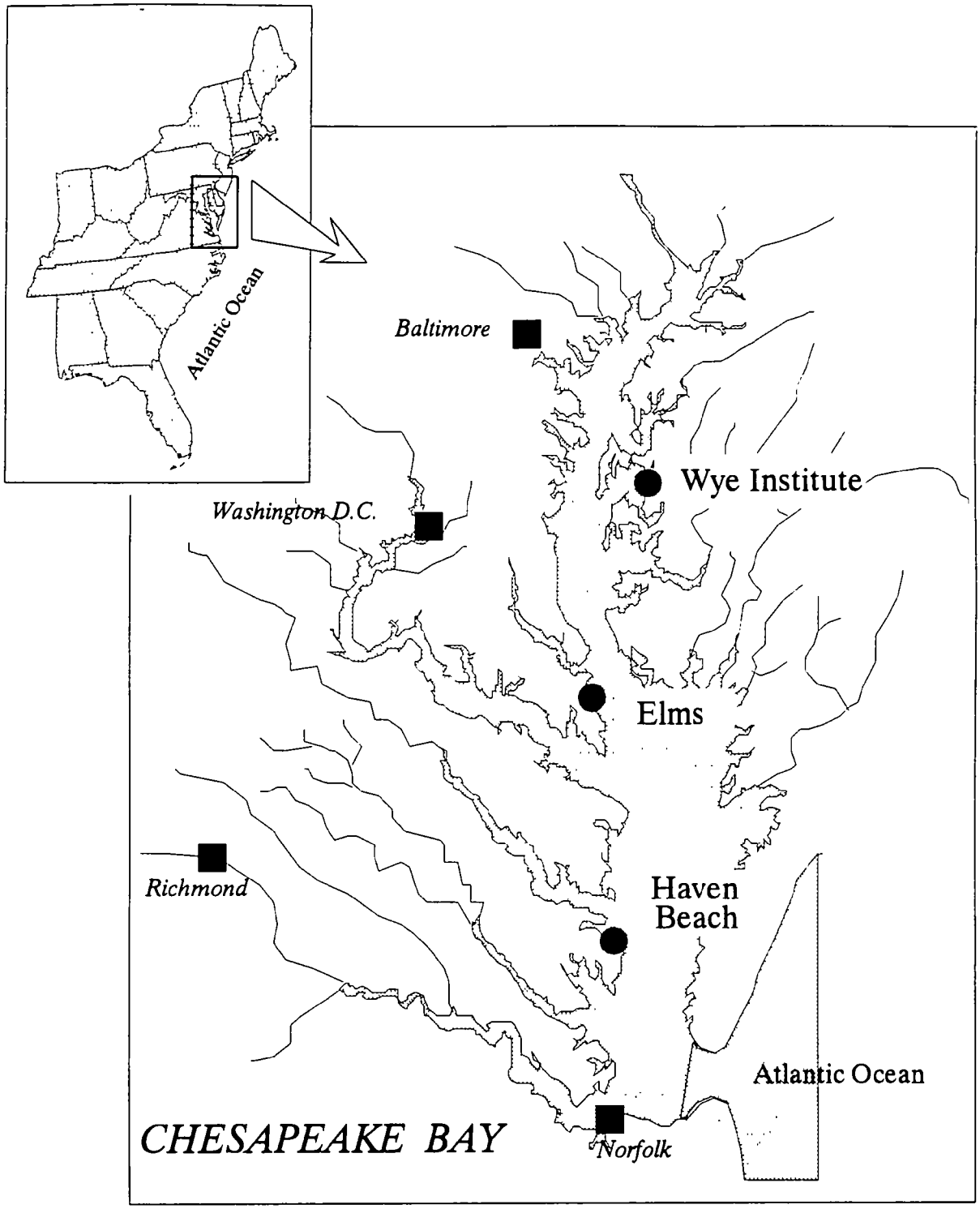


Figure 11.2.1. Chesapeake Bay atmospheric deposition sites. Organic contaminant data collected at the Elms and Haven Beach stations only.

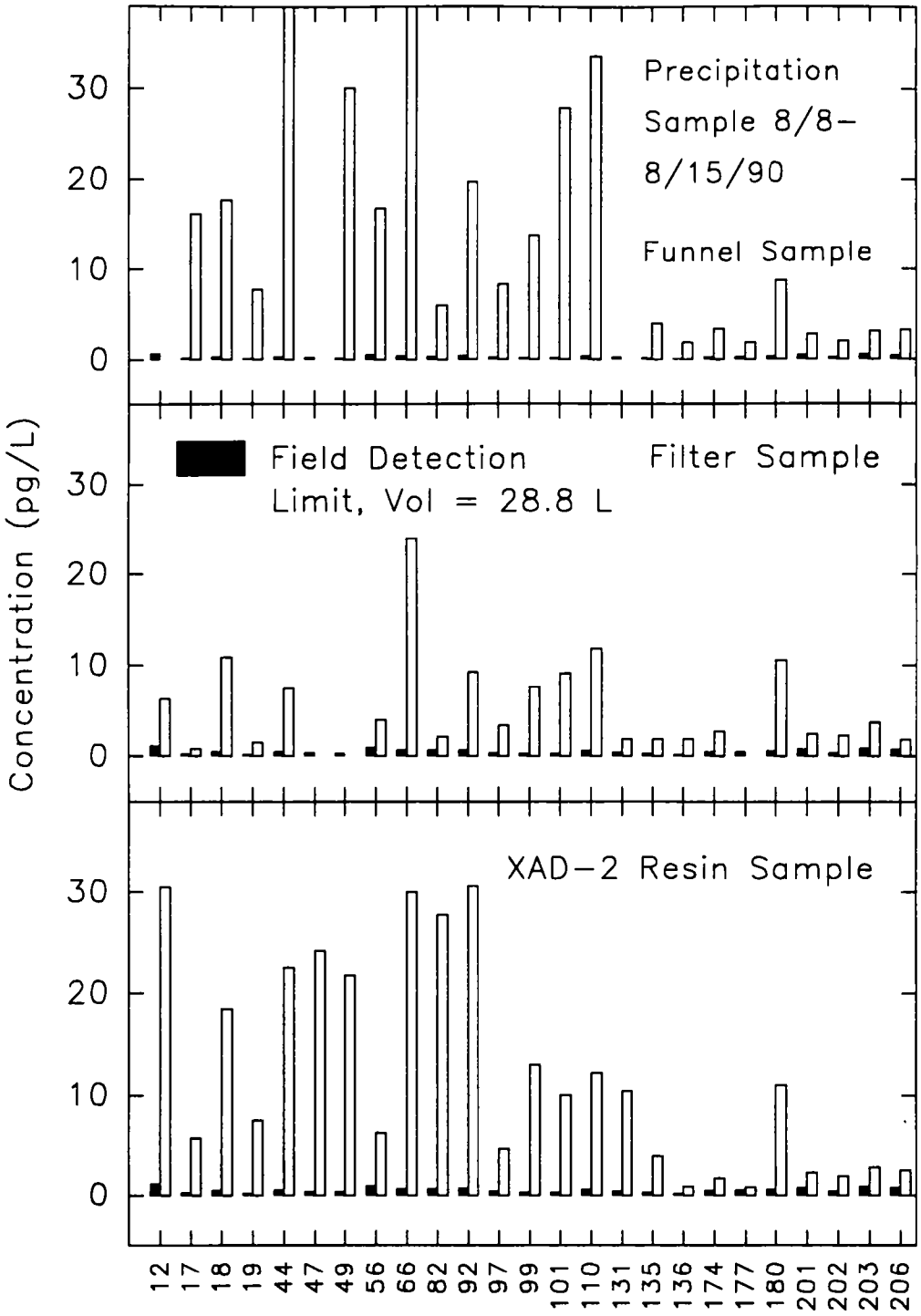


Figure III.1.1. Comparison of several PCB congeners in a precipitation sample to field detection limits. Field detection limits assume an annual precipitation rate of 75 cm. The sample volume is 54 L.

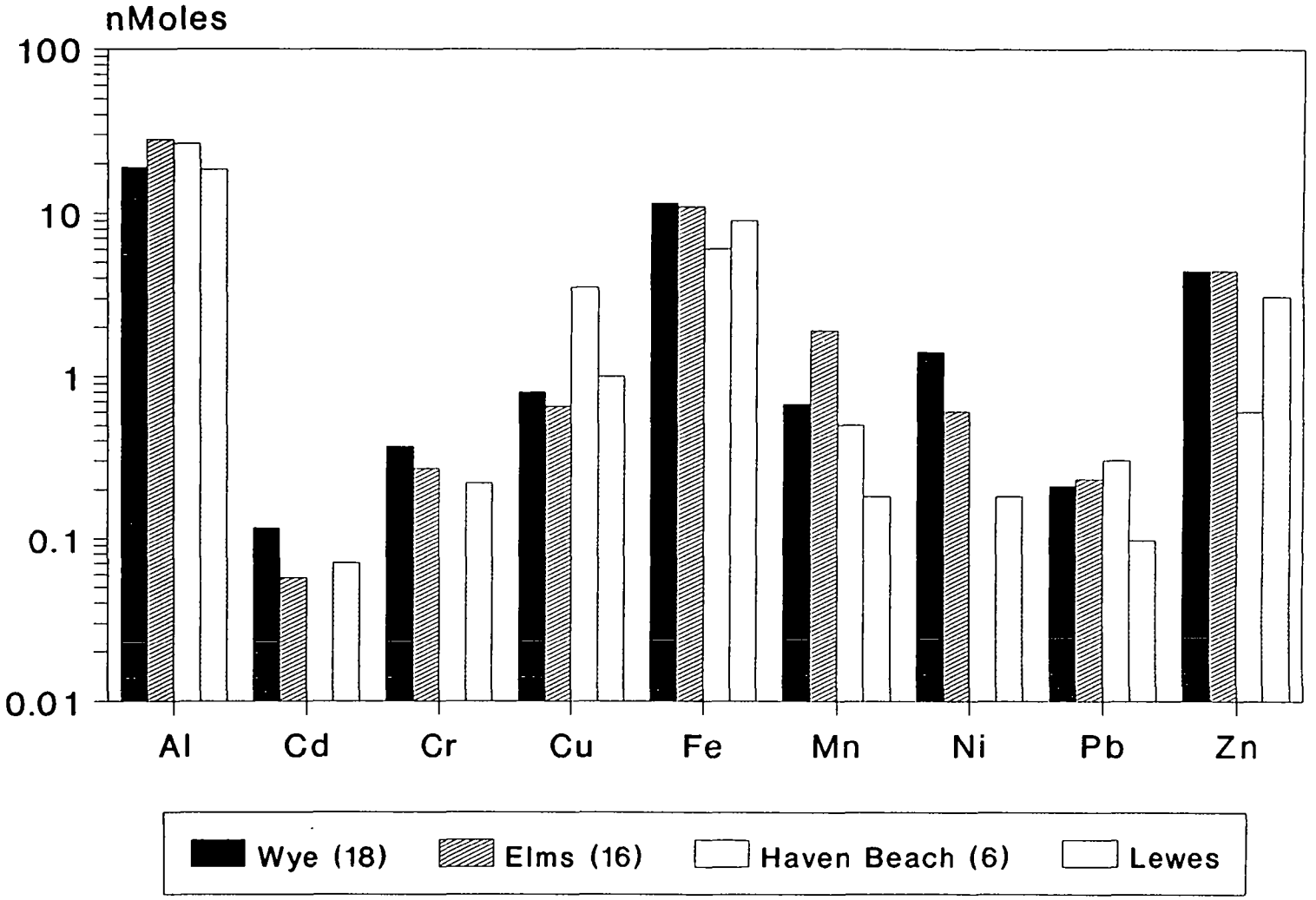
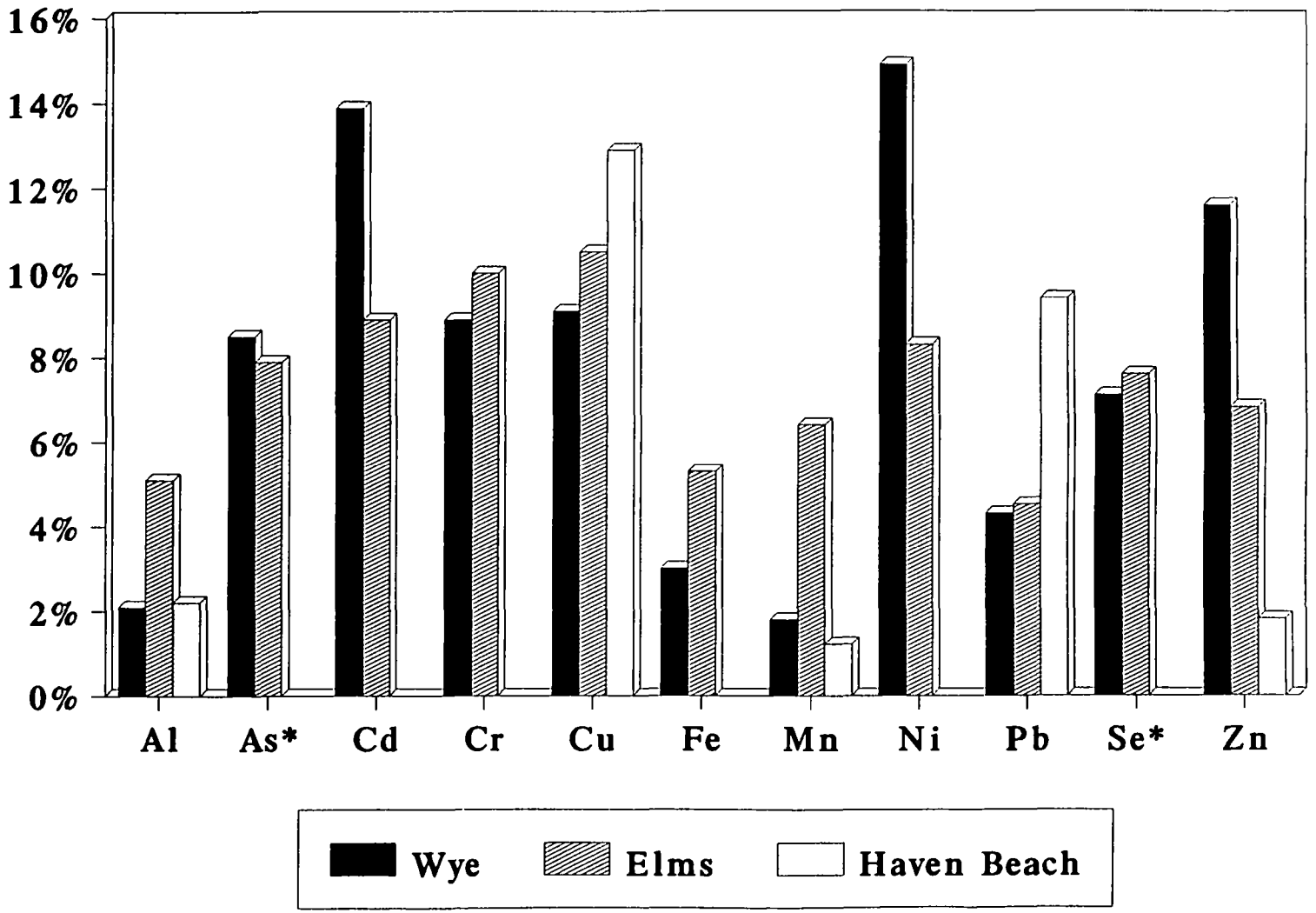
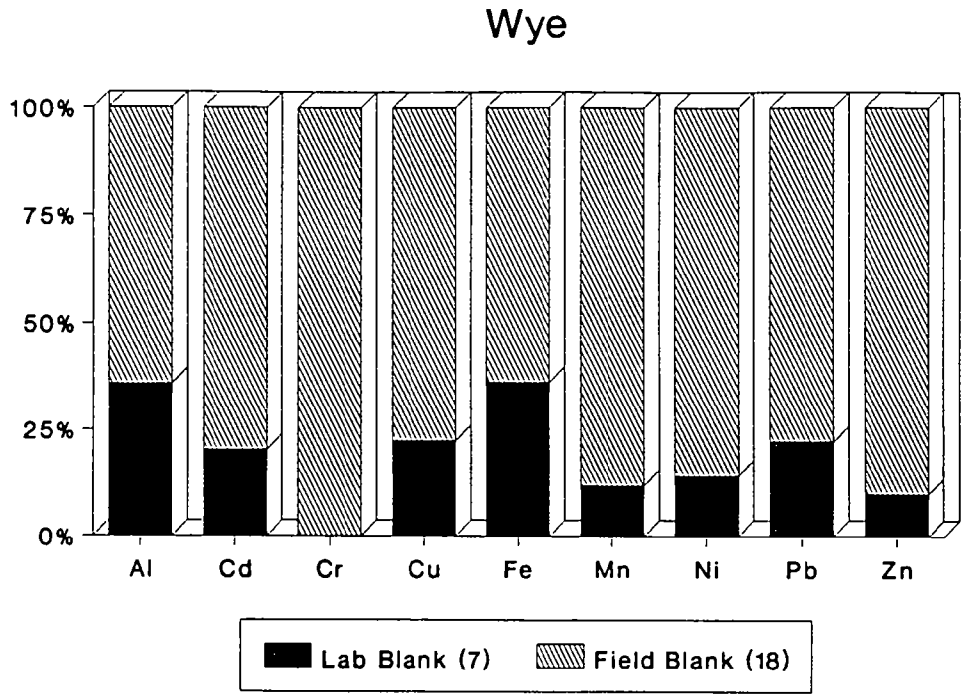


Figure III.3.1 Comparison of absolute field blank contributions at 3 CBADS sites to those measured at Lewes, DE.



***As & Se FB est from Detection Limits**

Figure III.3.2 A comparison of field blanks at 3 CBADS sites, shown as a percentage of the average sample concentration.



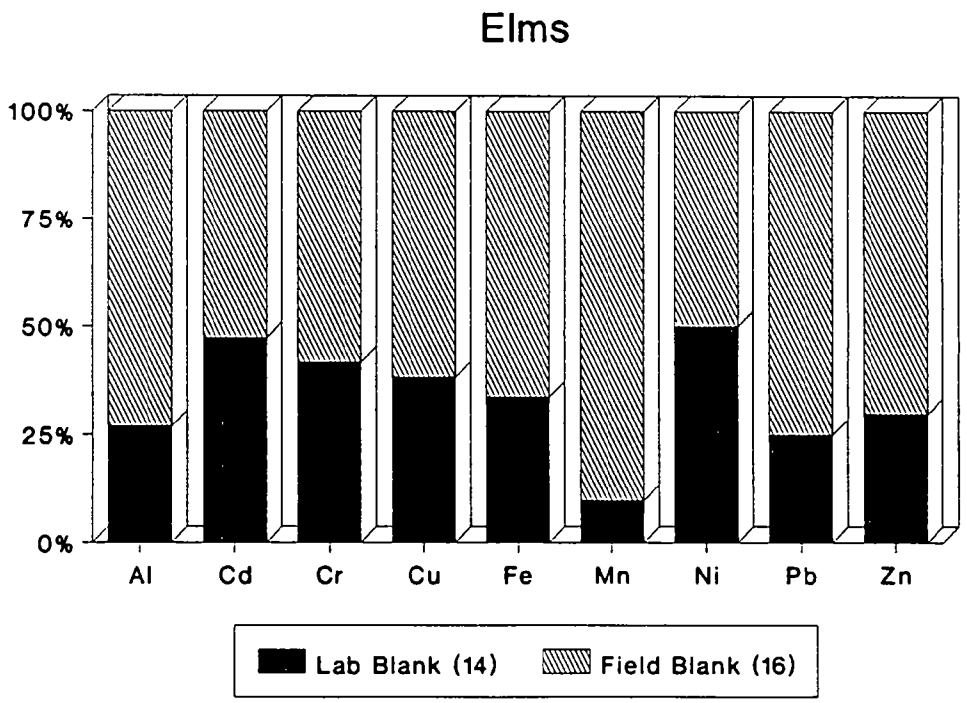


Figure III.3.3 A comparison of laboratory blanks to field blanks at 2 CBADS sites.

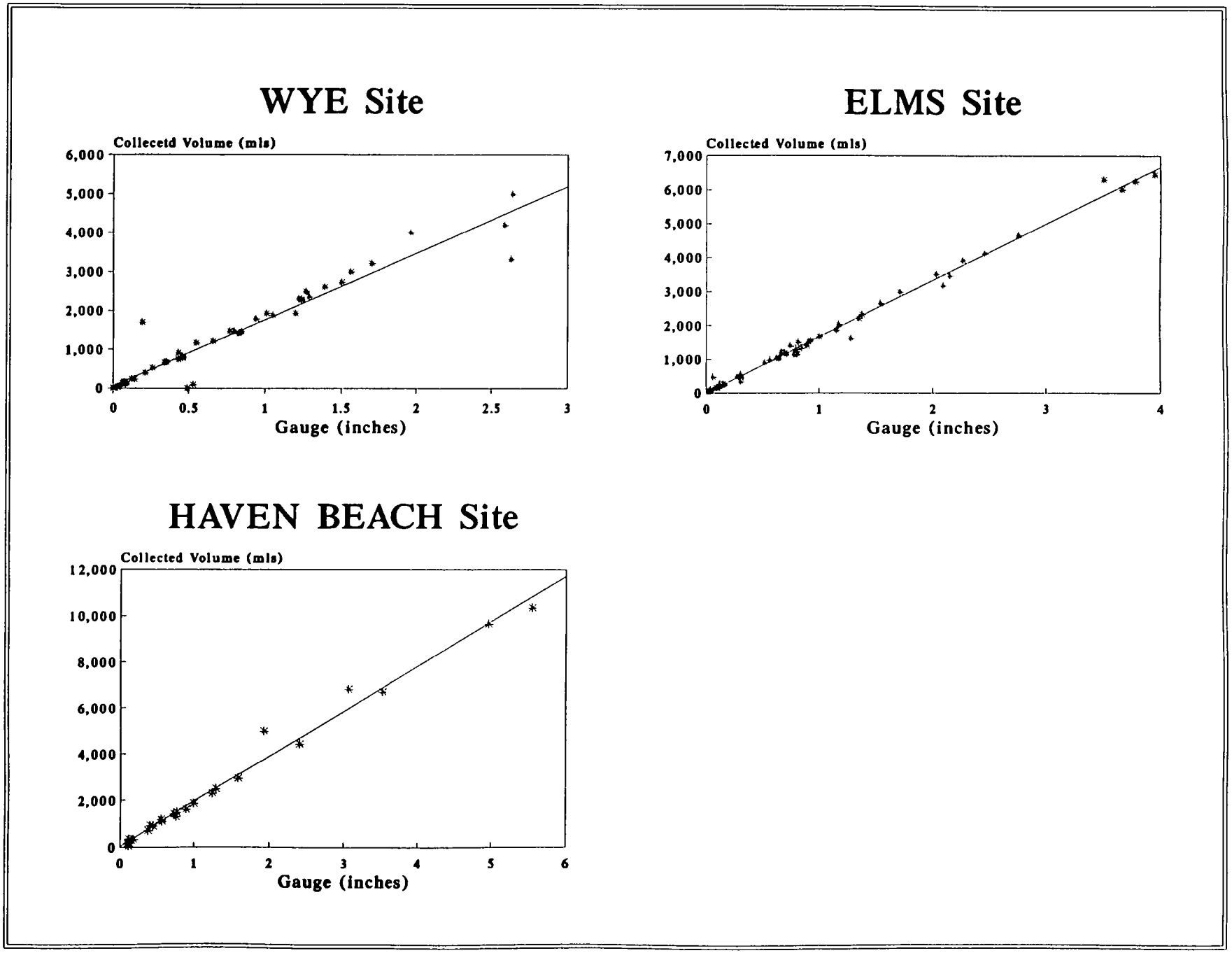
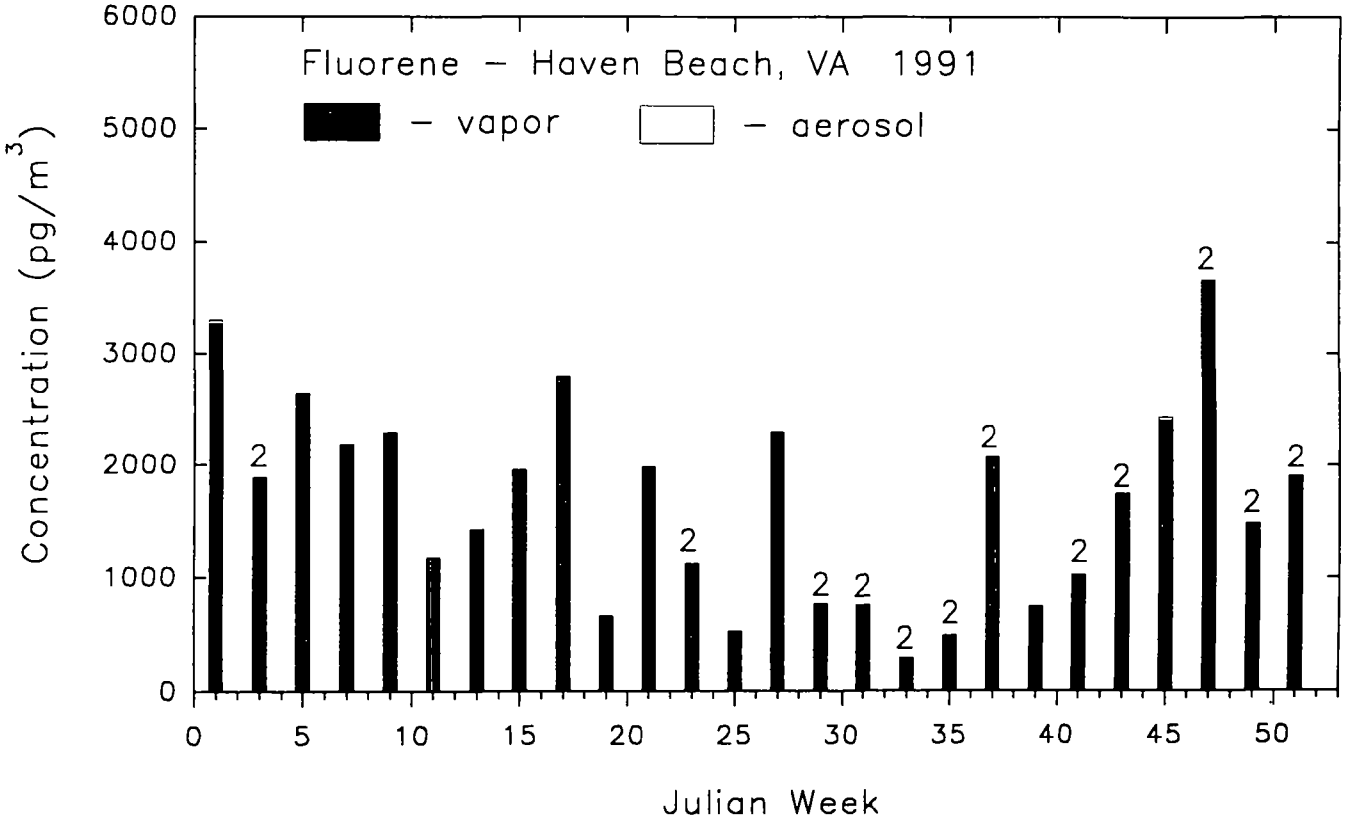


Figure III.3.4 A comparison of the predicted volume (from gauge) to the collected volume as an indication of the efficiency of the collector.

Figure IV.1.1 Fluorene concentrations in air collected at the Elms and Haven Beach sites. (1=not quantifiable in vapor phase, 2=not quantifiable on filter, 3=not detected in vapor phase, 4=not detected on filter, *=lost vapor sample, **=lost particulate sample)



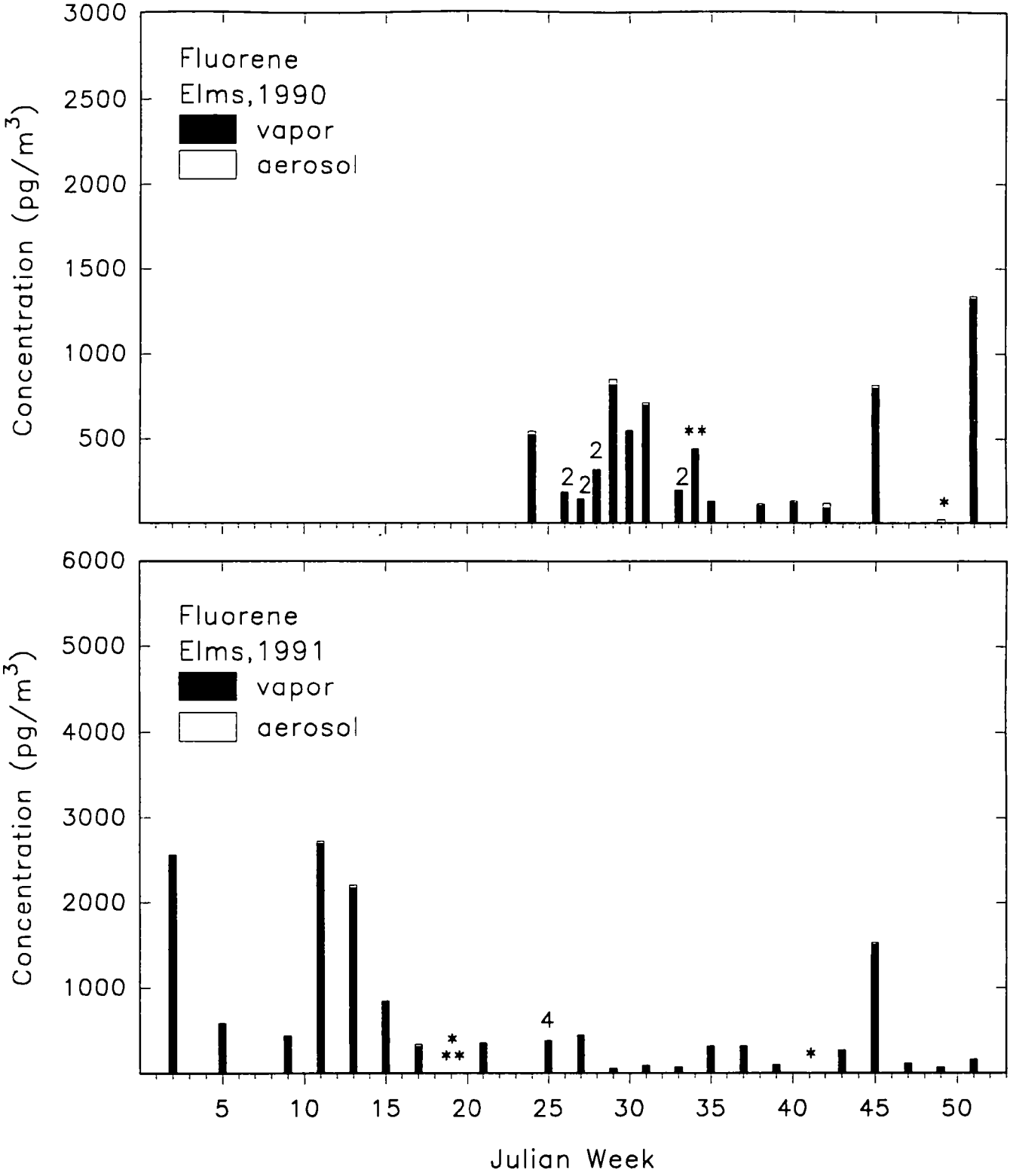
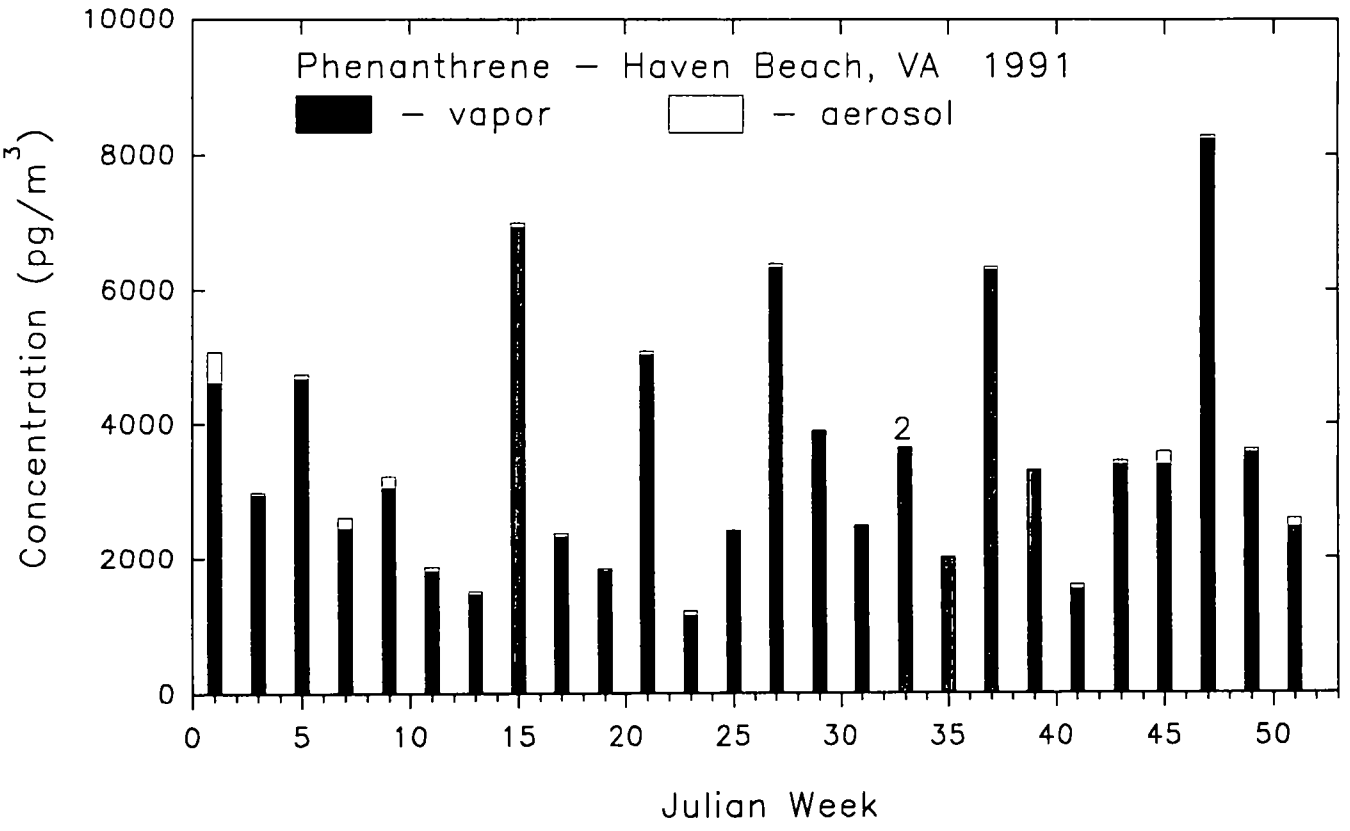
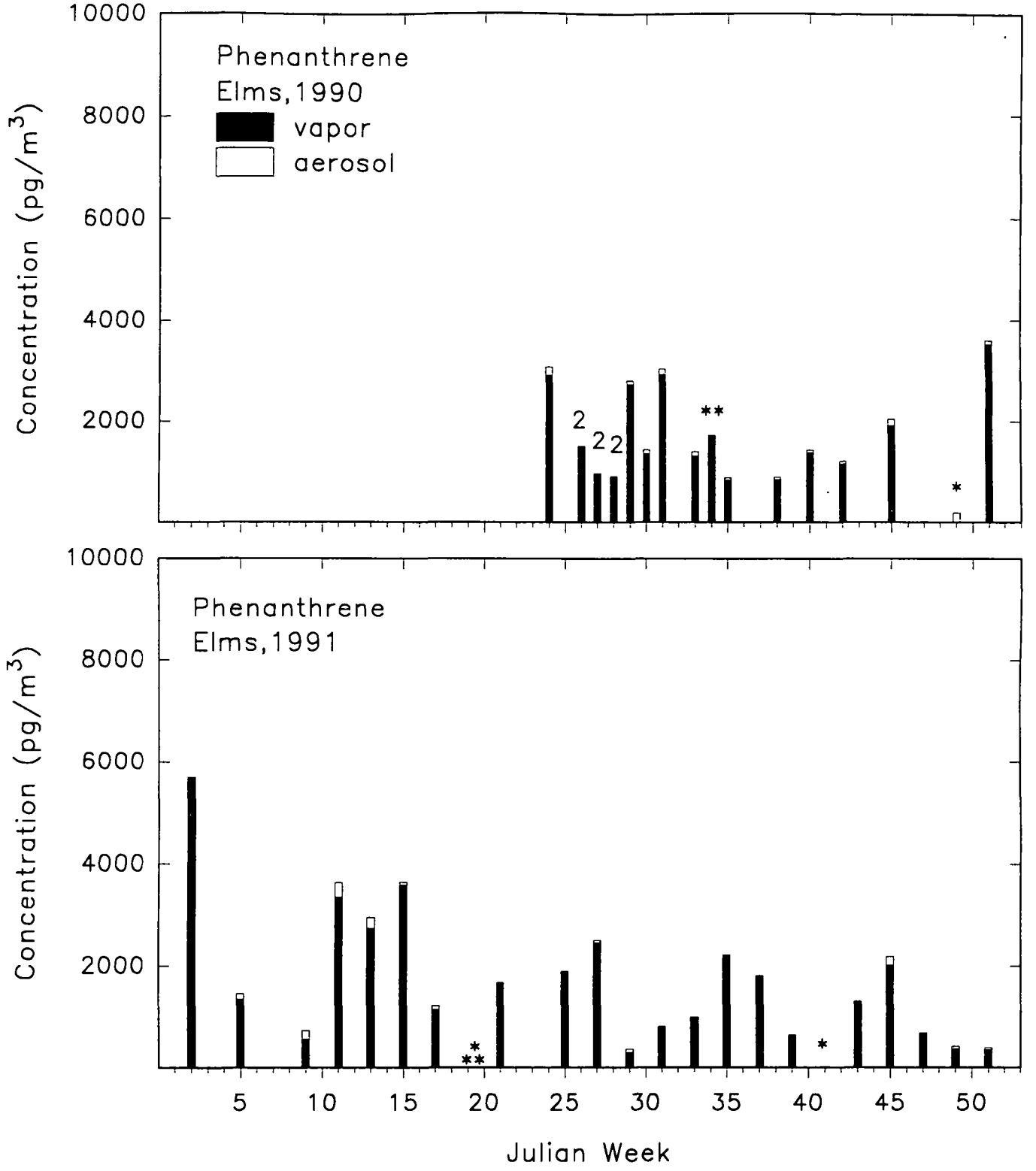

Fluorene
Elms,1990
vapor
aerosol
Concentration (pg/m3)
3000
2500
2000
1500
1000
500
2
2
2
2
2
**
*
Fluorene
Elms,1991
vapor
aerosol
Concentration (pg/m3)
6000
5000
4000
3000
2000
1000
*
**
4
*
5
10
15
20
25
30
35
40
45
50
Julian Week

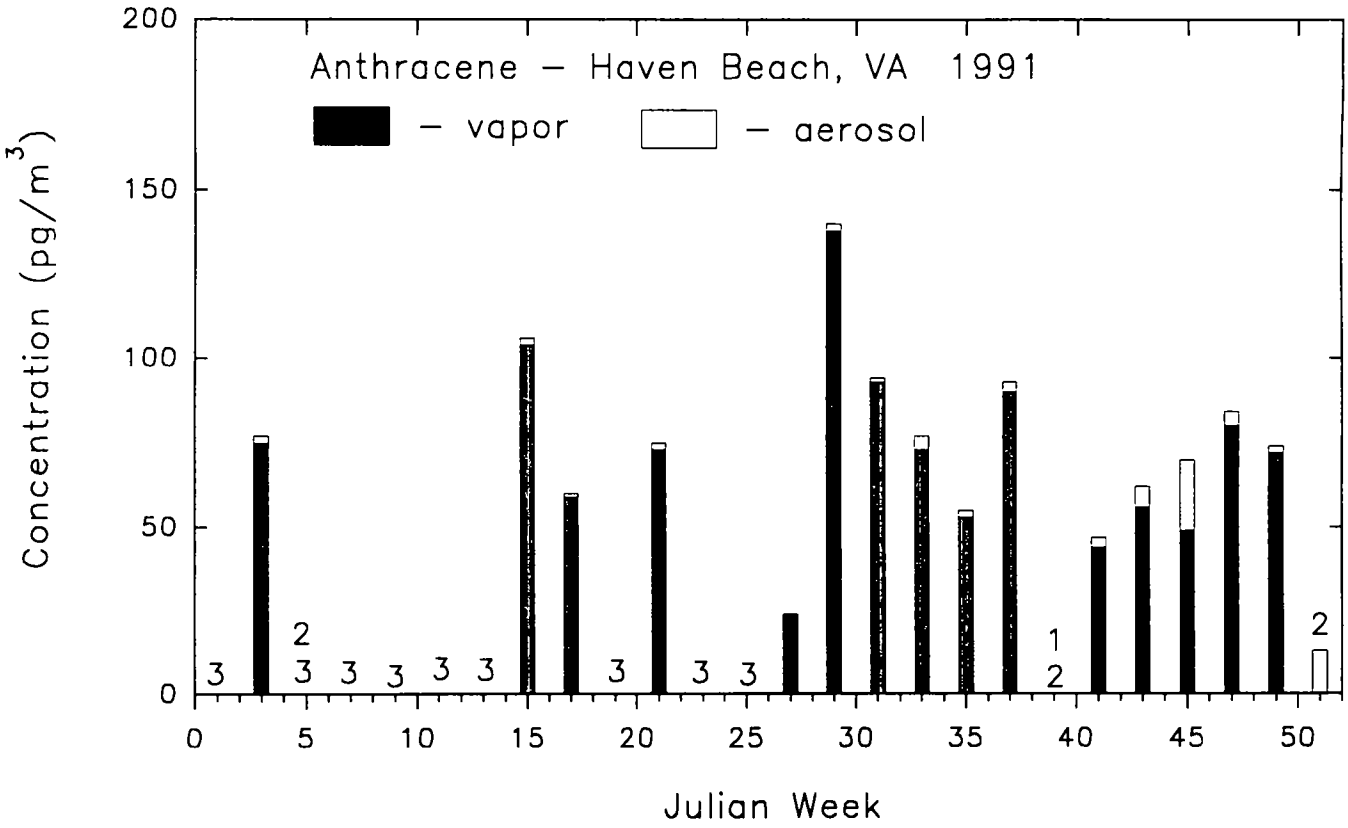
Figure IV.1.2 Phenanthrene concentrations in air collected at the Elms and Haven Beach sites. (1=not quantifiable in vapor phase, 2=not quantifiable on filter, 3=not detected in vapor phase, 4=not detected on filter, *=lost vapor sample, **=lost particulate sample)




Phenanthrene
Elms,1990
vapor
aerosol
Concentration (pg/m3)
10000
8000
6000
4000
2000
2
2
2
**
*
Phenanthrene
Elms,1991
Concentration (pg/m3)
10000
8000
6000
4000
2000
*
**
*
5
10
15
20
25
30
35
40
45
50
Julian Week

por

Figure IV.1.3 Anthracene concentrations in air collected at Elms and Haven Beach sites. (1=not quantifiable in vapor phase, 2=not quantifiable on filter, 3=not detected in vapor phase, 4=not detected on filter, *=lost vapor sample, **=lost particulate sample)



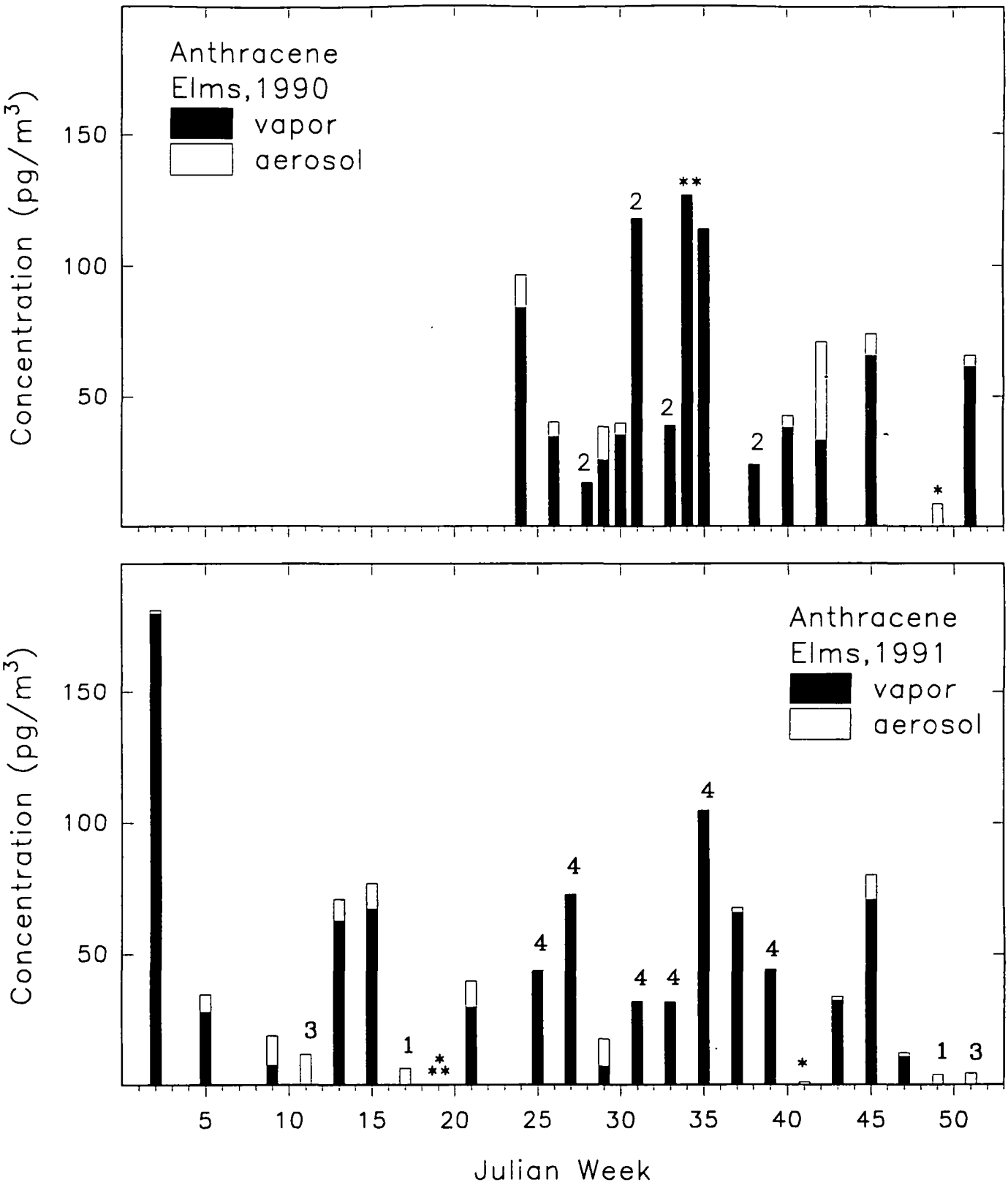
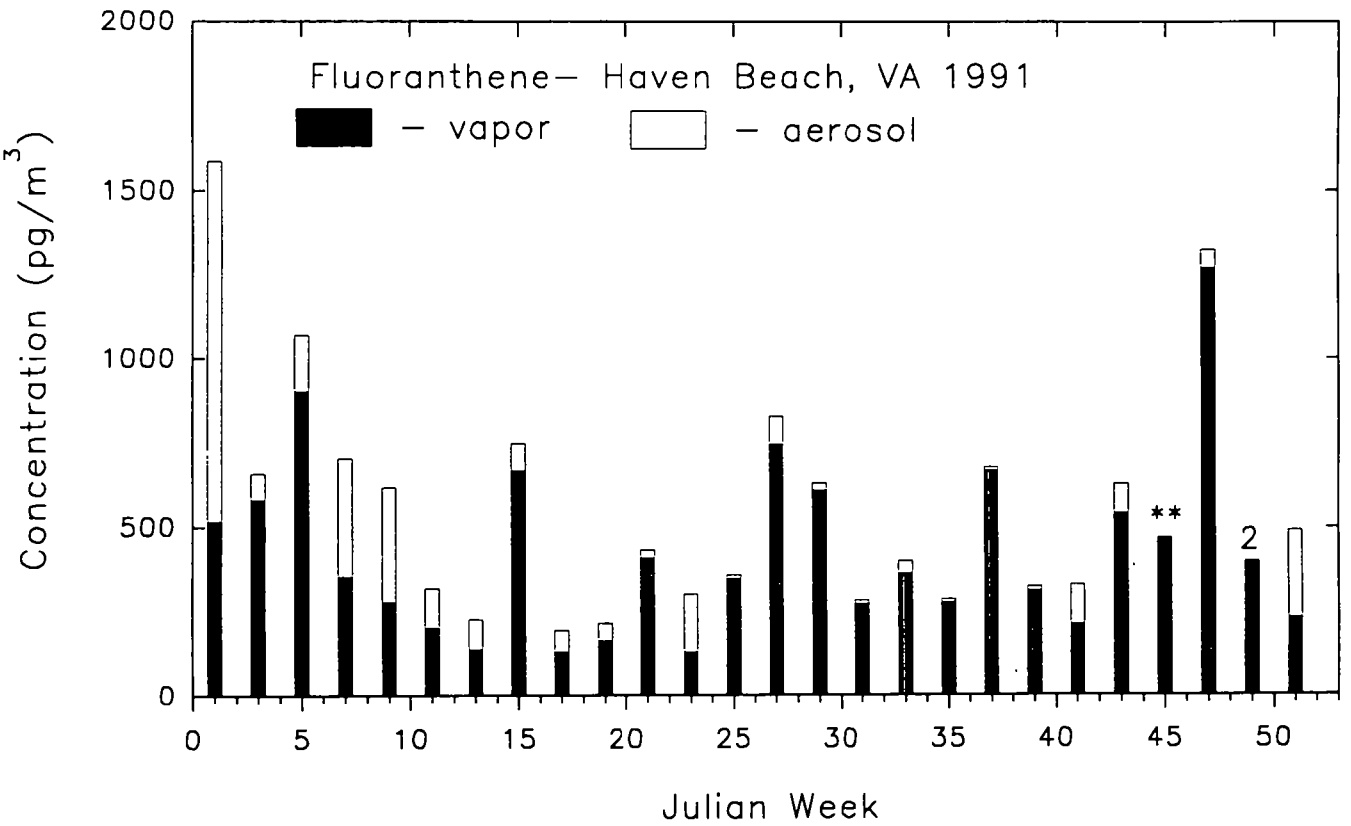

Anthracene
Elms,1990
vapor
aerosol
Concentration (pg/m3)
150
100
50
2
2
2
2
**
*
Anthracene
Elms,1991
vapor
aerosol
Concentration (pg/m3)
150
100
50
3
1
*
**
4
4
4
4
4
4
*
1
3
5
10
15
20
25
30
35
40
45
50
Julian Week

Figure IV.1.4 Fluoranthene concentrations in air collected at the Elms and Haven Beach sites. (1=not quantifiable in vapor phase, 2=not quantifiable on filter, 3=not detected in vapor phase, 4=not detected on filter, *=lost vapor sample, **=lost particulate sample)



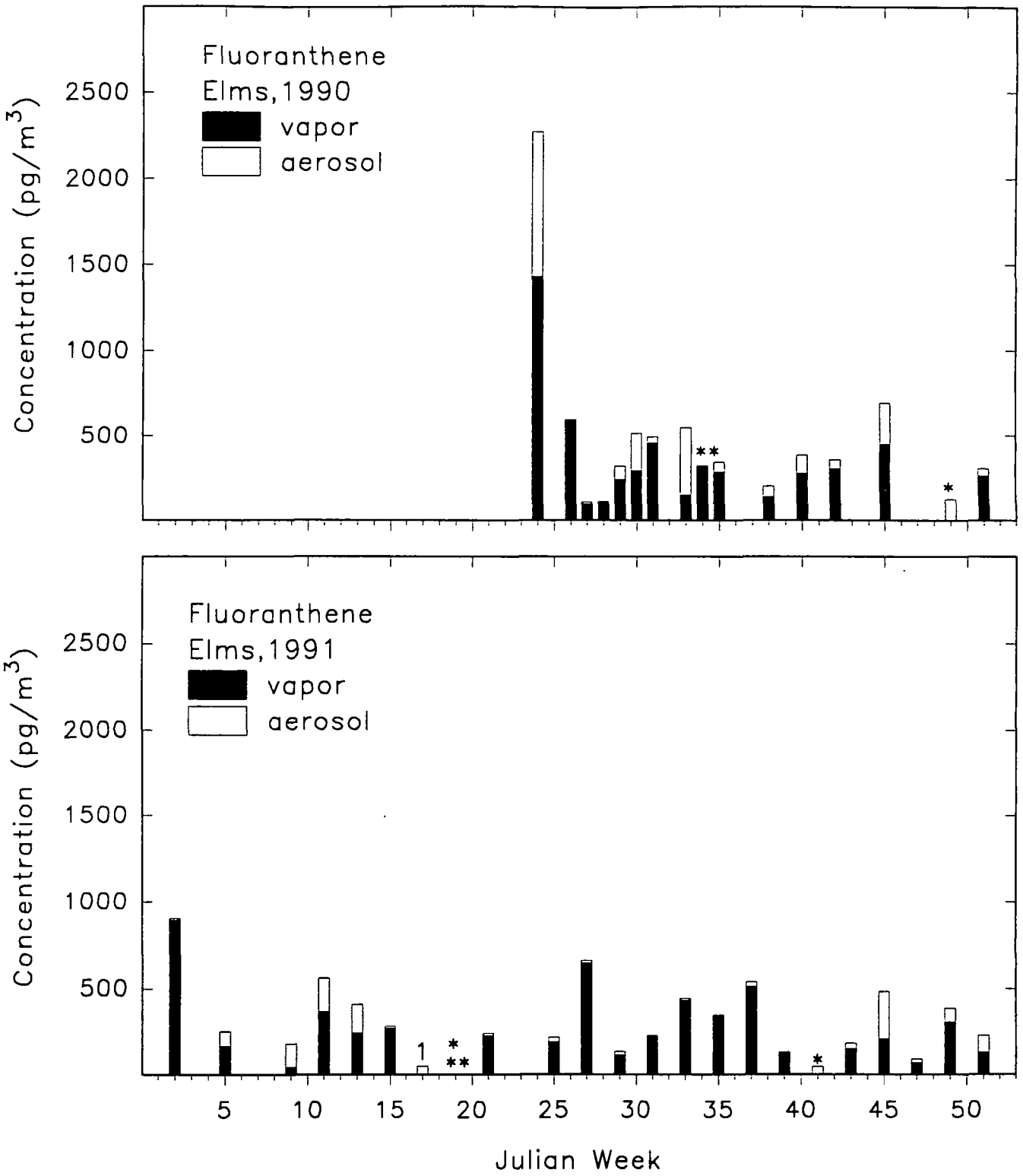
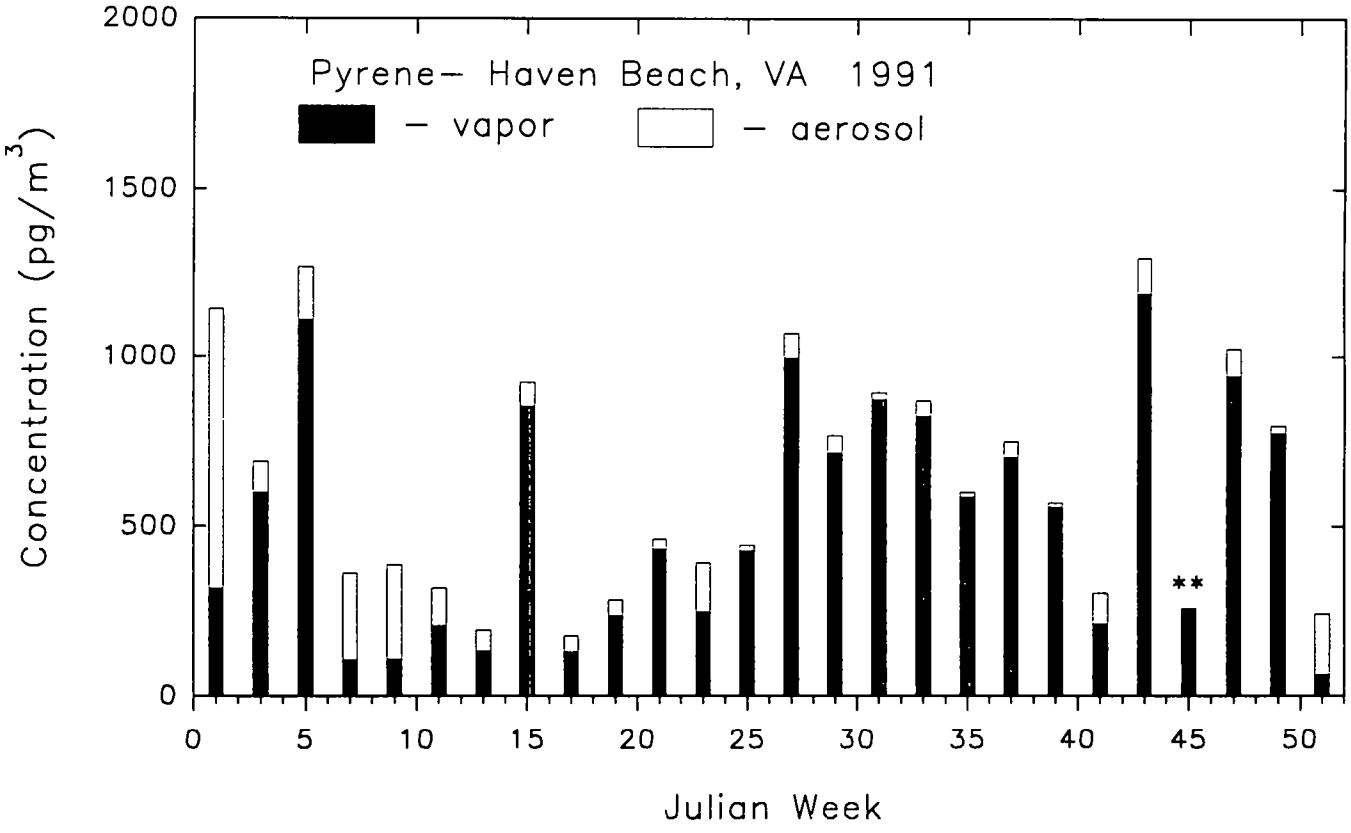

Fluoranthene
Elms,1990
vapor
aerosol
Concentration (pg/m3)
2500
2000
1500
1000
500
Fluoranthene
Elms,1991
vapor
aerosol
Concentration (pg/m3)
2500
2000
1500
1000
500
5
10
15
20
25
30
35
40
45
50
Julian Week

Figure IV.1.5 Pyrene concentrations in air collected at the Elms and Haven Beach sites. (1=not quantifiable in vapor phase, 2=not quantifiable on filter, 3=not detected in vapor phase, 4=not detected on filter, *=lost vapor sample, **=lost particulate sample)



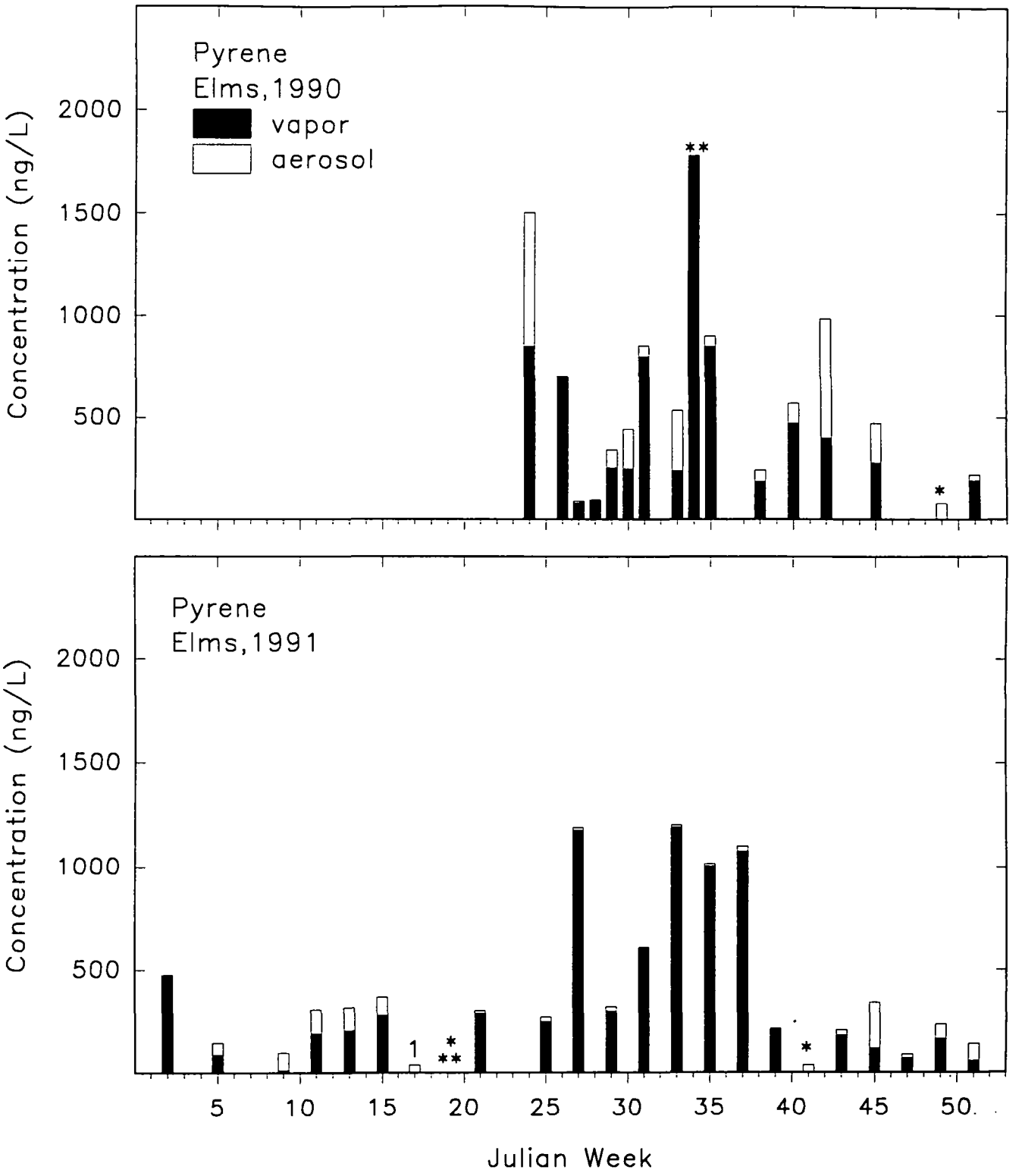
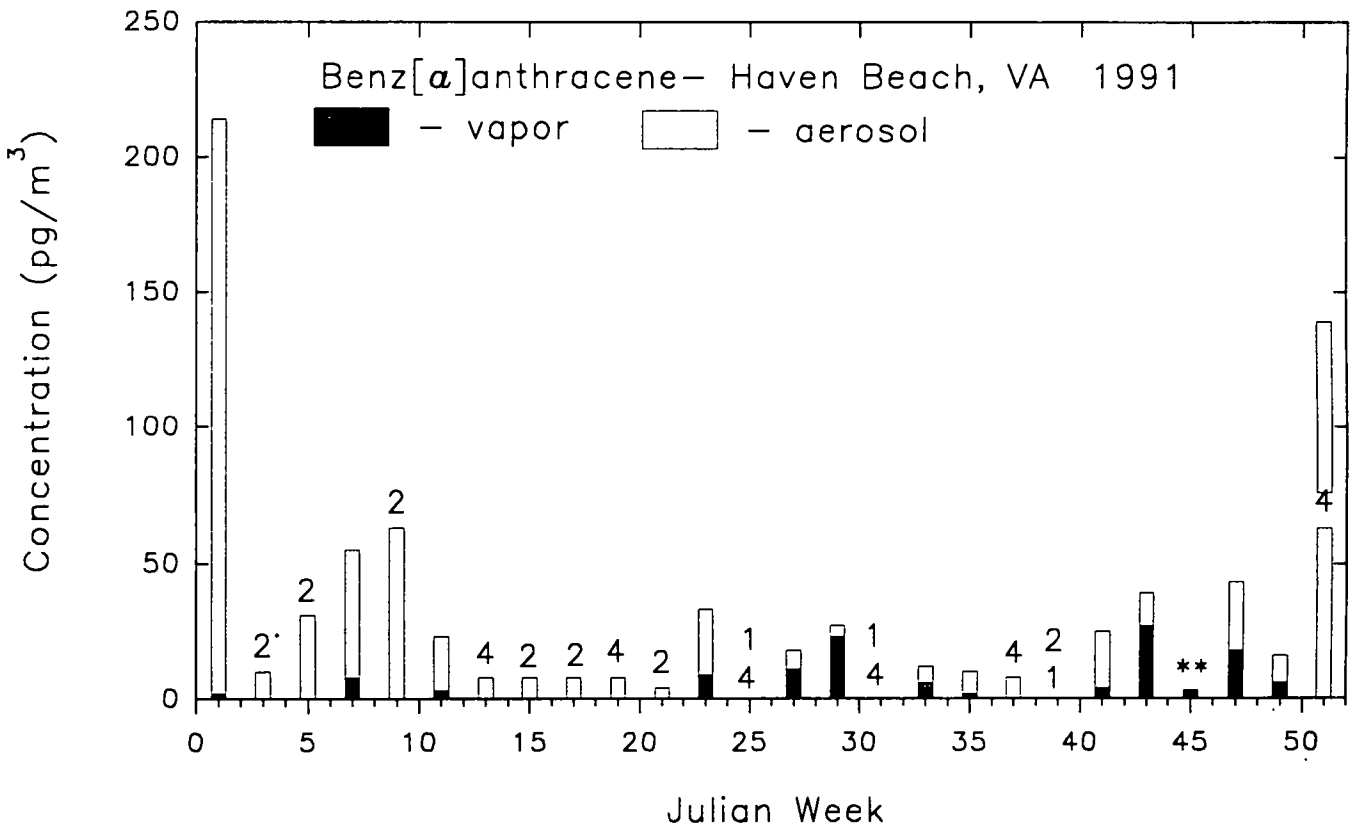

Pyrene
Elms,1990
vapor
aerosol
Concentration (ng/L)
2000
1500
1000
500
Pyrene
Elms,1991
Concentration (ng/L)
2000
1500
1000
500
5
10
15
20
25
30
35
40
45
50
Julian Week

Figure IV.1.6 Benz[*a*]anthracene concentrations in air collected at Elms and Haven Beach sites. (1= not quantifiable in vapor phase, 2=not quantifiable on filter, 3=not detected in vapor phase, 4=not detected on filter, *=lost vapor sample, **=lost particulate sample)



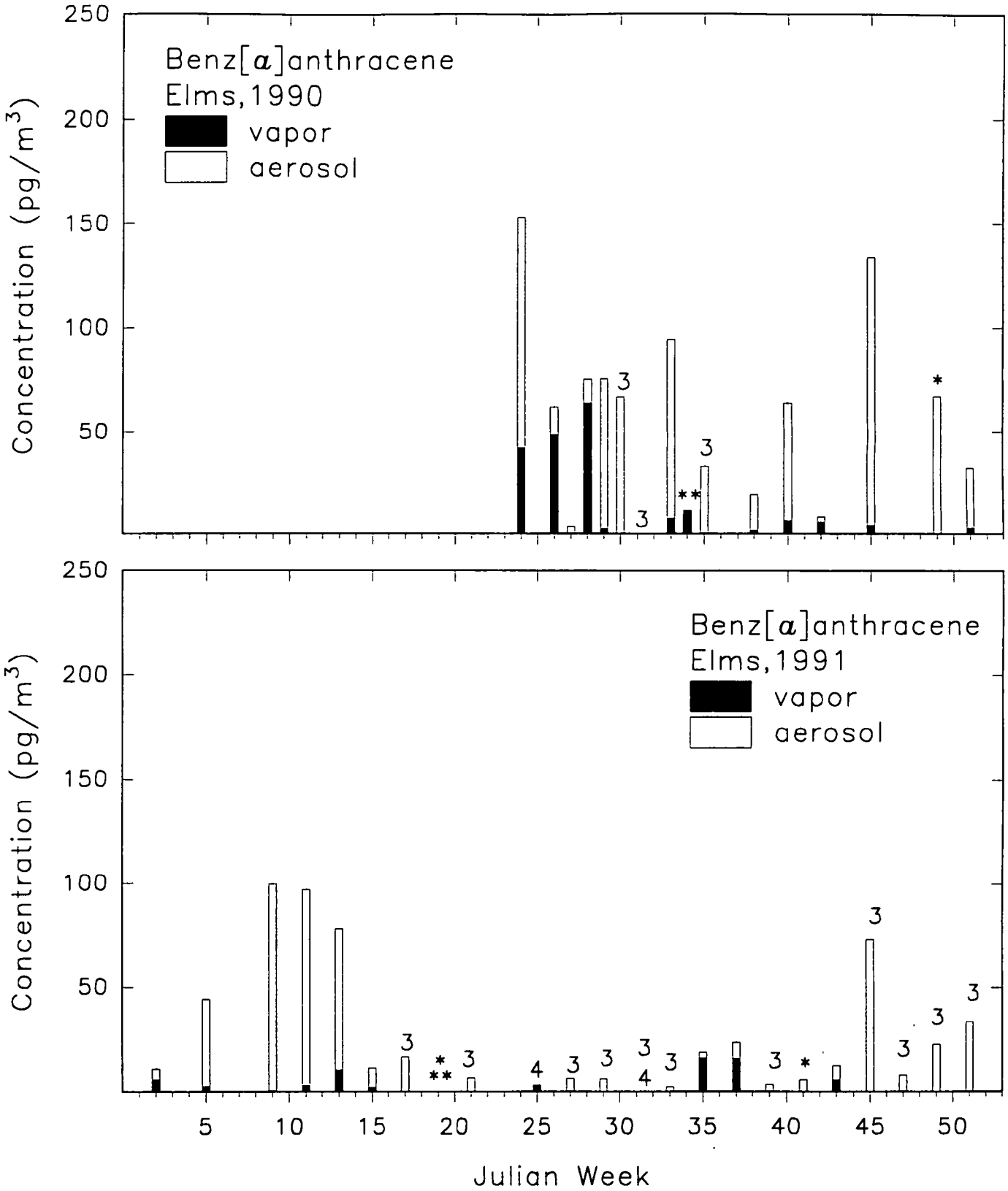
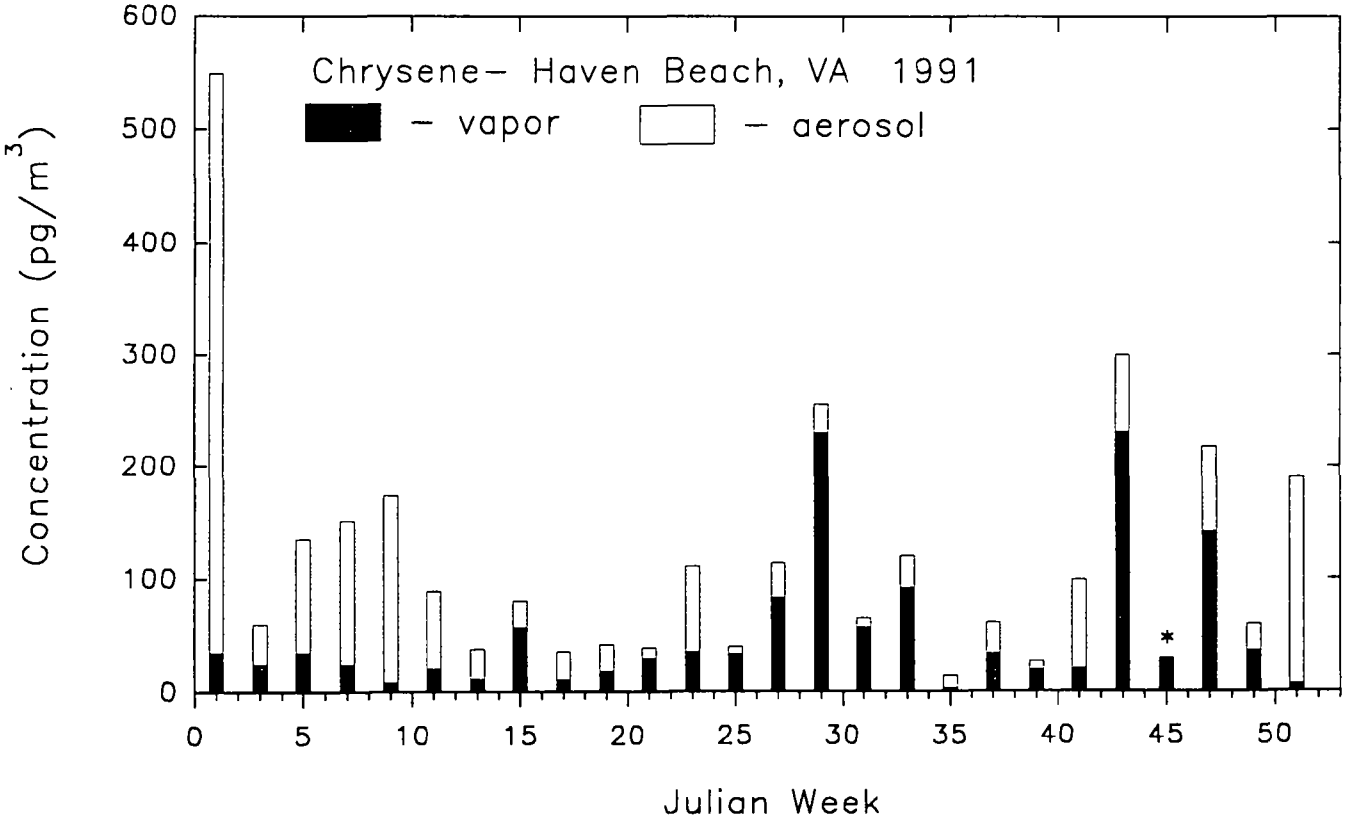

Benz[a]anthracene
Elms,1990
vapor
aerosol
Concentration (pg/m3)
250
200
150
100
50
Benz[a]anthracene
Elms,1991
vapor
aerosol
Concentration (pg/m3)
250
200
150
100
50
5
10
15
20
25
30
35
40
45
50
Julian Week

Figure IV.1.7 Chrysene concentrations in air collected at the Elms and Haven Beach sites. (1=not quantifiable in vapor phase, 2=not quantifiable on filter, 3=not detected in vapor phase, 4=not detected on filter, *=lost vapor sample, **=lost particulate sample)



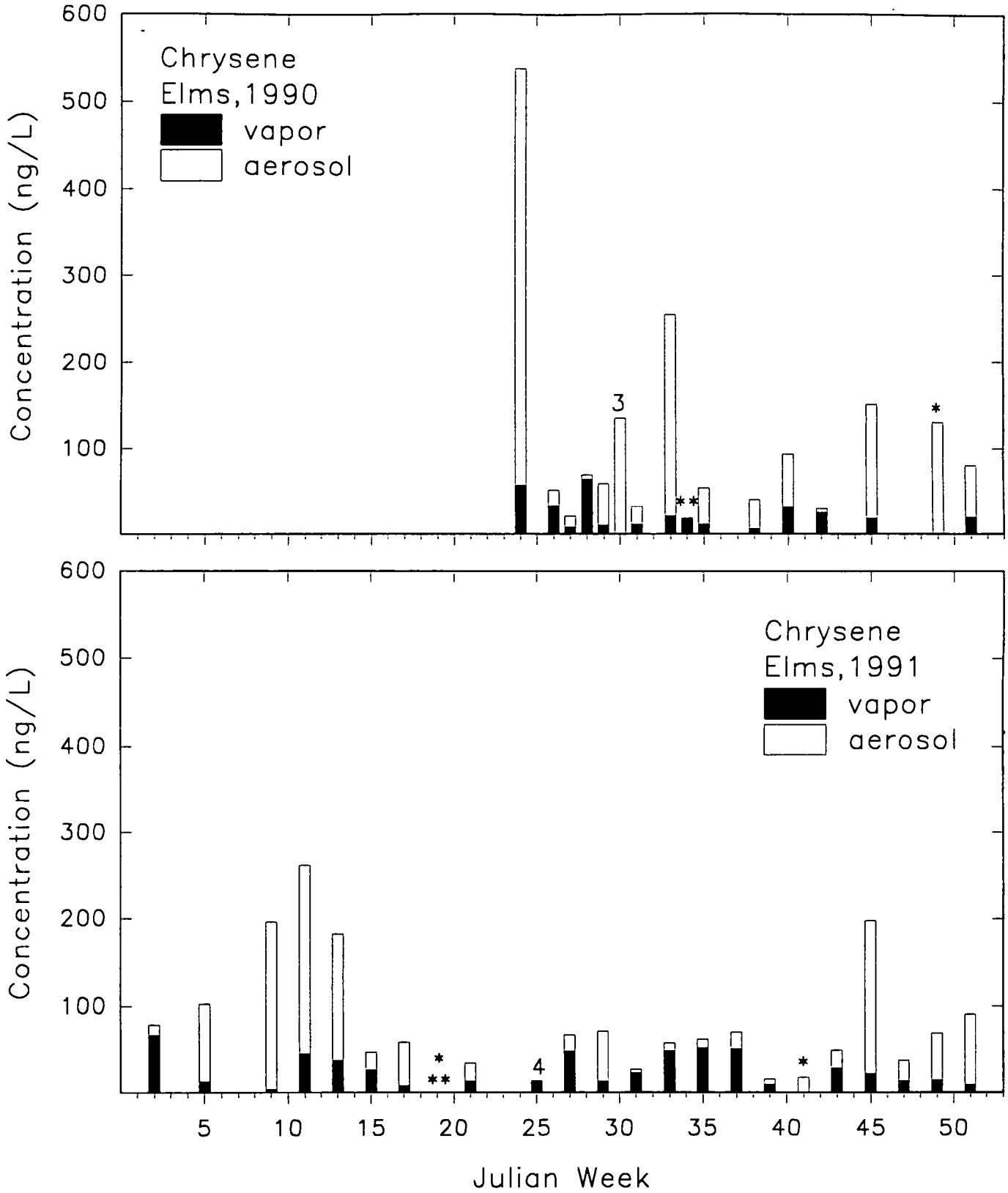
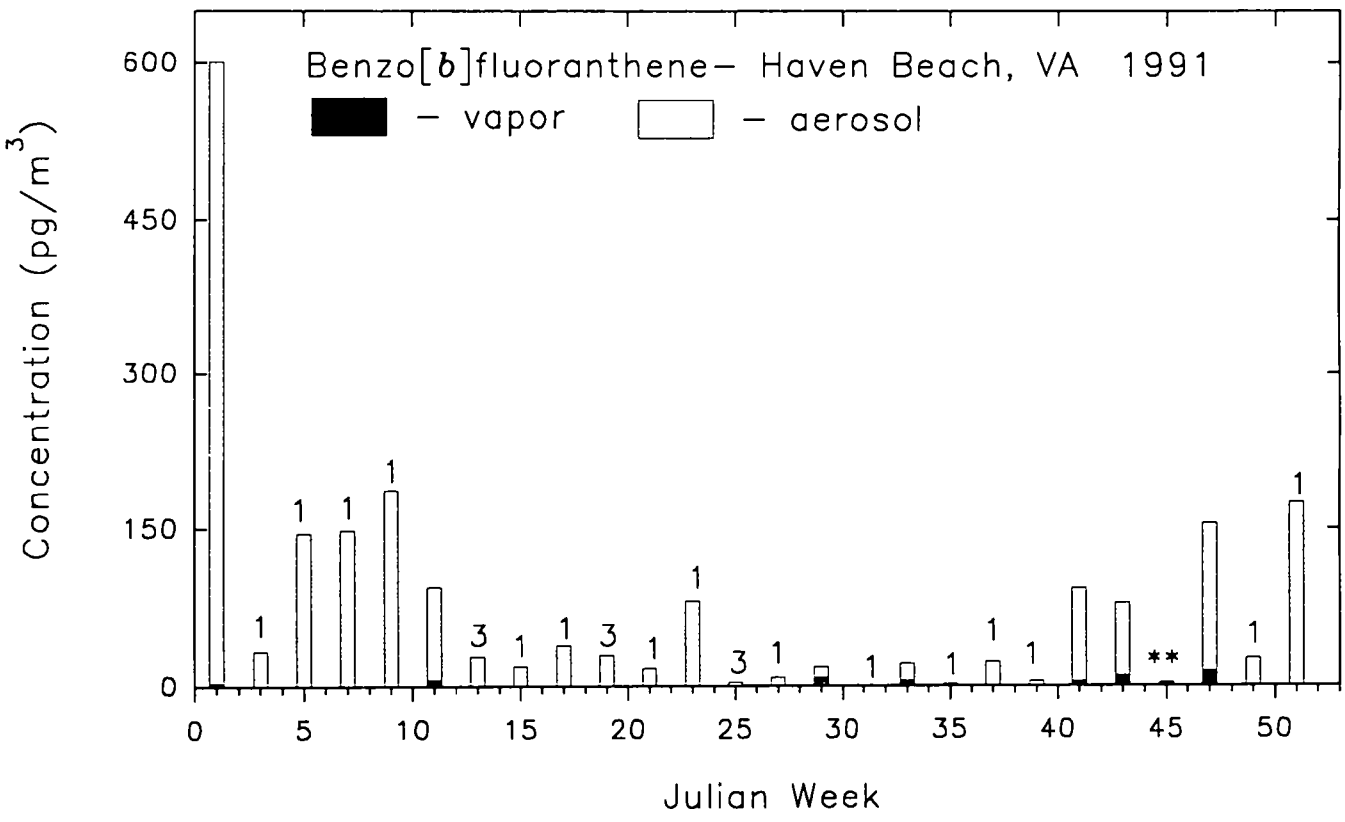

Chrysene
Elms,1990
vapor
aerosol
Concentration (ng/L)
600
500
400
300
200
100
3
*
**
Chrysene
Elms,1991
vapor
aerosol
Concentration (ng/L)
600
500
400
300
200
100
*
**
4
*
5
10
15
20
25
30
35
40
45
50
Julian Week

Figure IV.1.8 Benzo[*b*]fluoranthene concentrations in air collected at Elms and Haven Beach sites. (1=not quantifiable in vapor phase, 2=not quantifiable on filter, 3=not detected in vapor phase, 4=not detected on filter, *=lost vapor sample, **=lost particulate sample)



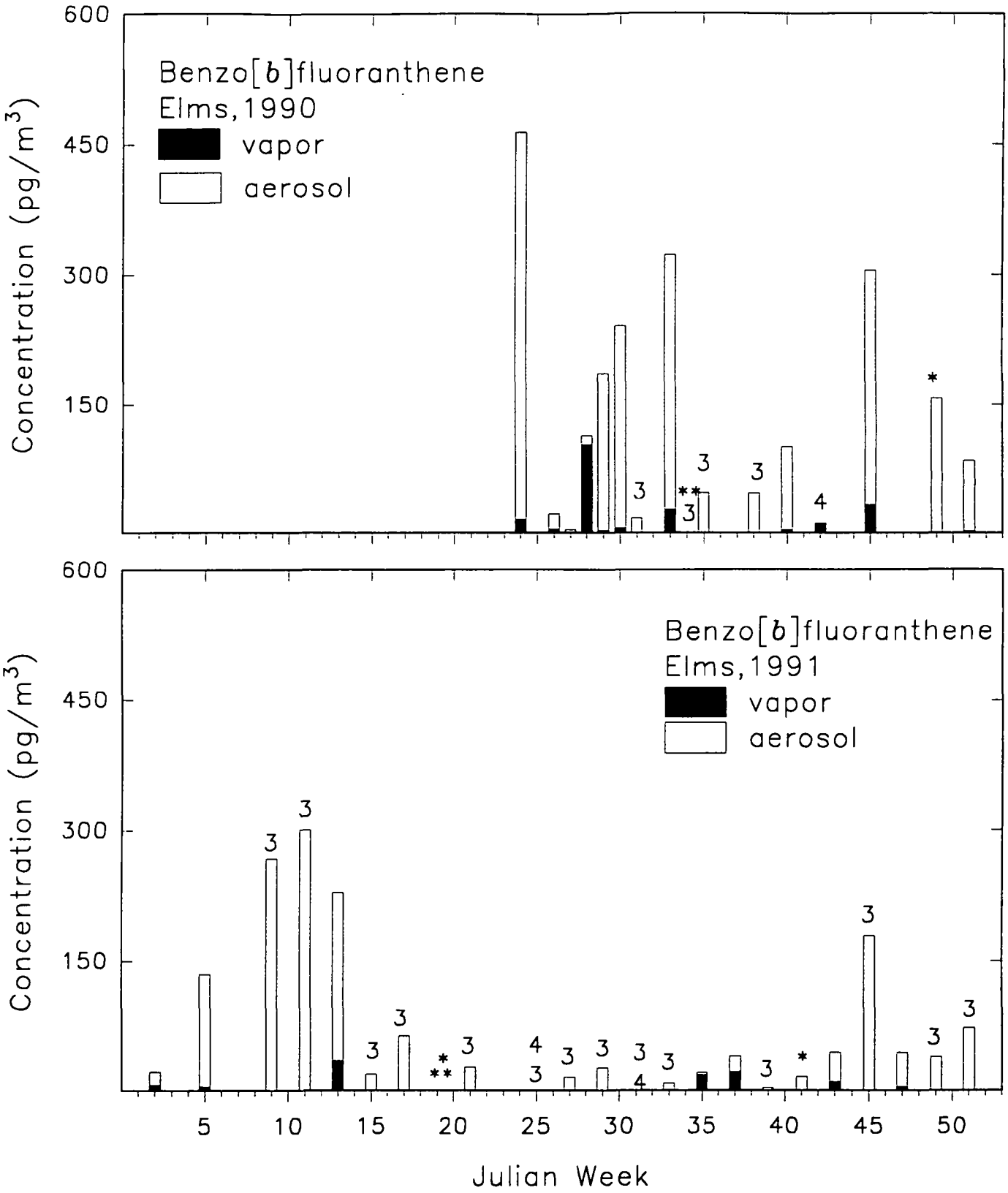
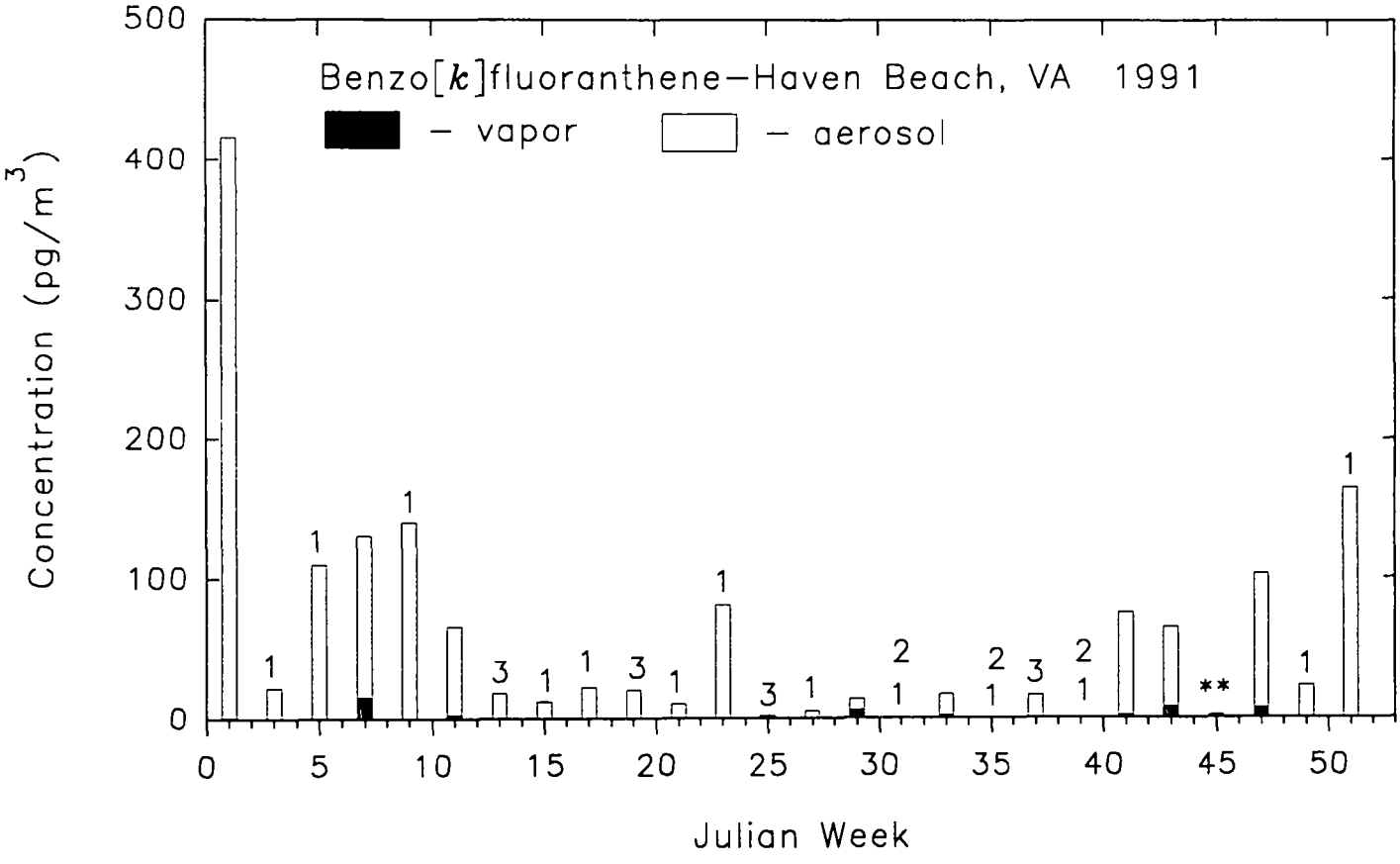

Benzo[b]fluoranthene
Elms, 1990
vapor
aerosol
Concentration (pg/m3)
600
450
300
150
Benzo[b]fluoranthene
Elms, 1991
vapor
aerosol
Concentration (pg/m3)
600
450
300
150
5
10
15
20
25
30
35
40
45
50
Julian Week

Figure IV.1.9 Benzo[*k*]fluoranthene concentrations in air collected at the Elms and Haven Beach sites. (1=not quantifiable in vapor phase, 2=not quantifiable on filter, 3=not detected in vapor phase, 4=not detected on filter, *=lost vapor sample, **=lost particulate sample)



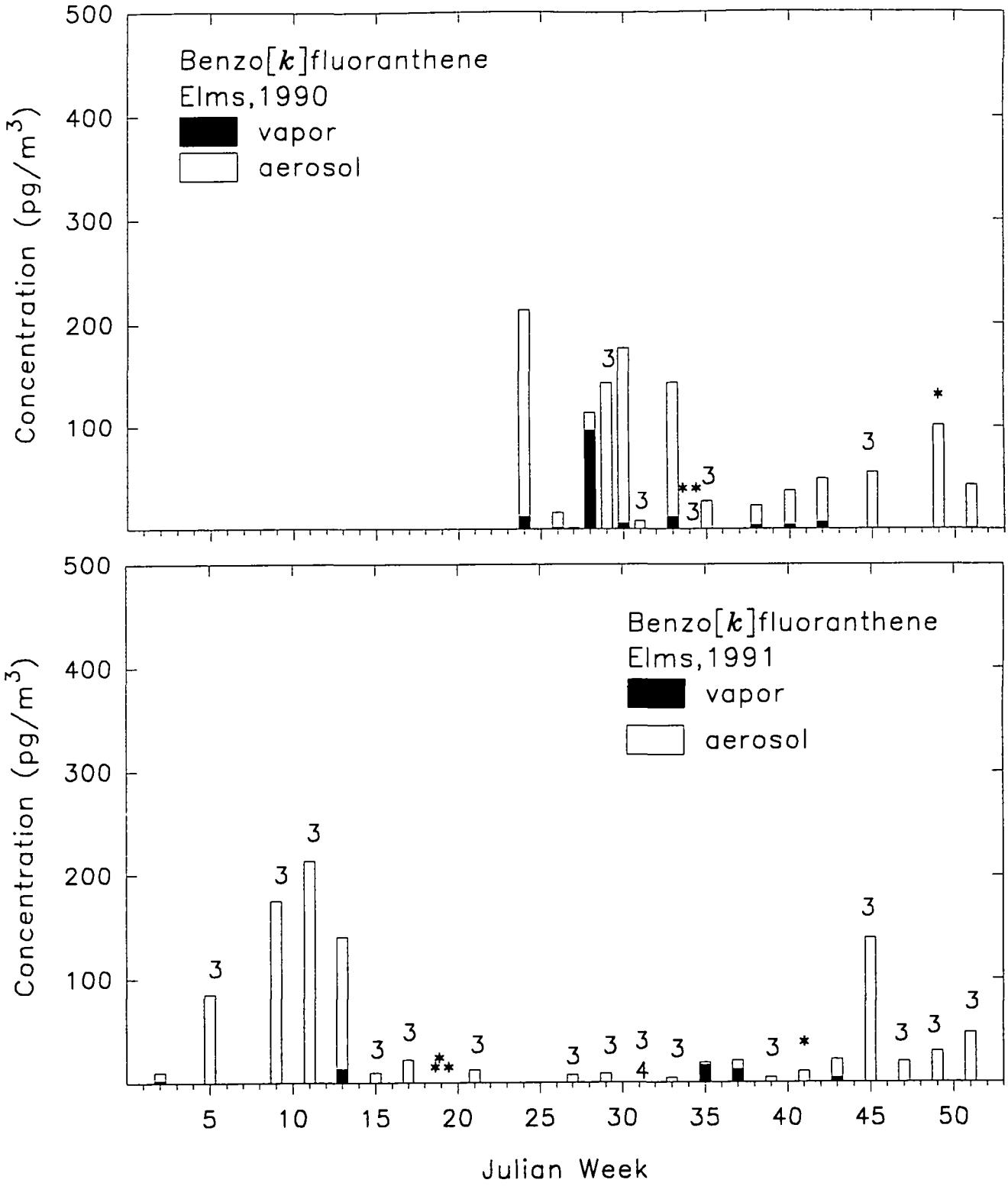
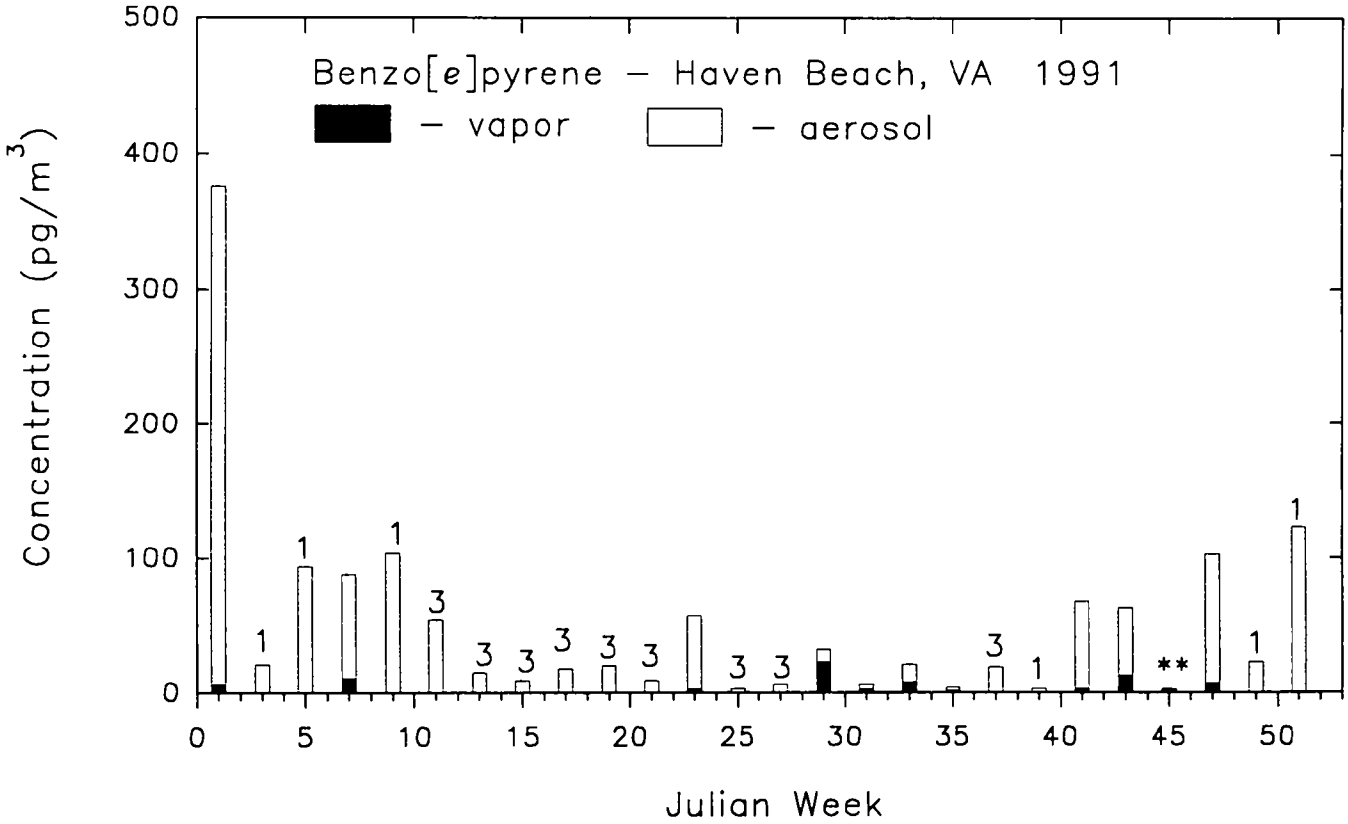

Benzo[k]fluoranthene
Elms,1990
vapor
aerosol
Concentration (pg/m3)
500
400
300
200
100
Benzo[k]fluoranthene
Elms,1991
vapor
aerosol
Concentration (pg/m3)
500
400
300
200
100
5
10
15
20
25
30
35
40
45
50
Julian Week

Figure IV.1.10 Benzo[*e*]pyrene concentrations in air collected at the Elms and Haven Beach sites. (1=not quantifiable in vapor phase, 2=not quantifiable on filter, 3=not detected in vapor phase, 4=not detected on filter, 5=not analyzed, *=lost vapor sample, **=lost particulate sample)



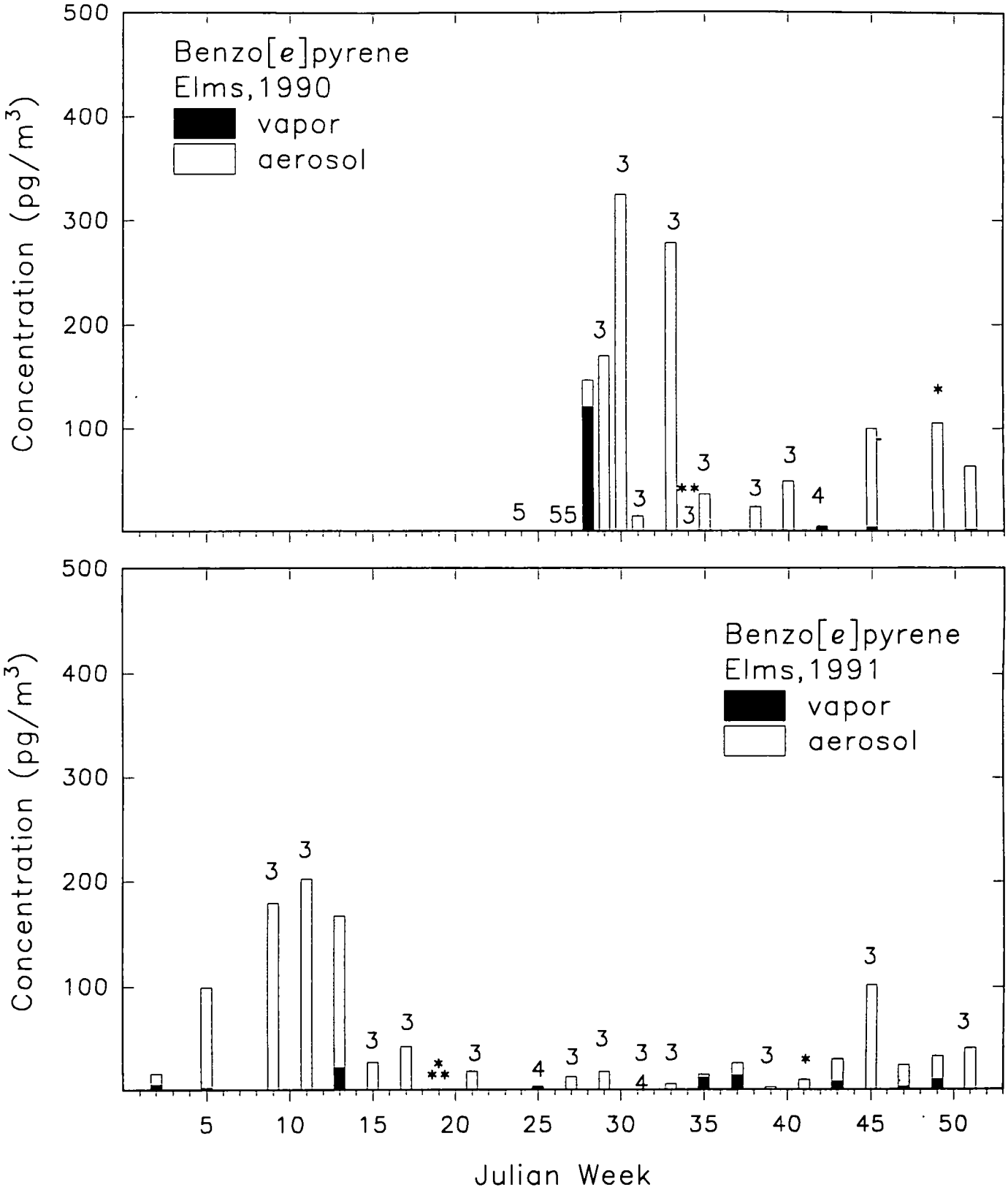
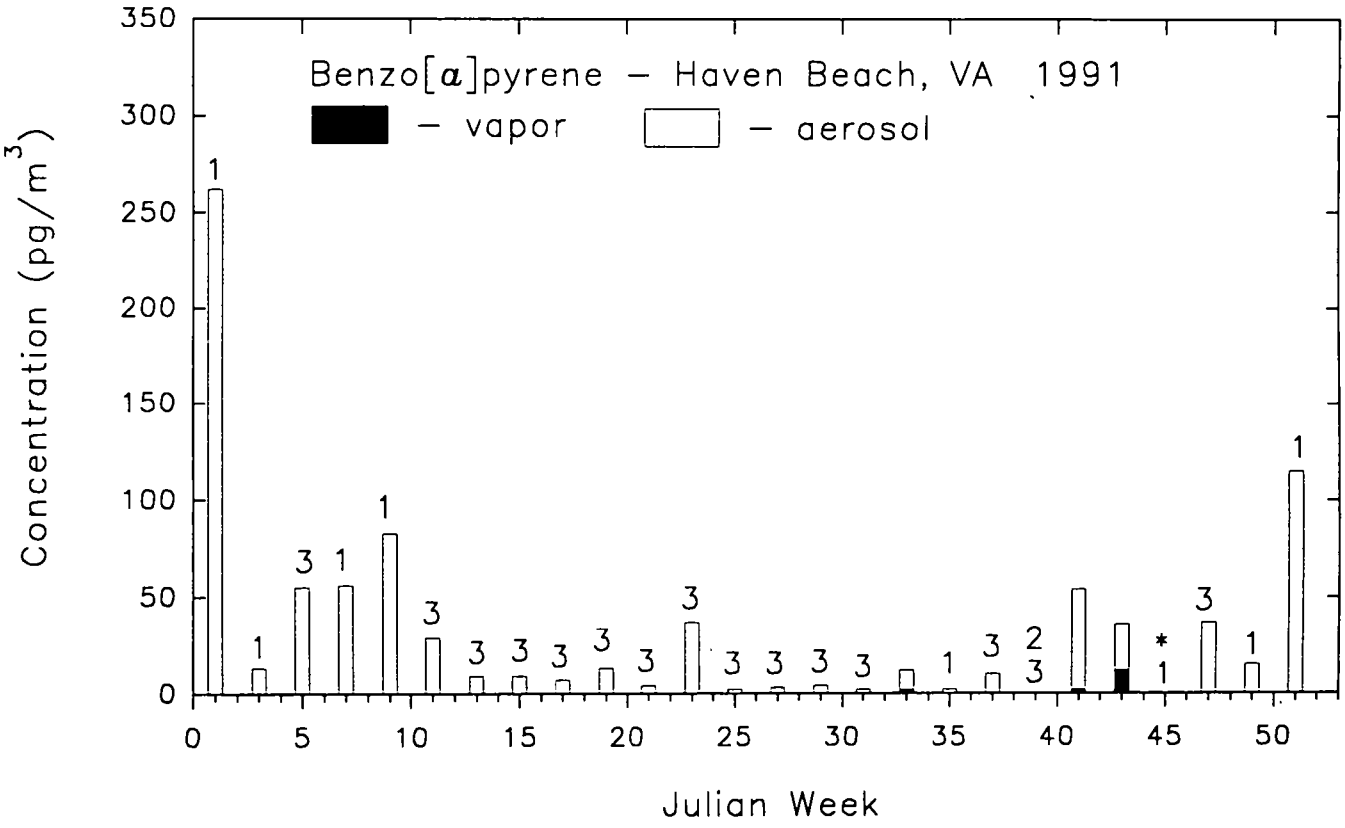

Benzo[e]pyrene
Elms, 1990
vapor
aerosol
Concentration (pg/m3)
500
400
300
200
100
Benzo[e]pyrene
Elms, 1991
vapor
aerosol
Concentration (pg/m3)
500
400
300
200
100
5
10
15
20
25
30
35
40
45
50
Julian Week

Figure IV.1.11 Benzo[*a*]pyrene concentrations in air collected at Elms and Haven Beach sites. (1=not quantifiable in vapor phase, 2=not quantifiable on filter, 3=not detected in vapor phase, 4=not detected on filter, *=lost vapor sample, **=lost particulate sample)



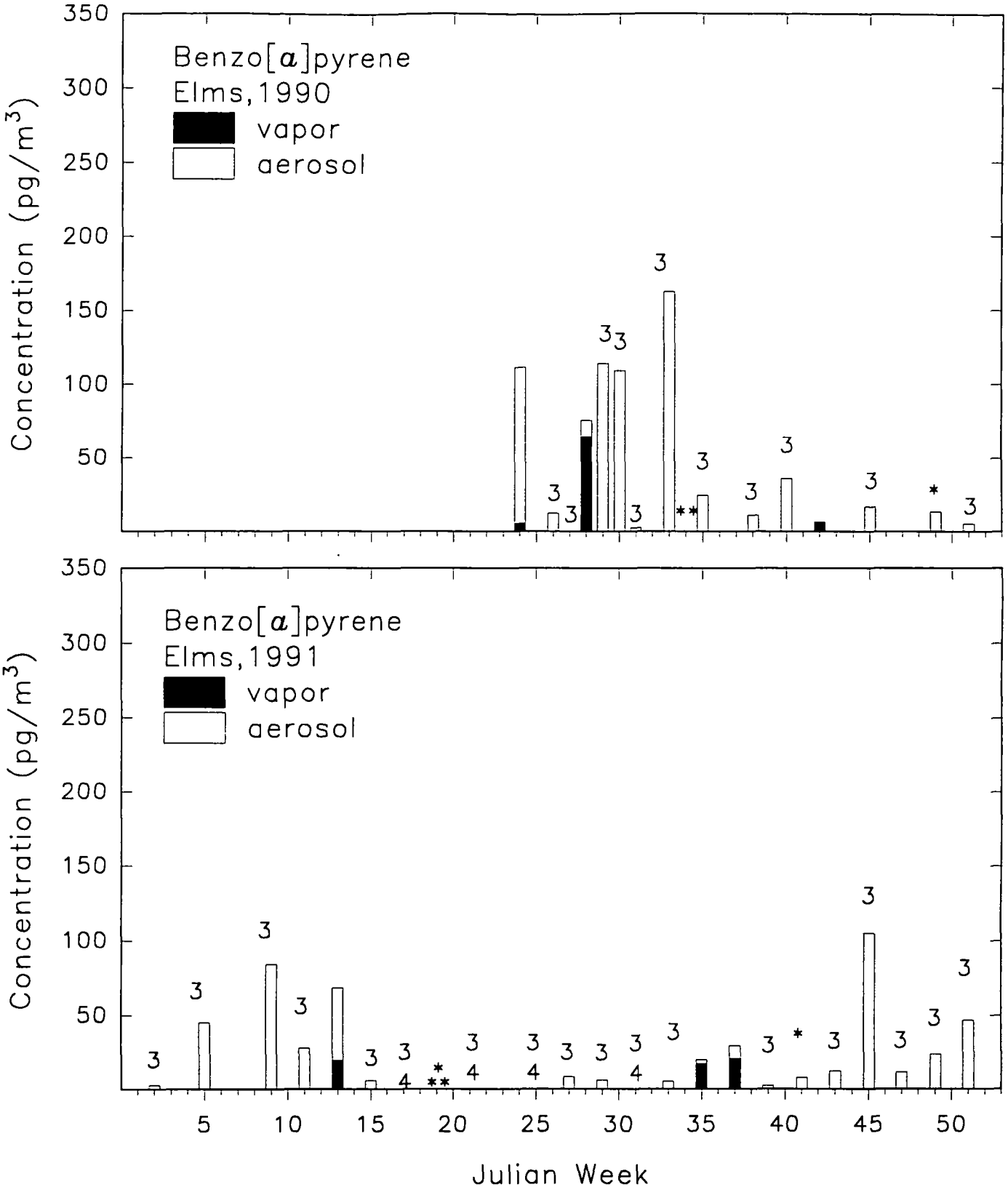
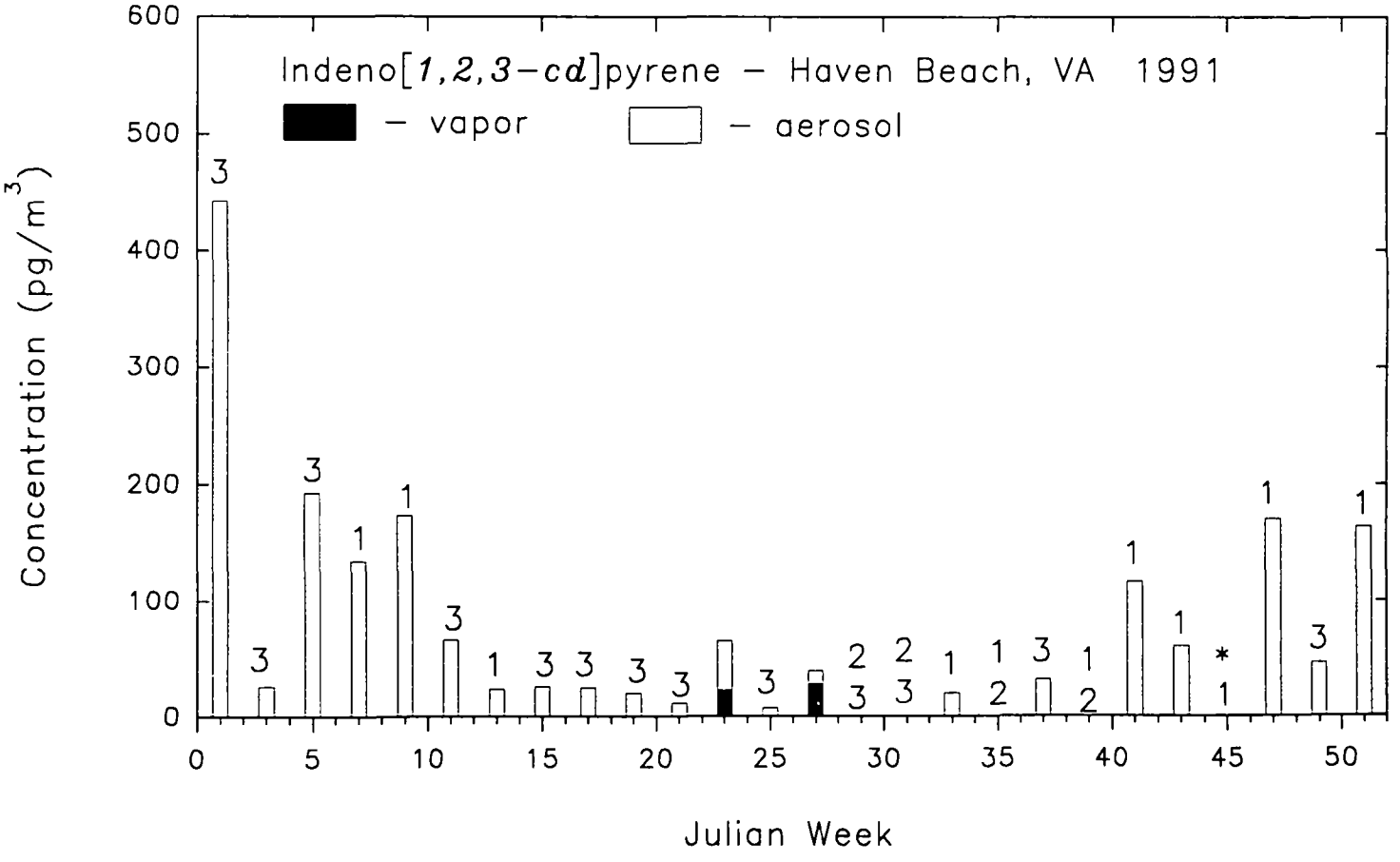

Benzo[a]pyrene
Elms,1990
vapor
aerosol
Concentration (pg/m3)
Benzo[a]pyrene
Elms,1991
vapor
aerosol
Concentration (pg/m3)
Julian Week

Figure IV.1.12. Indeno[*1,2,3-cd*]pyrene concentrations in air collected biweekly at the Elms and Haven Beach sites.(1=not quantifiable in vapor phase, 2=not quantifiable on filter,3= not detected in vapor phase 4=not detected on filter,*=lost vapor sample, **=lost particulate sample.



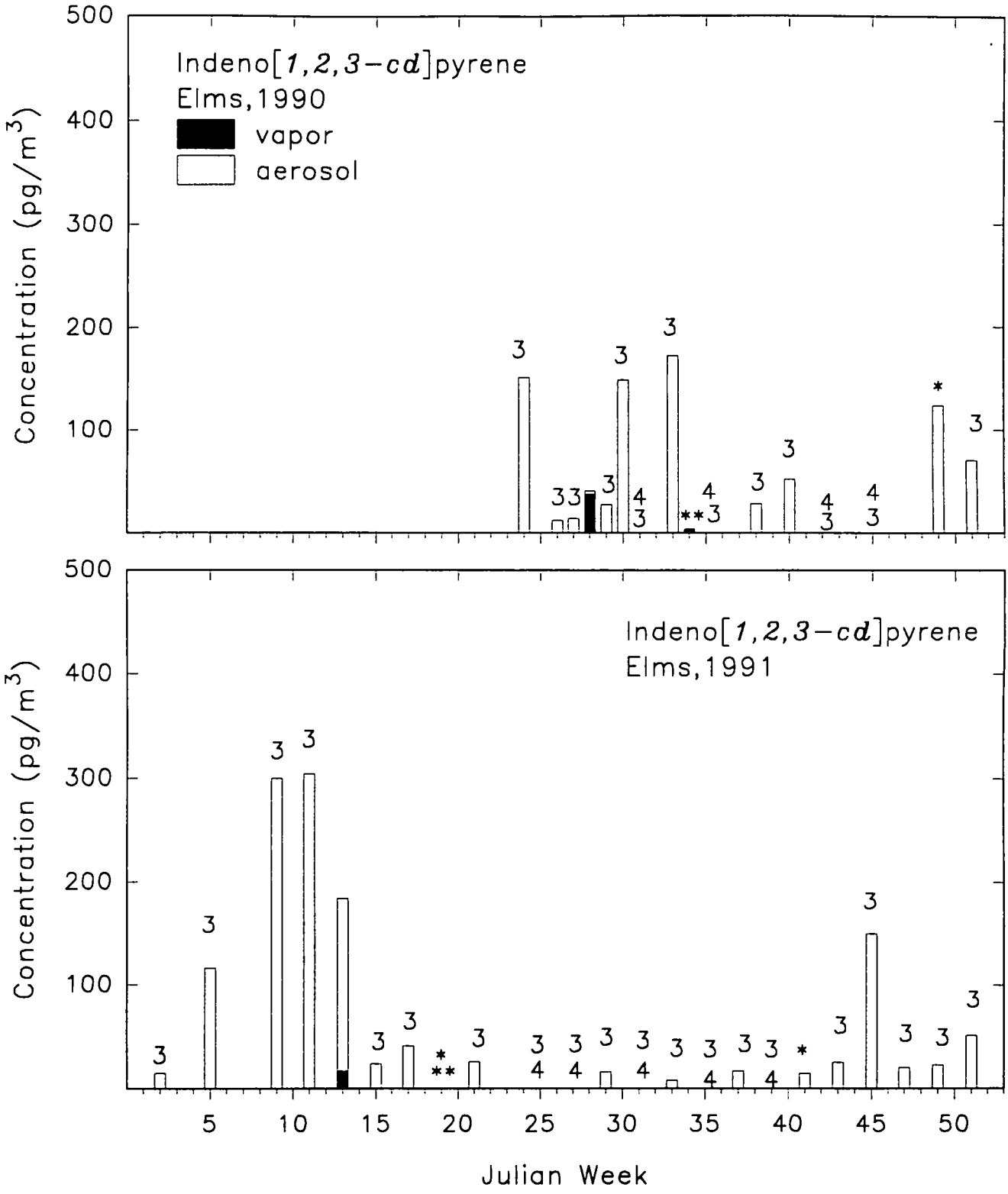
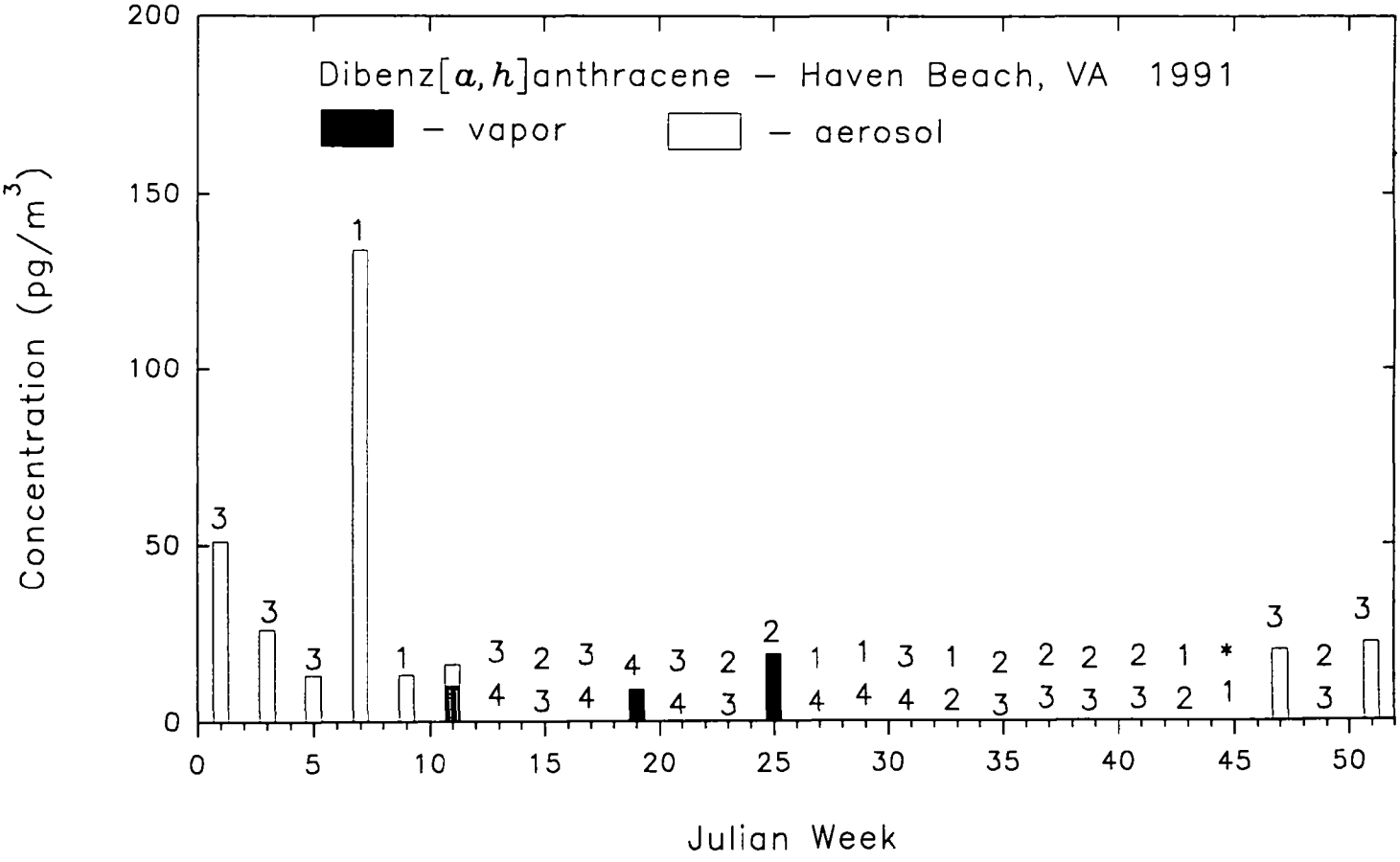

Indeno[1,2,3-cd]pyrene
Elms,1990
vapor
aerosol
Concentration (pg/m3)
Indeno[1,2,3-cd]pyrene
Elms,1991
Concentration (pg/m3)
Julian Week

Figure IV.1.13. Dibenz[*a,h*]anthracene concentrations in air collected biweekly at the Elms and Haven Beach sites.(1= not quantifiable in vapor phase, 2=not quantifiable on filter, 3=not detected in vapor phase, 4= not detected on filter, *=lost vapor sample, **=lost particulate sample.



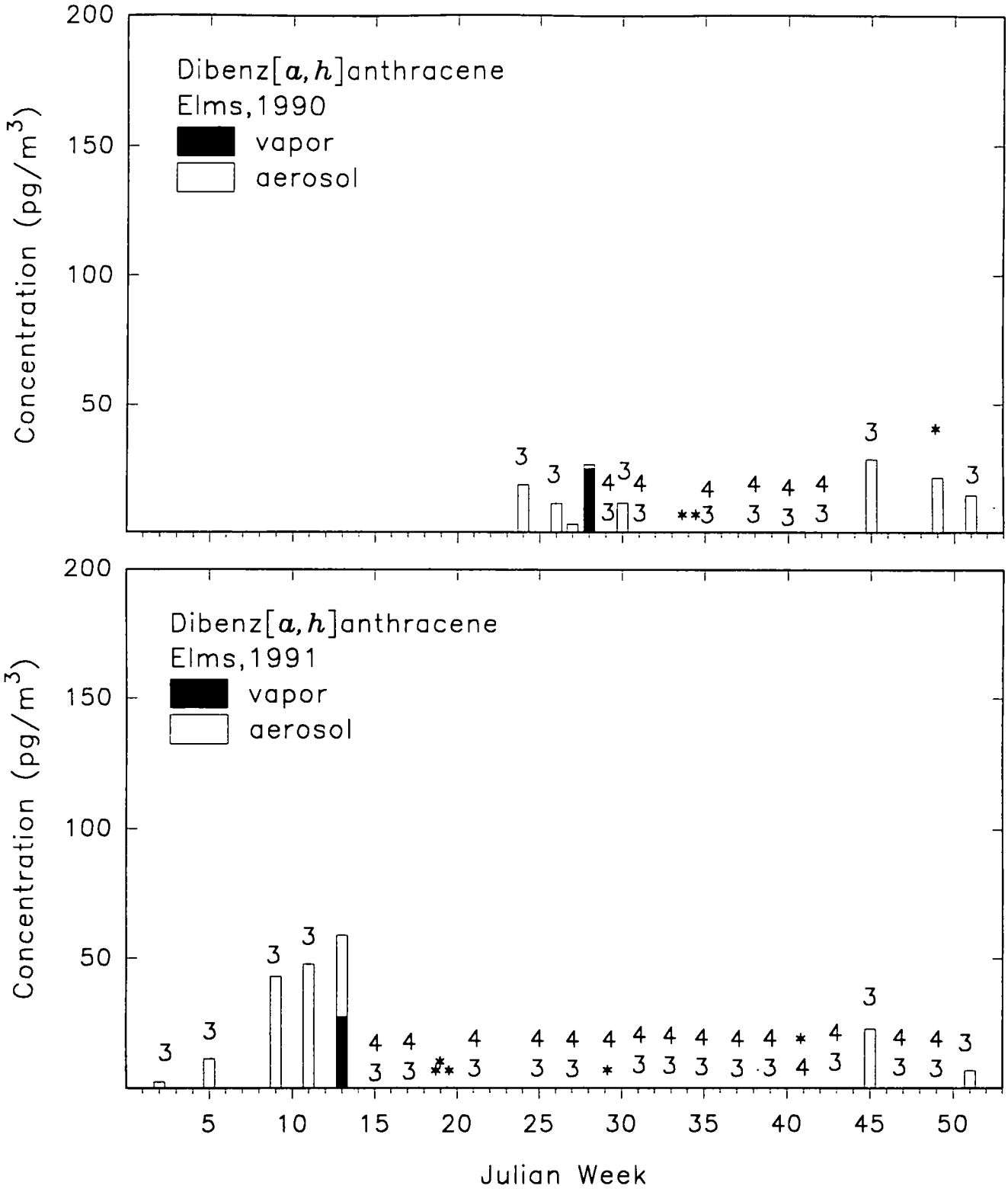
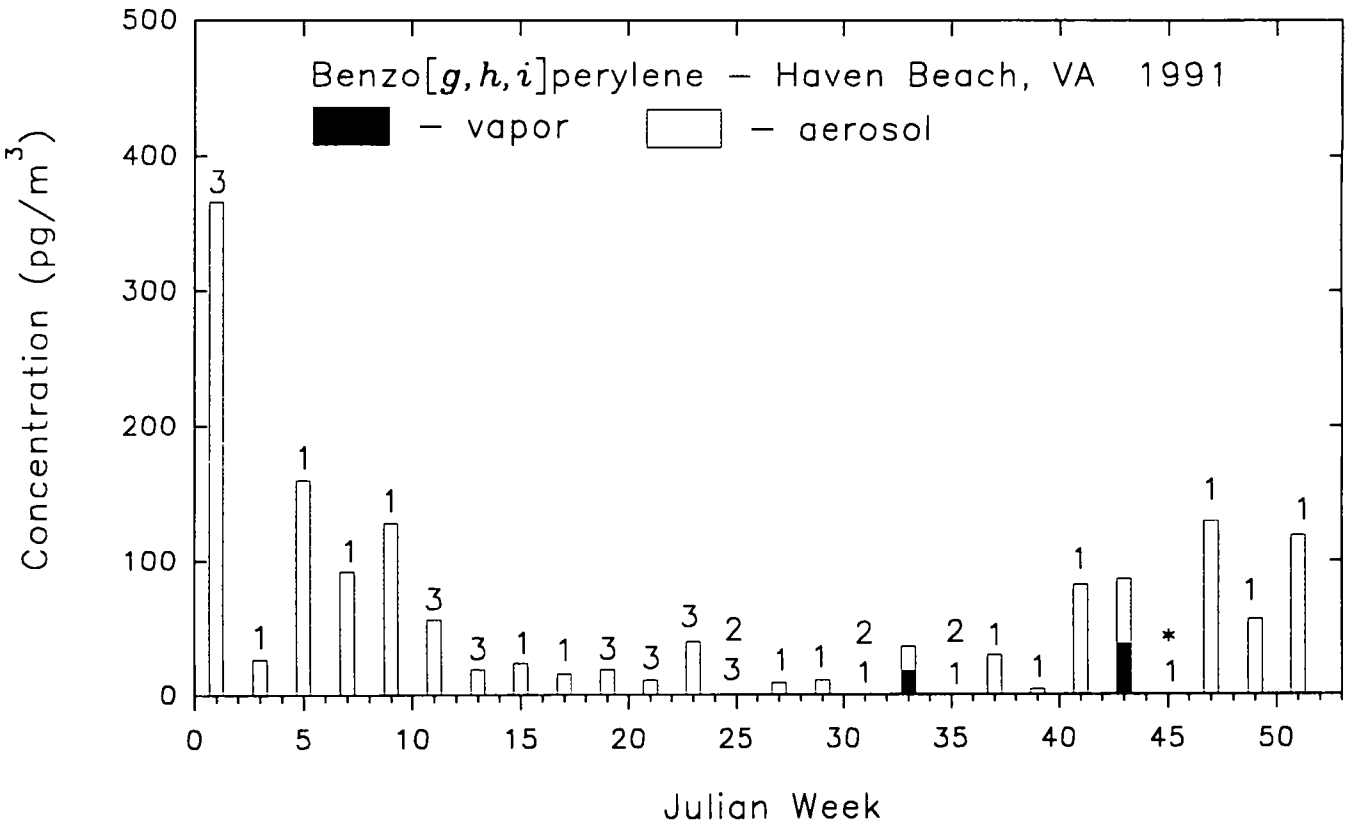

Dibenz[a,h]anthracene
Elms,1990
vapor
aerosol
Concentration (pg/m3)
200
150
100
50
Dibenz[a,h]anthracene
Elms,1991
vapor
aerosol
Concentration (pg/m3)
200
150
100
50
5
10
15
20
25
30
35
40
45
50
Julian Week

Figure IV.1.14 Benzo[*g,h,i*]perylene concentrations in air collected at Elms and Haven Beach sites. 1=not quantifiable in vapor phase, 2=not quantifiable on filter, 3=not detected in vapor phase, 4=not detected on filter, *=lost vapor sample, **=lost particulate sample)



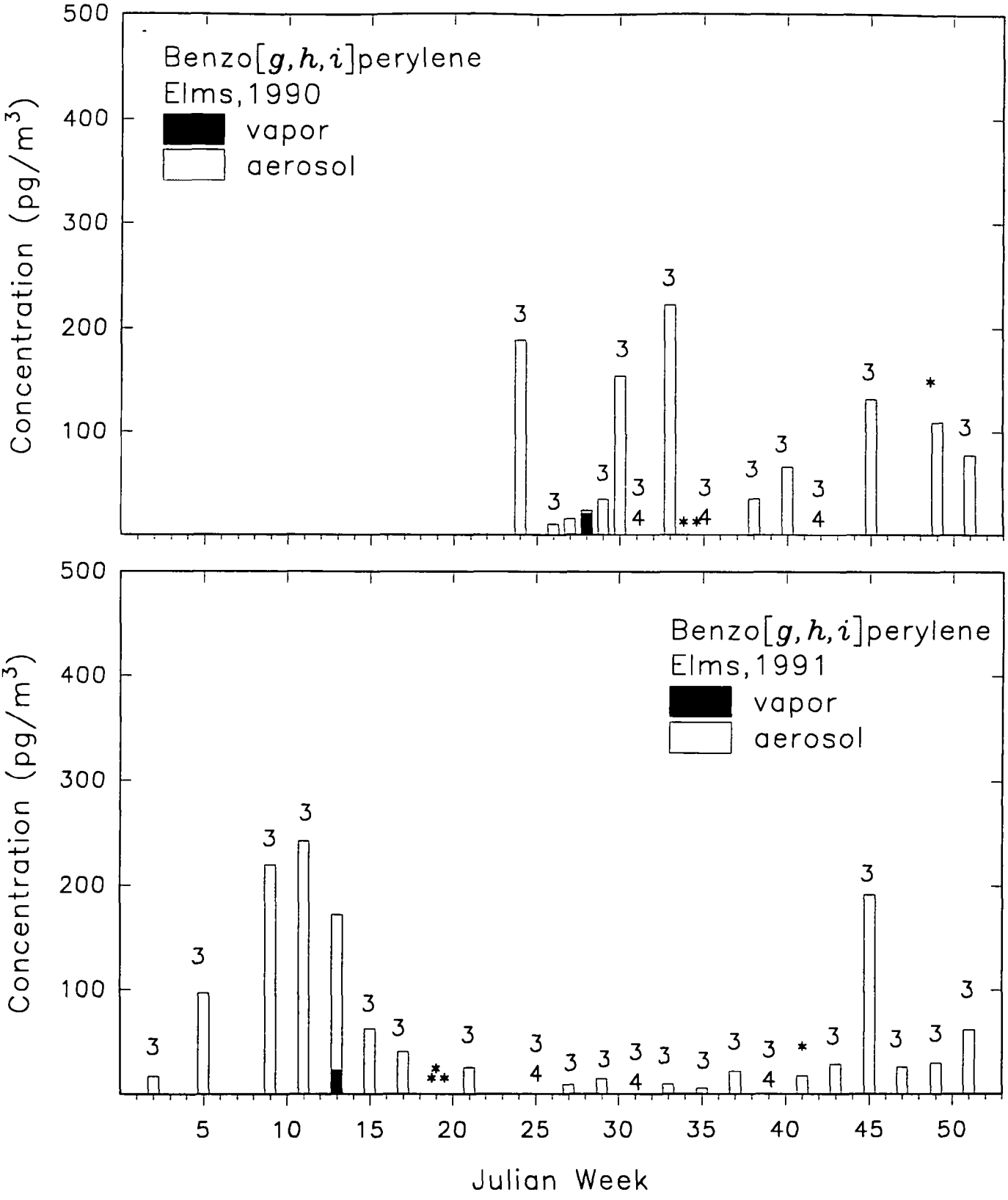
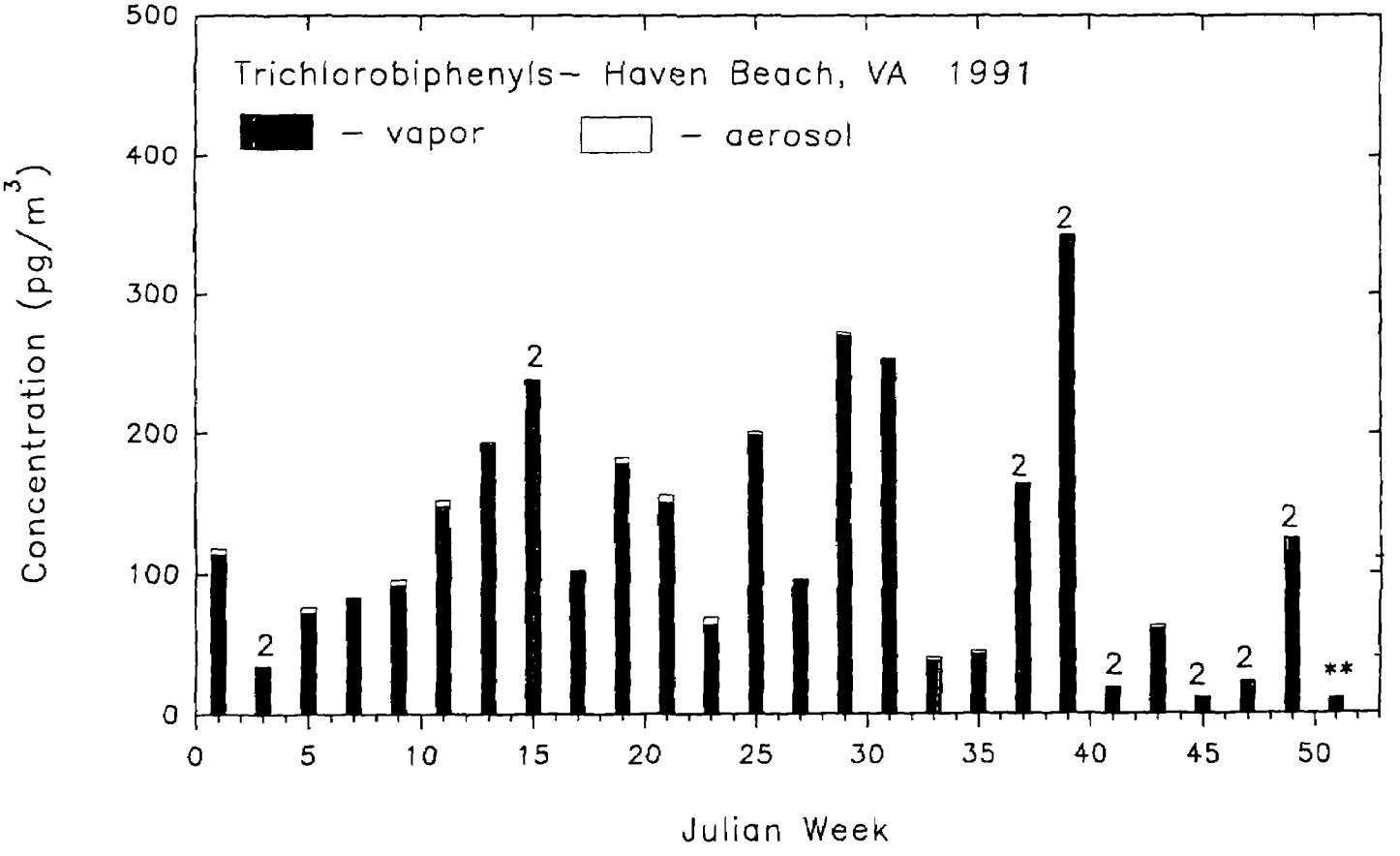

Benzo[g,h,i]perylene
Elms,1990
vapor
aerosol
Concentration (pg/m3)
Benzo[g,h,i]perylene
Elms,1991
vapor
aerosol
Concentration (pg/m3)
Julian Week

Figure IV.1.15. Total trichlorobiphenyl concentrations in air collected biweekly at the Elms and Haven Beach sites.(1= not quantifiable in vapor phase, 2=not quantifiable on filter, 3=not detected in vapor phase, 4= not detected on filter, *=lost vapor sample, **=lost particulate sample.



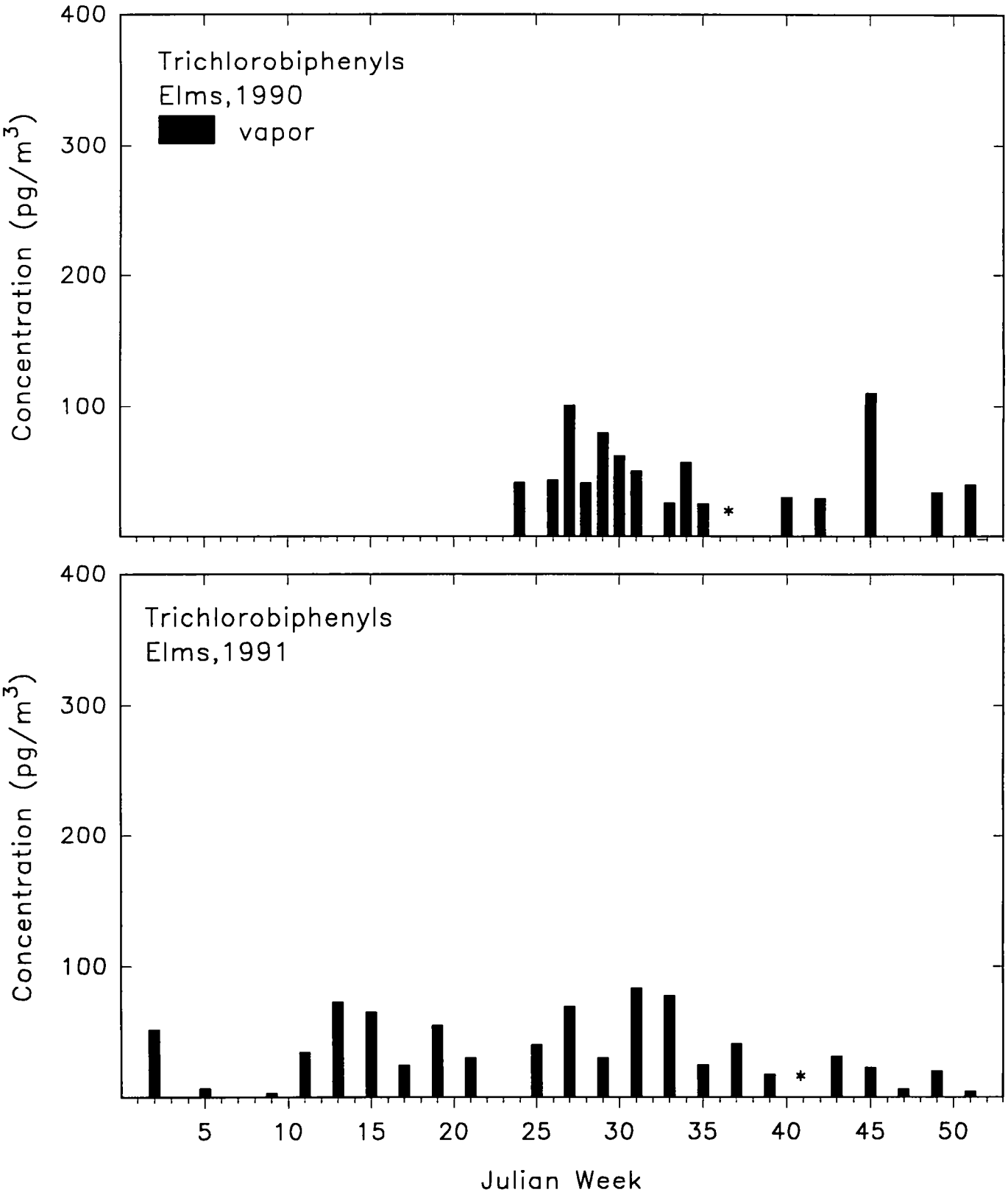
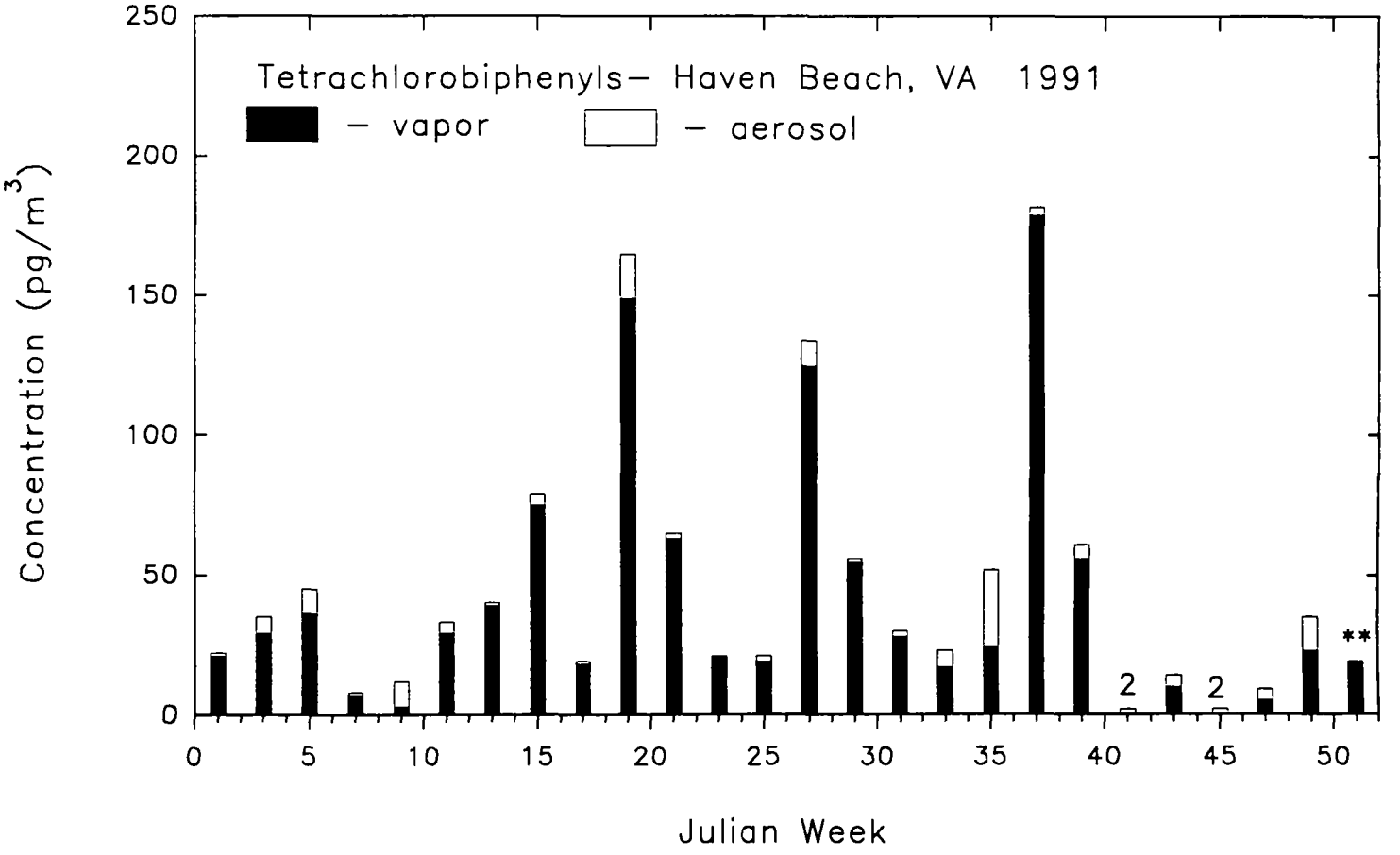

Trichlorobiphenyls
Elms,1990
vapor
Concentration (pg/m3)
400
300
200
100
Trichlorobiphenyls
Elms,1991
Concentration (pg/m3)
400
300
200
100
5
10
15
20
25
30
35
40
45
50
Julian Week

Figure IV.1.16. *Total tetrachlorobiphenyl concentrations in air collected* biweekly at the Elms and Haven Beach sites.(1= not quantifiable in vapor phase, 2=not quantifiable on filter, 3=not detected in vapor phase, 4= not detected on filter, *=lost vapor sample, **=lost particulate sample.



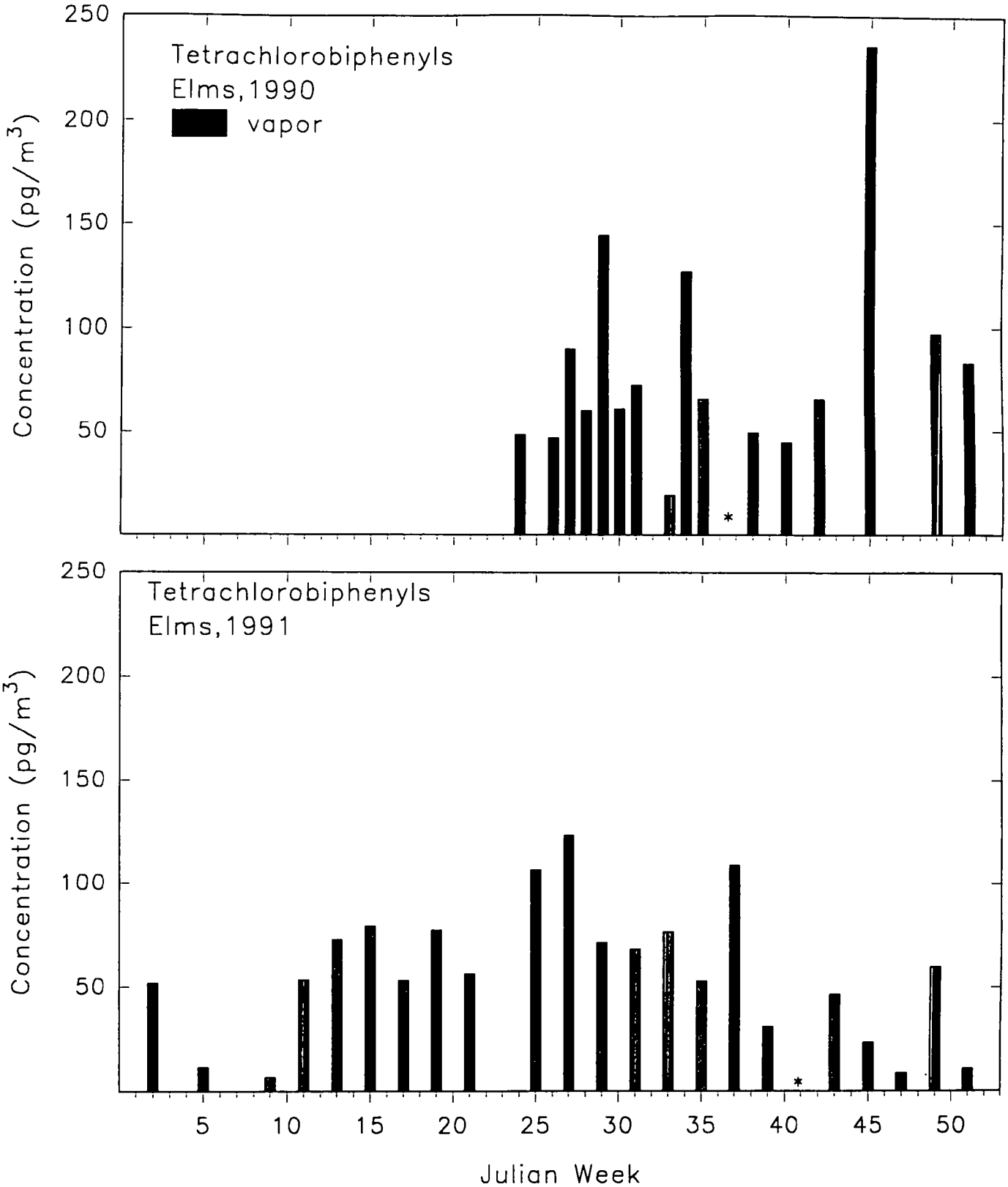
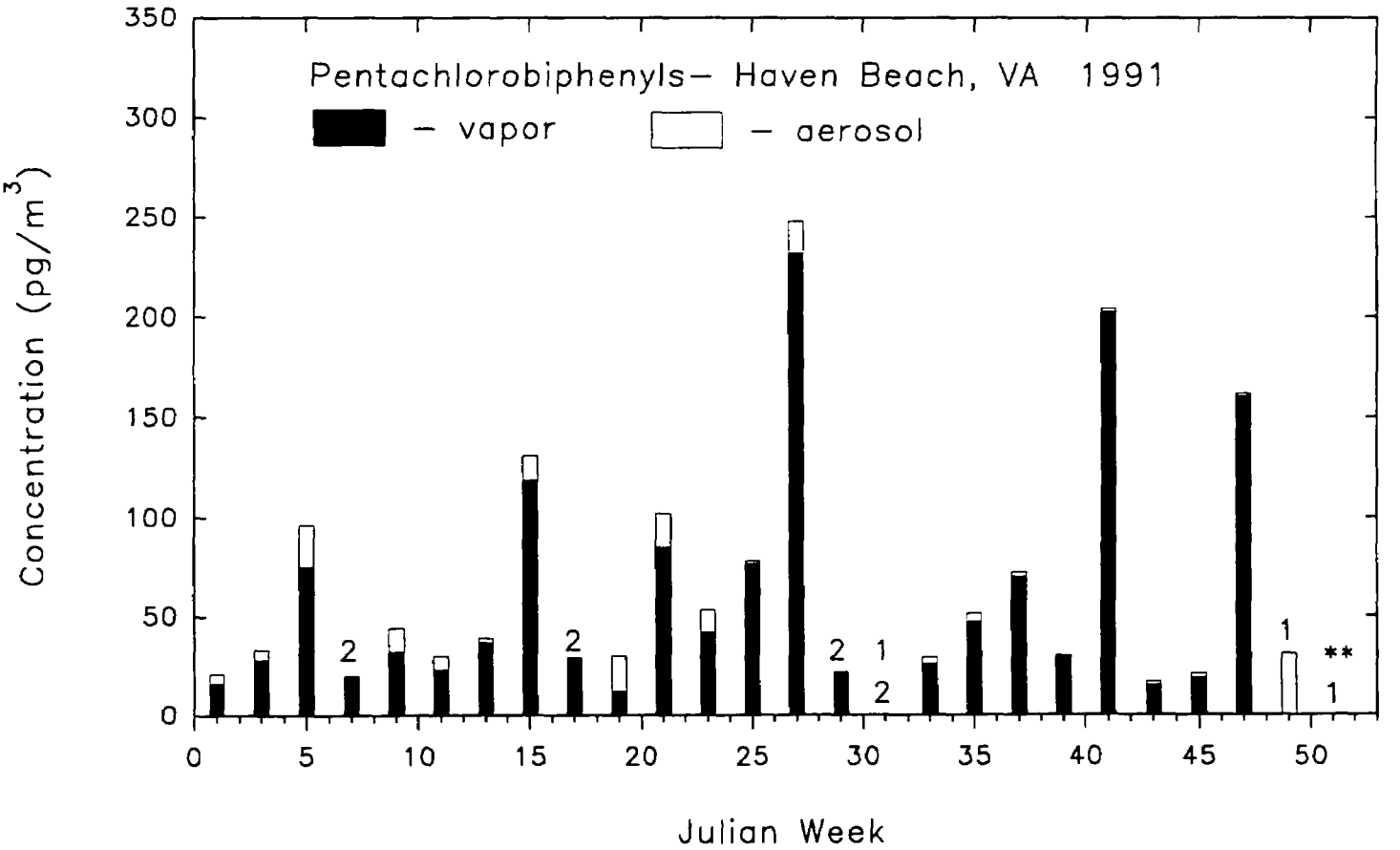

Tetrachlorobiphenyls
Elms, 1990
vapor
Concentration (pg/m3)
250
200
150
100
50
Tetrachlorobiphenyls
Elms, 1991
Concentration (pg/m3)
250
200
150
100
50
5
10
15
20
25
30
35
40
45
50
Julian Week

Figure IV.1.17 Total pentachlorobiphenyl concentrations in air collected biweekly at the Elms and Haven Beach sites. (1=not quantifiable in vapor phase, 2=not quantifiable on filter, 3=not detected in vapor phase, 4=not detected on filter, * =lost vapor sample, ** =lost particulate sample)



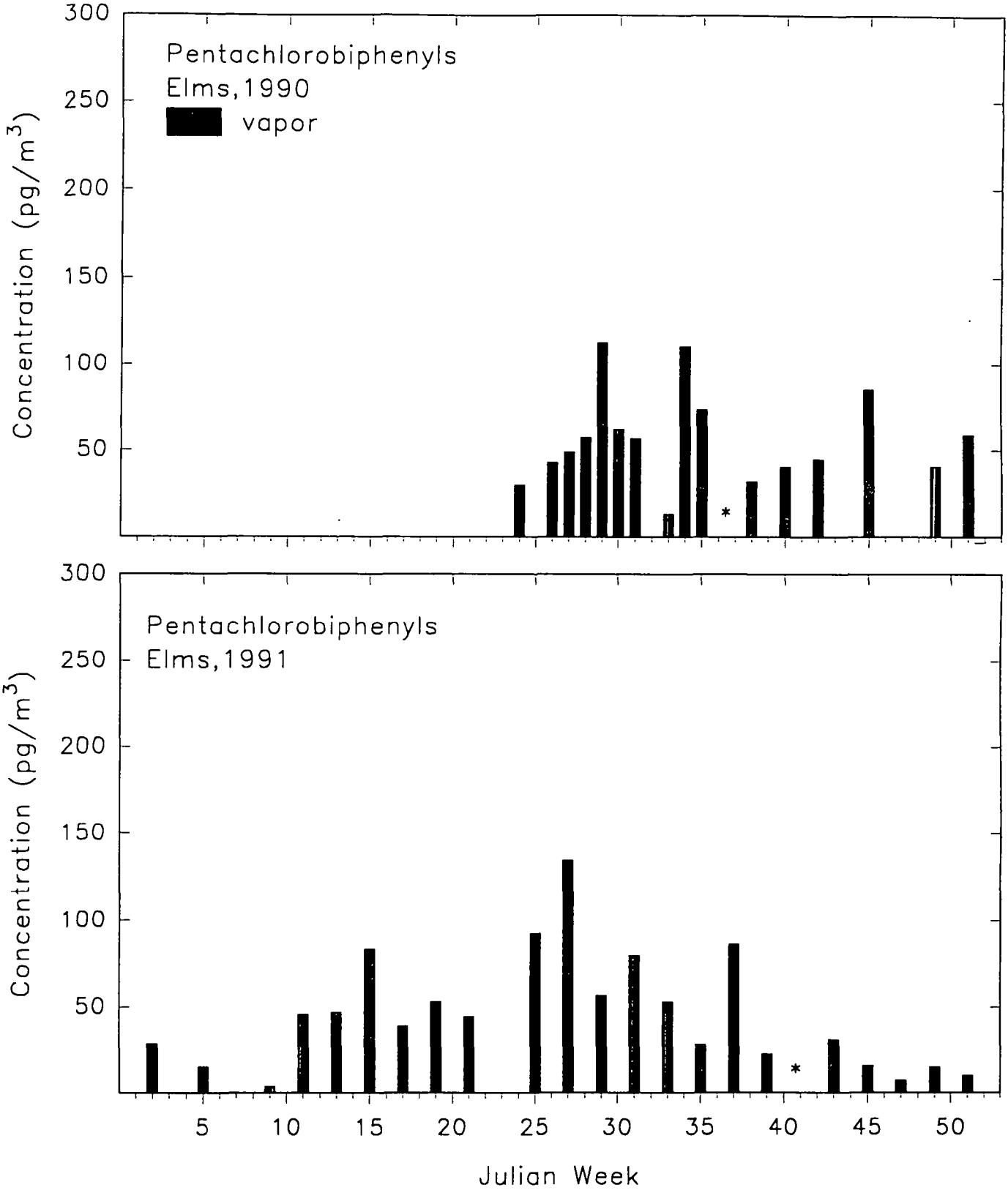
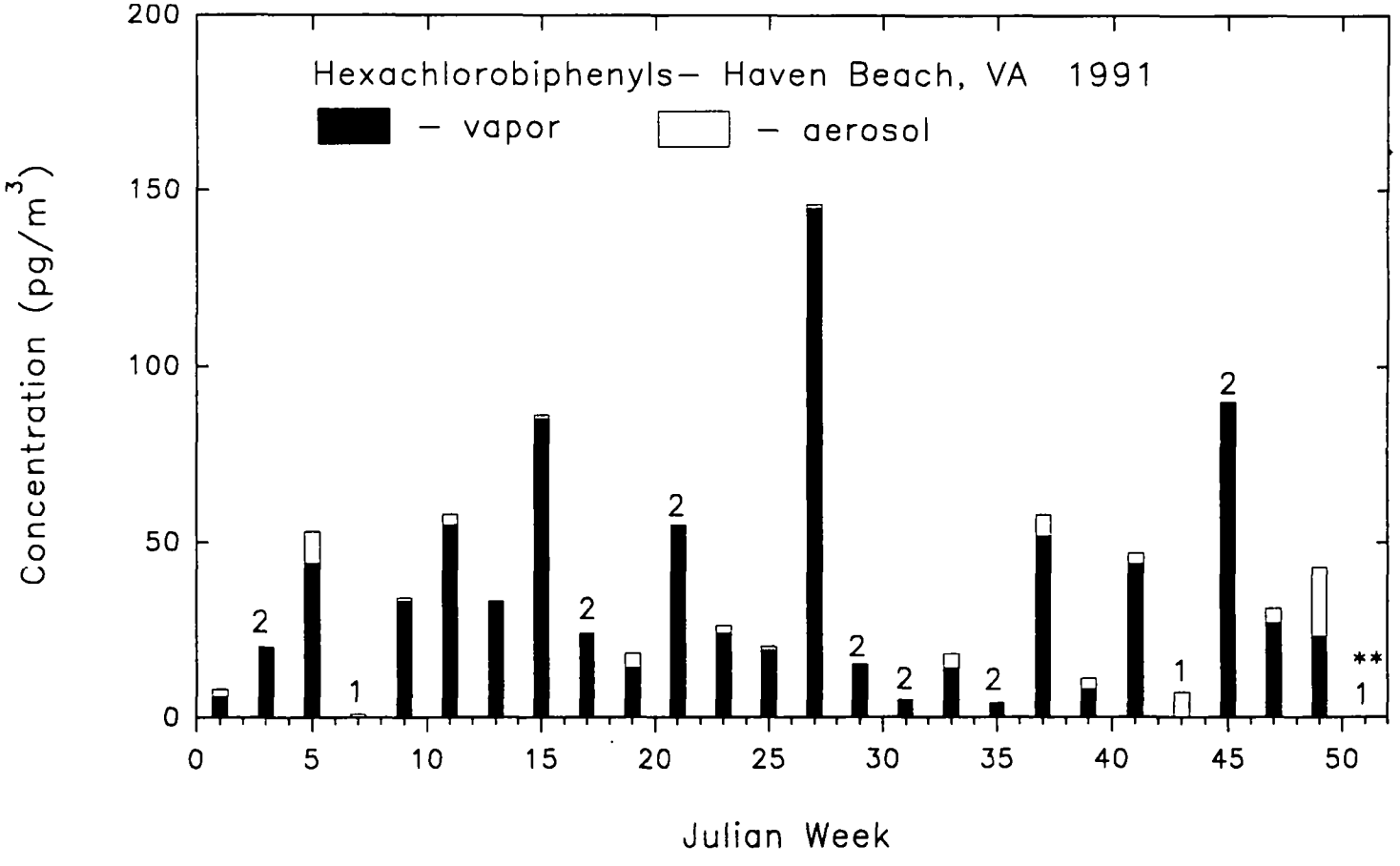

Pentachlorobiphenyls
Elms, 1990
vapor
Concentration (pg/m3)
300
250
200
150
100
50
Pentachlorobiphenyls
Elms, 1991
Concentration (pg/m3)
300
250
200
150
100
50
5
10
15
20
25
30
35
40
45
50
Julian Week

Figure IV.1.18. Total hexachlorobiphenyl concentrations in air collected biweekly at the Elms and Haven Beach sites. (1=not quantifiable in vapor phase, 2=not quantifialbe on filter, 3=not detected in vapor phase, 4=not detected filter, *= lost vapor phase, **=lost particulate sample.



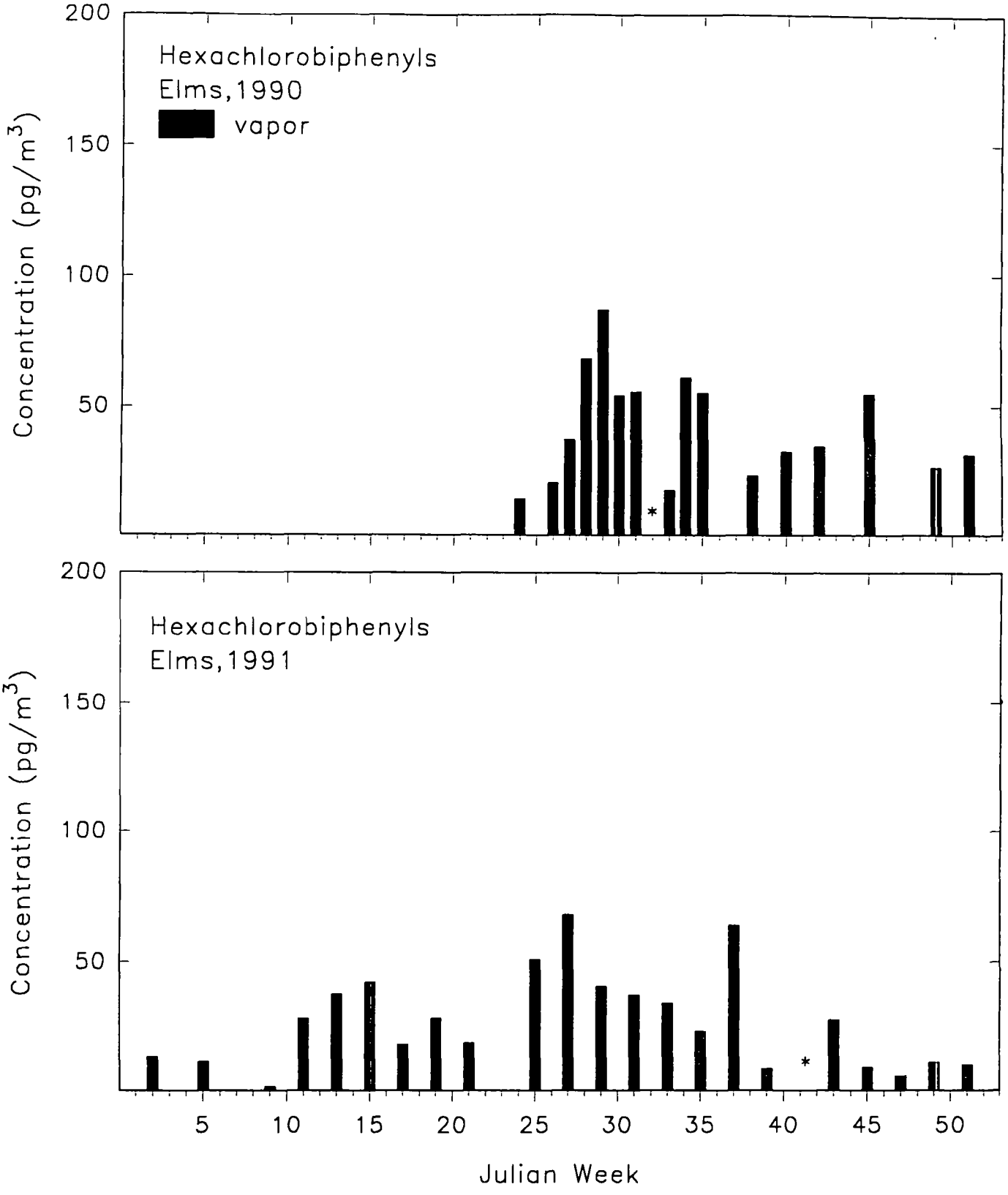
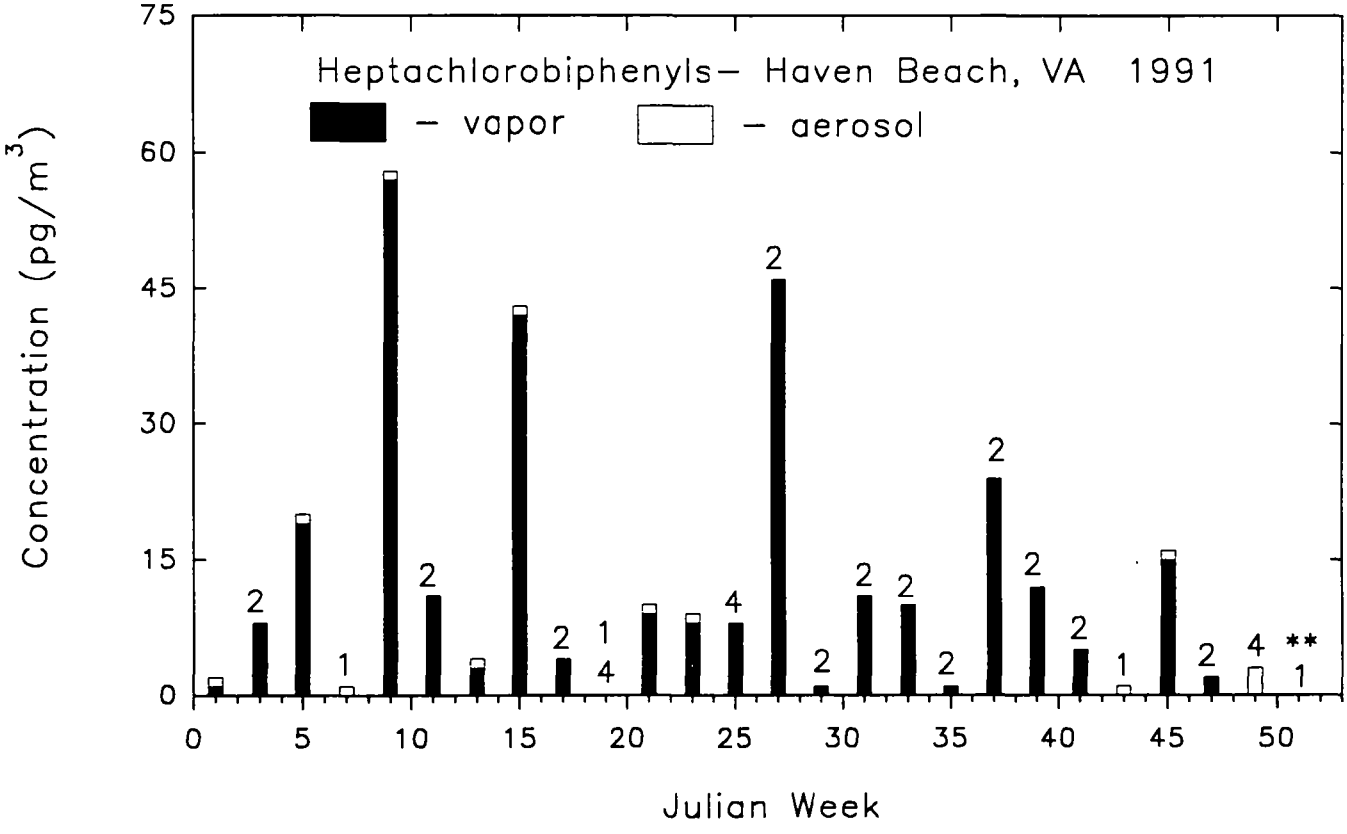

Hexachlorobiphenyls
Elms,1990
vapor
Concentration (pg/m3)
200
150
100
50
*
Hexachlorobiphenyls
Elms,1991
Concentration (pg/m3)
200
150
100
50
*
5
10
15
20
25
30
35
40
45
50
Julian Week

Figure IV.1.19. Total heptachlorobiphenyl concentrations in air at the Elms and Haven Beach sites. (1=not quantifiable in vapor phase, 2=not quantifiable on filter, 3=not detected in vapor phase, 4=not detected on filter, *=lost vapor sample, **=lost particulate sample)



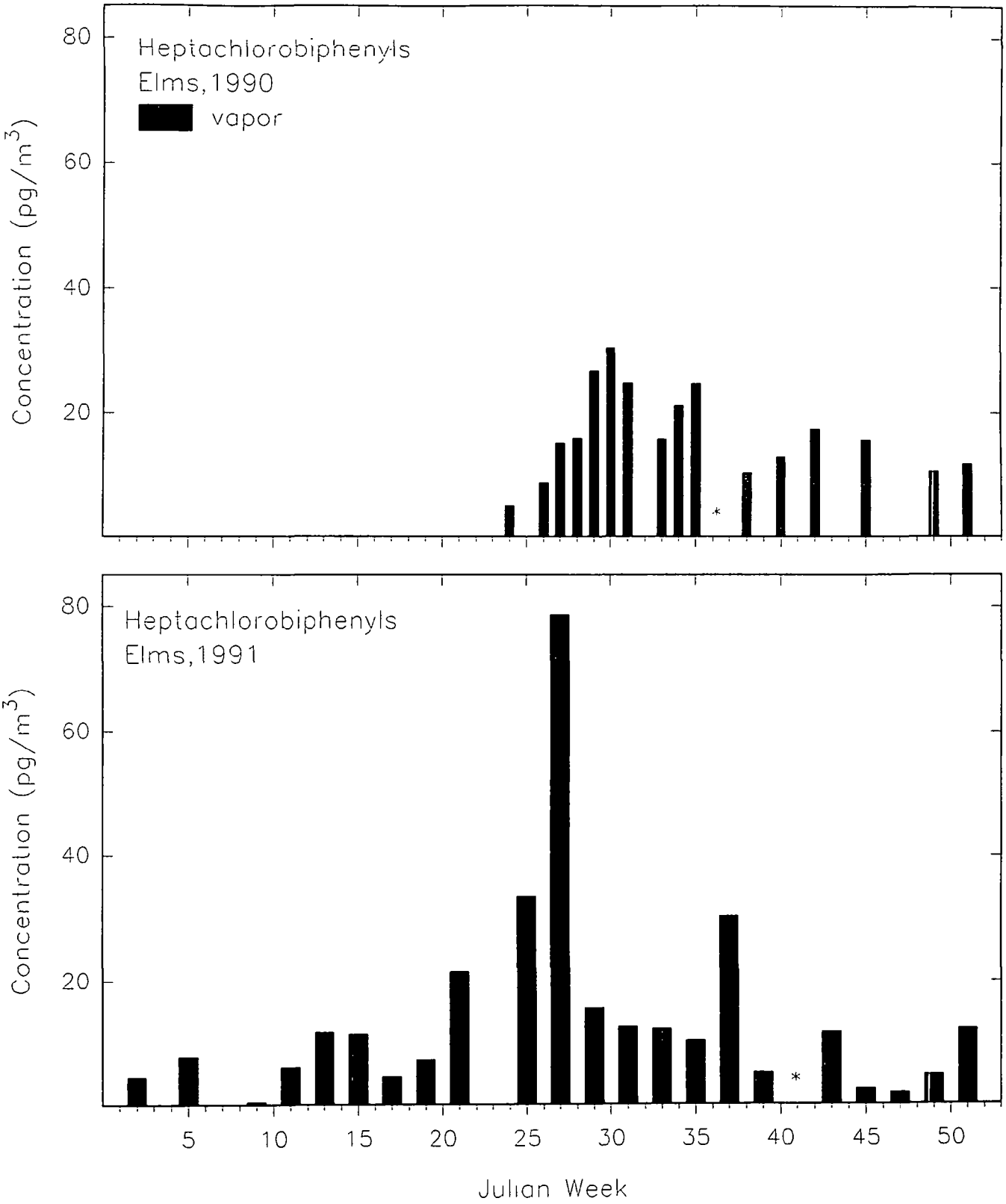
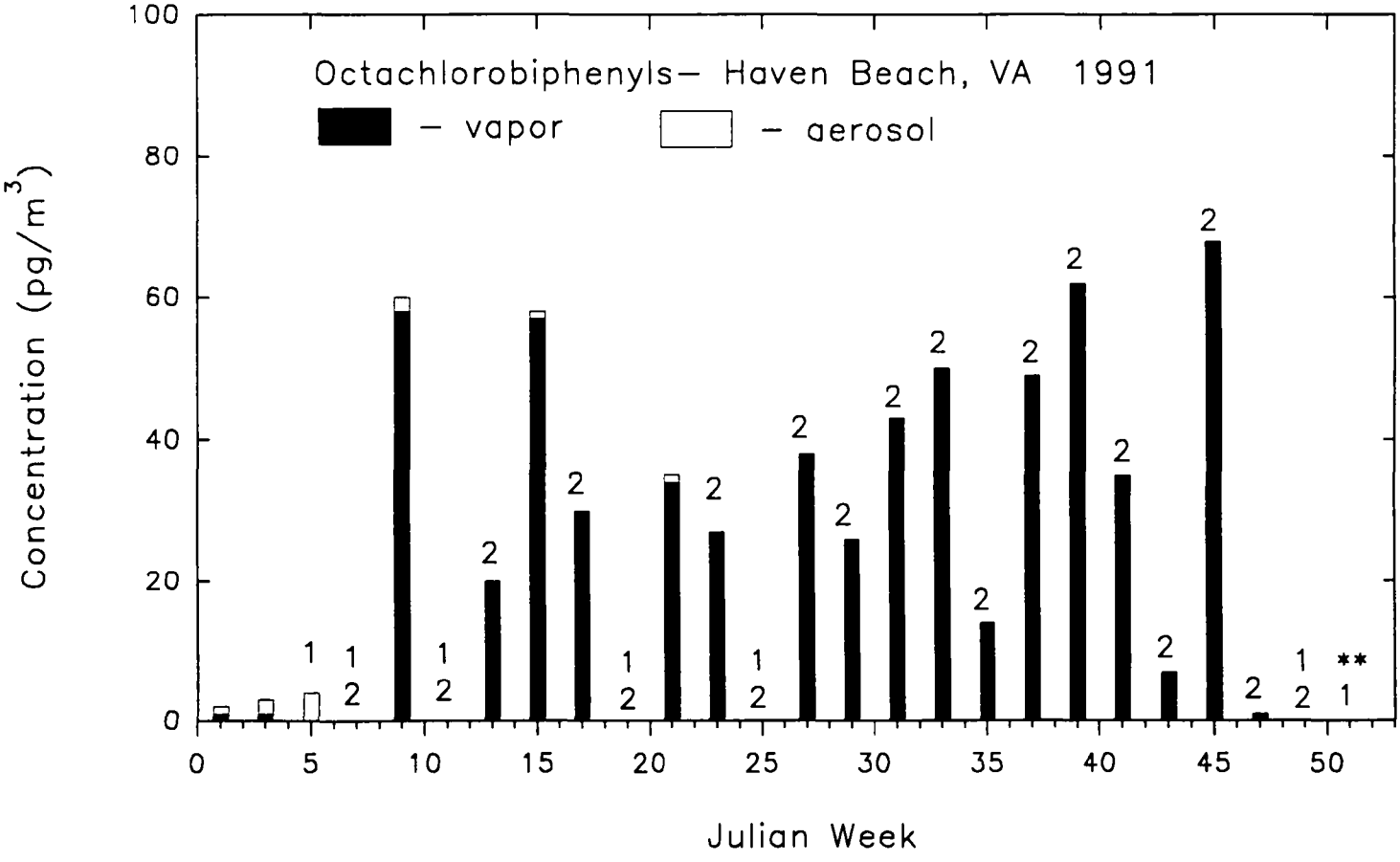

Heptachlorobiphenyls
Elms, 1990
vapor
Concentration (pg/m3)
80
60
40
20
Heptachlorobiphenyls
Elms, 1991
Concentration (pg/m3)
80
60
40
20
5
10
15
20
25
30
35
40
45
50
Julian Week

Figure IV.1.20 Total octachlorobiphenyl conoentrations in air collected biweekly at the Elms and Haven Beach sites. (1=not quantifiable in vapor phase, 2=not quantifiable on filter, 3=not detected in vapor phase, 4=not detected on filter, * =lost vapor sample, ** =lost particulate sample)



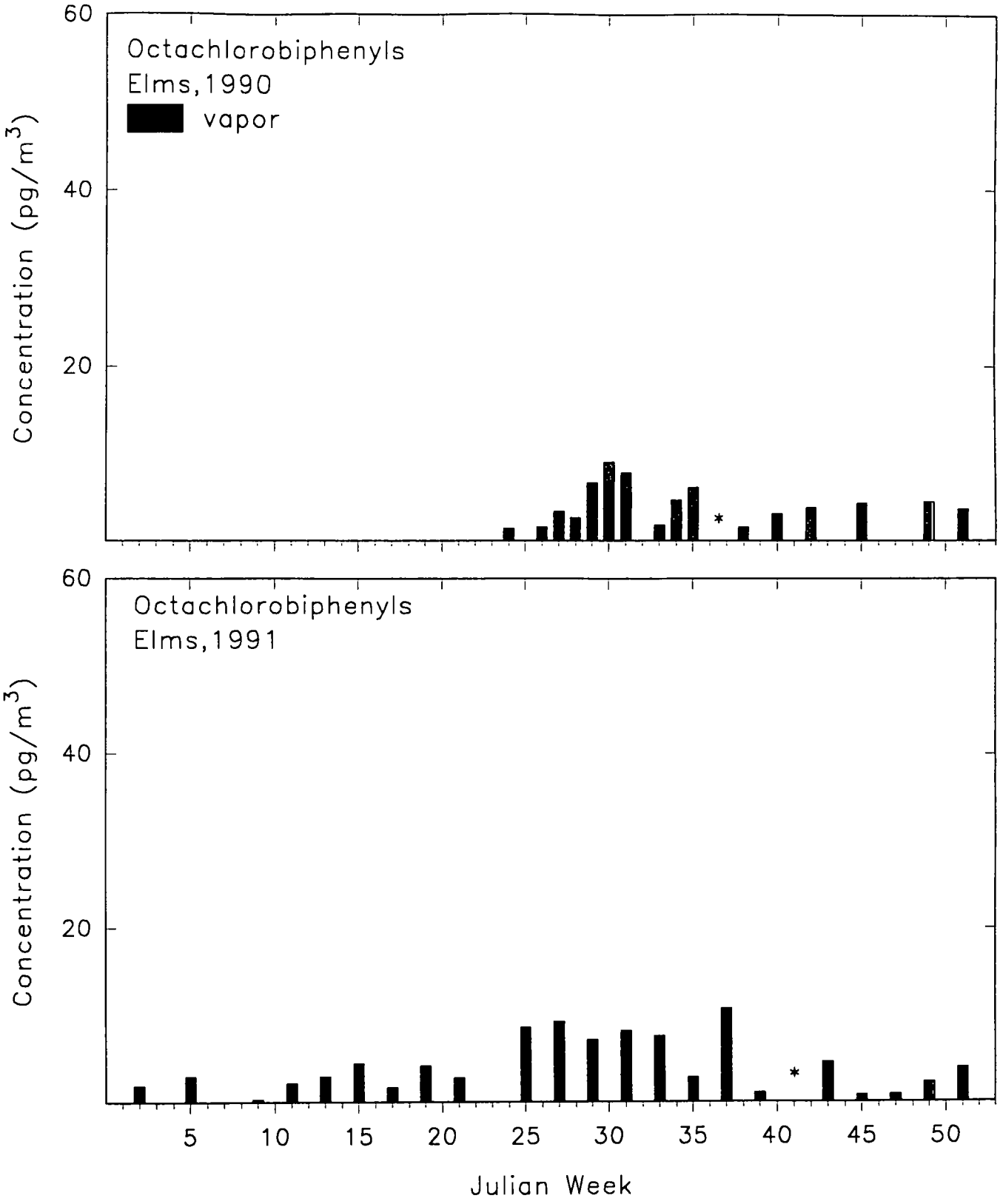
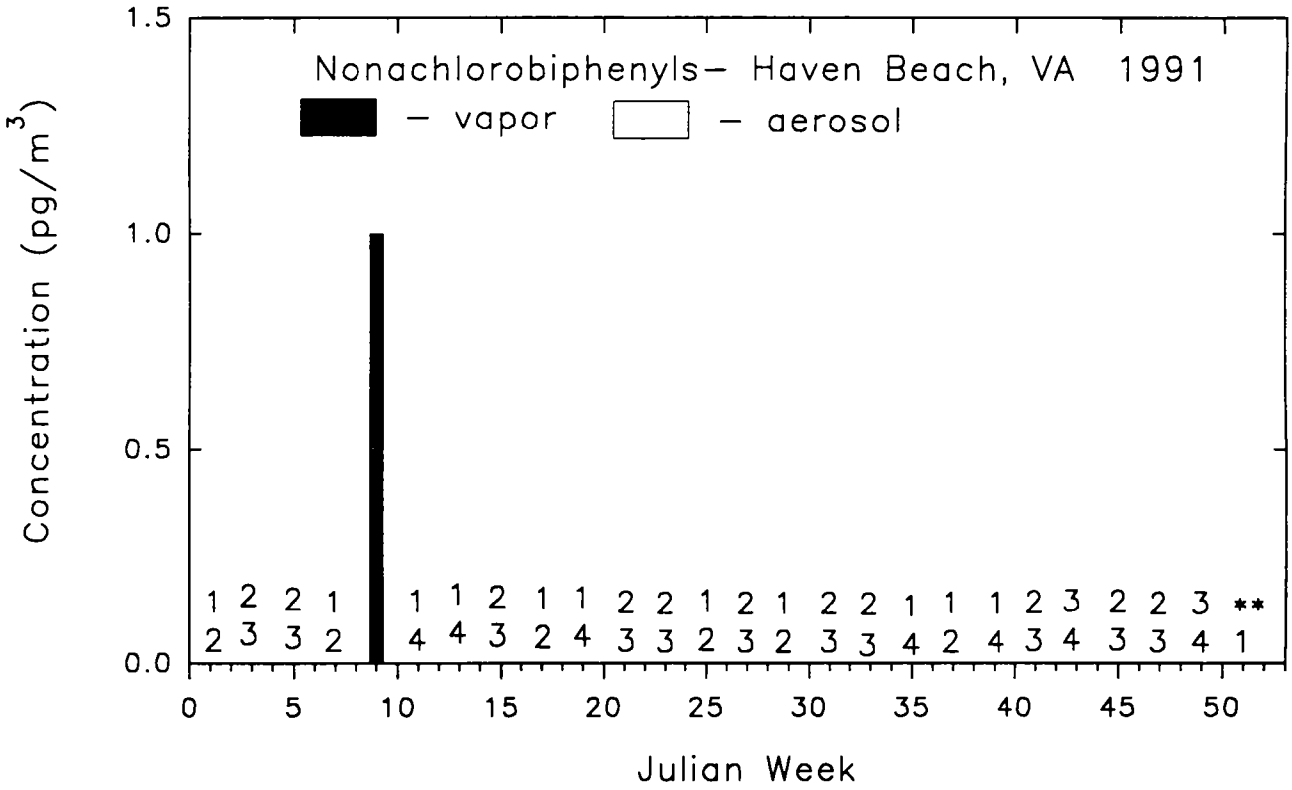

Octachlorobiphenyls
Elms,1990
vapor
Concentration (pg/m3)
60
40
20
Octachlorobiphenyls
Elms,1991
Concentration (pg/m3)
60
40
20
5
10
15
20
25
30
35
40
45
50
Julian Week

Figure IV.1.21 Total nonachlorobiphenyl concentrations in air collected biweekly at the Elms and Haven Beach sites. (1=not quantifiable in vapor phase, 2=not quantifiable on filter, 3=not detected in vapor phase, 4=not detected on filter, * =lost vapor sample, ** =lost particulate sample)



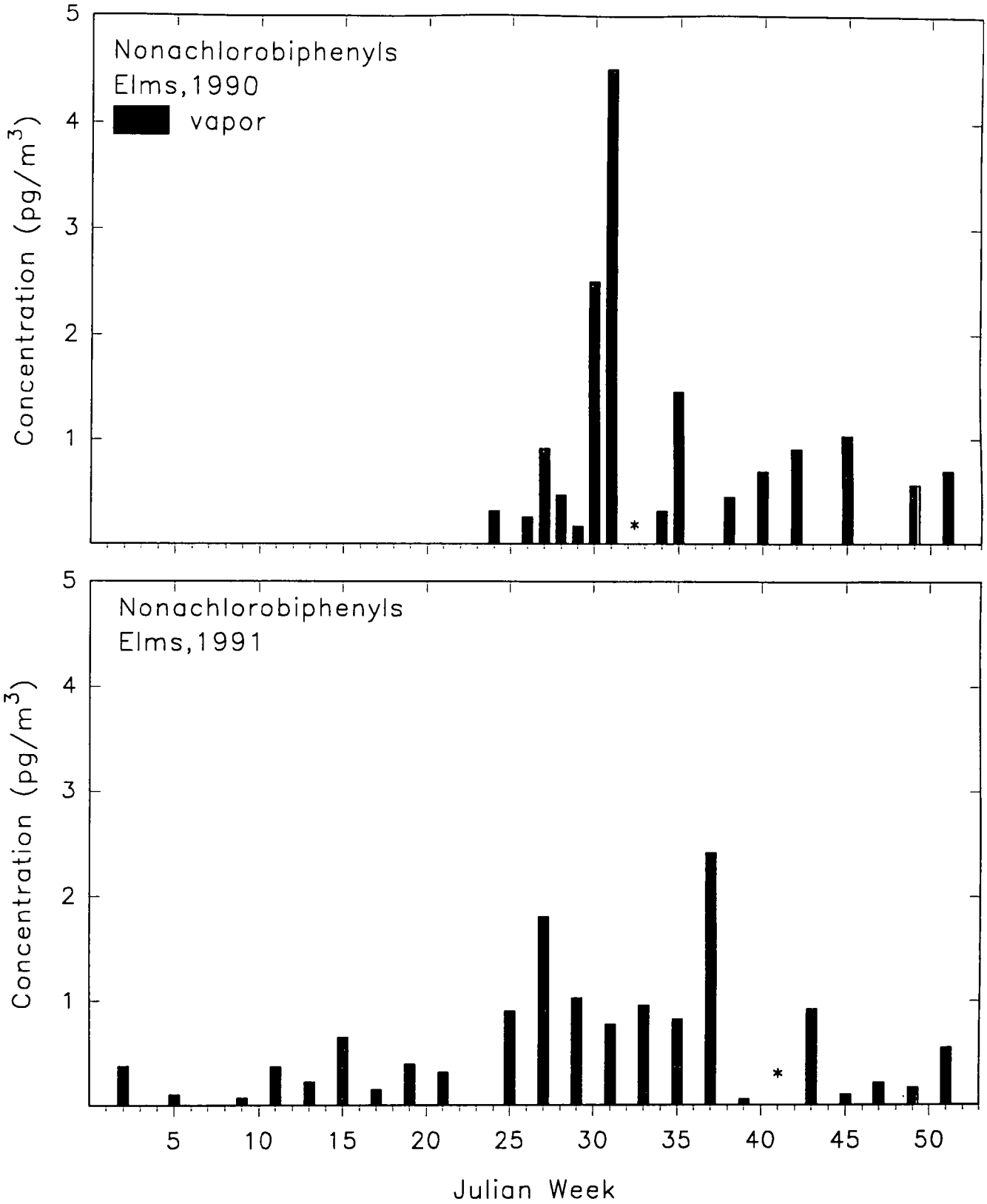
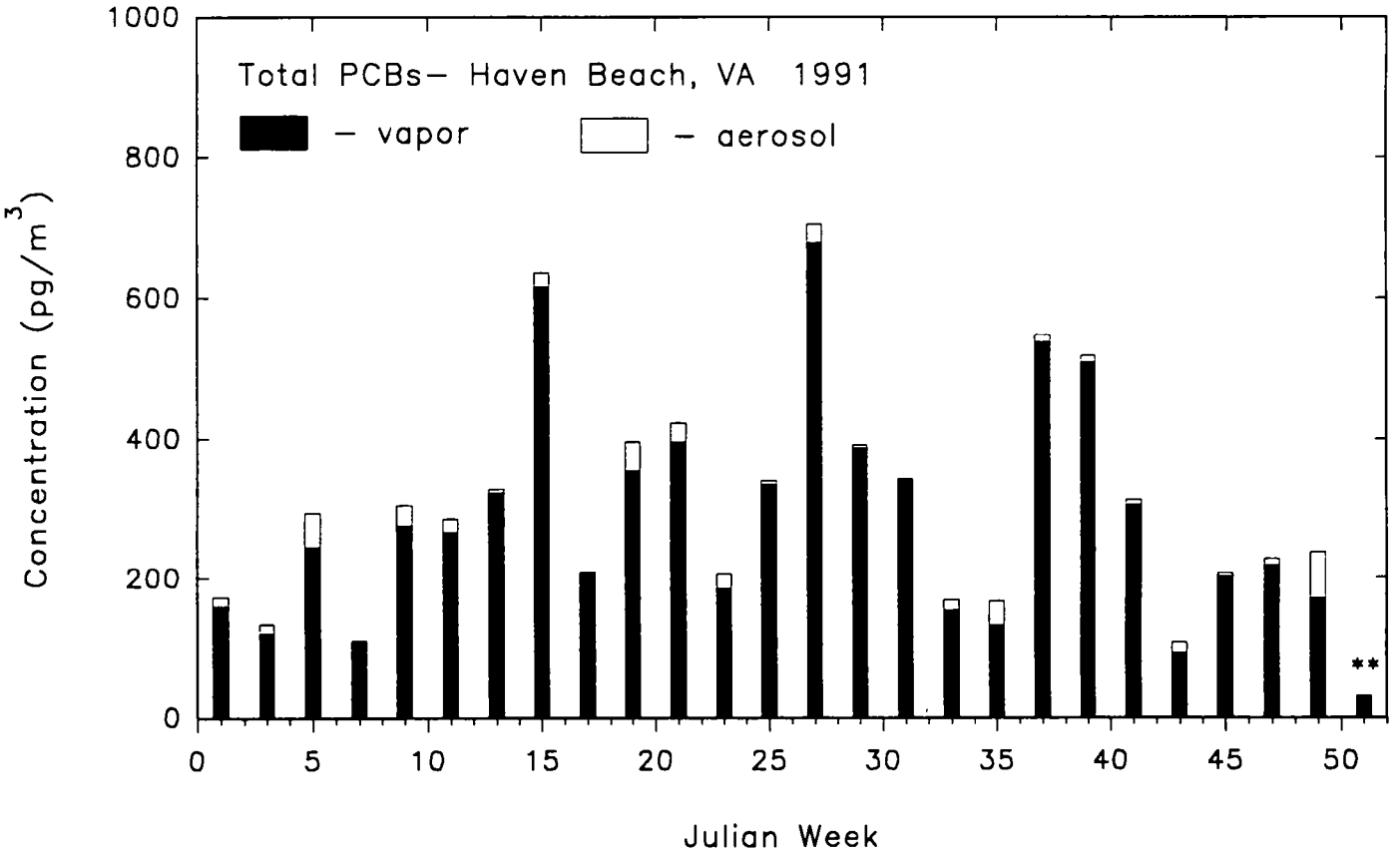
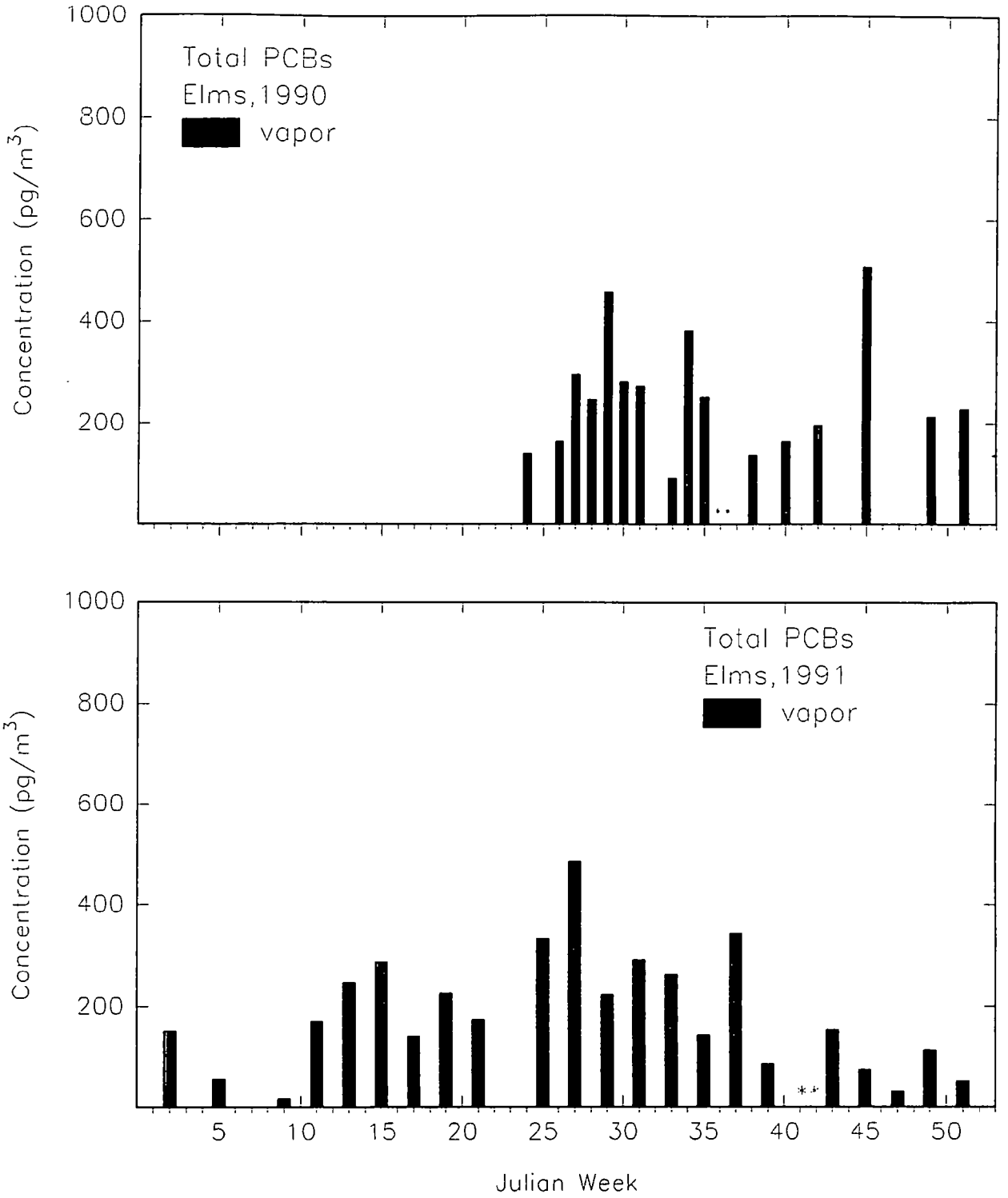

Nonachlorobiphenyls
Elms,1990
vapor
Concentration (pg/m3)
Nonachlorobiphenyls
Elms,1991
Concentration (pg/m3)
Julian Week

Figure IV.1.22. Total PCB concentrations in air collected biweekly at the Elms and Haven Beach sites.(1= not quantifiable in vapor phase, 2=not quantifiable on filter, 3=not detected in vapor phase, 4= not detected on filter, *=lost vapor sample, **=lost particulate sample.




Total PCBs
Elms,1990
vapor
Concentration (pg/m3)
1000
800
600
400
200
Total PCBs
Elms,1991
vapor
Concentration (pg/m3)
1000
800
600
400
200
5
10
15
20
25
30
35
40
45
50
Julian Week

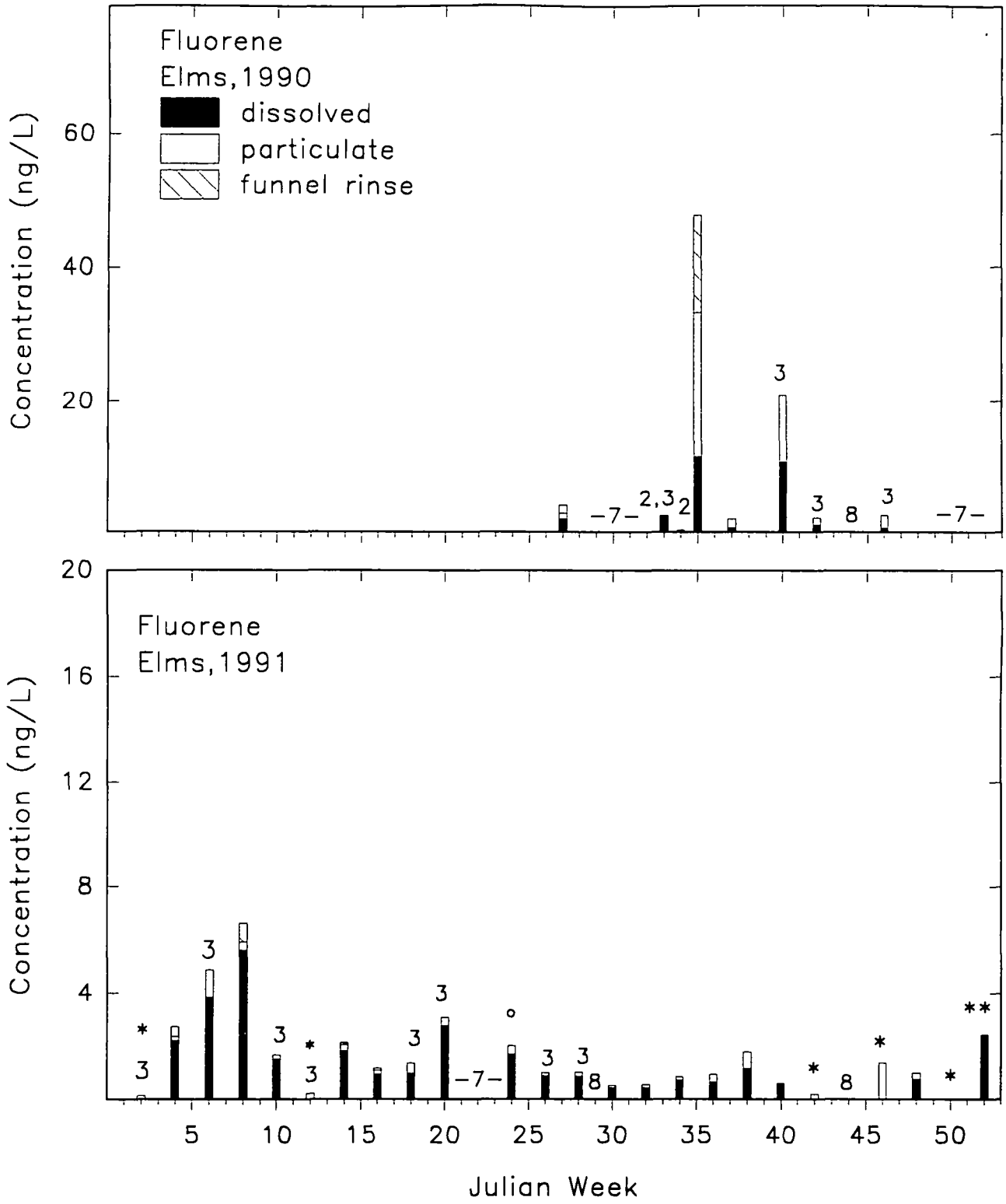
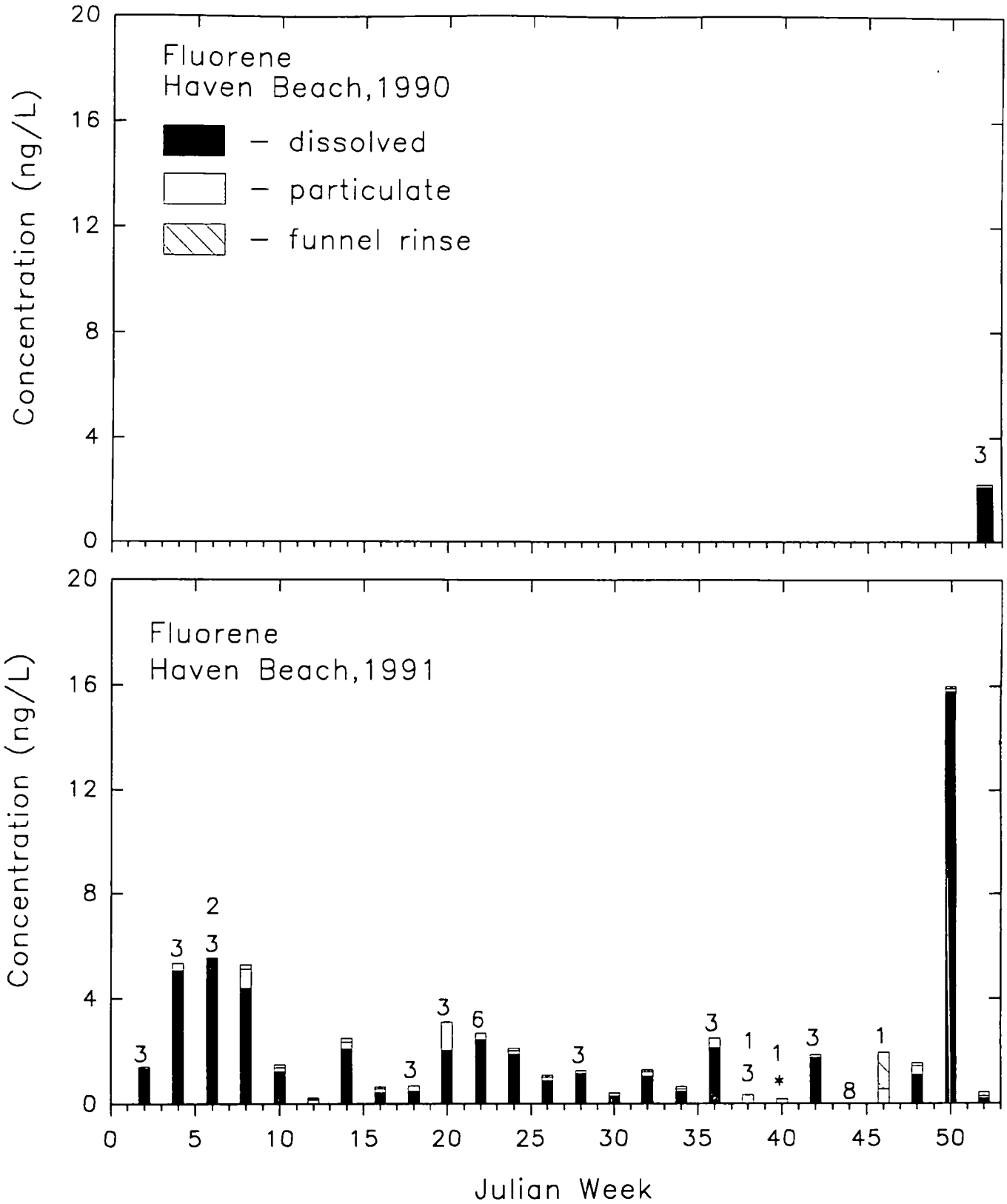


Figure IV.1.23 Fluorene concentrations in precipitation integrated biweekly at the Elms and Haven Beach sites. (1=not quantifiable in dissolved phase, 2=not quantifiable on filter, 3=not quantifiable in funnel, 4=not detected in dissolved phase, 5=not detected on filter, 6=not detected in funnel, 7=sampler down, 8=field blank, *=lost dissolved sample, **=lost particulate sample, ° = lost funnel rinse). Funnel rinse combined with particulate fractions after week 30, 1991.


Fluorene
Haven Beach,1990
– dissolved
– particulate
– funnel rinse
Concentration (ng/L)
Fluorene
Haven Beach,1991
Concentration (ng/L)
Julian Week

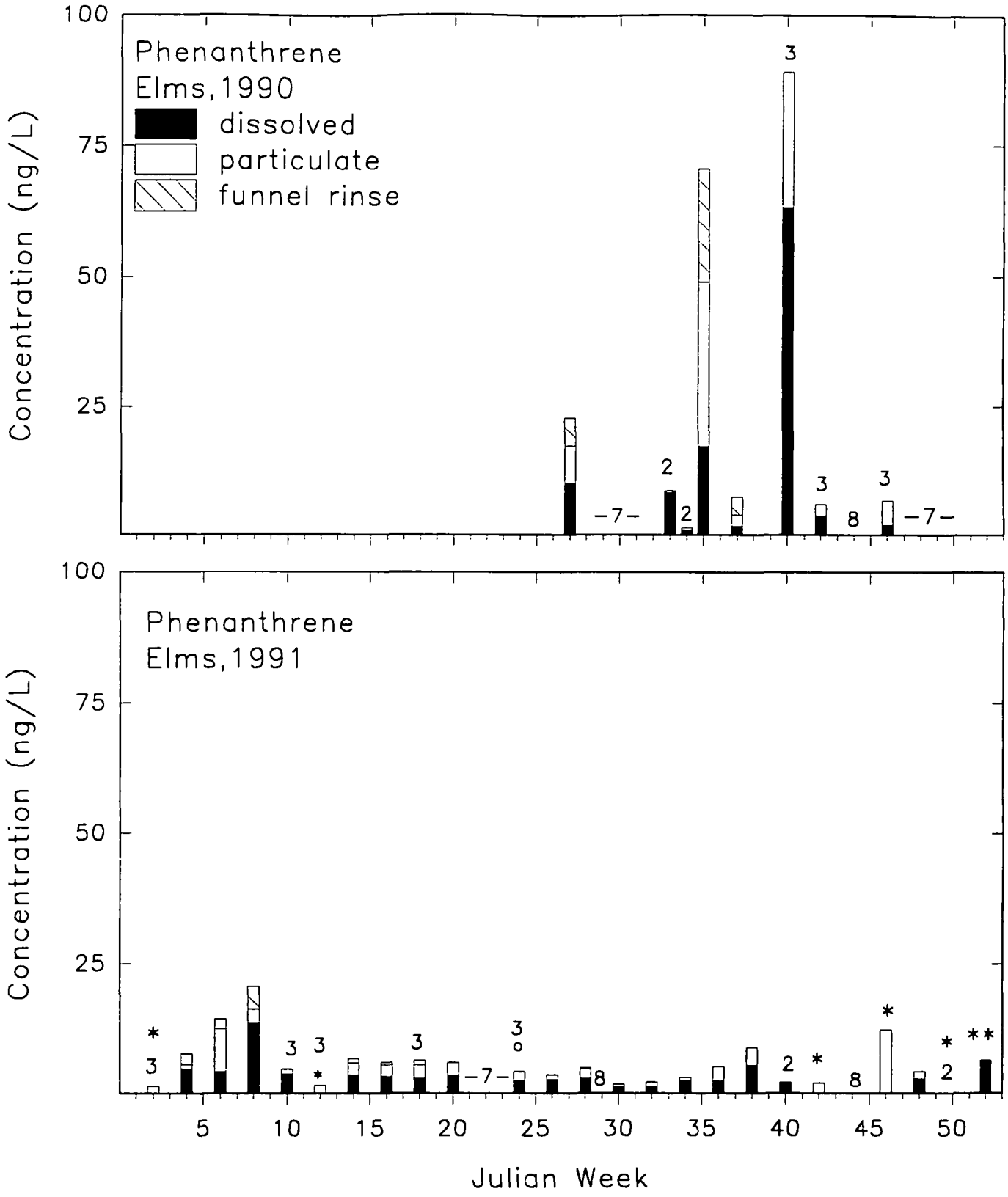
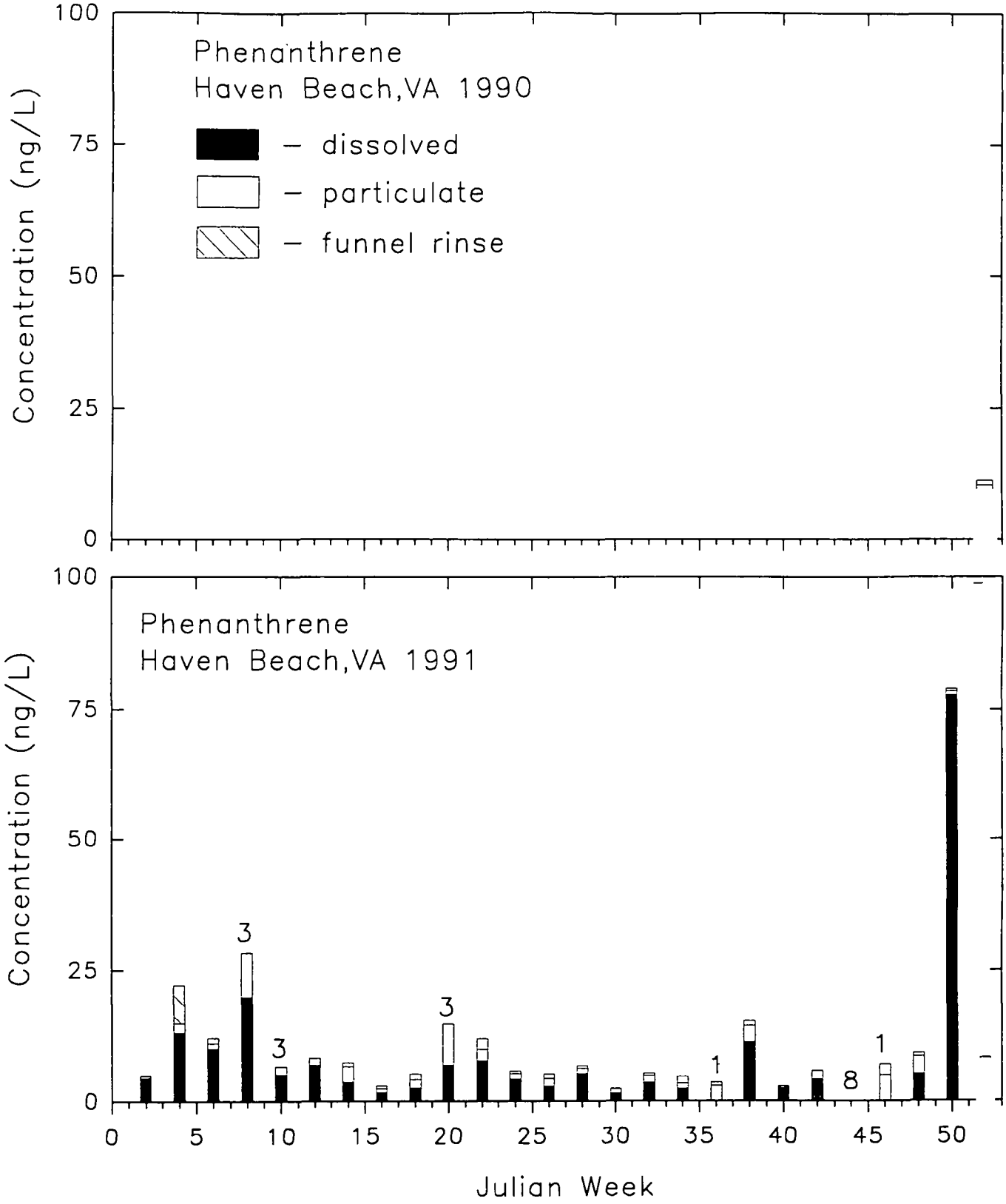


Figure IV.1.24. Phenanthrene concentrations in precipitation integrated biweekly at the Elms and Haven Beach sites. (1=not quantifiable in dissolved phase, 2=not quantifiable on filter, 3=not quantifiable in funnel, 4=not detected in dissolved phase, 5=not detected on filter, 6=not detected in funnel, *=lost dissolved sample, **=lost particulate sample, ° = lost funnel rinse, 7 = sampler down and 8 = field blank, no ppt.). Funnel rinse combined with particulate fractions after Week 30, 1991.


Phenanthrene
Haven Beach,VA 1990
– dissolved
– particulate
– funnel rinse
Concentration (ng/L)
100
75
50
25
0
Phenanthrene
Haven Beach,VA 1991
Concentration (ng/L)
3
3
3
1
8
1
0
5
10
15
20
25
30
35
40
45
50
Julian Week

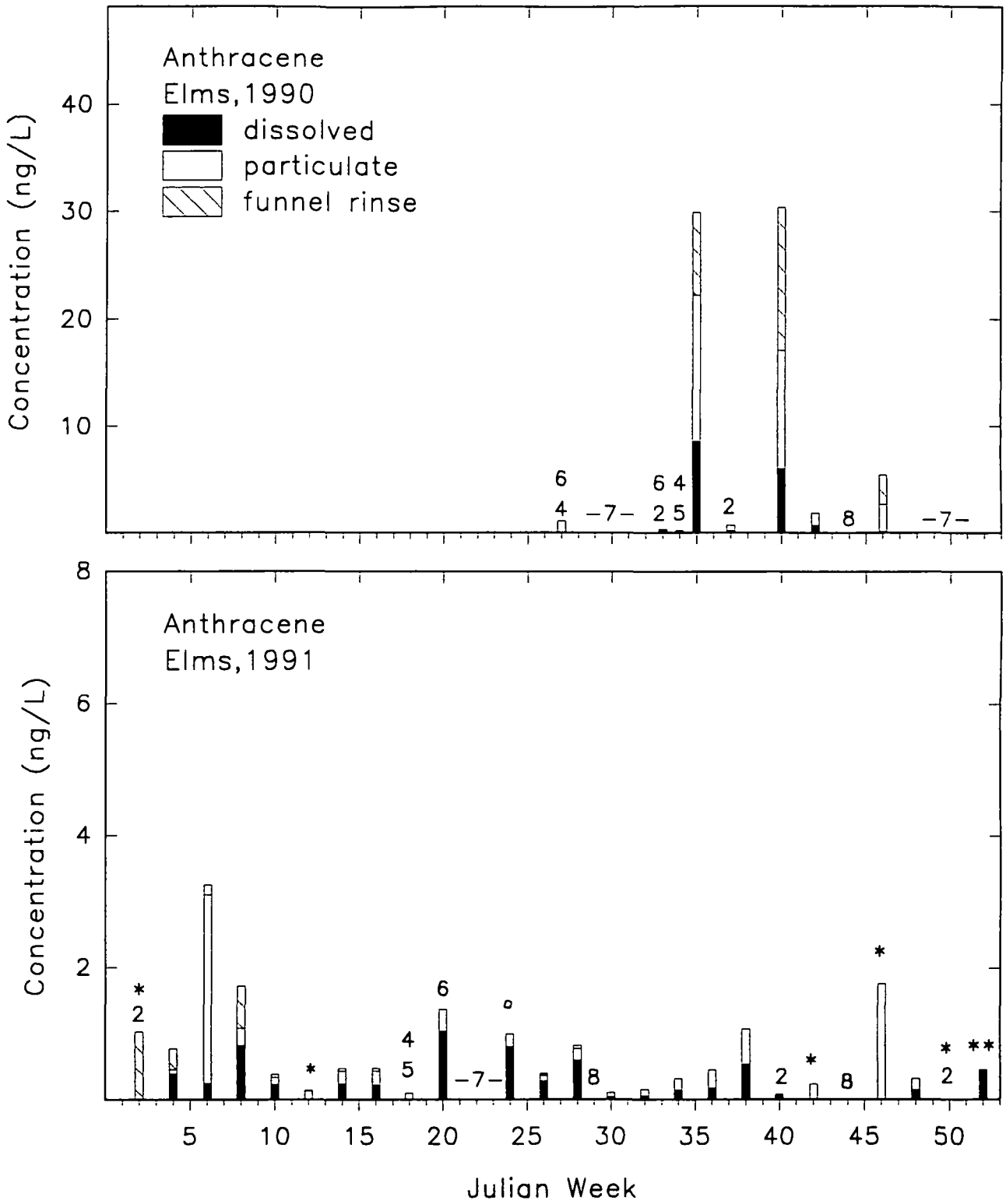
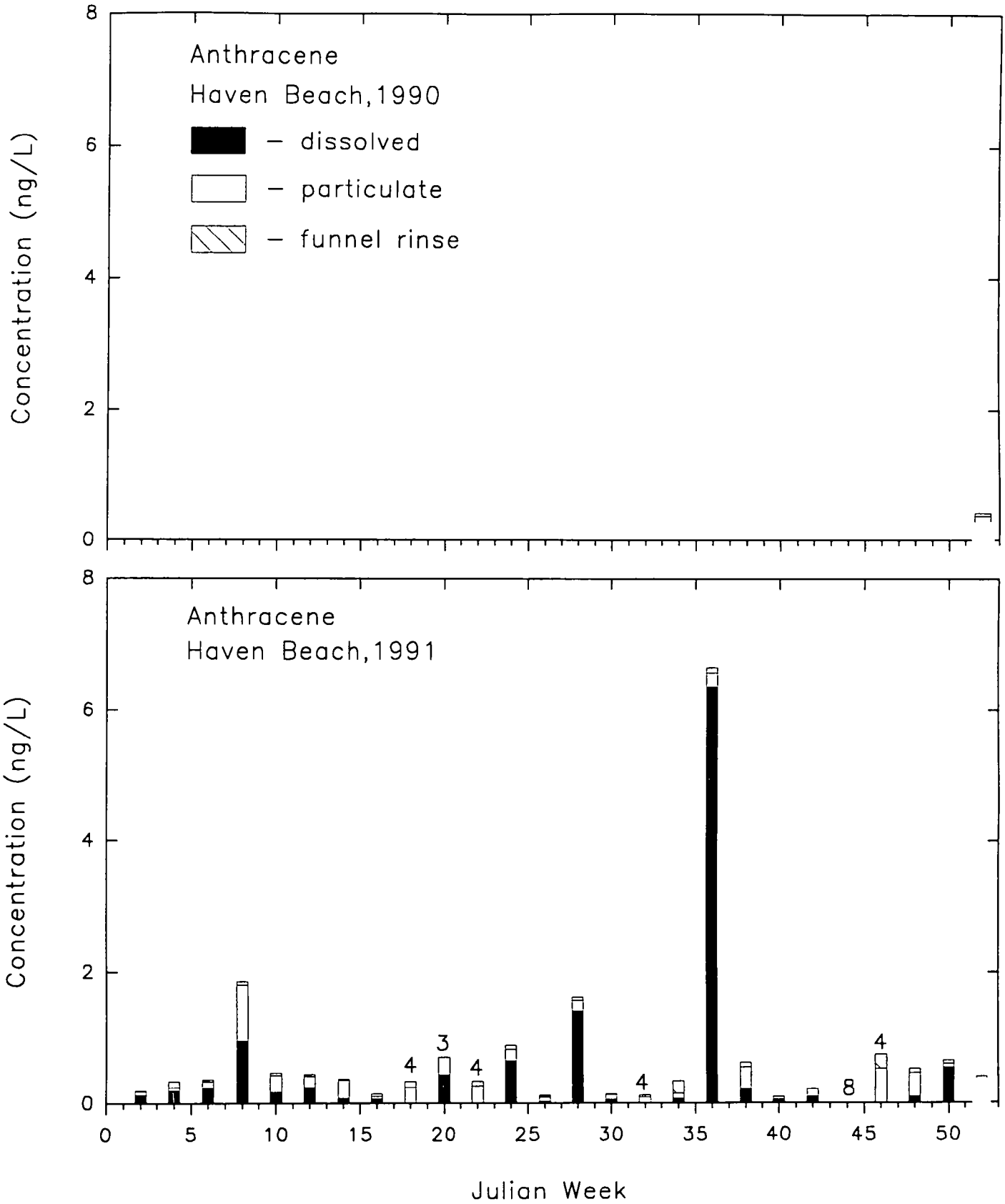


Figure IV.1.25 Anthracene concentrations in precipitation integrated biweekly at the Elms and Haven Beach sites. (1=not quantifiable in dissolved phase, 2= not quantifiable on filter, 3=not quantifiable in funnel, 4=not detected in dissolvedphase, 5=not detected on filter, 6=not detected in funnel, 7=sampler down, 8=field blank, *=lost dissolved sample, **=lost particulate sample,° = lost funnel rinse). Funnel rinse combined with particulate fractions after week 30, 1991.


Anthracene
Haven Beach,1990
– dissolved
– particulate
– funnel rinse
Concentration (ng/L)
Anthracene
Haven Beach,1991
Concentration (ng/L)
4
3
4
4
8
4
Julian Week

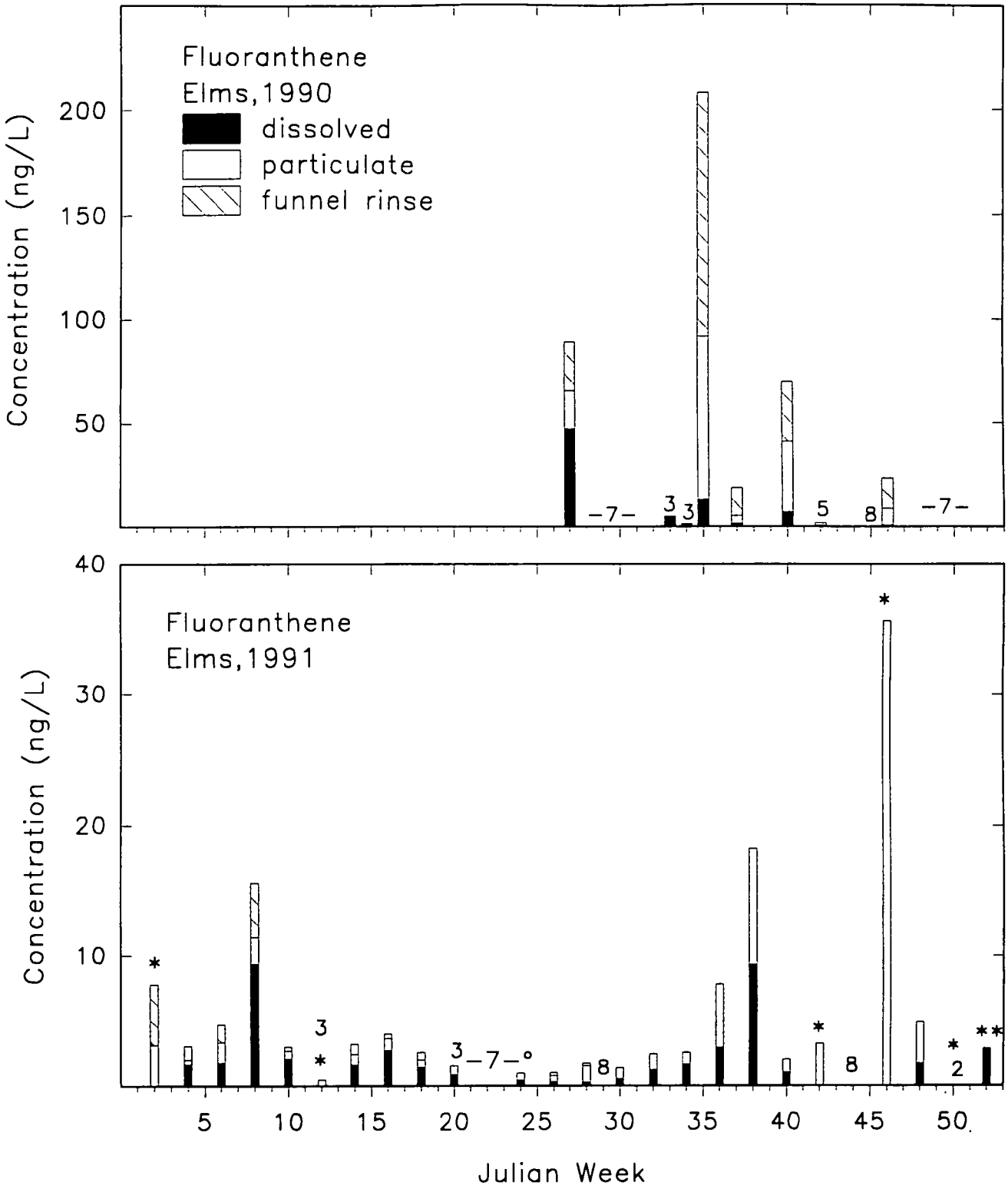
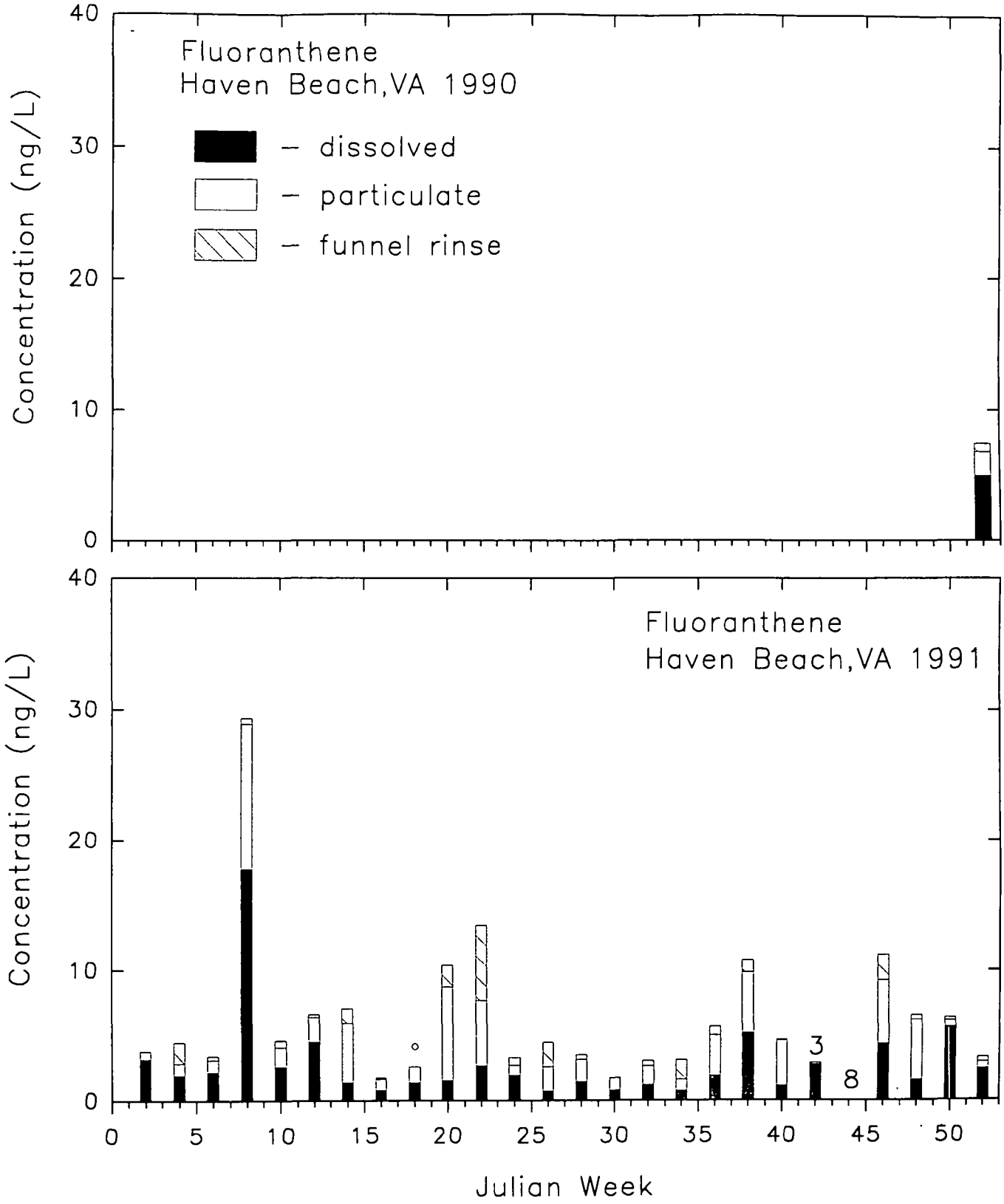


Figure IV.1.26. Fluoranthene concentrations in precipitation integrated biweekly at the Elms and Haven Beach sites.(1=not quantifiable in dissolved phase, 2=not quantifiable on filter, 3=not quantifiable in funnel, 4=not detected in dissolved phase, 5=not detected on filter, 6=not detected in funnel, 7=sampler down, 8=field blank, *=lost dissolved sample, **=lost particulate sample, ° = lost funnel rinst). Funnel rinse combined with particulate fractions after week 30, 1991.


Fluoranthene
Haven Beach,VA 1990
– dissolved
– particulate
– funnel rinse
Concentration (ng/L)
Fluoranthene
Haven Beach,VA 1991
Concentration (ng/L)
3
8
Julian Week

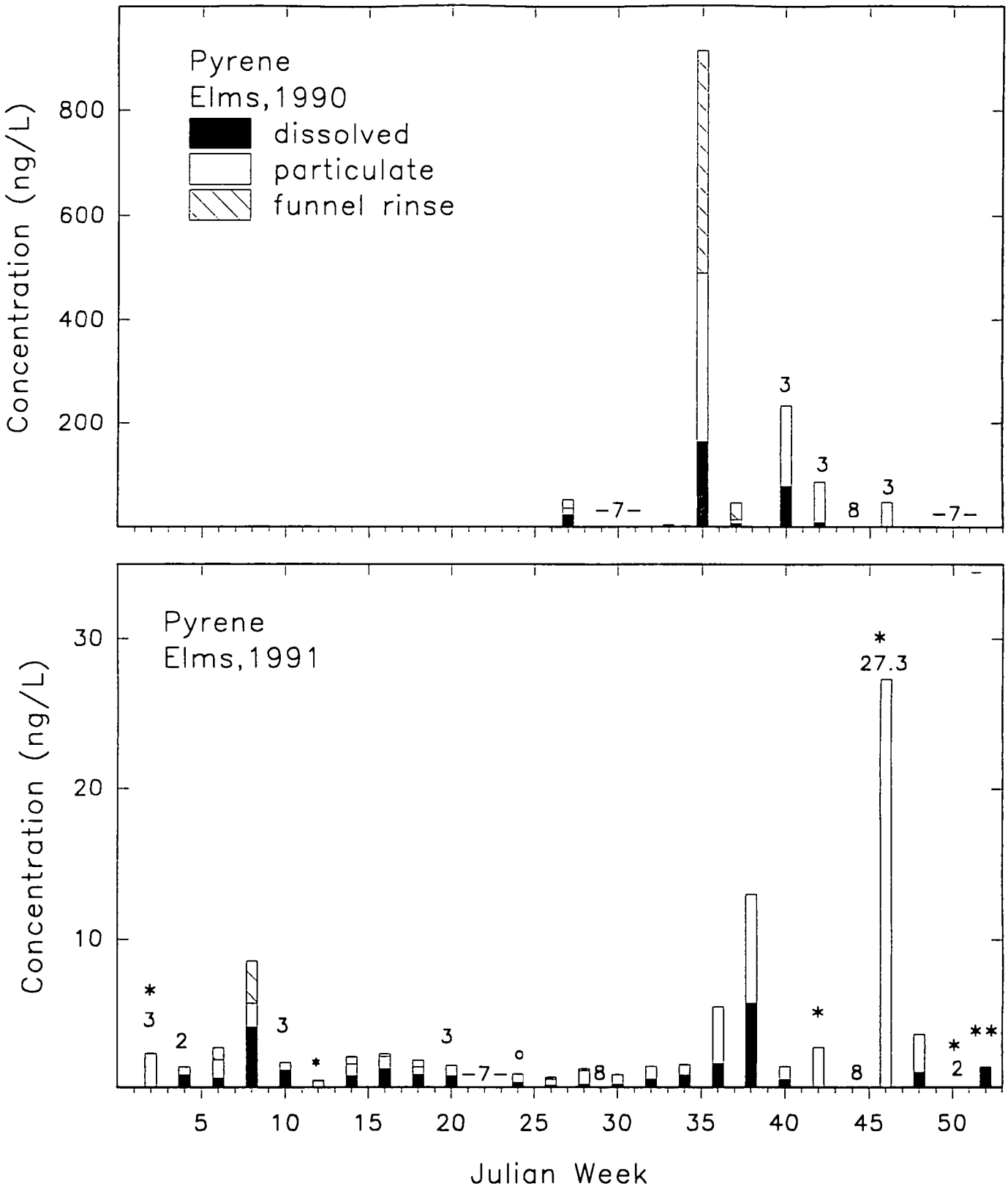
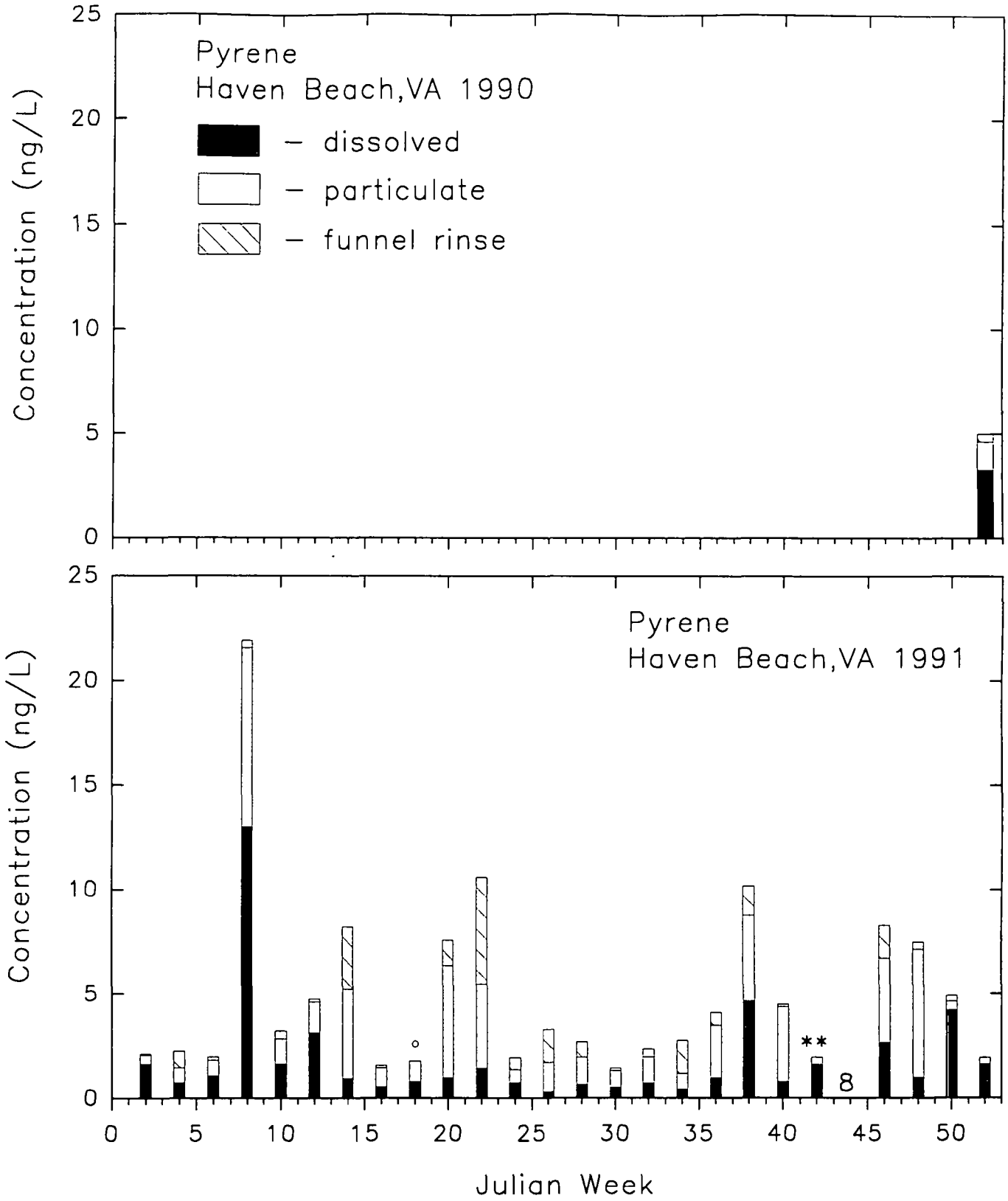


Figure IV.1.27. Pyrene concentrations in precipitation integrated biweekly at the Elms and Haven Beach sites. (1=not quantifiable in dissolved phase, 2=not quantifiable on filter, 3=not quantifiable in funnel, 4=not detected in dissolved phase, 5=not detected on filter, 6=not detected in funnel, 7=sampler down, 8=field blank, *=lost dissolved sample, **=lost particulate sample, ° = lost funnel rinse). Funnel rinse combined with particulate fractions after week 30, 1991


Pyrene
Haven Beach,VA 1990
– dissolved
– particulate
– funnel rinse
Concentration (ng/L)
Pyrene
Haven Beach,VA 1991
Concentration (ng/L)
Julian Week

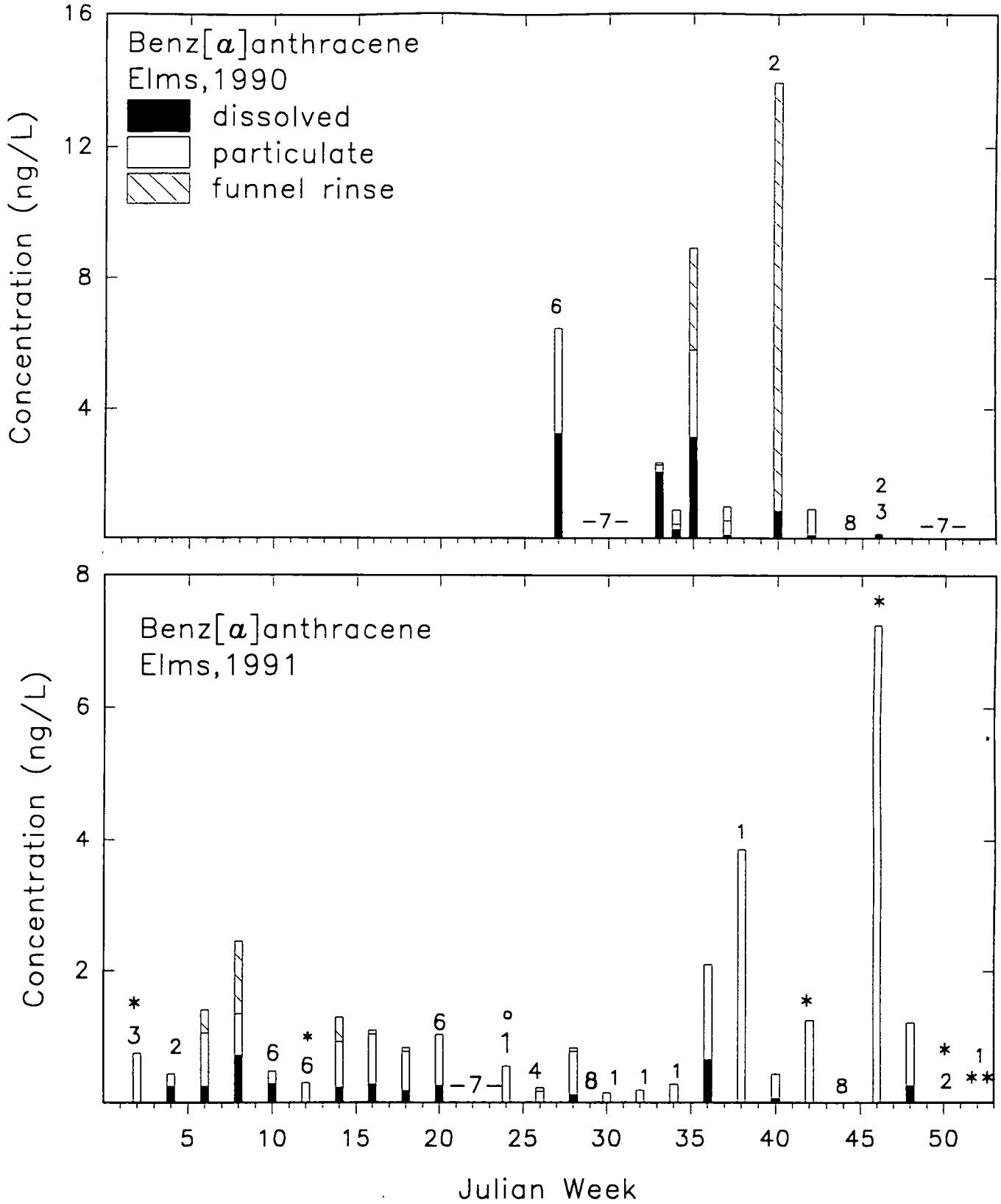
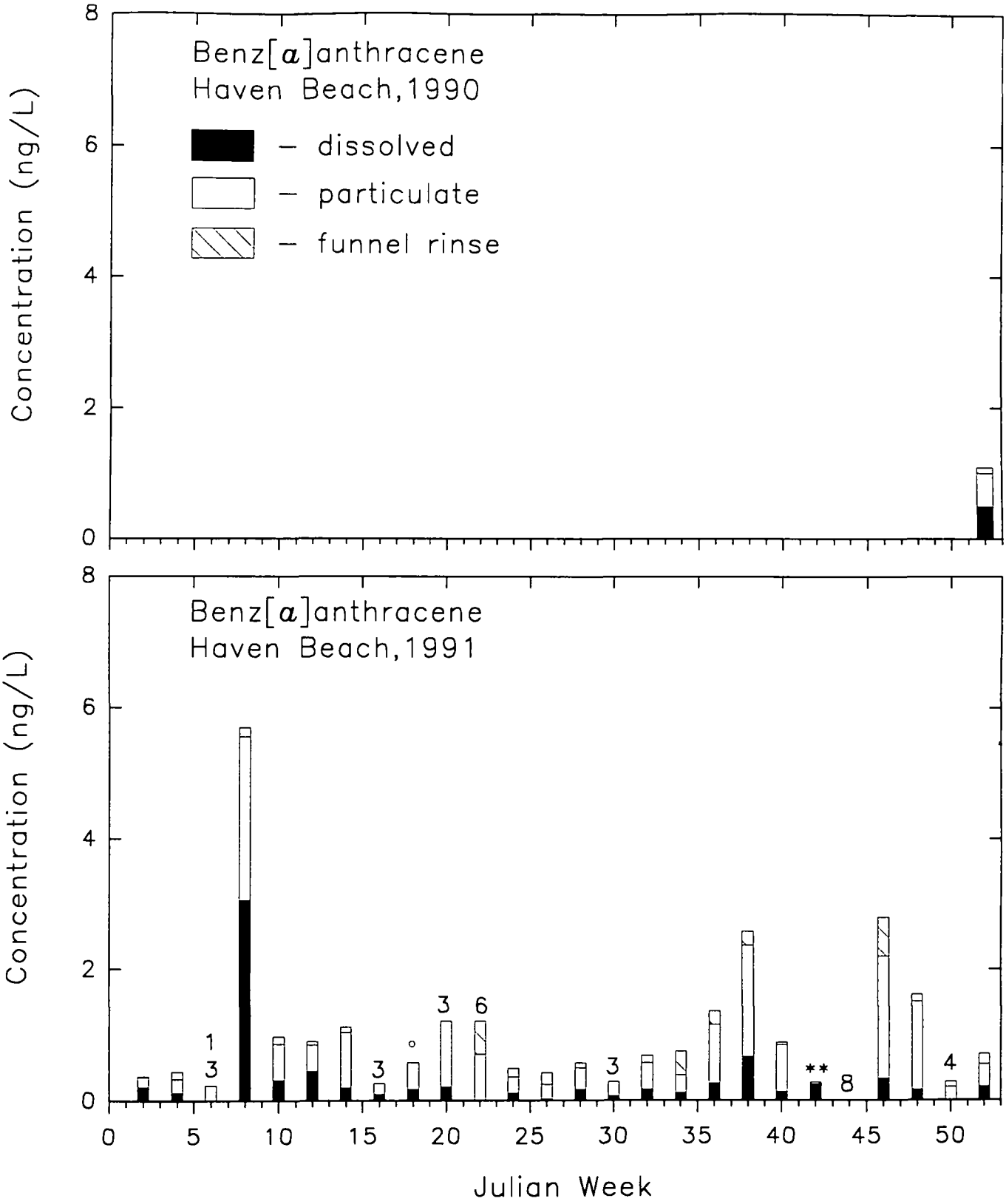


Figure IV.1.28 Benz[a]anthracene concentrations in precipitation integrated biweekly at the Elms and Haven Beach sites. (1=not quantifiable in dissolved phase, 2=not quantifiable on filter, 3=not quantifiable in funnel, 4=not detected in dissolved phase, 5=not detected on filter, 6=not detected in funnel, 7=sampler down, 8=field blank, *=lost dissolved sample, **=lost particulate sample, ° = lost funnel rinse). Funnel rinse combined with particulate fractions after week 30, 1991.


Benz[a]anthracene
Haven Beach,1990
– dissolved
– particulate
– funnel rinse
Concentration (ng/L)
Benz[a]anthracene
Haven Beach,1991
Concentration (ng/L)
1
3
3
°
3
6
3
**
8
4
Julian Week

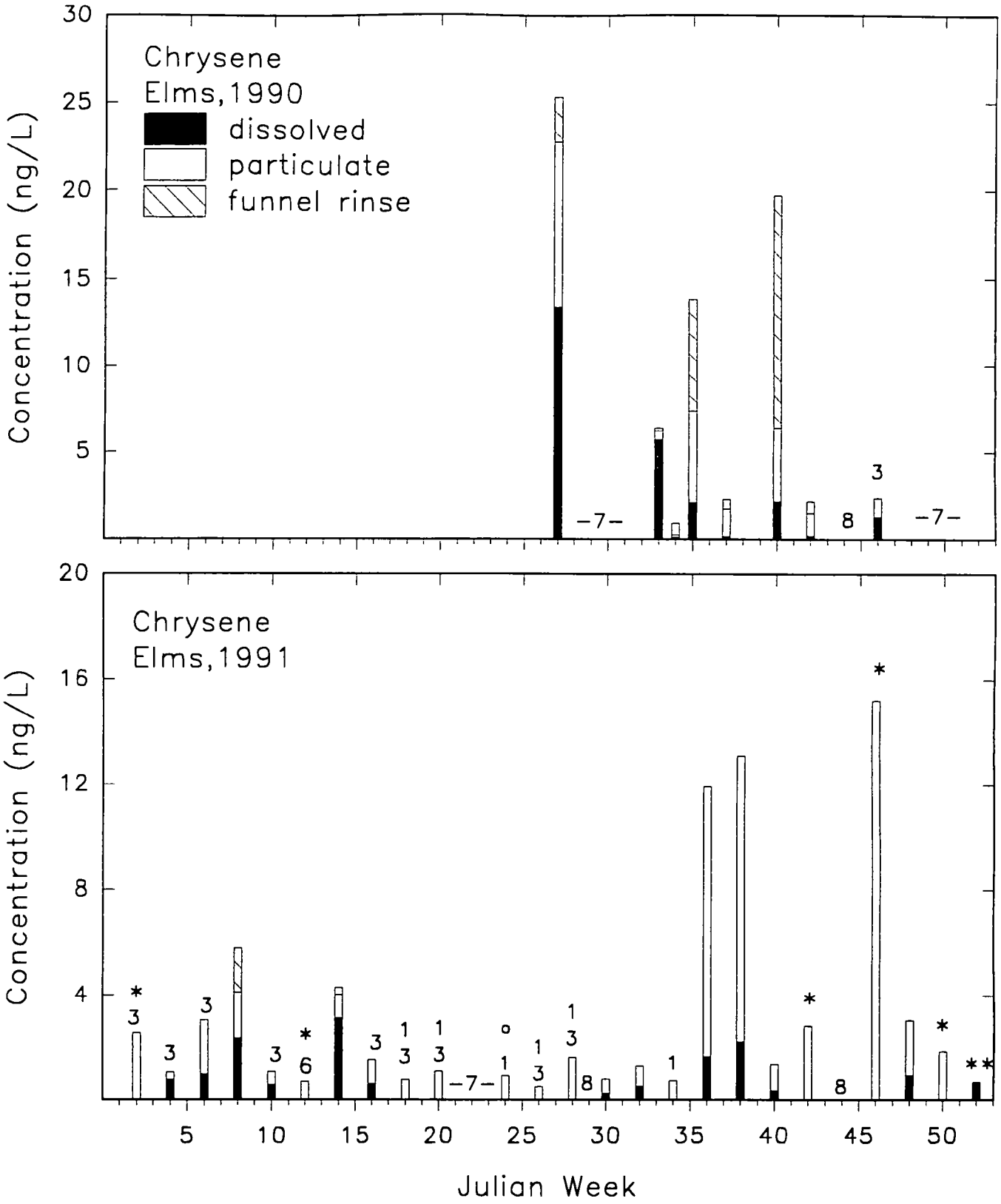
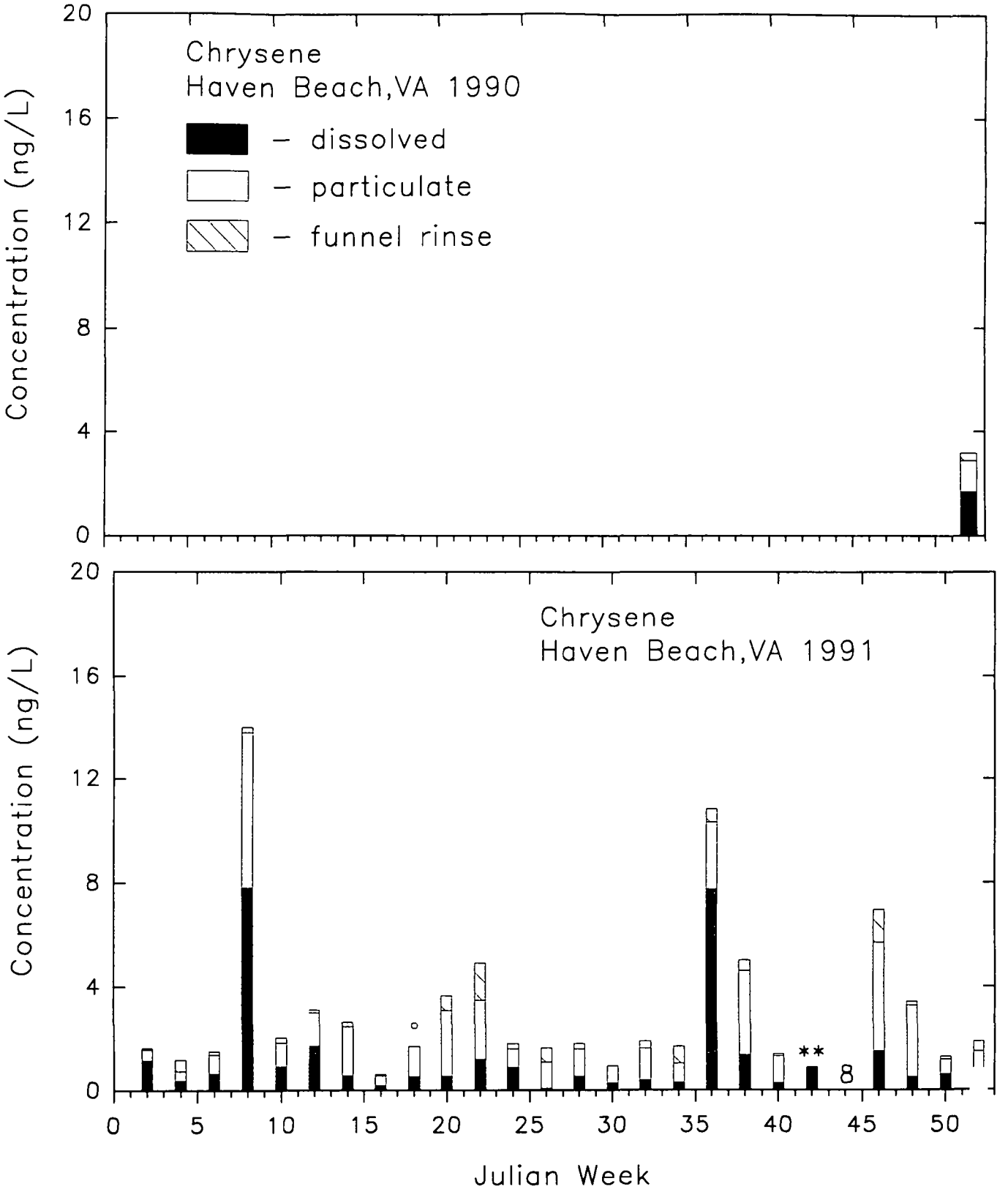


Figure IV.1.29. Chrysene concentrations in precipitation integrated biweekly at the Elms site. (1=not quantifiable in dissolved phase, 2=not quantifiable on filter, 3=not quantifiable in funnel, 4=not detected in dissolved phase, 5=not detected on filter, 6=not detected in funnel, 7=sampler down, 8=field blank, 8=lost dissolved sample, **=lost particulate sample, ° = lost funnel rinse). Funnel rinse combined with particulate fractions after week 30, 1991.


Chrysene
Haven Beach,VA 1990
– dissolved
– particulate
– funnel rinse
Concentration (ng/L)
Chrysene
Haven Beach,VA 1991
Concentration (ng/L)
Julian Week

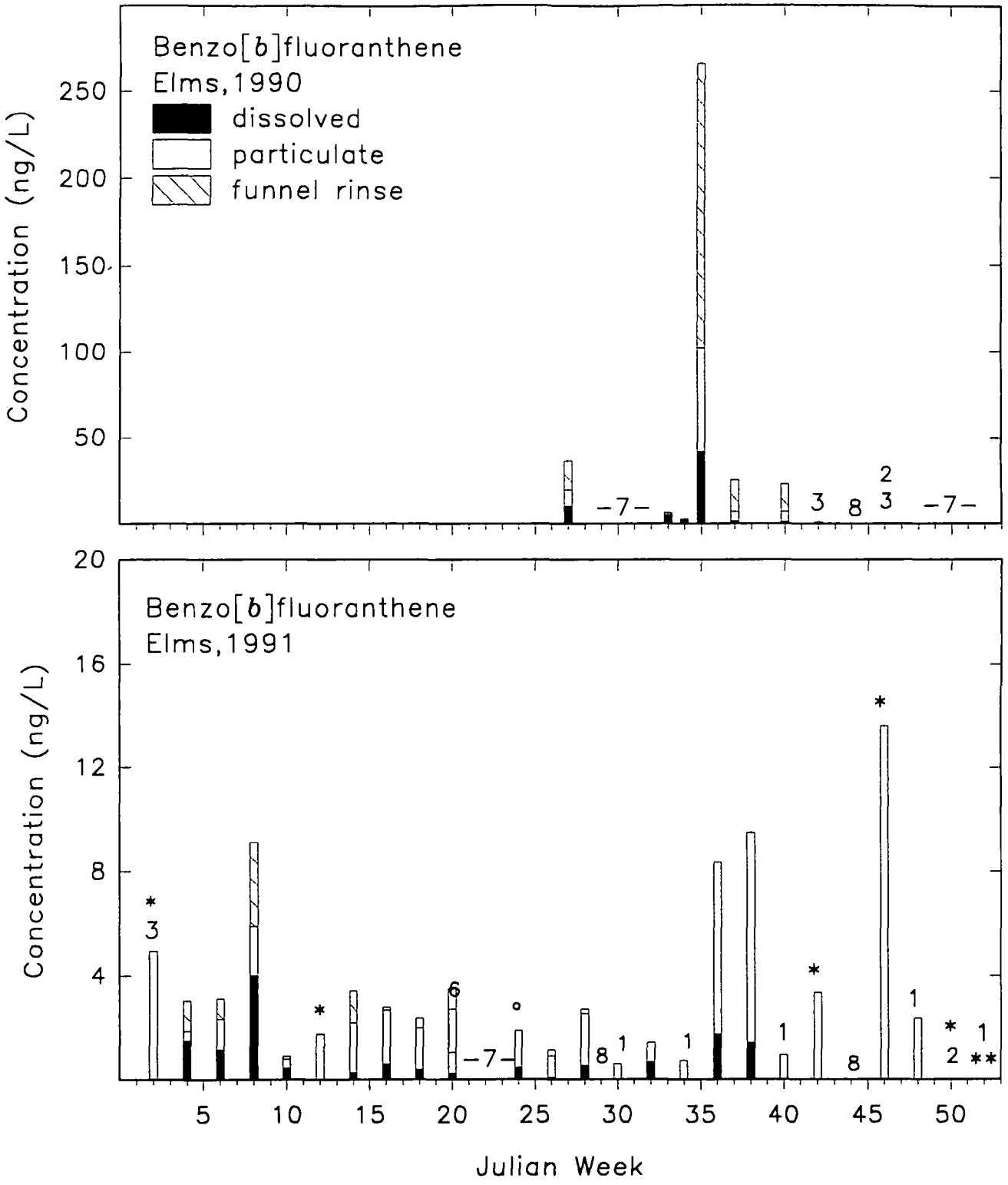
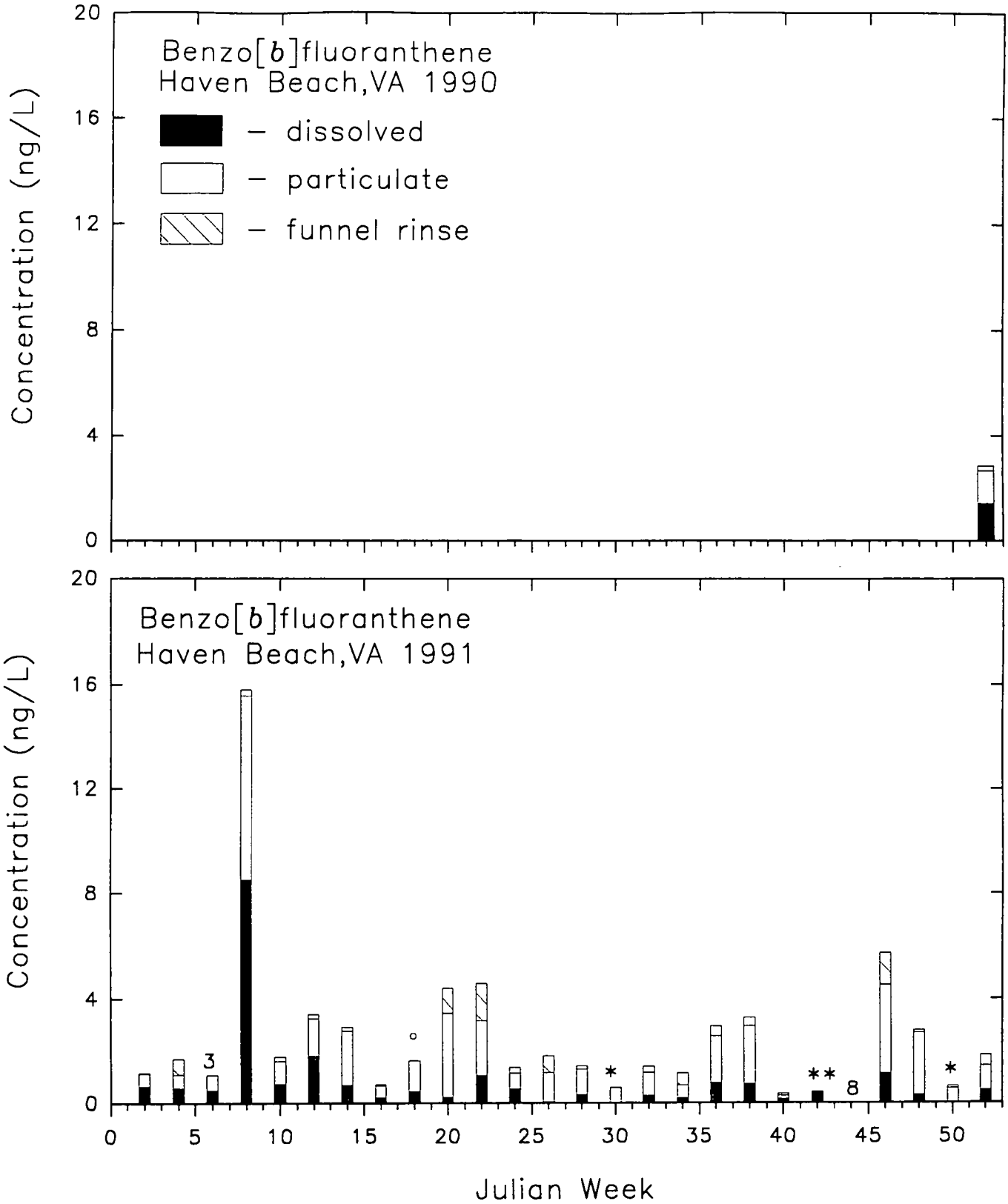


Figure IV.1.30. Benzo[*b*]fluoranthene concentrations in precipitation integrated biweekly at the Elms and Haven Beach sites. (1=not quantifiable in dissolved phase, 2=not quantifiable on filter, 3=not quantifiable in funnel, 4=not detected in dissolved phase, 5=not detected on filter, 6=not detected in funnel, 7=sampler down, 8=field blank, *=lost dissolved sample, **=lost particulate sample, ° = lost funnel rinse). Funnel rinse combined with particulate fractions after week 30, 1991.


Benzo[b]fluoranthene
Haven Beach,VA 1990
– dissolved
– particulate
– funnel rinse
Concentration (ng/L)
Benzo[b]fluoranthene
Haven Beach,VA 1991
Concentration (ng/L)
Julian Week

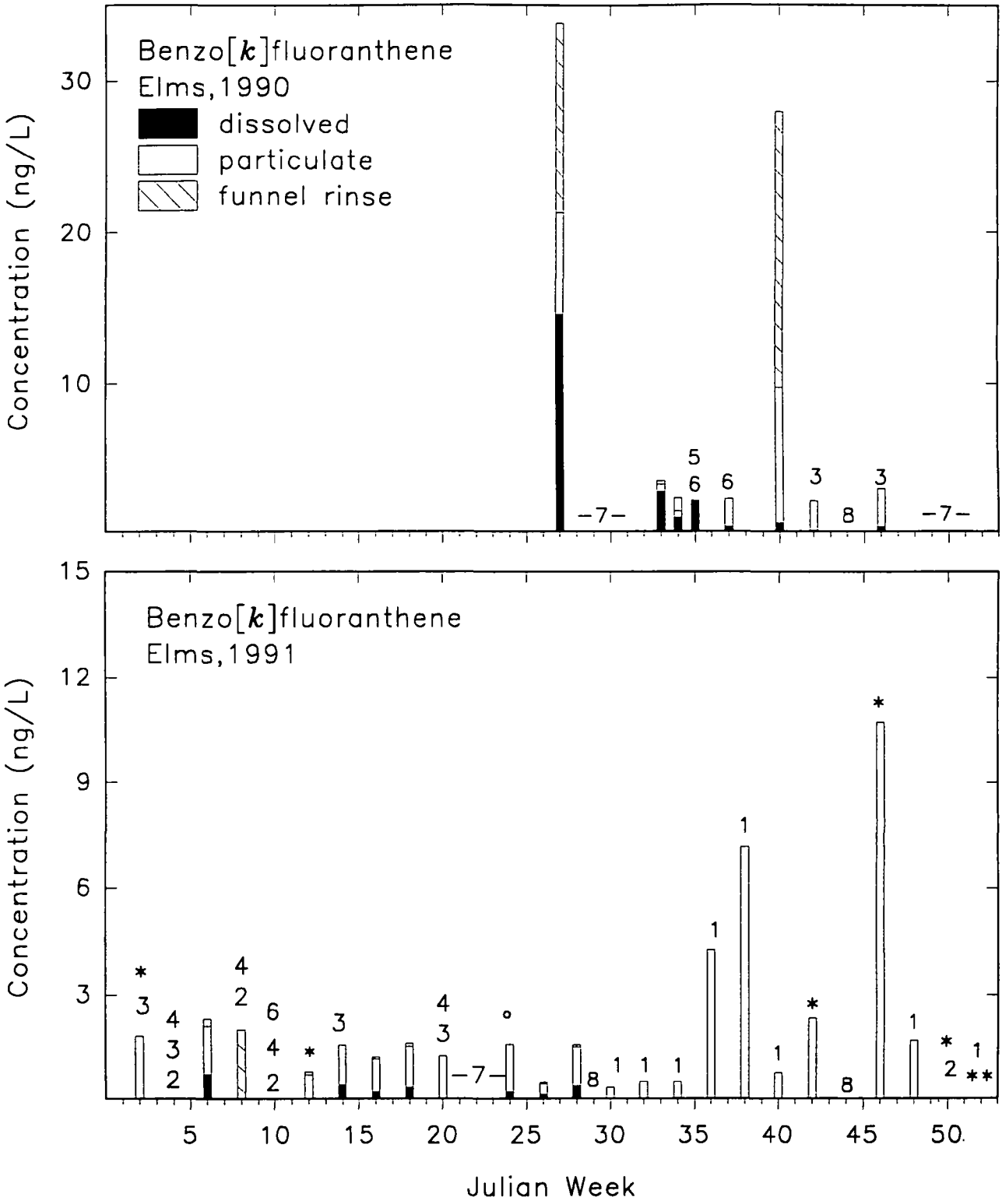
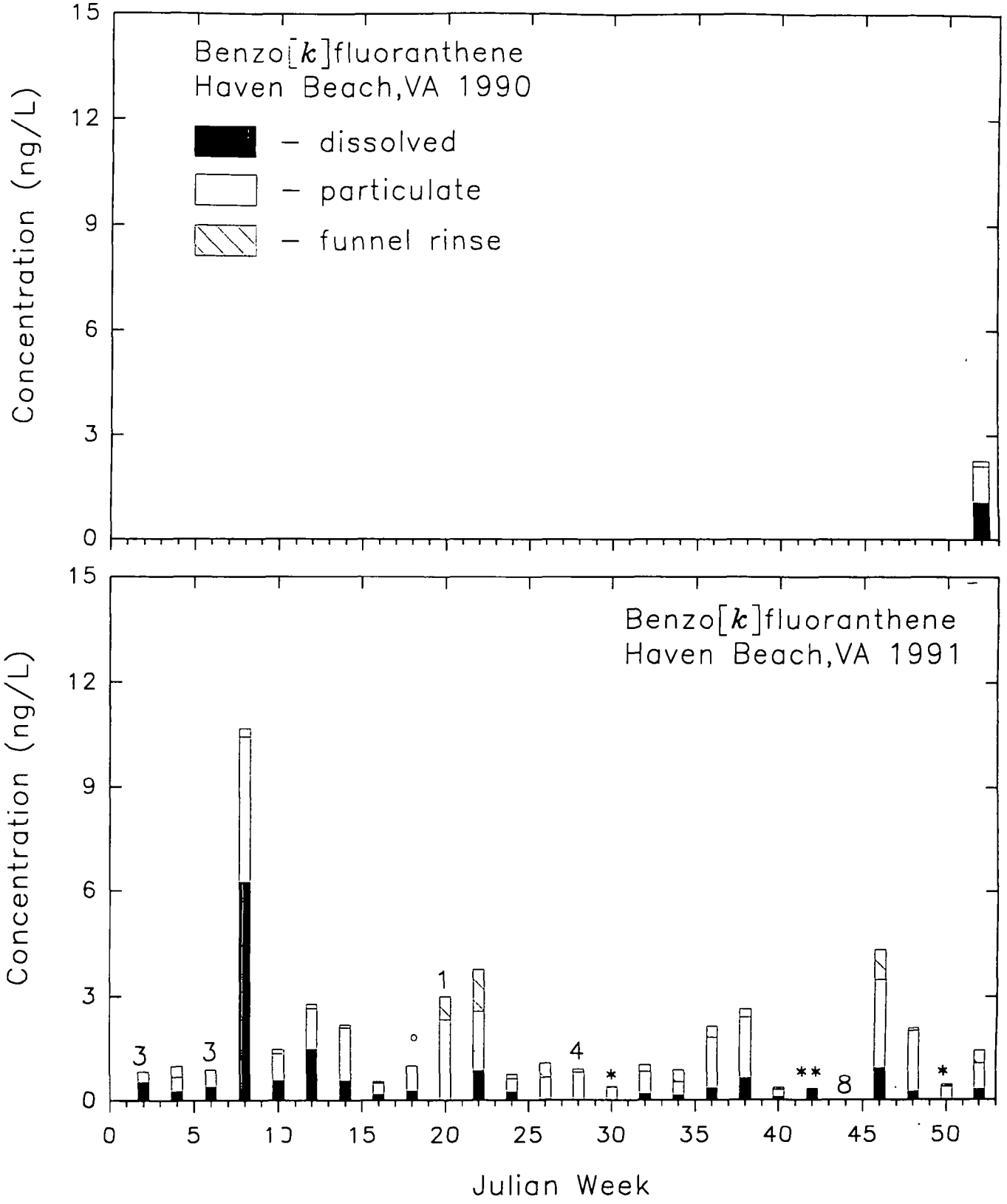


Figure IV.1.31. Benzo[*k*]fluoranthene concentrations in precipitation integrated biweekly at the Elms and Haven Beach sites.(1=not quantifiable in dissolved phase, 2=not quantifiable on filter, 3=not quantifiable in funnel, 4=not detected in dissolved phase, 5=not detected on filter, 6=not detected in funnel, 7=sampler down, 8=field blank, *=lost dissolved sample, **=lost particulate sample, ° = lost funnel rinse). Funnel rinse combined with particulate fractions after week 30, 1991.


Benzo[k]fluoranthene
Haven Beach,VA 1990
– dissolved
– particulate
– funnel rinse
Concentration (ng/L)
Benzo[k]fluoranthene
Haven Beach,VA 1991
Concentration (ng/L)
Julian Week

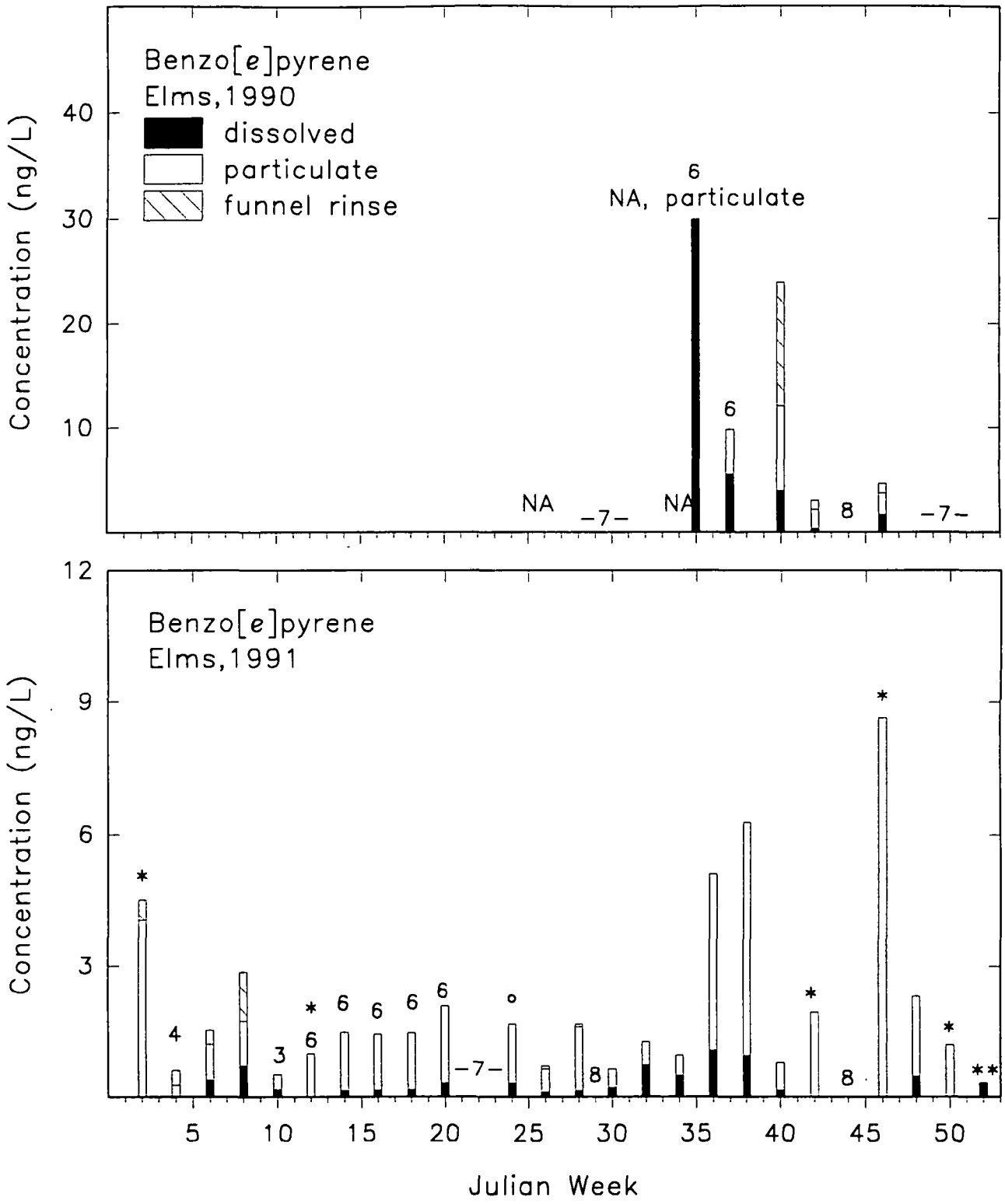
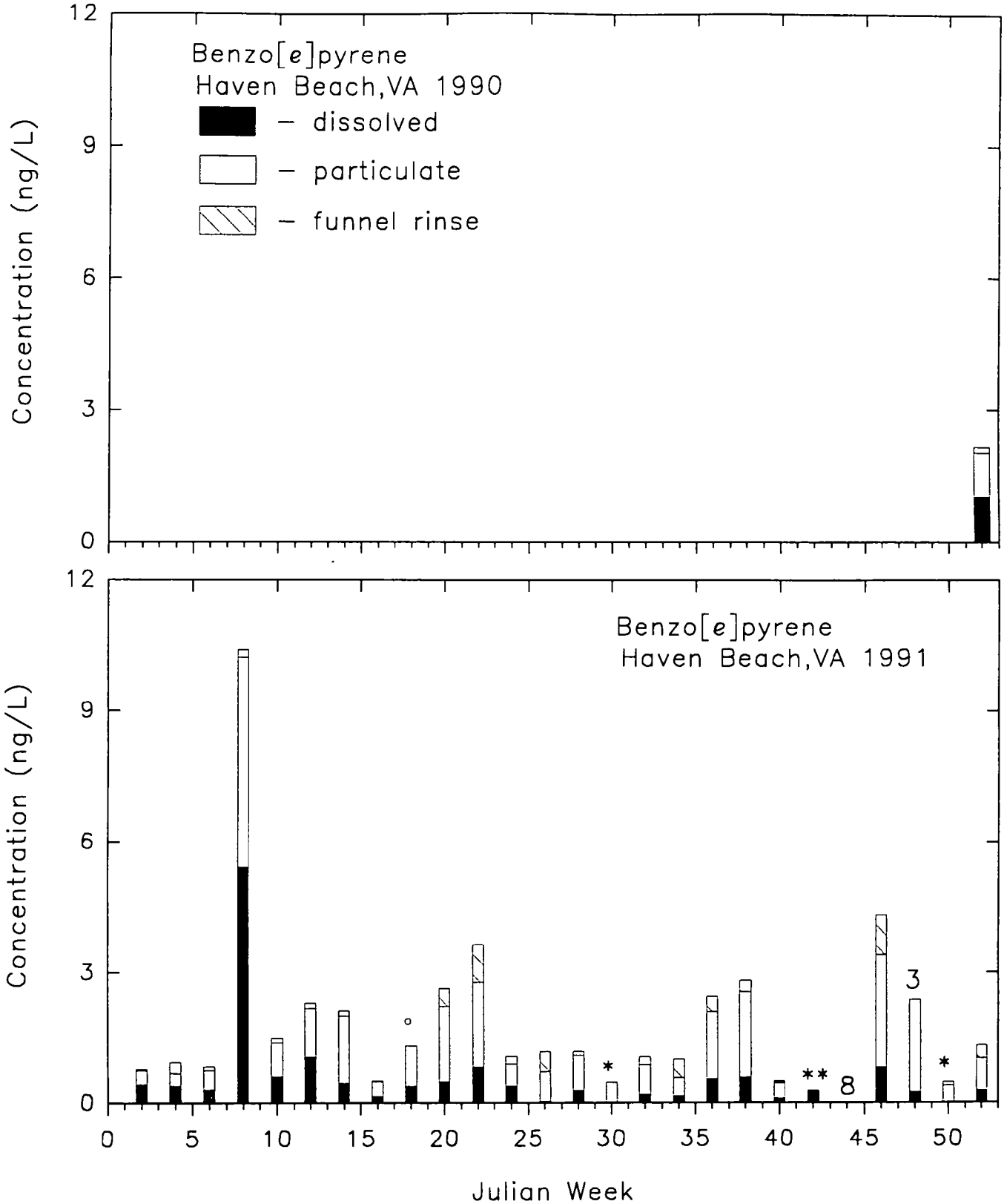


Figure IV.1.32. Benzo[e]pyrene concentrations in precipitation integrated biweekly at the Elms and Haven Beach sites. (1=not quantifiable in dissolved phase, 2=not quantifiable on filter, 3=not quantifiable in funnel, 4=not detected in dissolved phase, 5=not detected on filter, 6=not detected in funnel, 7=sampler down, 8=field blank, *=lost dissolved sample, **=lost particulate sample, ° = lost funnel rinse, NA = not analyzed for). Funnelrinse combined with particulate fractions after week 30, 1991.


Benzo[e]pyrene
Haven Beach,VA 1990
– dissolved
– particulate
– funnel rinse
Concentration (ng/L)
Benzo[e]pyrene
Haven Beach,VA 1991
Concentration (ng/L)
Julian Week

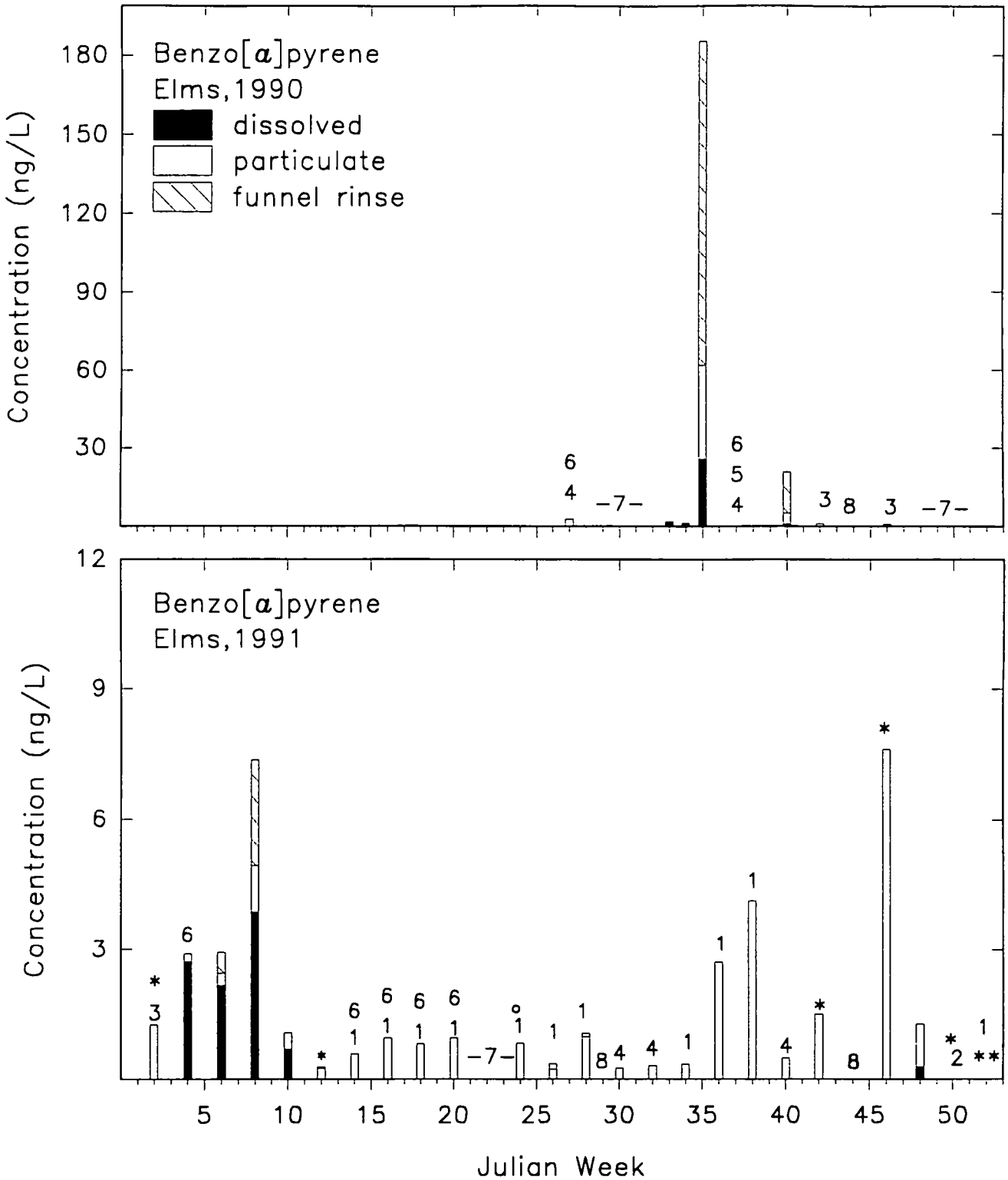
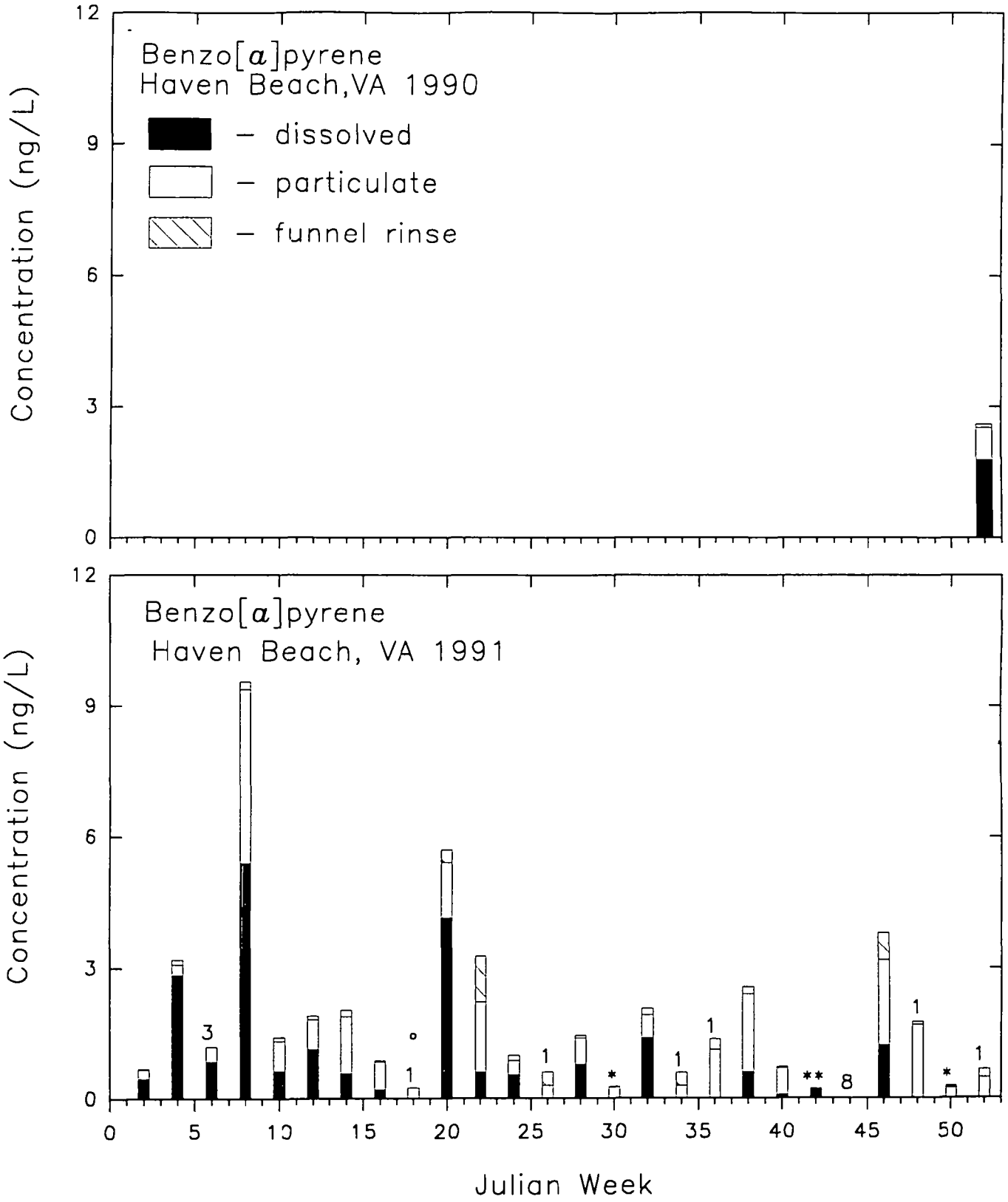


Figure IV.1.33. Benzo[a]pyrene concentrations in precipitation integrated biweekly at the Elms and Haven Beach sites. (1=not quantifiable in dissolved phase, 2=not quantifiable on filter, 3=not quantifiable in funnel, 4=not detected in dissolved phase, 5=not detected on filter, 6=not detected in funnel, 7=sampler down, 8=field blank, *=lost dissolved sample, **=lost particulate sample, ° = lost funnel rinse). Funnel rinse combined with particulate fractions after week 30, 1991.


Benzo[a]pyrene
Haven Beach,VA 1990
– dissolved
– particulate
– funnel rinse
Concentration (ng/L)
Benzo[a]pyrene
Haven Beach, VA 1991
Concentration (ng/L)
Julian Week

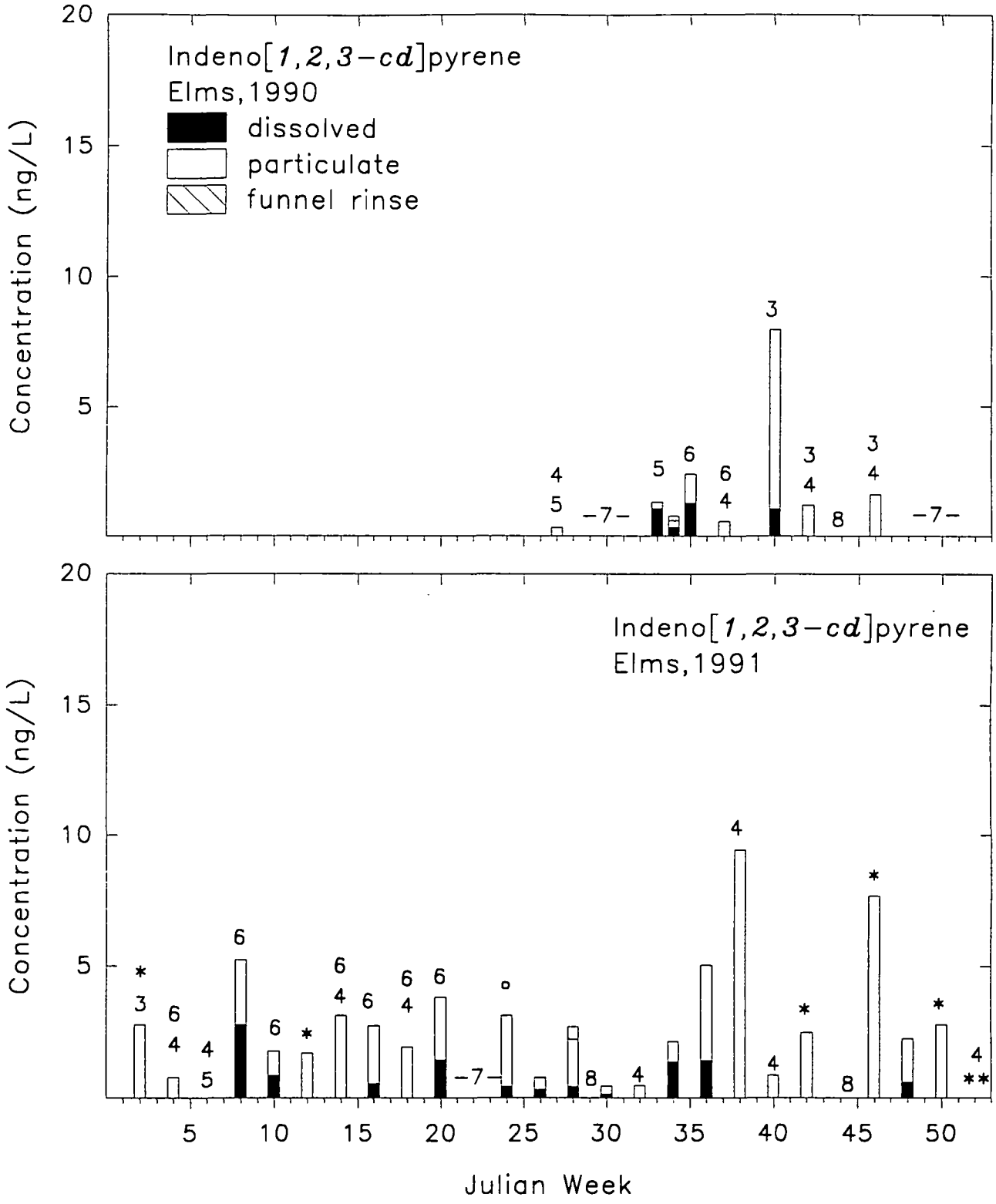
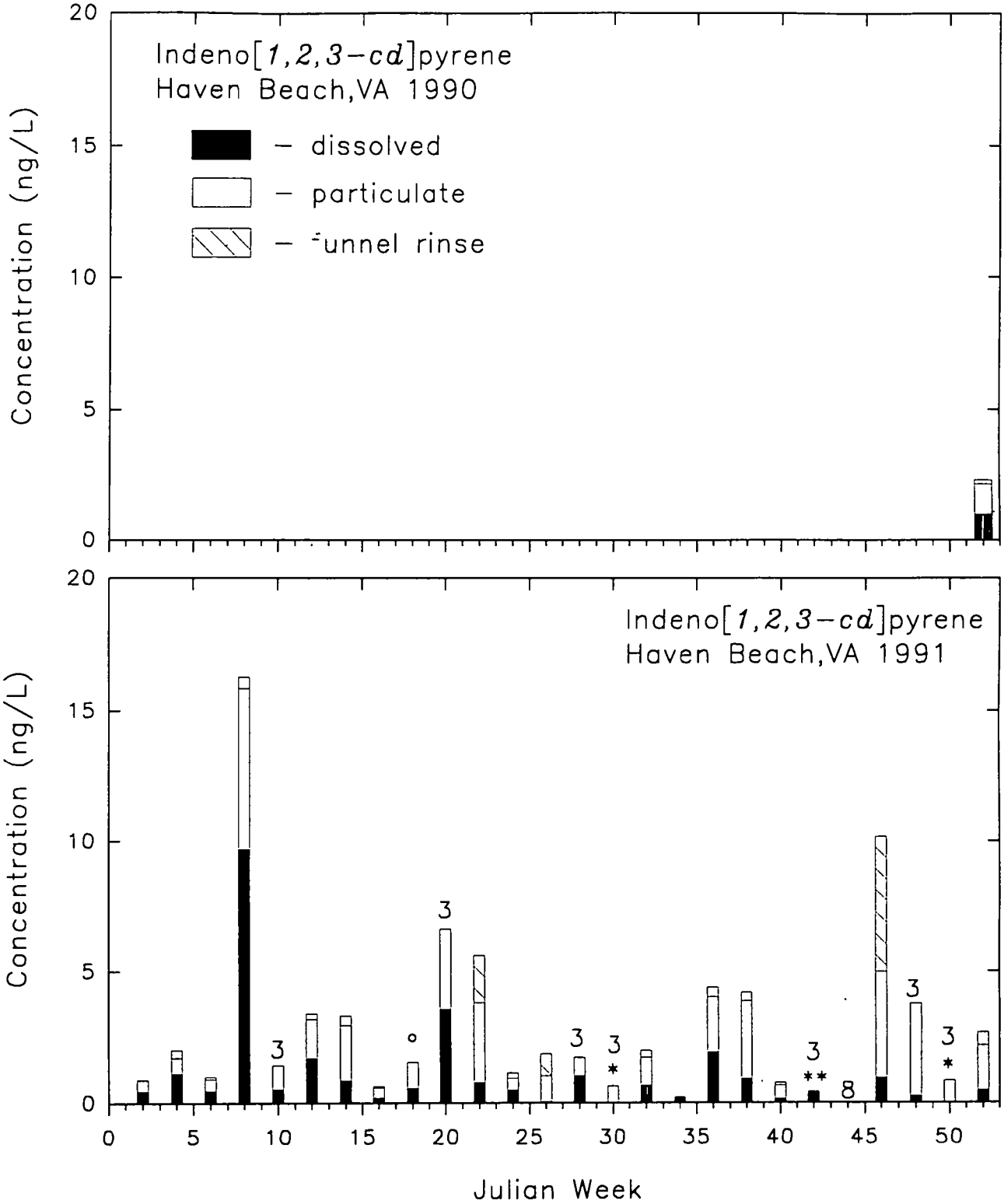


Figure IV.1.34. Indeno[*1,2,3-cd*]pyrene concentrations in precipitation integrated biweekly at the Elms and Haven Beach sites. (1=not quantifiable in dissolved phase, 2=not quantifiable on filter, 3=not quantifiable in funnel, 4=not detected in dissolved phase, 5=not detected on filter, 6=not detected in funnel, 7=sampler down, 8=field blank, *=lost dissolved sample, **=lost particulate sample, ° = lost funnel rinse). Funnel rinse combined with particulate fractions after week 30, 1991.


Indeno[1,2,3-cd]pyrene
Haven Beach,VA 1990
– dissolved
– particulate
– funnel rinse
Concentration (ng/L)
Indeno[1,2,3-cd]pyrene
Haven Beach,VA 1991
Concentration (ng/L)
Julian Week

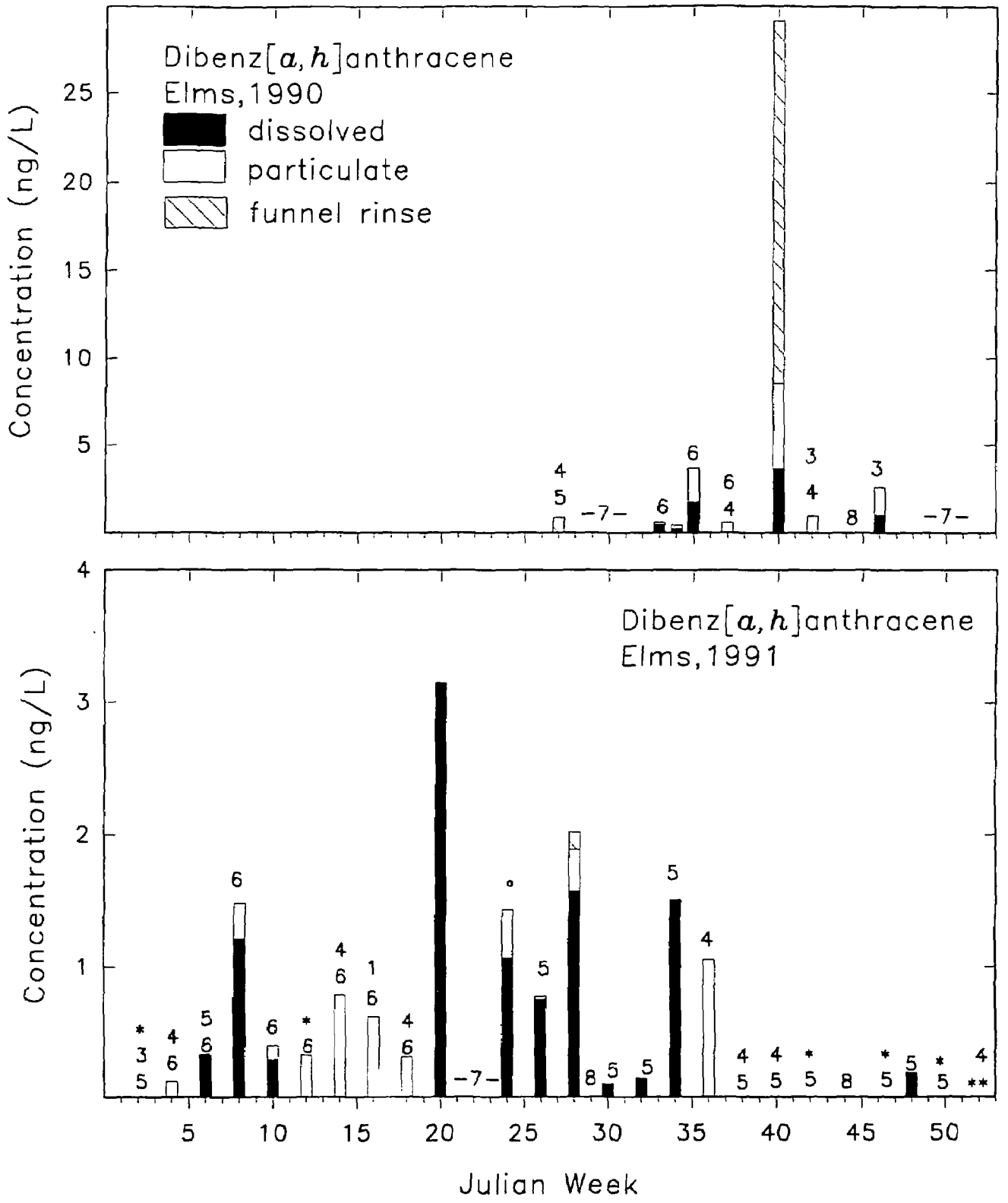
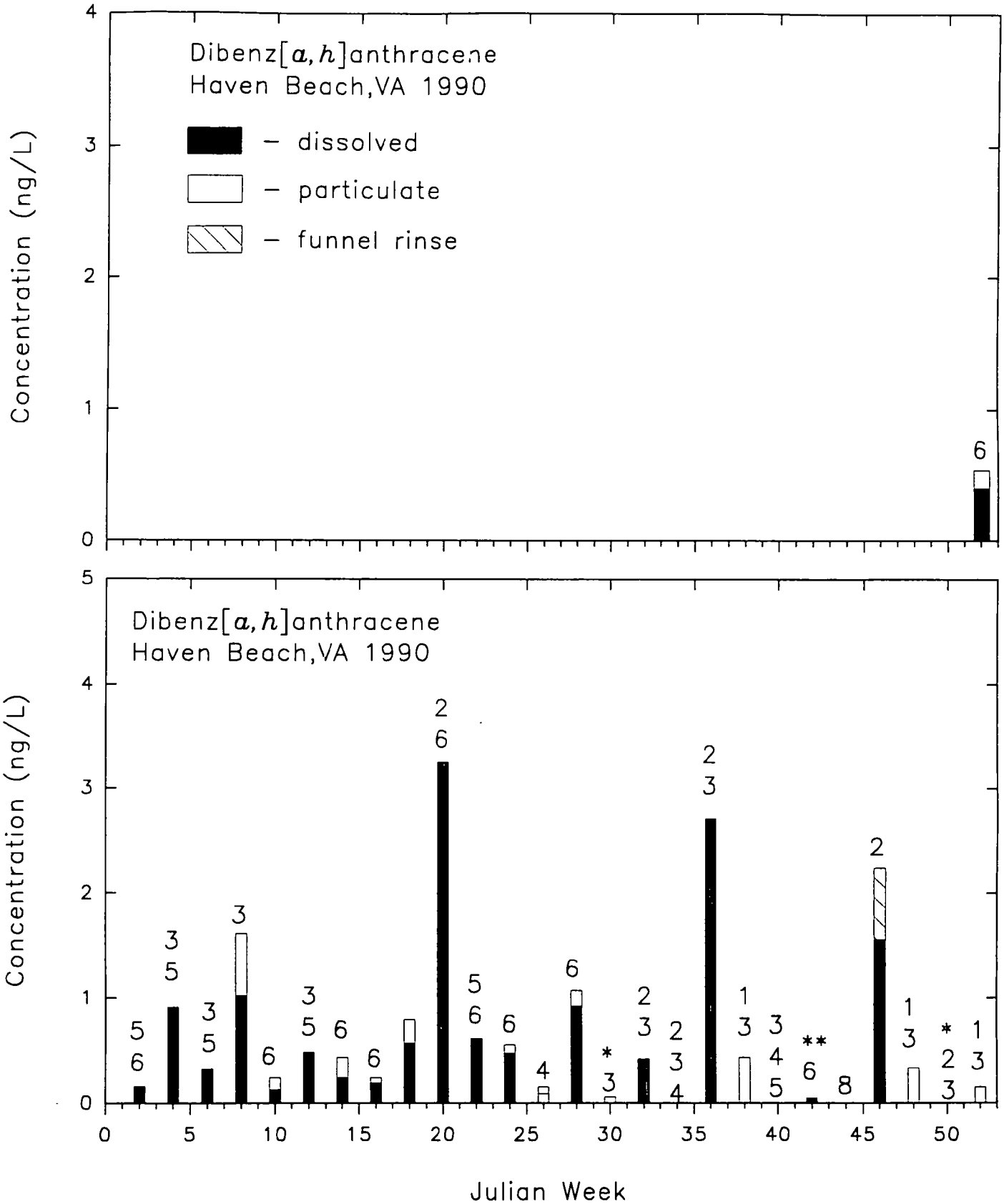


Figure IV.1.35. Dibenz[a,h]anthracene concentrations in precipitation integrated biweekly at the Elms and Haven Beach sites.(1=not quantifiable in dissolved phase, 2=not quantifiable on filter, 3=not quantifiable in funnel, 4=not detected in dissolved phase, 5=not detected on filter, 6=not detected in funnel, 7=sampler down, 8=field blank, *=lost dissolved sample, **=lost particulate sample, ° = lost funnel rinse). Funnel rinse combined with particulate fractions after week 30, 1991.


Dibenz[a,h]anthracene
Haven Beach,VA 1990
– dissolved
– particulate
– funnel rinse
Concentration (ng/L)
Dibenz[a,h]anthracene
Haven Beach,VA 1990
Concentration (ng/L)
Julian Week

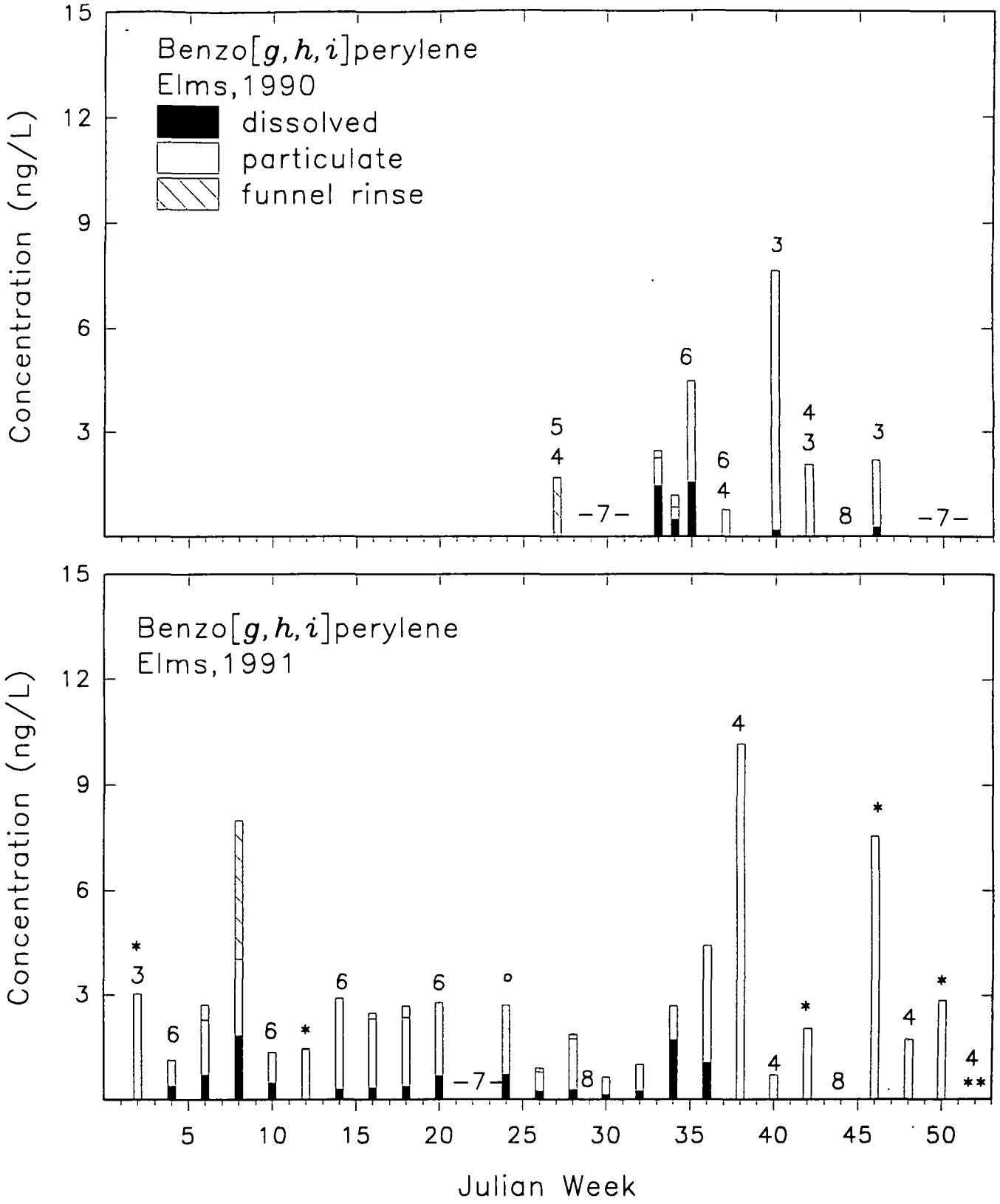
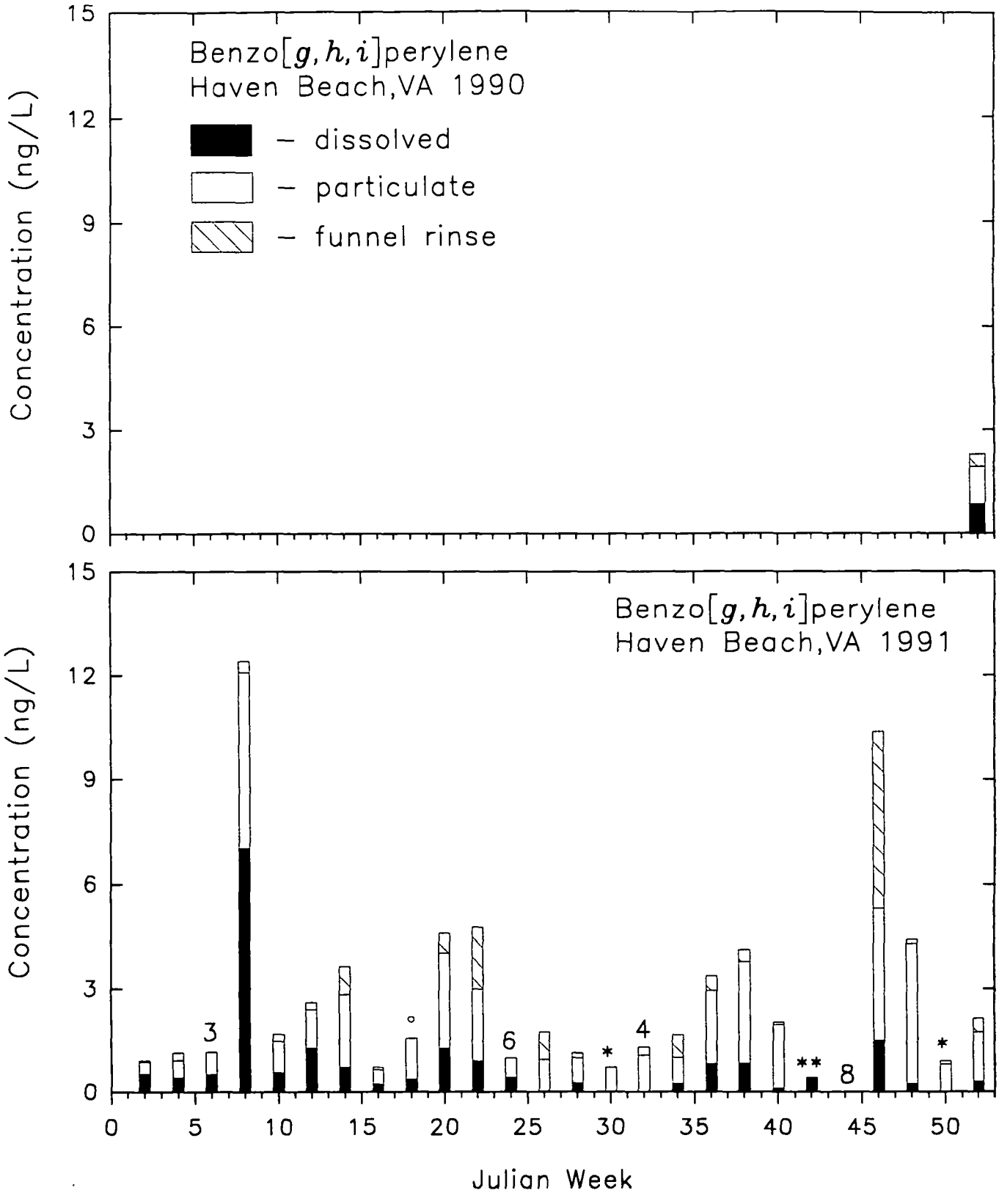


Figure IV.1.36. Benzo[g,h,i]perylene concentrations in precipitation integrated biweekly at the Elms and Haven Beach sites. (1=not quantifiable in dissolved phase, 2=not quantifiable on filter, 3=not quantifiable in funnel, 4=not detected in dissolved phase, 5=not detected on filter, 6=not detected in funnel, 7=sampler down, 8=field blank, *lost dissolved sample, **=lost particulate sample, ° = lost funnel rinse). Funnel rinse combined with particulate fractions after week 30, 1991.


Benzo[g,h,i]perylene
Haven Beach,VA 1990
– dissolved
– particulate
– funnel rinse
Concentration (ng/L)
Benzo[g,h,i]perylene
Haven Beach,VA 1991
Concentration (ng/L)
Julian Week

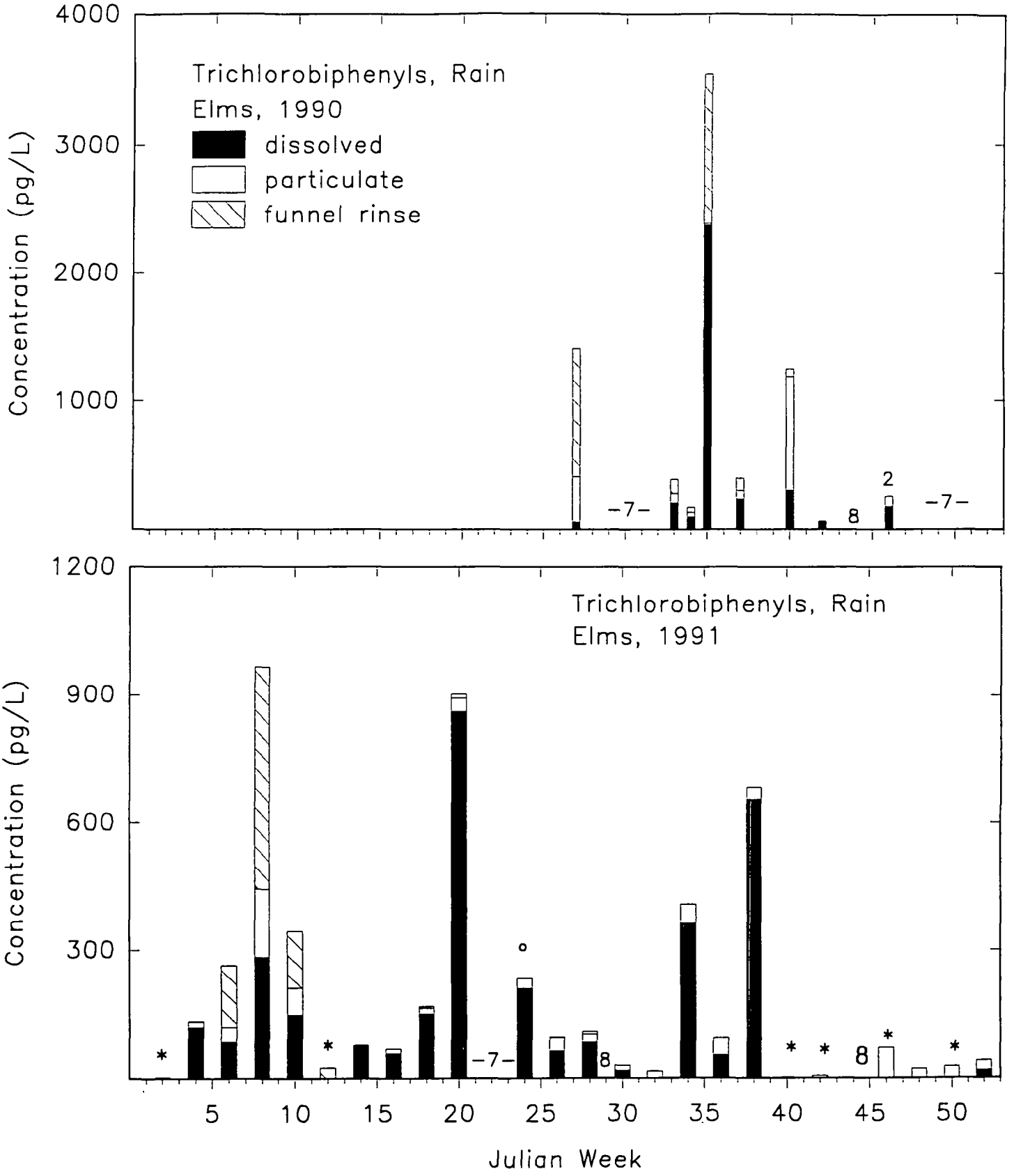
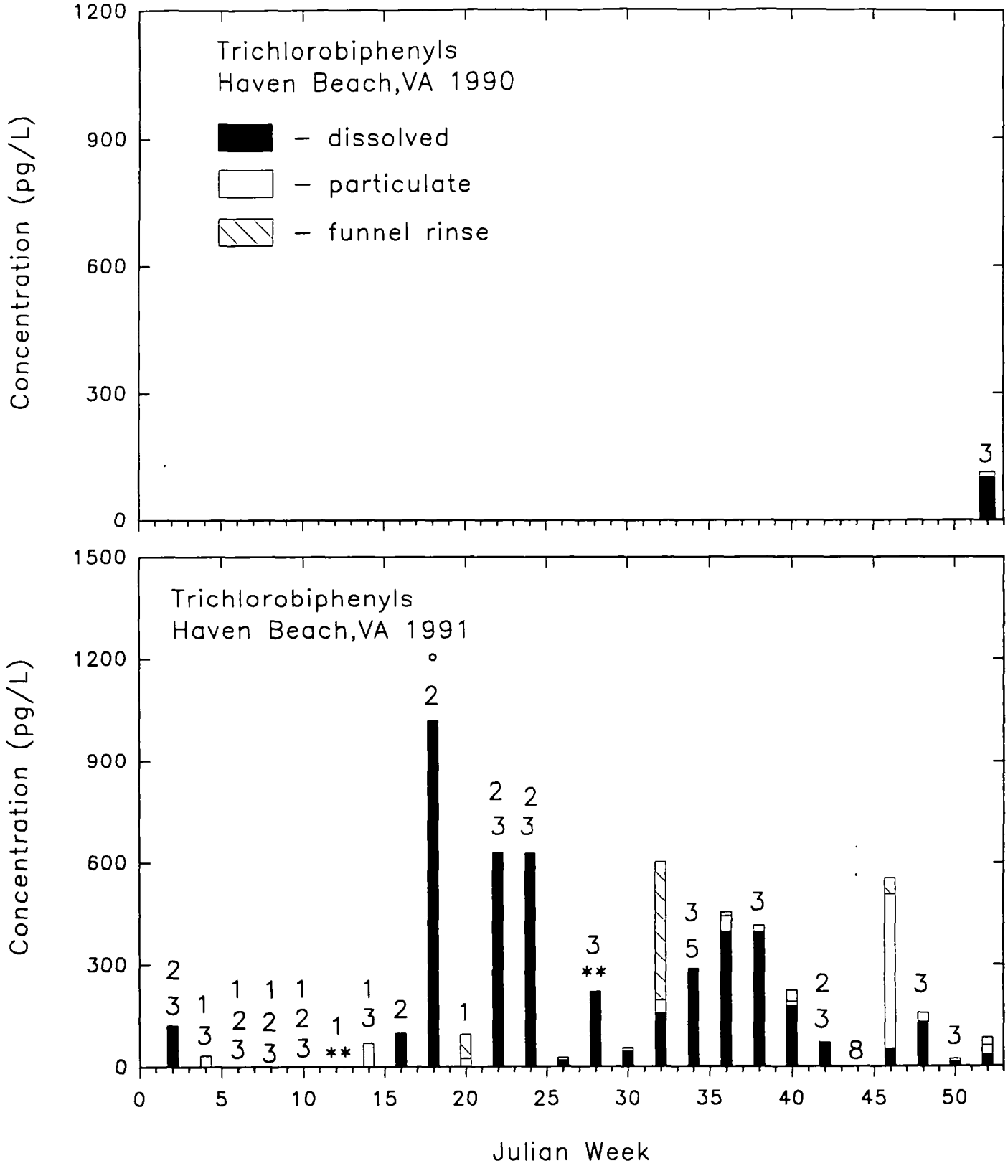


Figure IV.1.37. Total trichlorobiphenyl concentrations in precipitation integrated biweekly at the Elms and Haven Beach sites.1 = not quantifiable in dissolved 2 = not quantifiable on filter, 3 not quantifiable in funnel, 4 = not detected in dissolved phase, 5 = not detected on filter, 6 = not detected in funnel, 7 = sampler down, 8 = field blank, * = lost dissolved samples, ° = lost funnel rinse). Funnel rinse combined with particulate


Trichlorobiphenyls
Haven Beach,VA 1990
– dissolved
– particulate
– funnel rinse
Concentration (pg/L)
1200
900
600
300
0
Trichlorobiphenyls
Haven Beach,VA 1991
Concentration (pg/L)
1500
1200
900
600
300
0
0
5
10
15
20
25
30
35
40
45
50
Julian Week

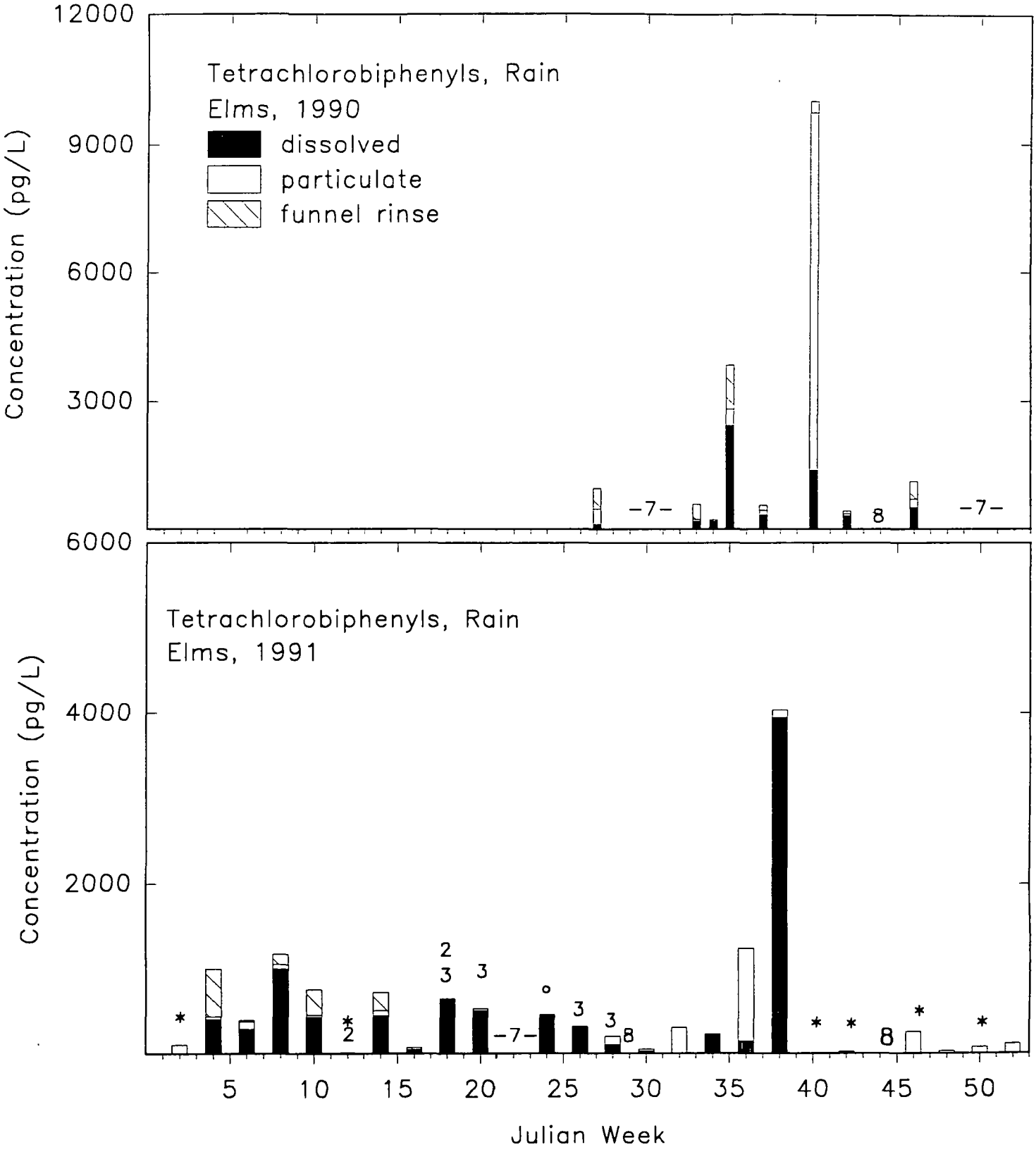
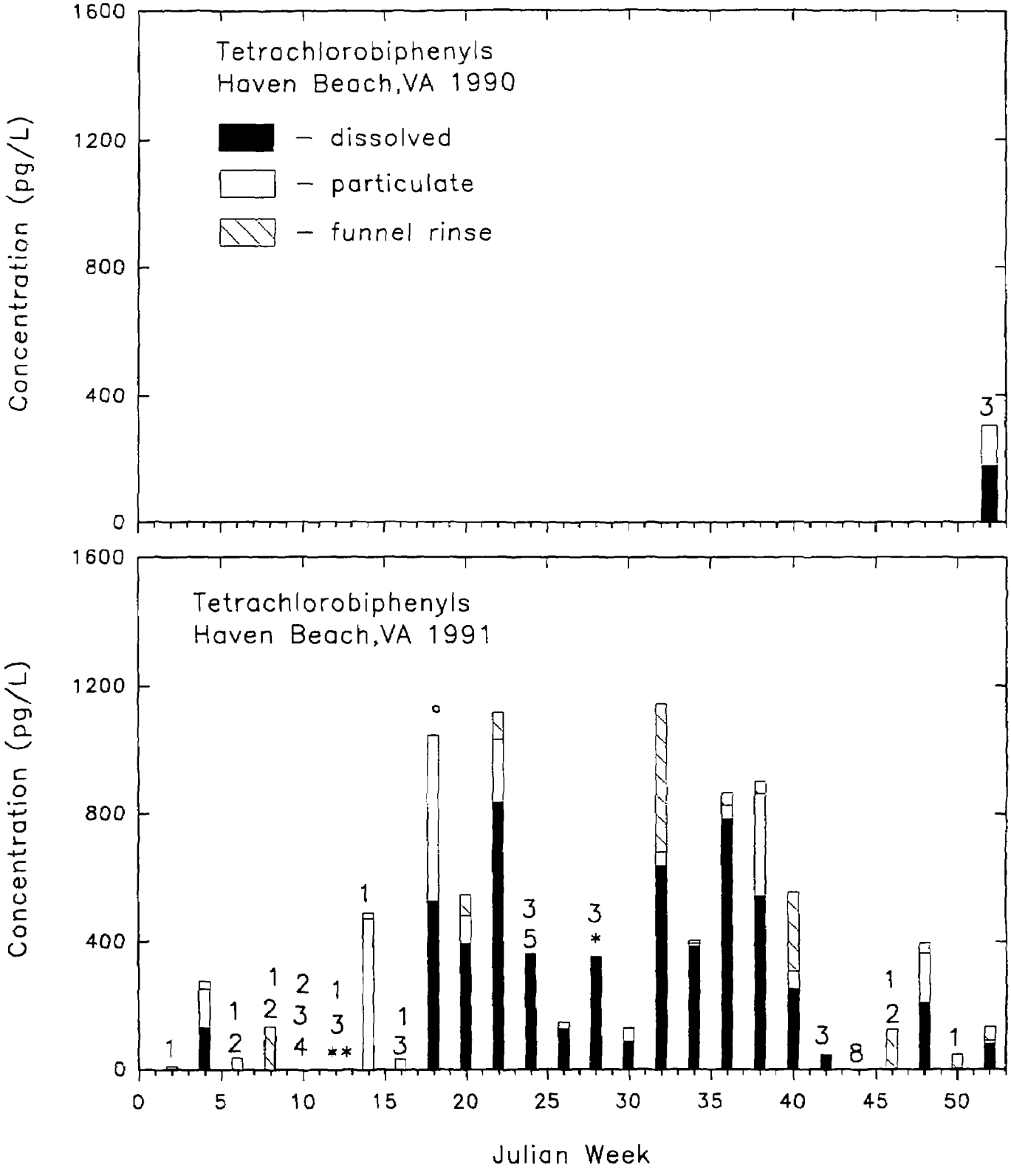


Figure IV.1.38. Total tetrachlorobipheynl concentrations in precipitation integrated phase, 2 = not quant'fiable on filter, 3 not quantifiable in funnel, 4 = = biweekly at the Elms and Haven Beach site.s (1 = not quantifiable in dissolved not detected in dissolved phase, 5 = not detected on filter, 6 = not detected in funnel, 7 = sampler down, 8 = field blank, * = lost dissolved samples, ° = lost funnel rinse). Funnel rinse combined with particulate fraction after week 30, 1991.


Tetrachlorobiphenyls
Haven Beach,VA 1990
– dissolved
– particulate
– funnel rinse
Concentration (pg/L)
1600
1200
800
400
0
Tetrachlorobiphenyls
Haven Beach,VA 1991
Concentration (pg/L)
0
5
10
15
20
25
30
35
40
45
50
Julian Week

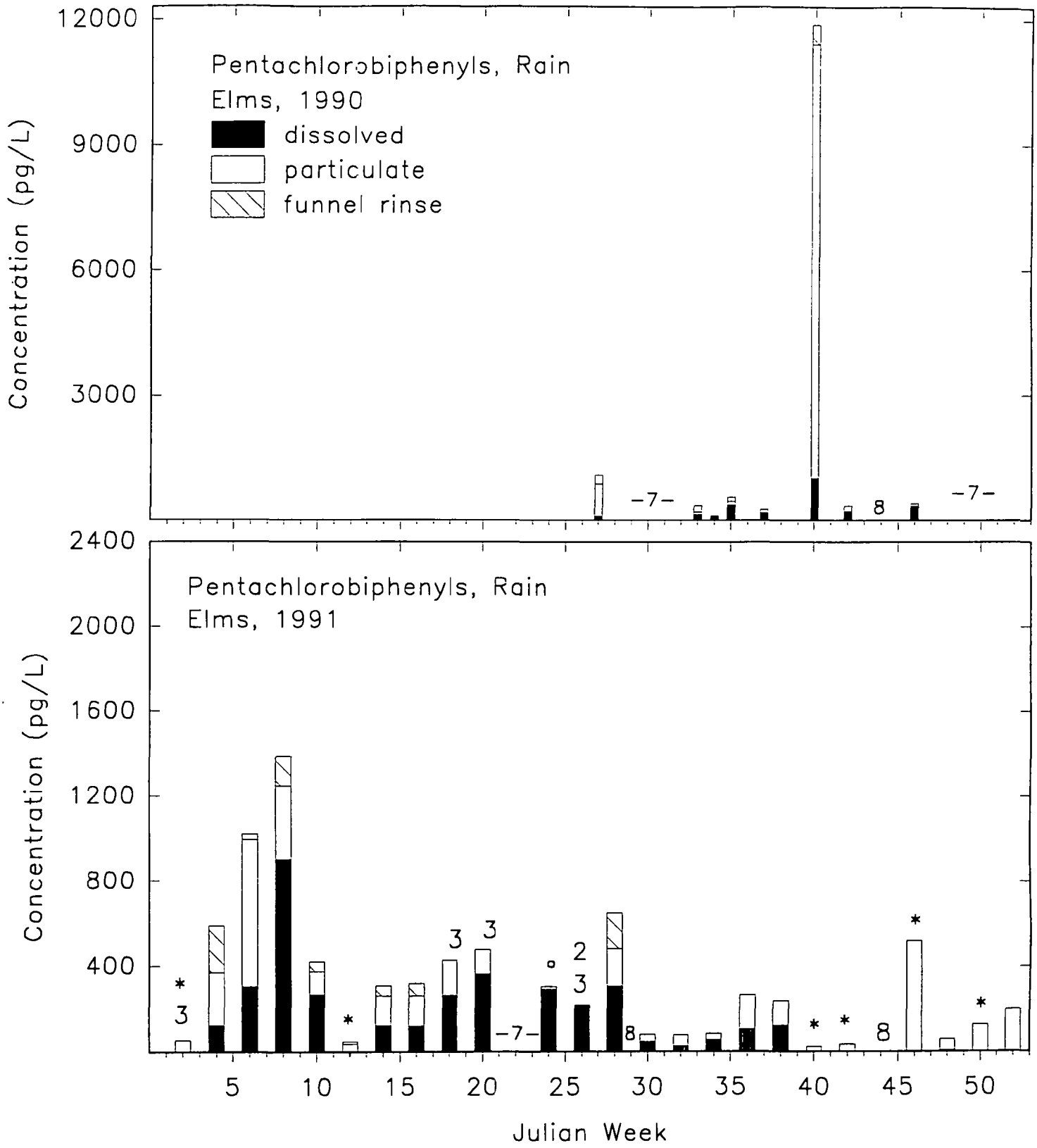
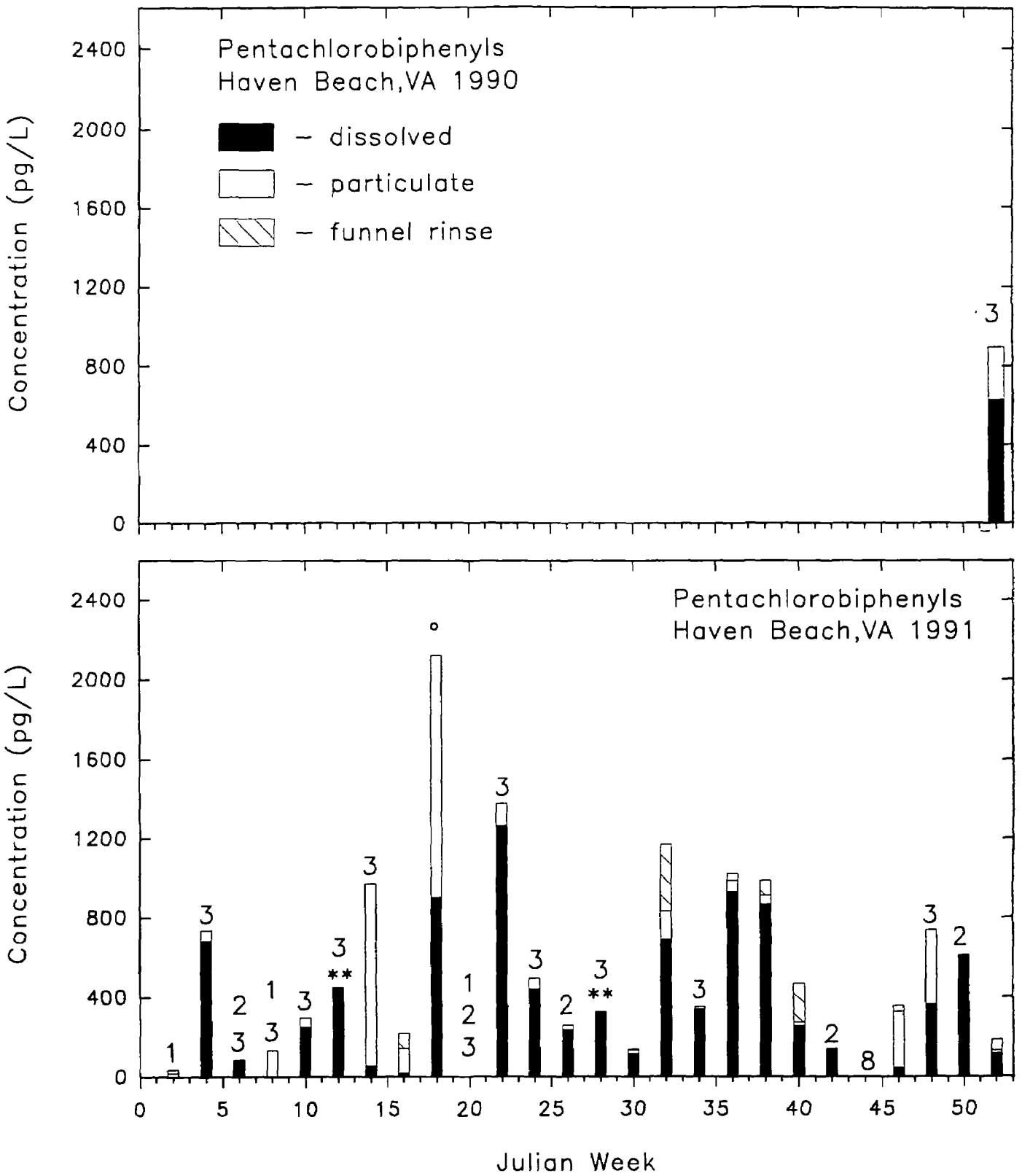


Figure IV.1.39. Total pentachlorobiphenyl concentrations in precipitation integrated biweekly at the Elms and Haven Beach sites. (1 = not quantifiable in dissolved phase, 2 = not quantifiable on filter, 3 not quantifiable in funnel, 4 = not detected in dissolved phase, 5 = not detected on filter, 6 = not detected in funnel, 7 = sampler down, 8 = field blank, * = lost dissolved samples, ° = lost funnel rinse). Funnel rinse combined with particulate fraction after week 30, 1991.


Pentachlorobiphenyls
Haven Beach,VA 1990
– dissolved
– particulate
– funnel rinse
Concentration (pg/L)
Pentachlorobiphenyls
Haven Beach,VA 1991
Concentration (pg/L)
Julian Week

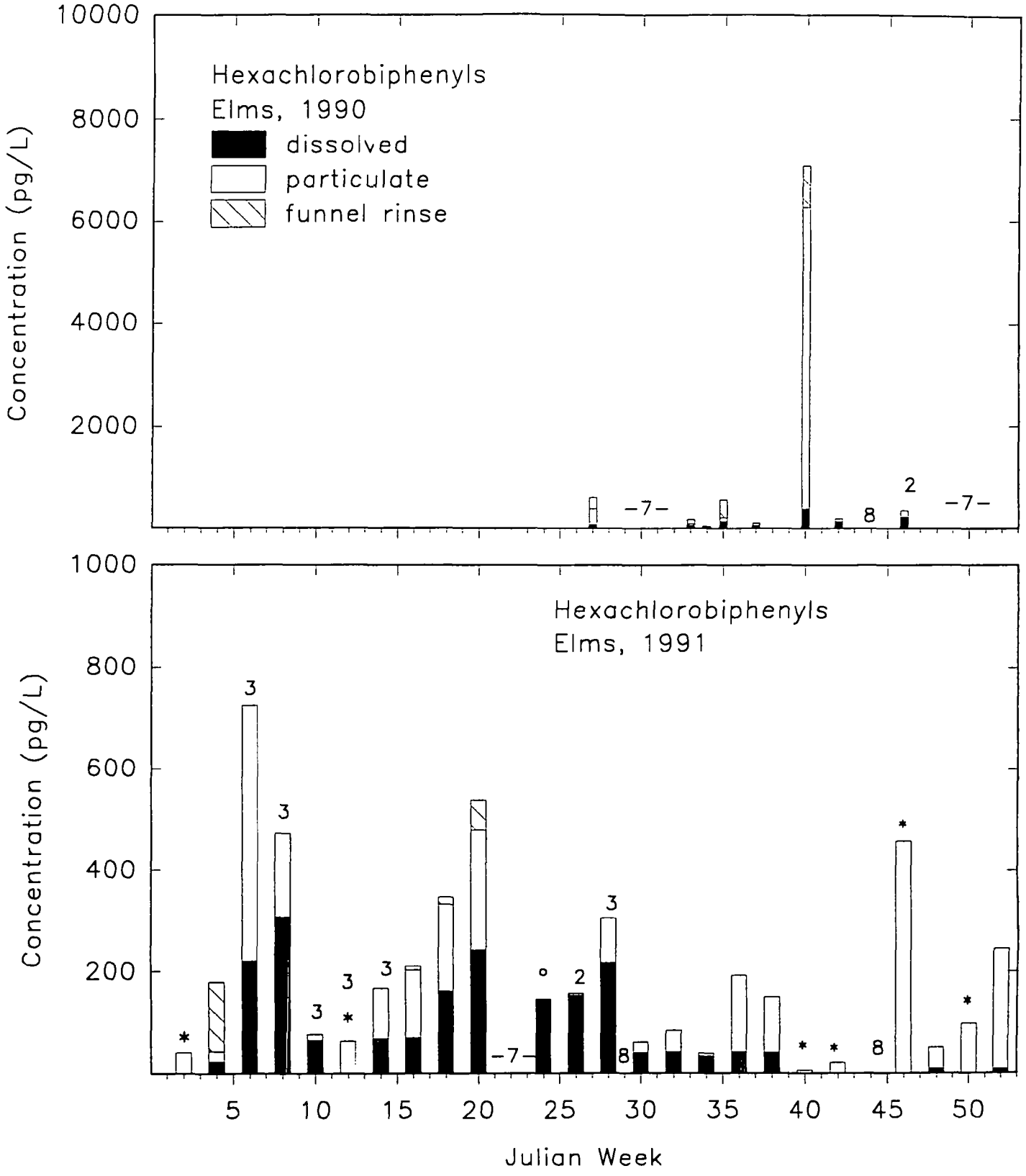
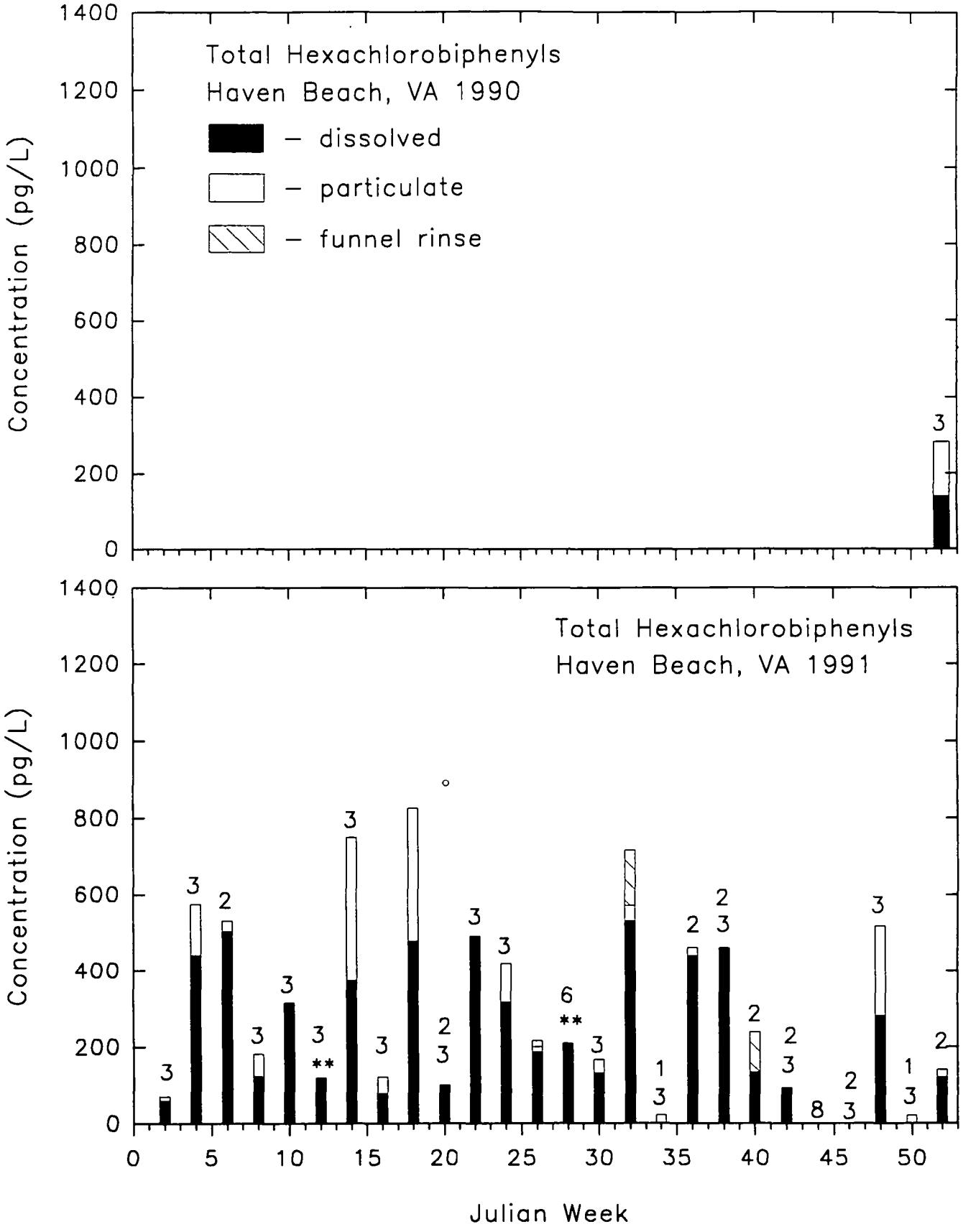


Figure IV.1.40. Total hexachlorobiphenyl concentrations in precipitation integrated biweekly at the Elms and Haven Beach sites.(1 = not quantifiable in dissolved phase 2 = not quantifiable on filter, 3 not quantifiable in funnel, 4 = not detected in dissolved phase, 5 = not detected on filter, 6 = not detected in funnel, 7 = sampler down, 8 = field blank, * = lost dissolved samples, ° = lost funnel rinse). Funnel rinse combined with particulate fraction after week 30, 1991.


Total Hexachlorobiphenyls
Haven Beach, VA 1990
– dissolved
– particulate
– funnel rinse
Concentration (pg/L)
Total Hexachlorobiphenyls
Haven Beach, VA 1991
Concentration (pg/L)
Julian Week

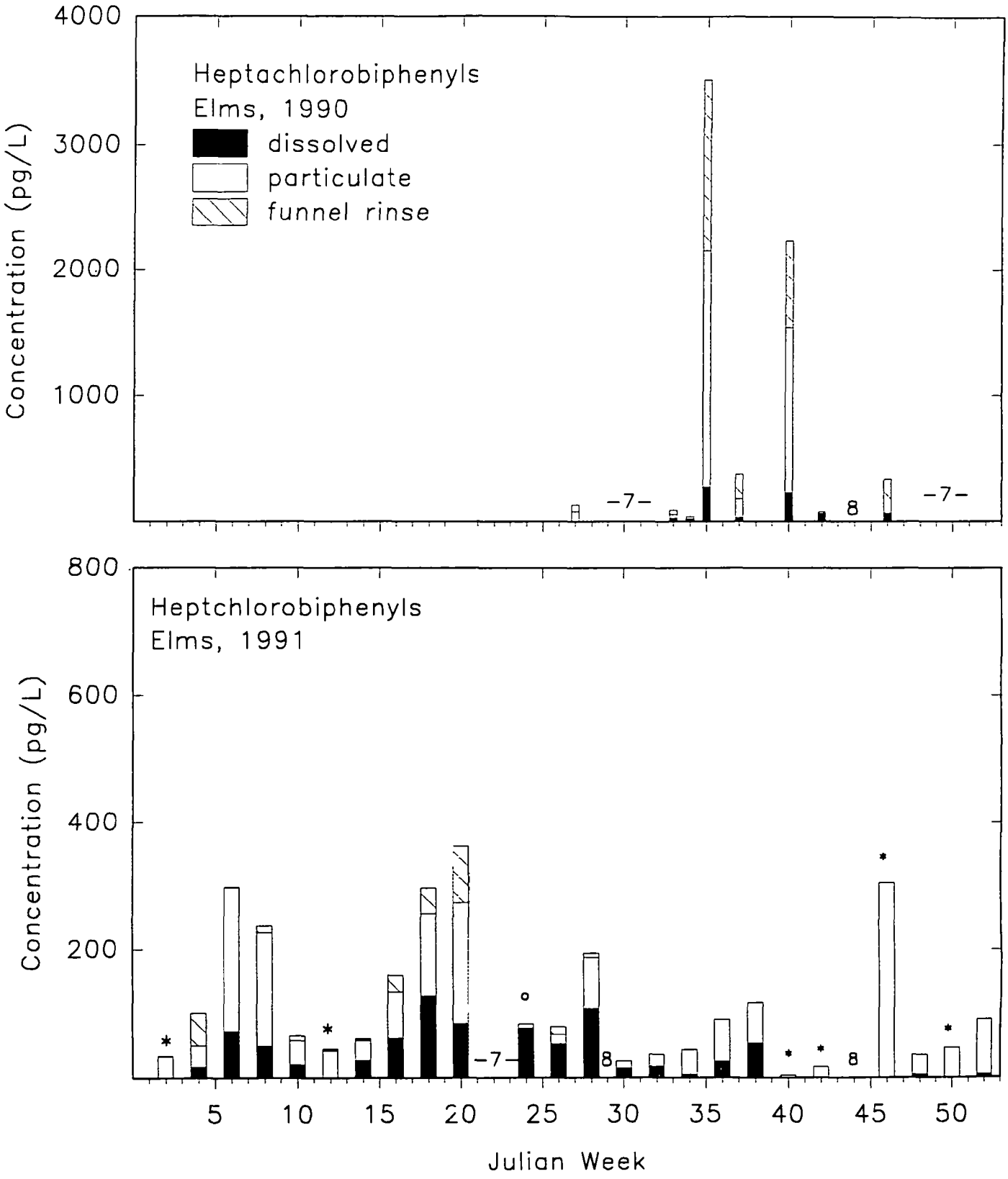
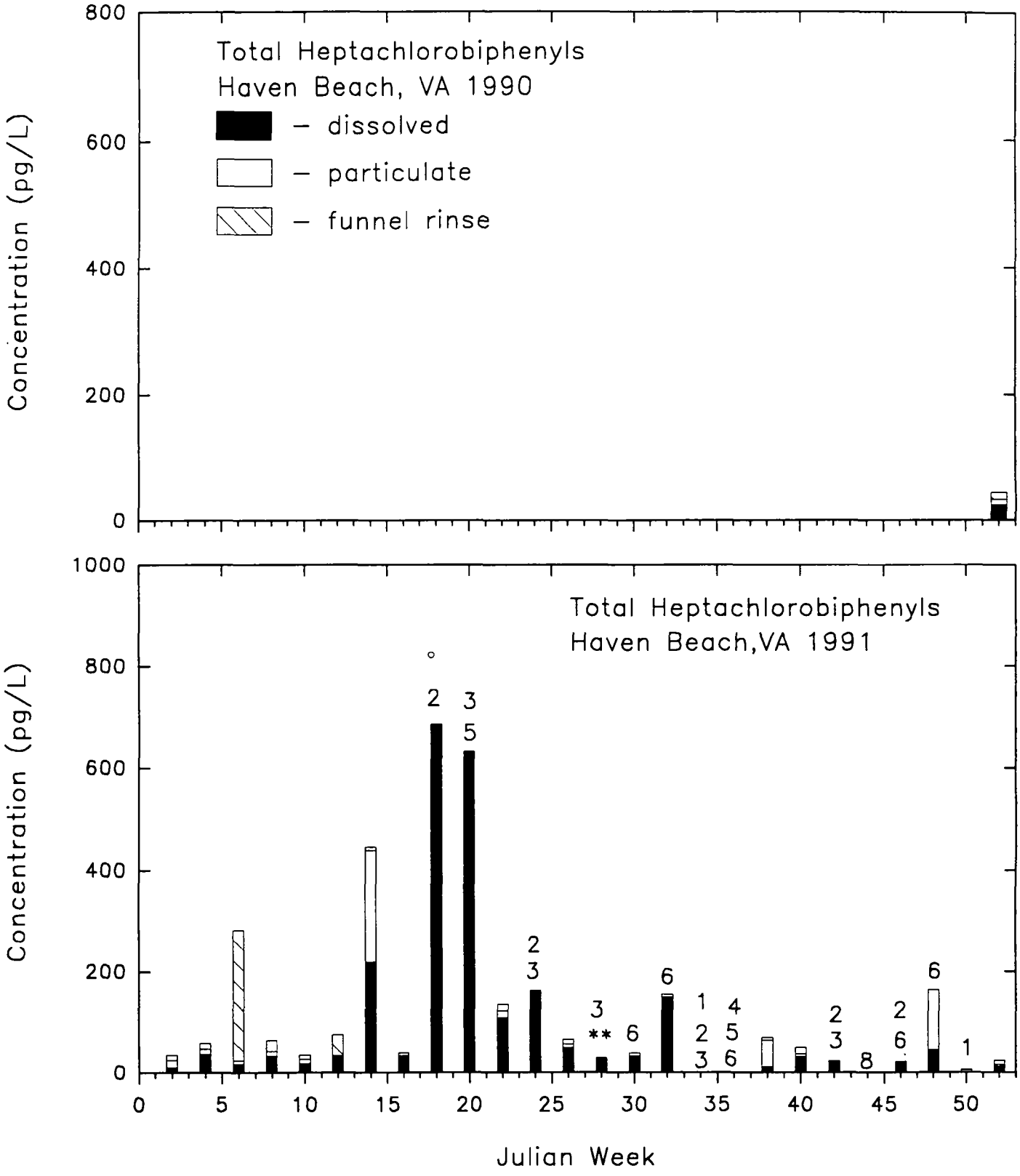


Figure IV.1.41. Total heptachlorobiphenyl concentrations in precipitation integrated biweekly at the Elms and Haven Beach sites. (1 = not quantifiable in dissolved phase, 2 = not quantifiable on filter, 3 not quantifiable in funnel, 4 = not detected in dissolved phase, 5 = not detected on filter, 6 = not detected in funnel, 7 = sampler down, 8 = field blank, * = lost dissolved samples, ° = lost funnel rinse). Funnel rinse combined with particulate fraction after week 30, 1991.


Total Heptachlorobiphenyls
Haven Beach, VA 1990
– dissolved
– particulate
– funnel rinse
Concentration (pg/L)
800
600
400
200
0
Total Heptachlorobiphenyls
Haven Beach,VA 1991
Concentration (pg/L)
1000
800
600
400
200
0
0
5
10
15
20
25
30
35
40
45
50
Julian Week

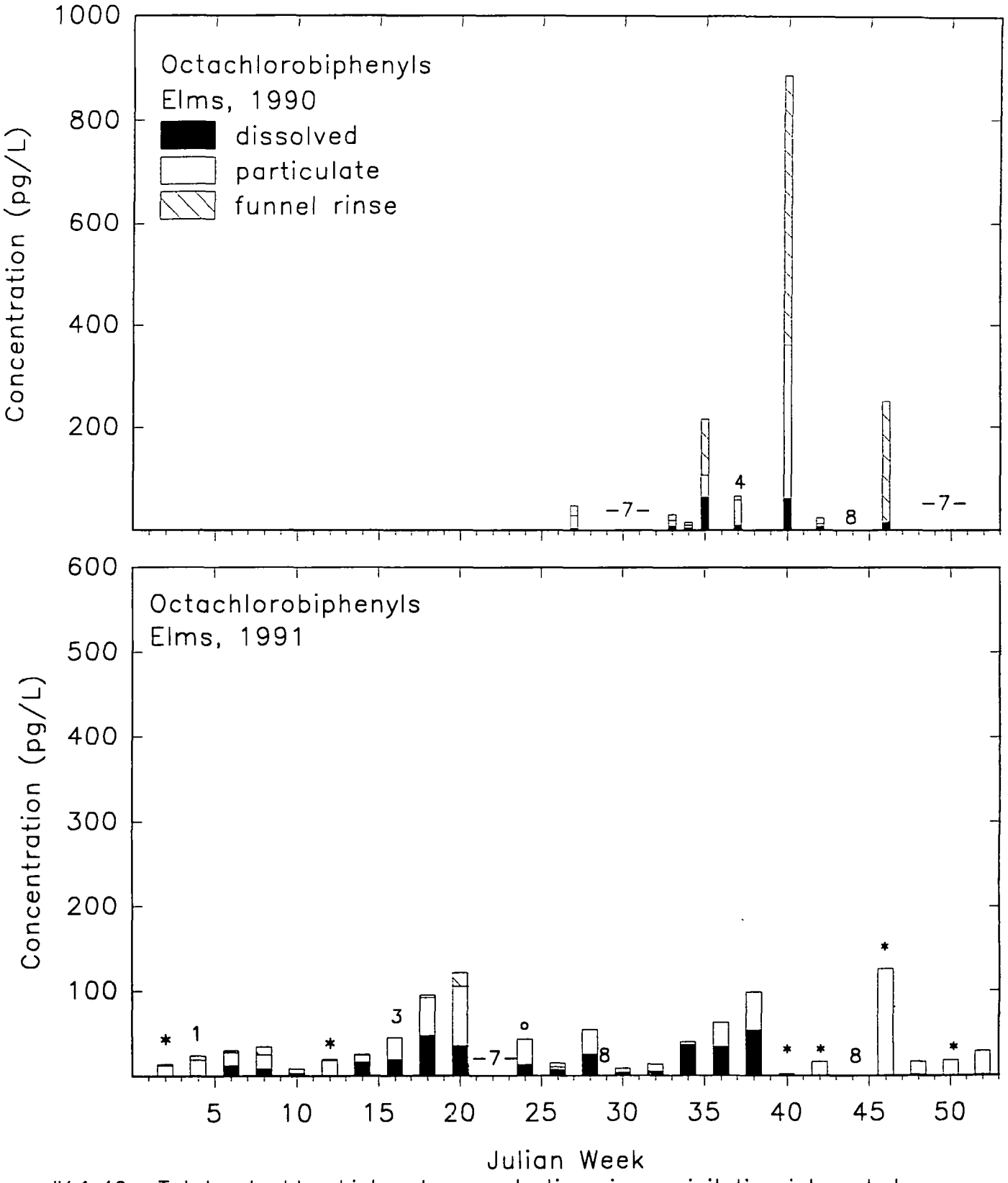
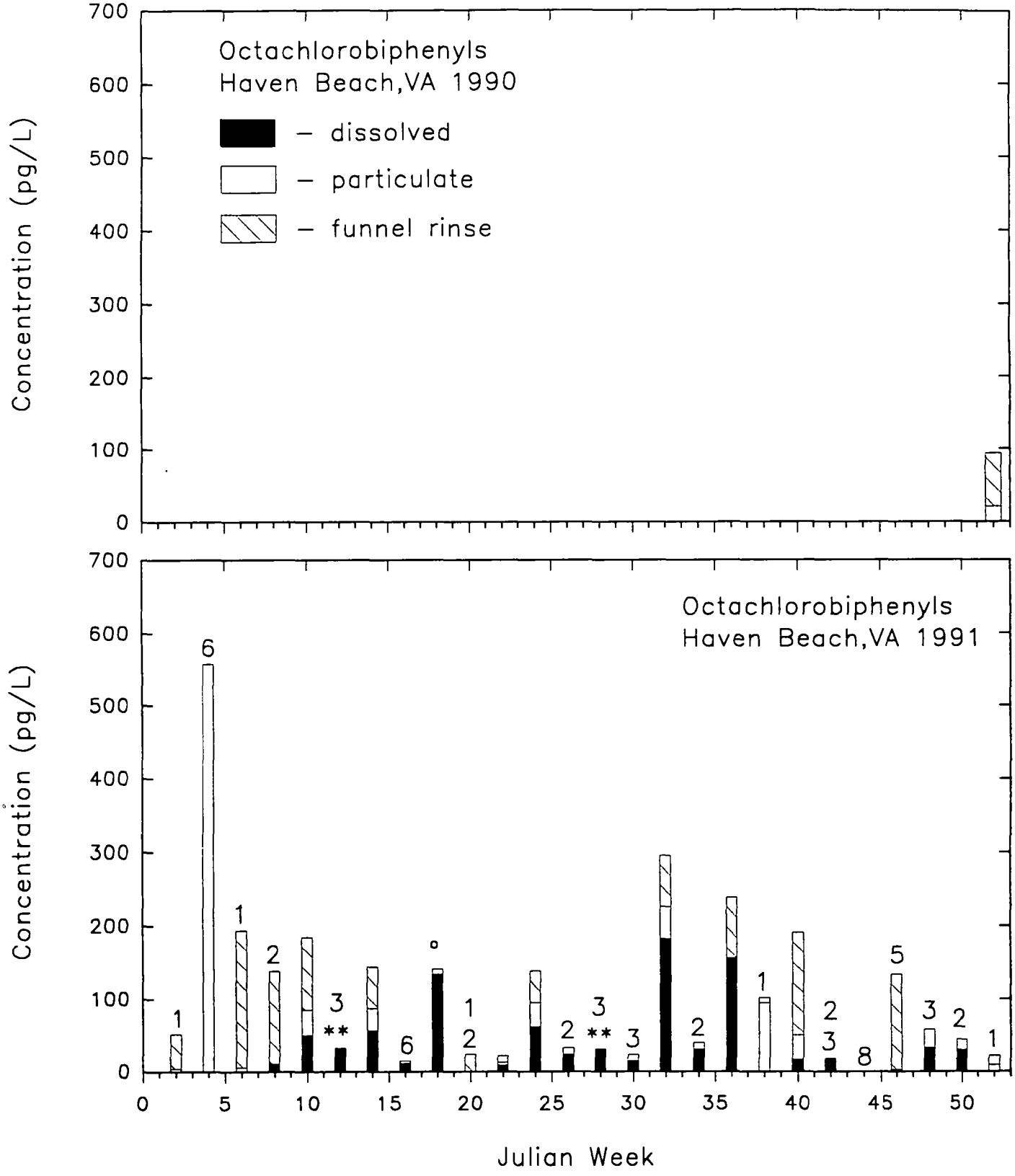


Figure IV.1.42. Total octachlorobiphenyl concentrations in precipitation integrated biweekly at the Elms and Haven Beach sites.(1 = not quantifiable in , dissolved phase, 2 = not quantifiable on filter, 3 not quantifiable in funnel, 4 = not detected in dissolved phase, 5 = not detected on filter, 6 = not detected in funnel, 7 = sampler down, 8 = field blank, * = lost dissolved samples, ° = lost funnel rinse). Funnel rinse combined with particulate fraction after week 30, 1990


Octachlorobiphenyls
Haven Beach,VA 1990
– dissolved
– particulate
– funnel rinse
Concentration (pg/L)
Octachlorobiphenyls
Haven Beach,VA 1991
Concentration (pg/L)
Julian Week

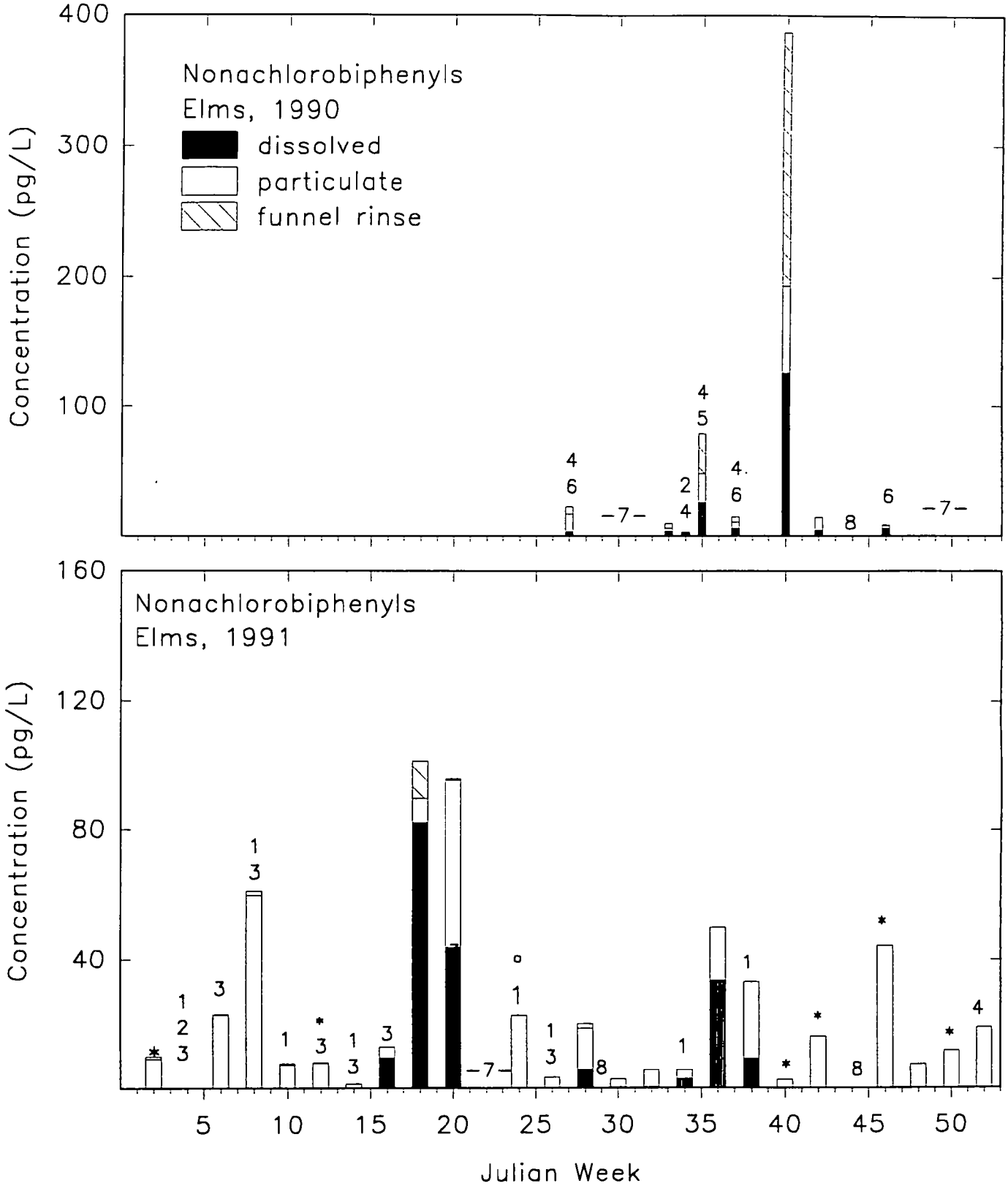
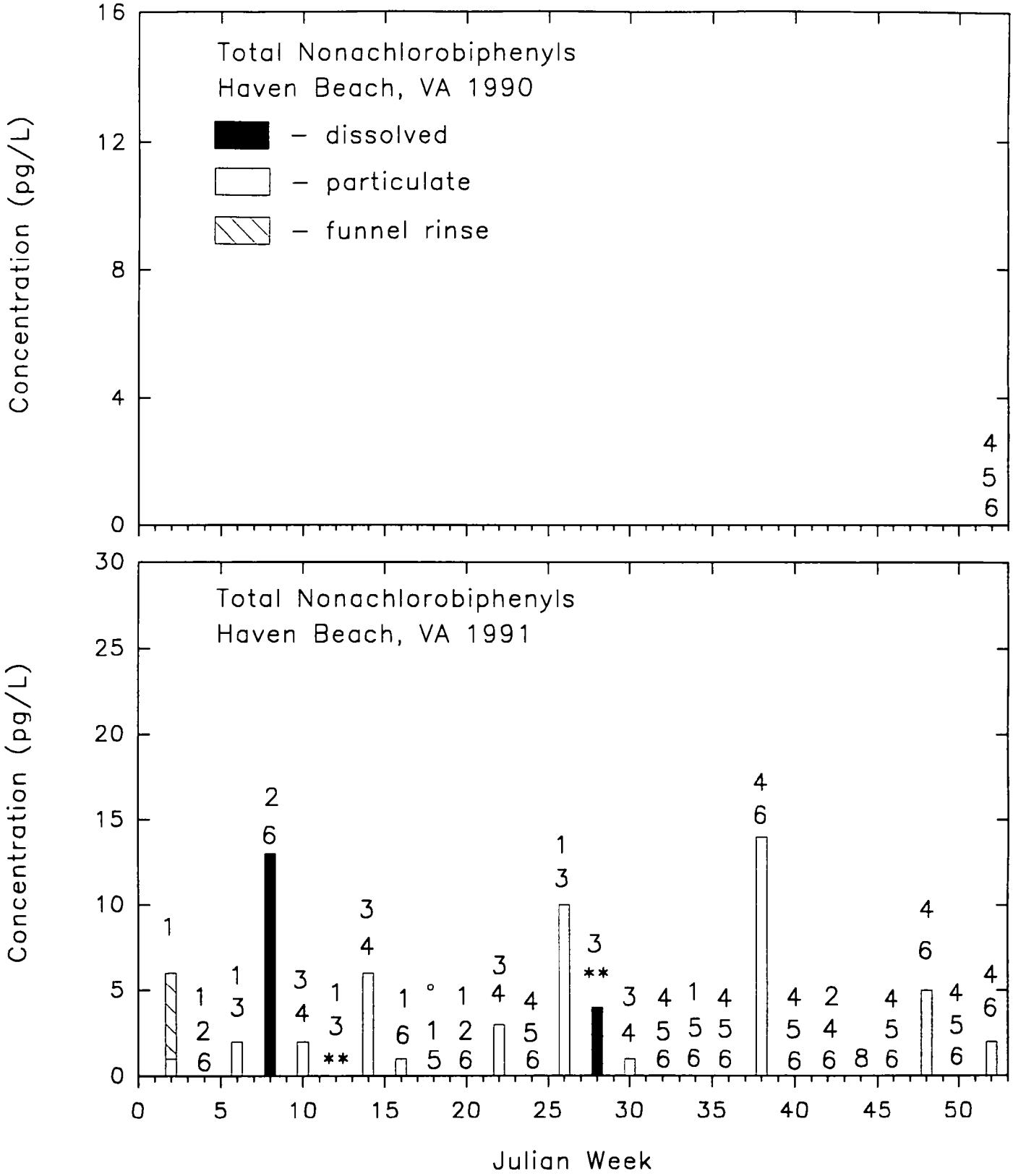


Figure IV.1.43. Total nonachlorobiphenyl concentrations in precipitation integrated biweekly at the Elms and Haven Beach sites. (1 = not quantifiable in dissolved phase, 2 = not quantifiable on filter, 3 = not quantifiable in funn 4= not detected in dissolved phase, 5 = not detected on filter, 6 = not detected in funnel, 7 = sampler down, 8 = field blank, * = lost dissolved samples, ° = lost funnel rinse). Funnel rinse combined with particulate fraction after week 30, 1991.


Total Nonachlorobiphenyls
Haven Beach, VA 1990
– dissolved
– particulate
– funnel rinse
Concentration (pg/L)
Total Nonachlorobiphenyls
Haven Beach, VA 1991
Concentration (pg/L)
Julian Week

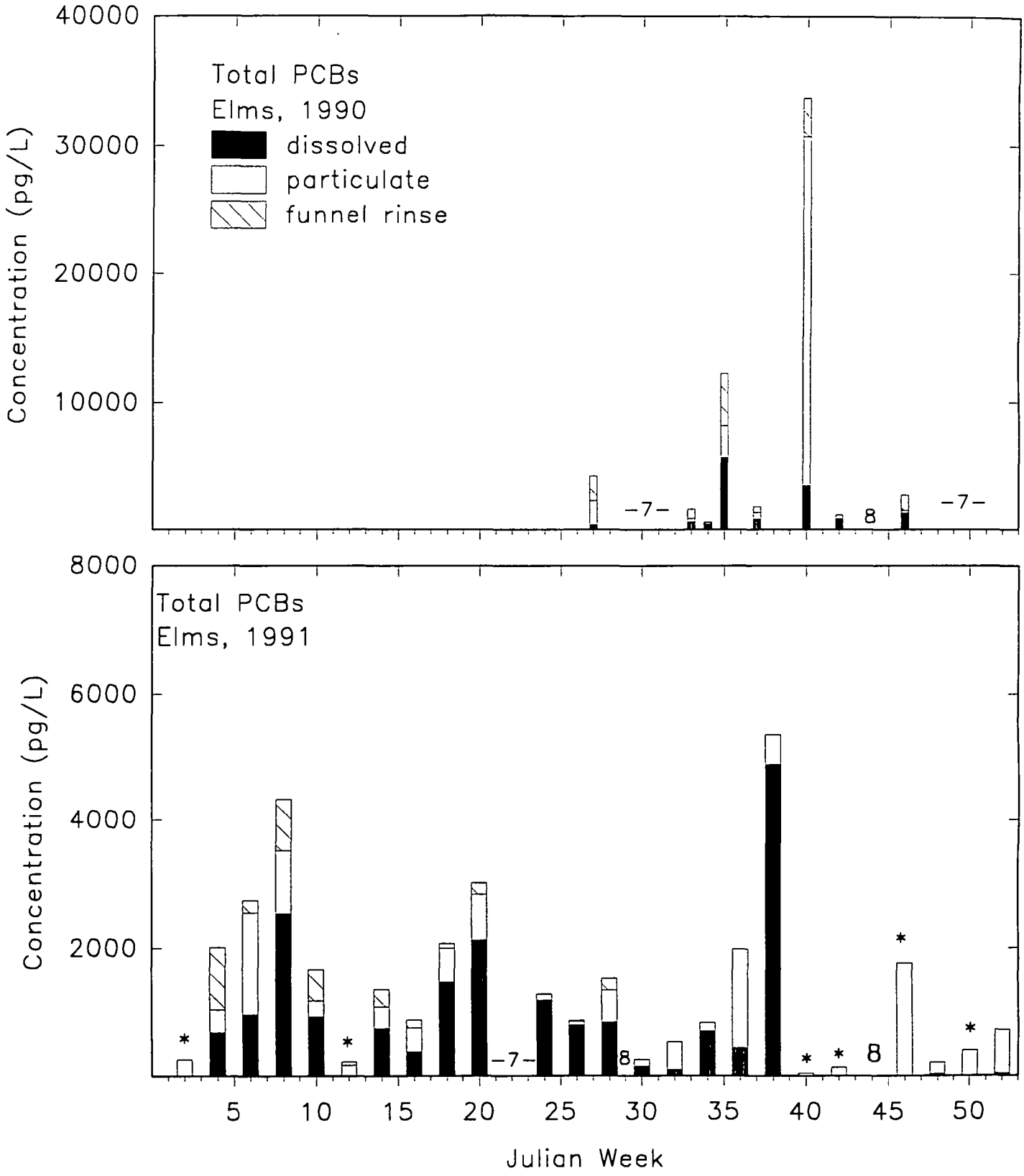


Figure IV.1.44. Total PCB concentration in precipitation integrated biweekly at the Elms and Haven Beach sites. (1=not quantifiable in dissolved phase, 2=not quantifiable on filter, 3=not quantifiable in funnel,4 =not detected in dissolved phase, 5=not detected on filter, 6= not detected in funnel,7= sampler down, *=lost dissolved samples). Funnel rinse combined with particulate fractions after week 30, 1991.

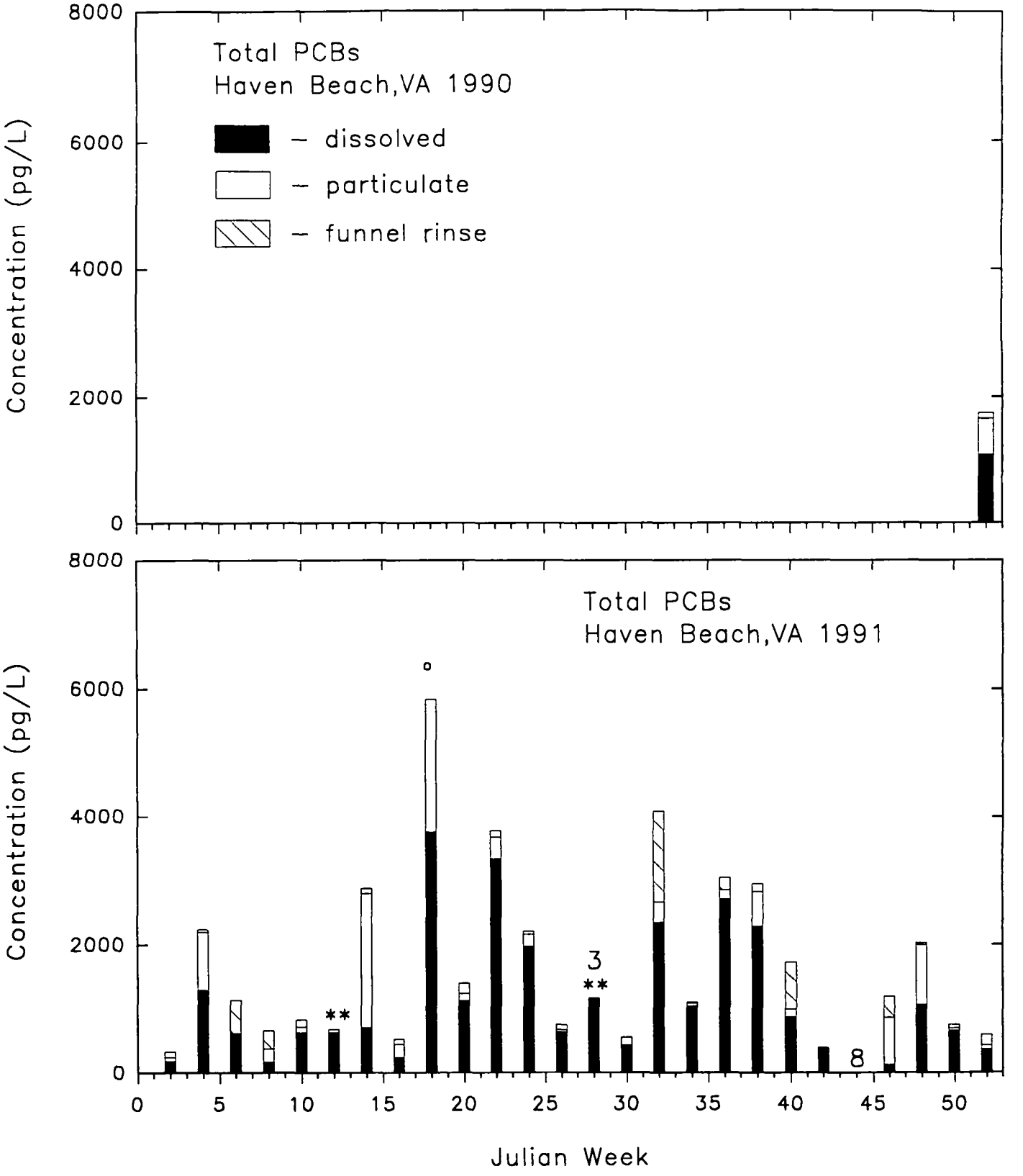
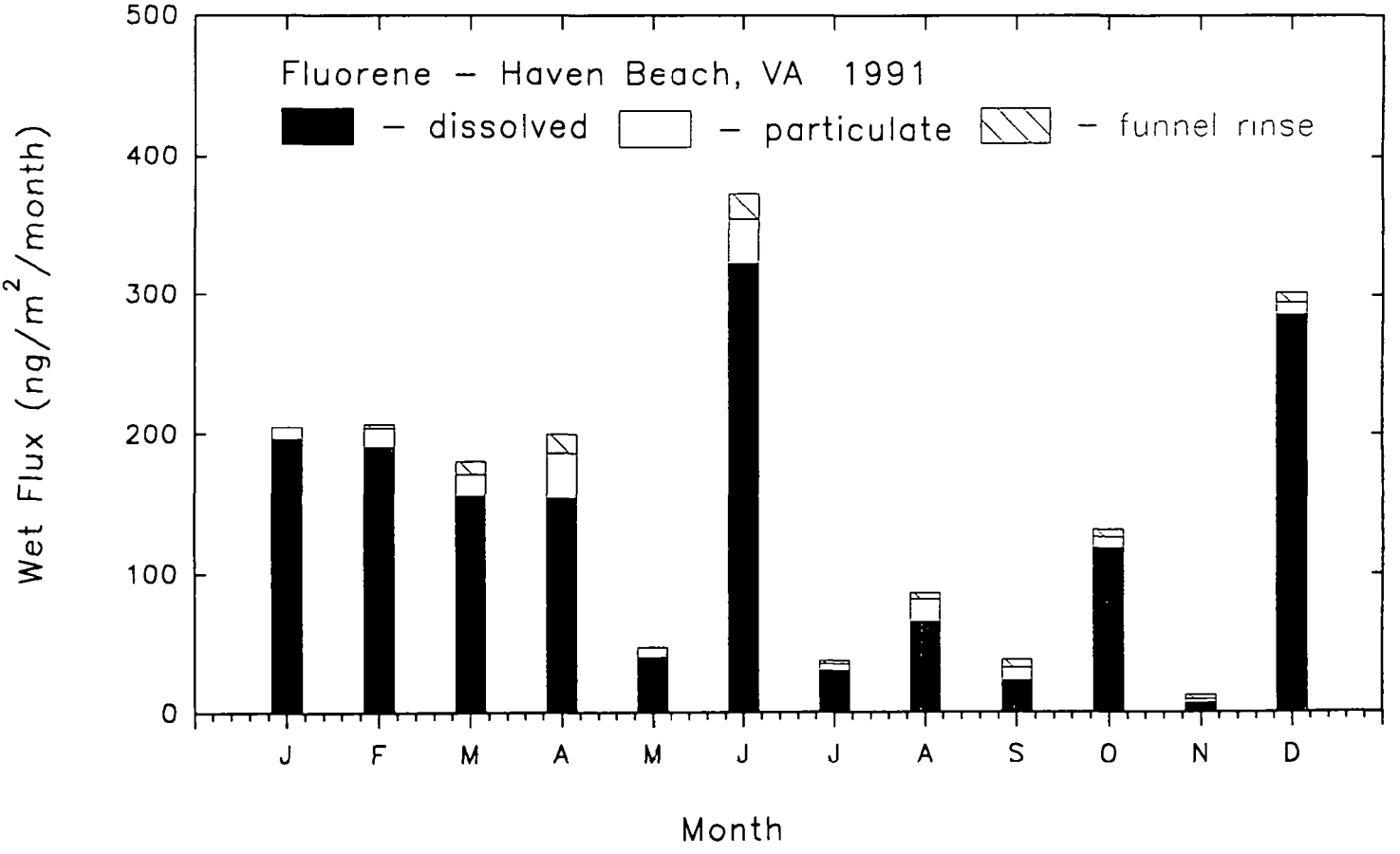

Total PCBs
Haven Beach,VA 1990
– dissolved
– particulate
– funnel rinse
Concentration (pg/L)
8000
6000
4000
2000
0
Total PCBs
Haven Beach,VA 1991
Concentration (pg/L)
8000
6000
4000
2000
0
o
**
3
**
8
0
5
10
15
20
25
30
35
40
45
50
Julian Week

Figure IV.1.45. Fluorene wet depositiona fluxes measured at the Elms and Haven Beach sites. (1=not quantifiable in dissolved phase, 2=not quantifiable on filter, 3=not quantifiable in funnel, 4=not detected in dissolved phase, 5=not detected on filter, 6=not detected in funnel, 7 = sampler down, * = lost dissolved samples). Particulate fraction after June, 1991 includes funnel rinse.



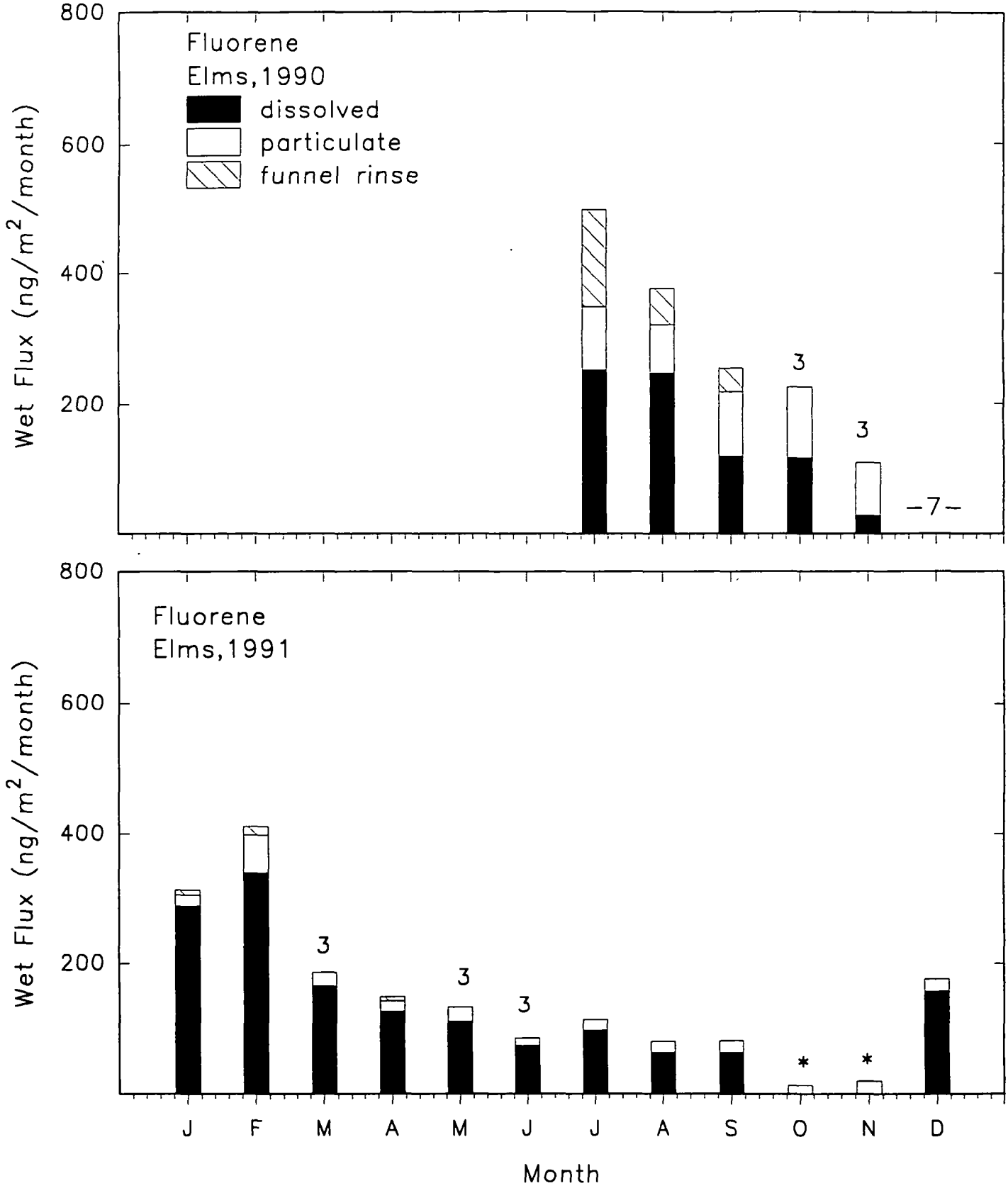
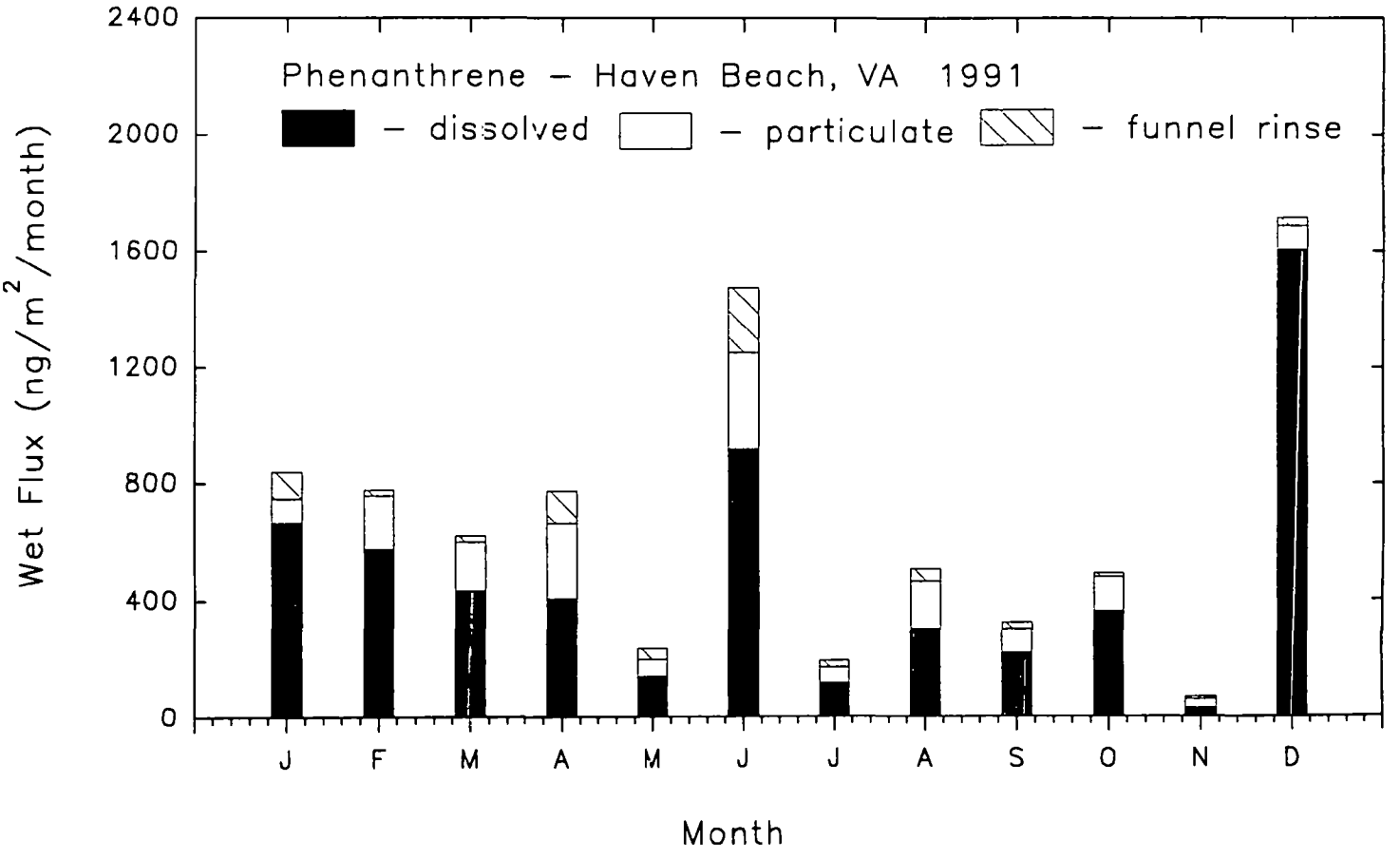

Fluorene
Elms,1990
dissolved
particulate
funnel rinse
Wet Flux (ng/m2/month)
800
600
400
200
3
3
-7-
Fluorene
Elms,1991
Wet Flux (ng/m2/month)
800
600
400
200
3
3
3
*
*
J
F
M
A
M
J
J
A
S
O
N
D
Month

Figure IV.1.46. Phenanthrene wet depositional fluxes measured at the Elms and Haven Beach sites. (1=not quantifiable in dissolved phase, 2=not quantifiable on filter, 3=not quantifiable in funnel, 4=not detected in dissolved phase, 5=not detected on filter, 6=not detected in funnel, 7 = sampler down, * = lost dissolved samples). Particulate fraction after June, 1991 includes funnel rinse.



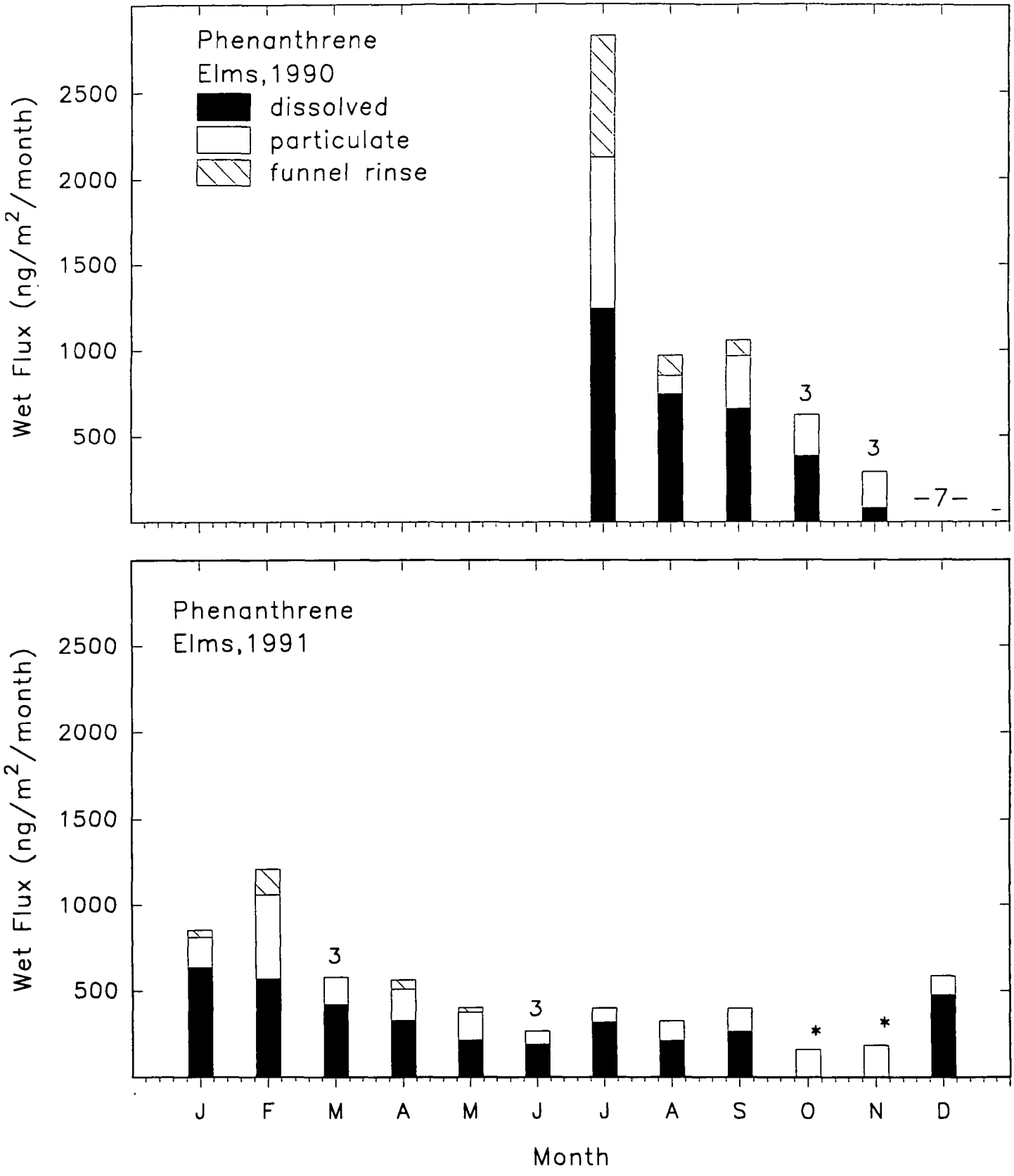
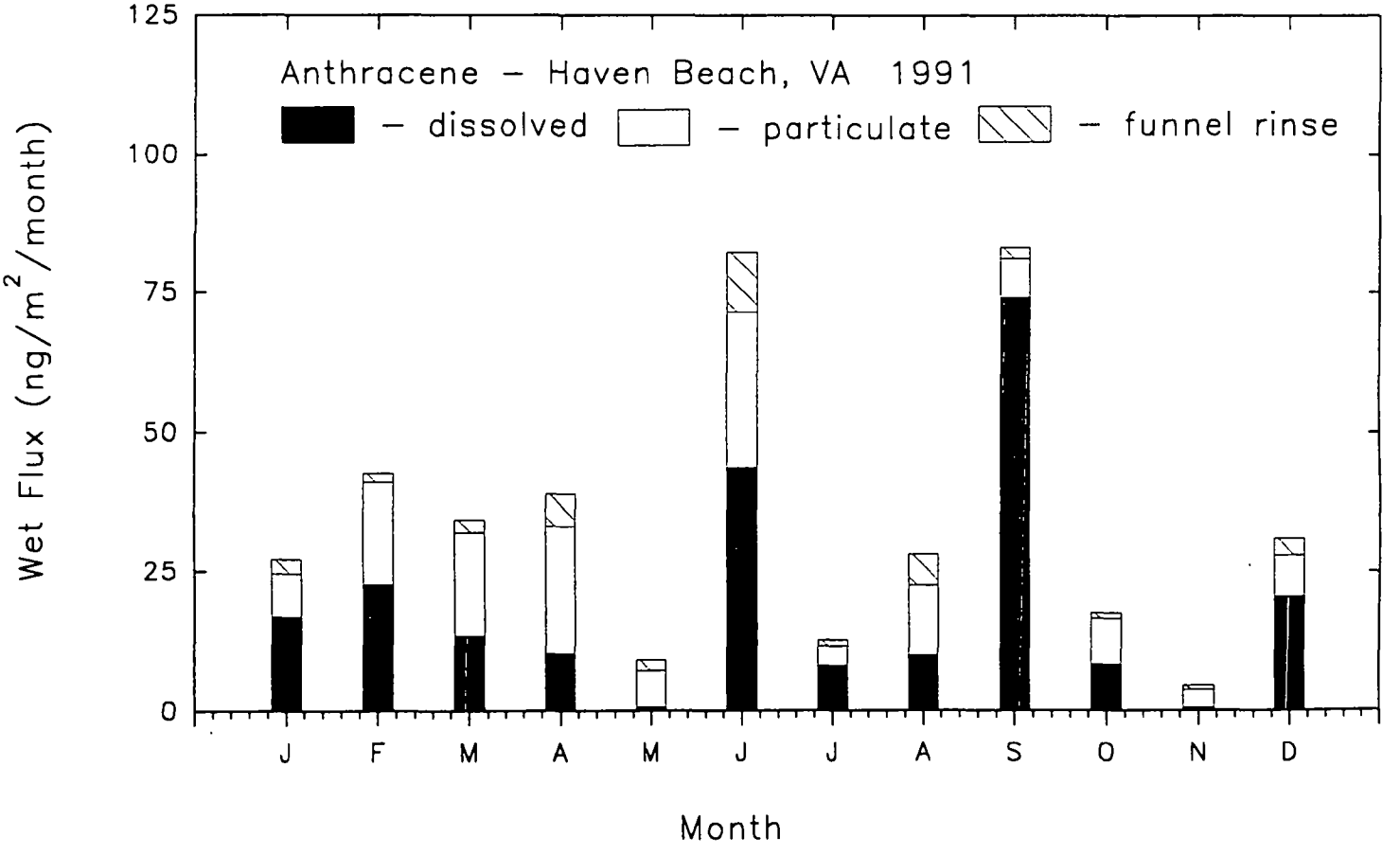

Phenanthrene
Elms,1990
dissolved
particulate
funnel rinse
Wet Flux (ng/m2/month)
2500
2000
1500
1000
500
3
3
-7-
Phenanthrene
Elms,1991
Wet Flux (ng/m2/month)
2500
2000
1500
1000
500
3
3
*
*
J
F
M
A
M
J
J
A
S
O
N
D
Month

Figure IV.1.47. Anthracene wet depositional fluxes measured at the Elms and Haven Beach sites.(1=not quantifiable in dissolved phase, 2=not quantifiable on filter, 3=not quantifiable in funnel, 4=not detected in dissolved phase, 5=not detected on filter, 6=not detected in funnel, 7 = sampler down, * = lost dissolved samples). Particulate fraction after June, 1991 includes funnel rinse.



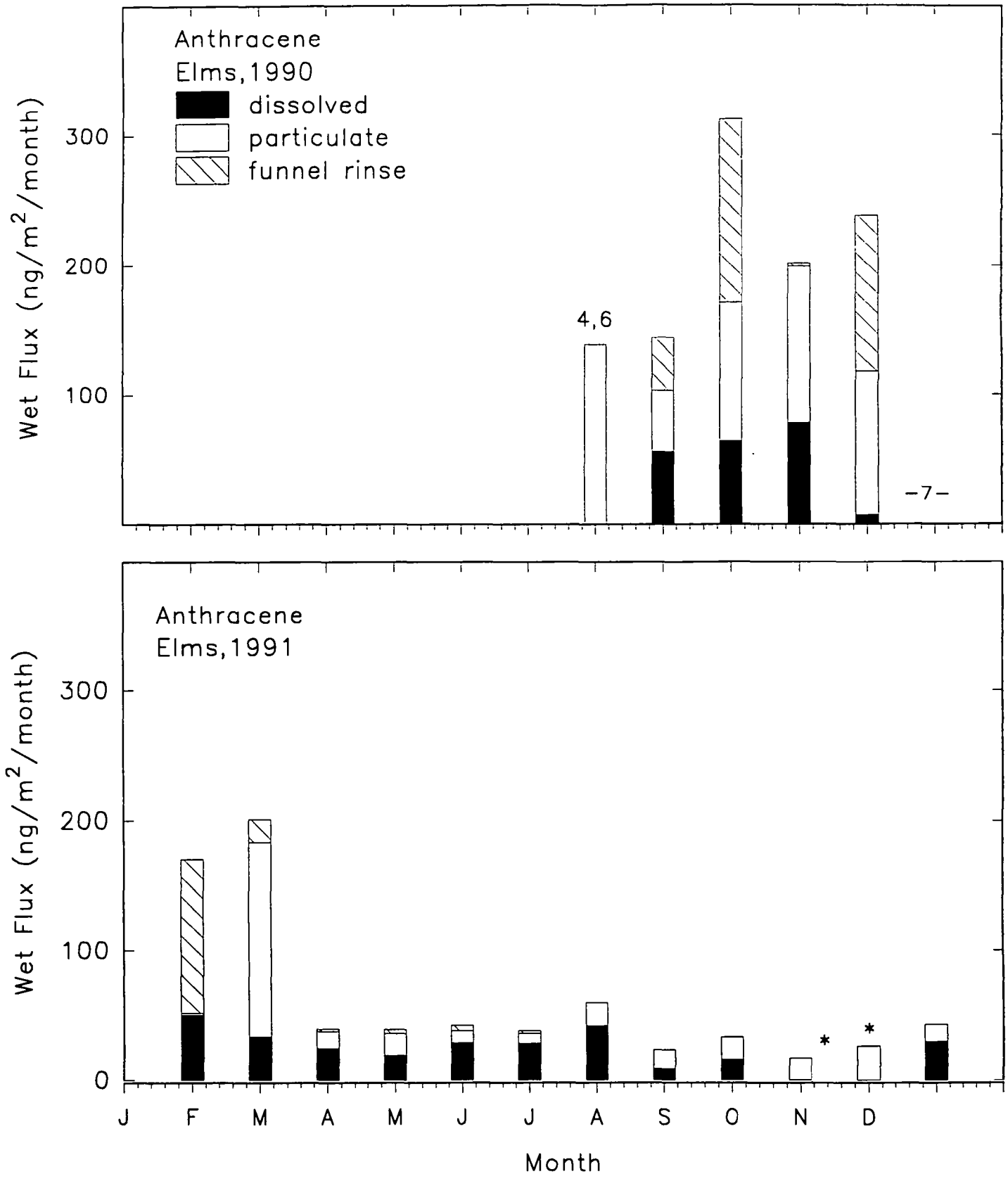
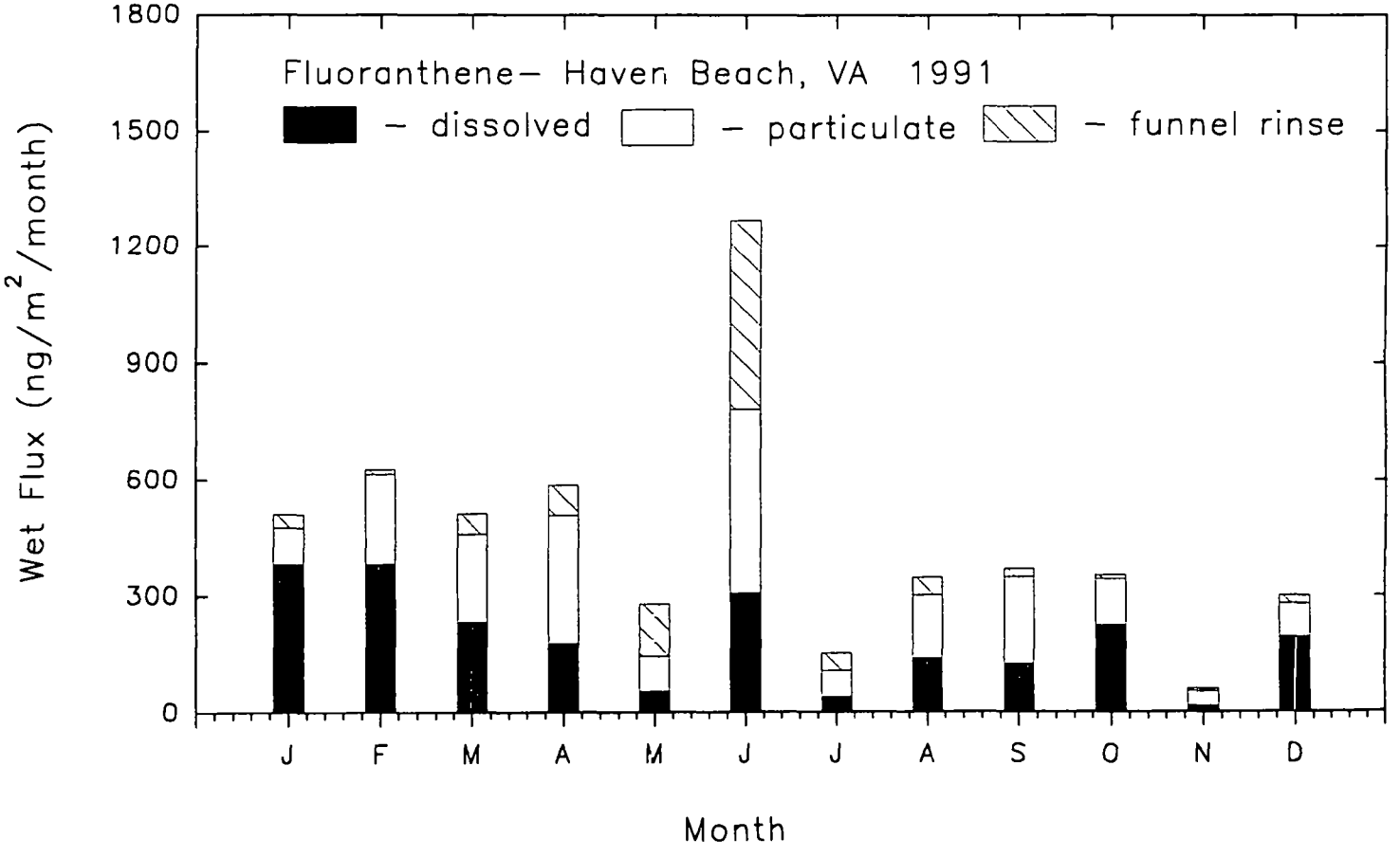

Anthracene
Elms,1990
dissolved
particulate
funnel rinse
Wet Flux (ng/m2/month)
300
200
100
4,6
-7-
Anthracene
Elms,1991
Wet Flux (ng/m2/month)
300
200
100
0
*
*
J
F
M
A
M
J
J
A
S
O
N
D
Month

Figure.IV.1.48. Fluoranthene wet depositional fluxes measured at the Elms and Haven Beach sites. (1 =not quantifiable in dissolved phase, 2 = not quantifiable on filter, 3 =not quantifiable in funnel, 4= not detected in dissolved phase, 5= not detected on filter, 6= not detected in funnel, 7= sampler doan, *= lost dissolved sample). Particulate fraction after June,1991 includes funnel rinse.



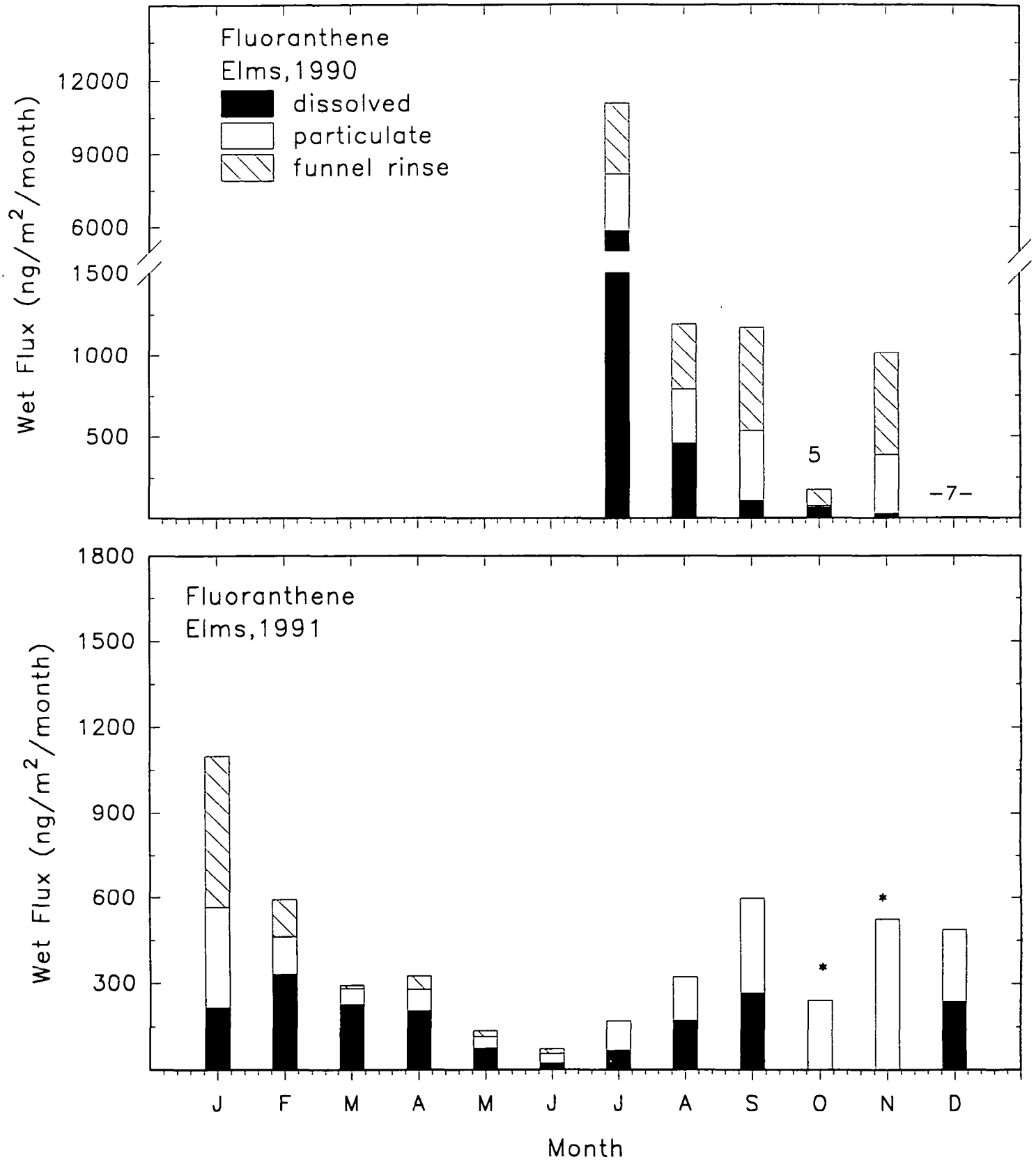
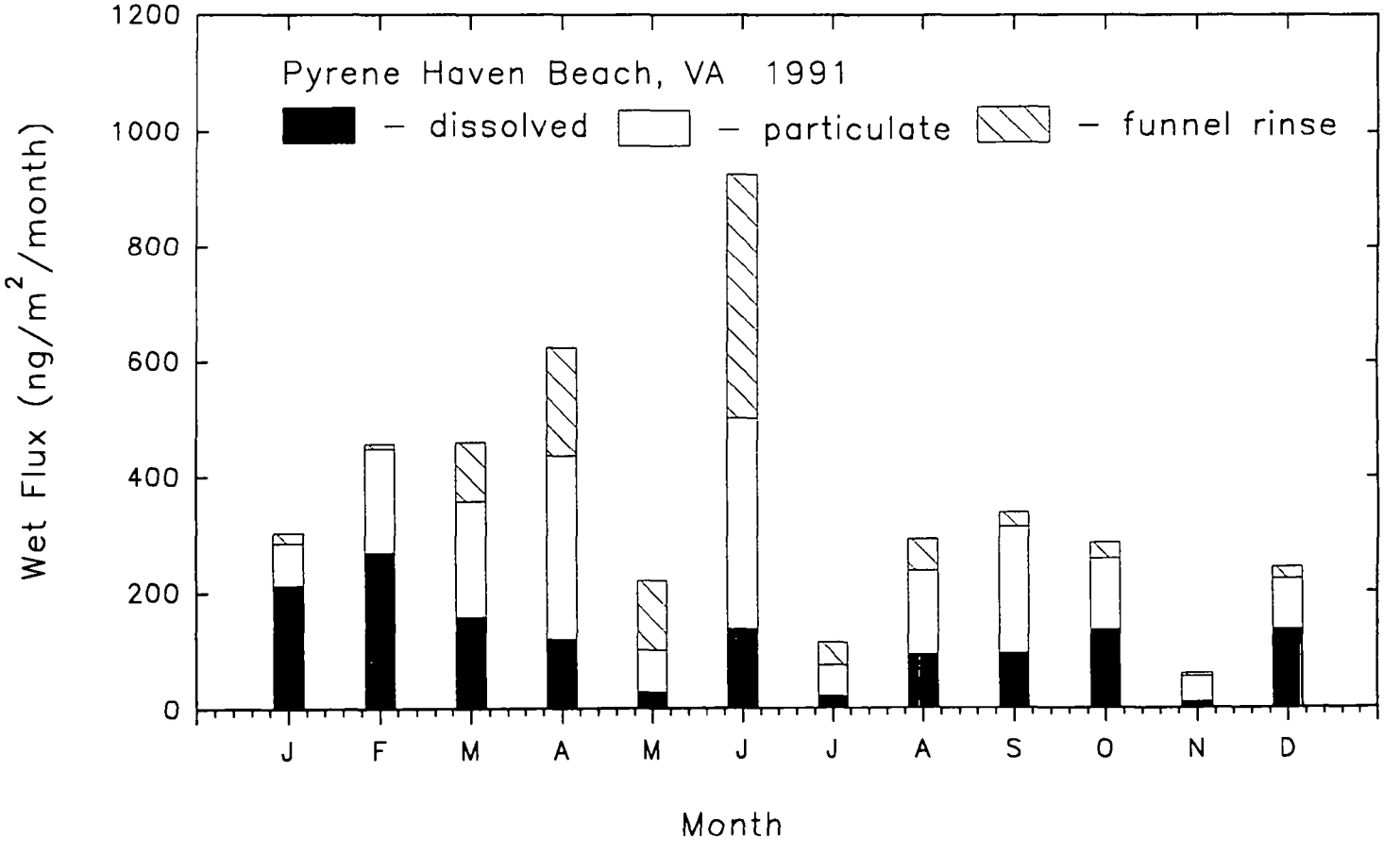

Fluoranthene
Elms,1990
dissolved
particulate
funnel rinse
Wet Flux (ng/m2/month)
12000
9000
6000
1500
1000
500
5
-7-
Fluoranthene
Elms,1991
1800
1500
1200
900
600
300
J
F
M
A
M
J
J
A
S
O
N
D
Month

Figure IV.1.49. Pyrene wet depositional fluxes measured at the Elms and Haven Beach sites. (1=not quantifiable in dissolved phase, 2=not quantifiable on filter, 3=not quantifiable in funnel, 4=not detected in dissolved phase, 5=not detected on filter, 6=not detected in funnel, 7 = sampler down, * = lost dissolved samples). Particulate fraction after June, 1991 includes funnel rinse.



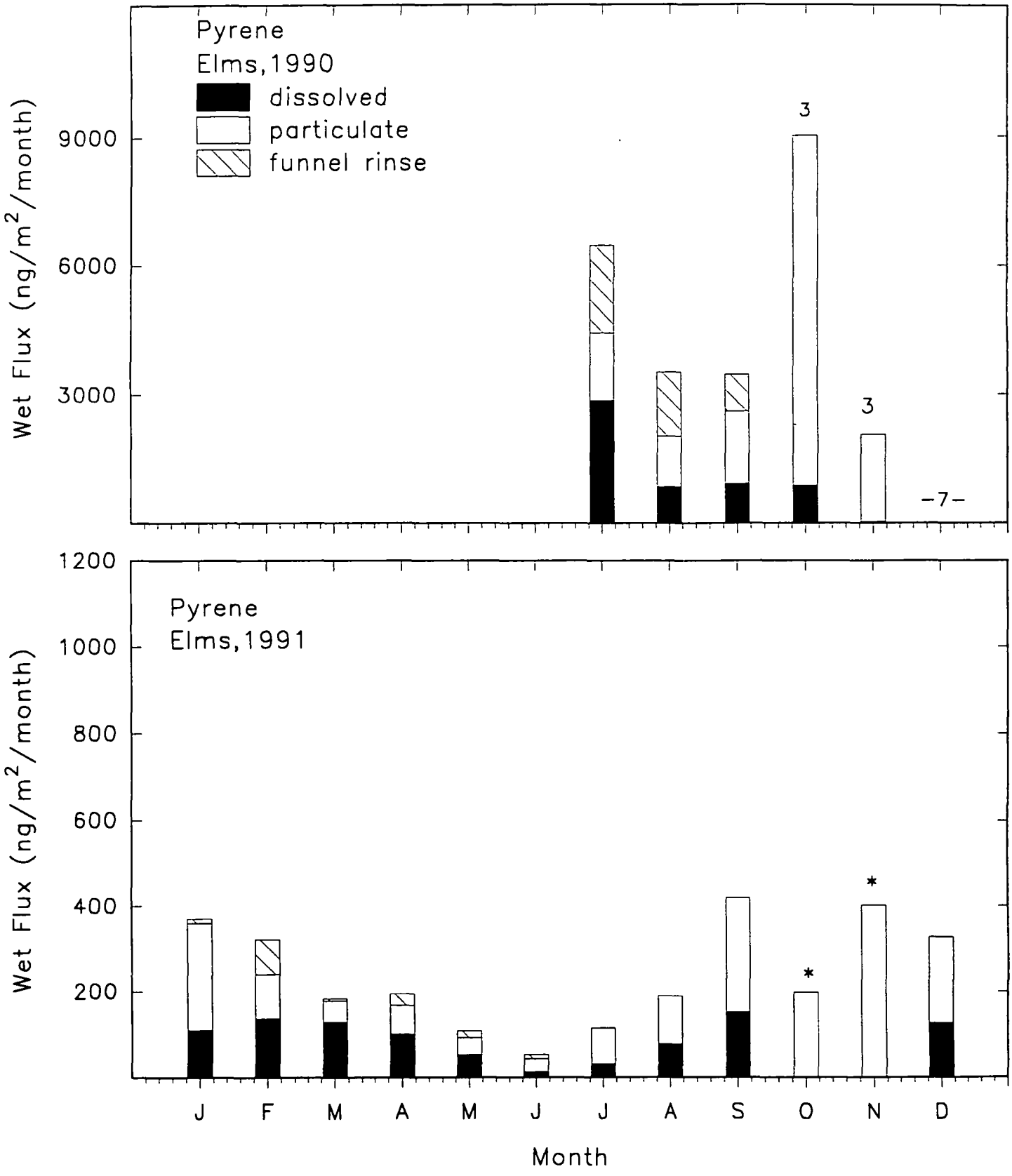
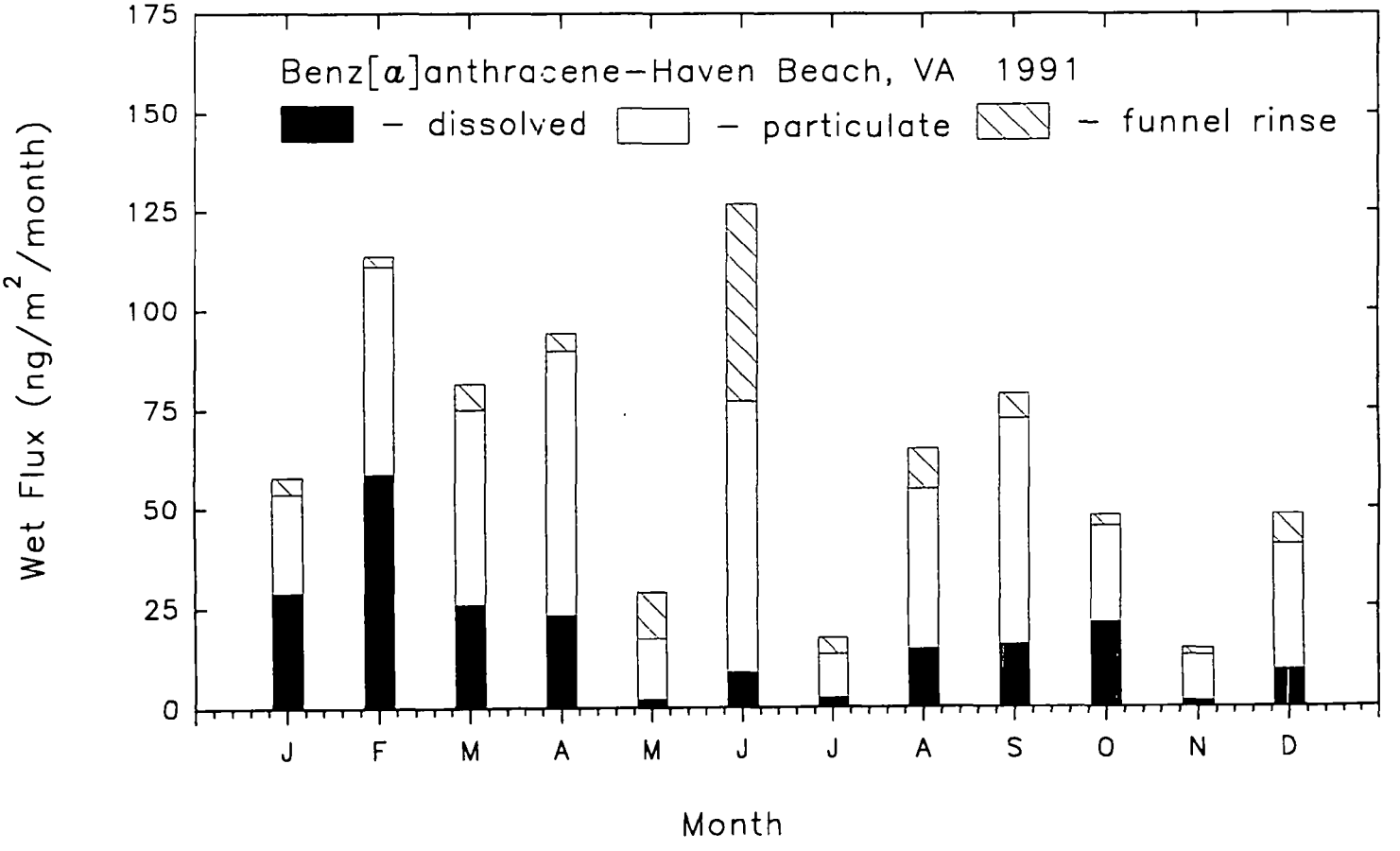

Pyrene
Elms,1990
dissolved
particulate
funnel rinse
Wet Flux (ng/m2/month)
9000
6000
3000
3
3
-7-
Pyrene
Elms,1991
1200
1000
800
600
400
200
*
*
J
F
M
A
M
J
J
A
S
O
N
D
Month

Figure IV.1.50. Benz[*a*]anthracene wet depositional fluxes measured at the Elms and Haven Beach sites.(1=not quantifiable in dissolved phase, 2=not quantifiable on filter, 3=not quantifiable in funnel, 4=not detected in dissolved phase, 5=not detected on filter, 6=not detected in funnel, 7 = lsampler down, * = lost dissolved samples). Particulate fraction after June, 1991 includes funnel rinse.



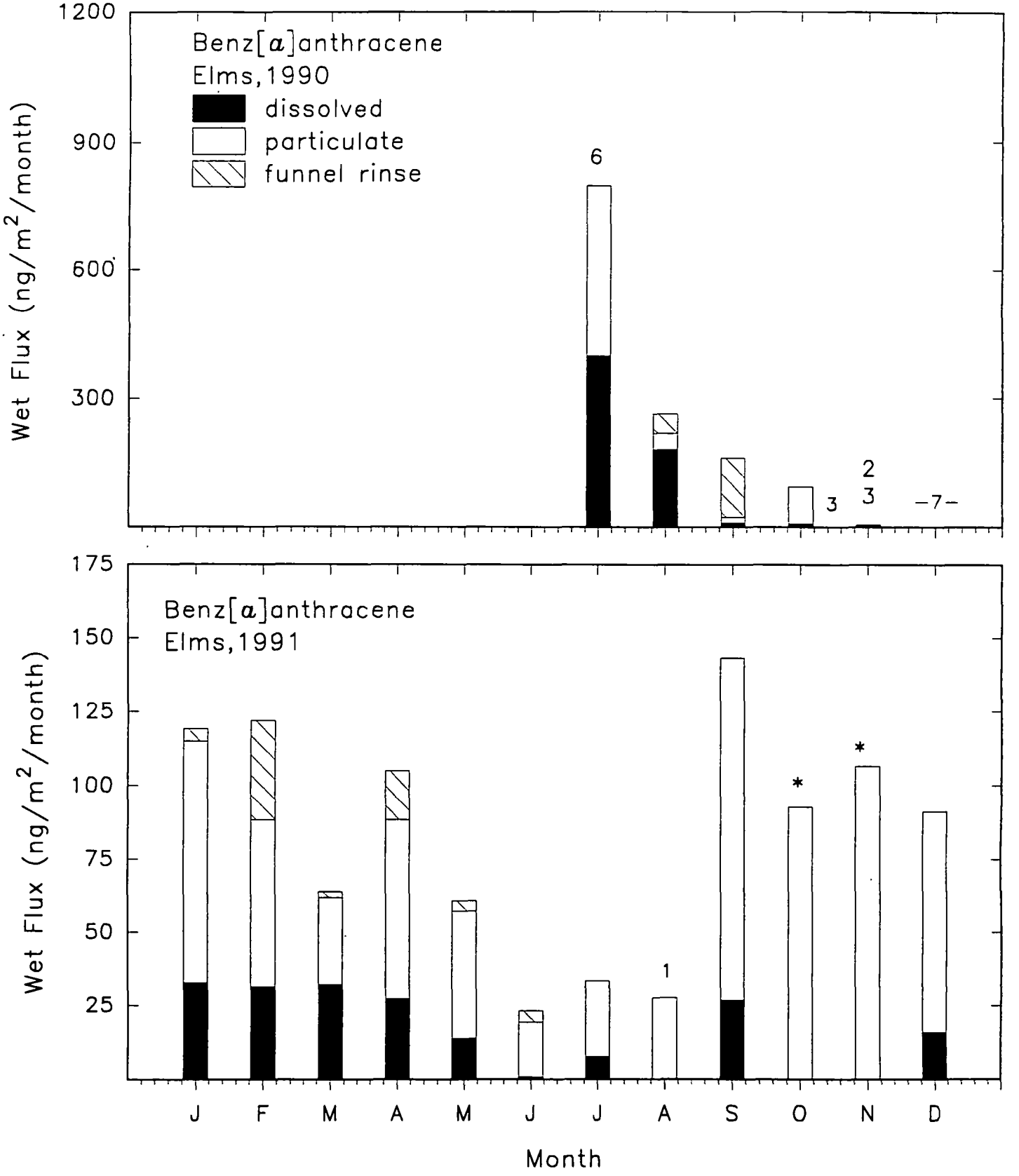
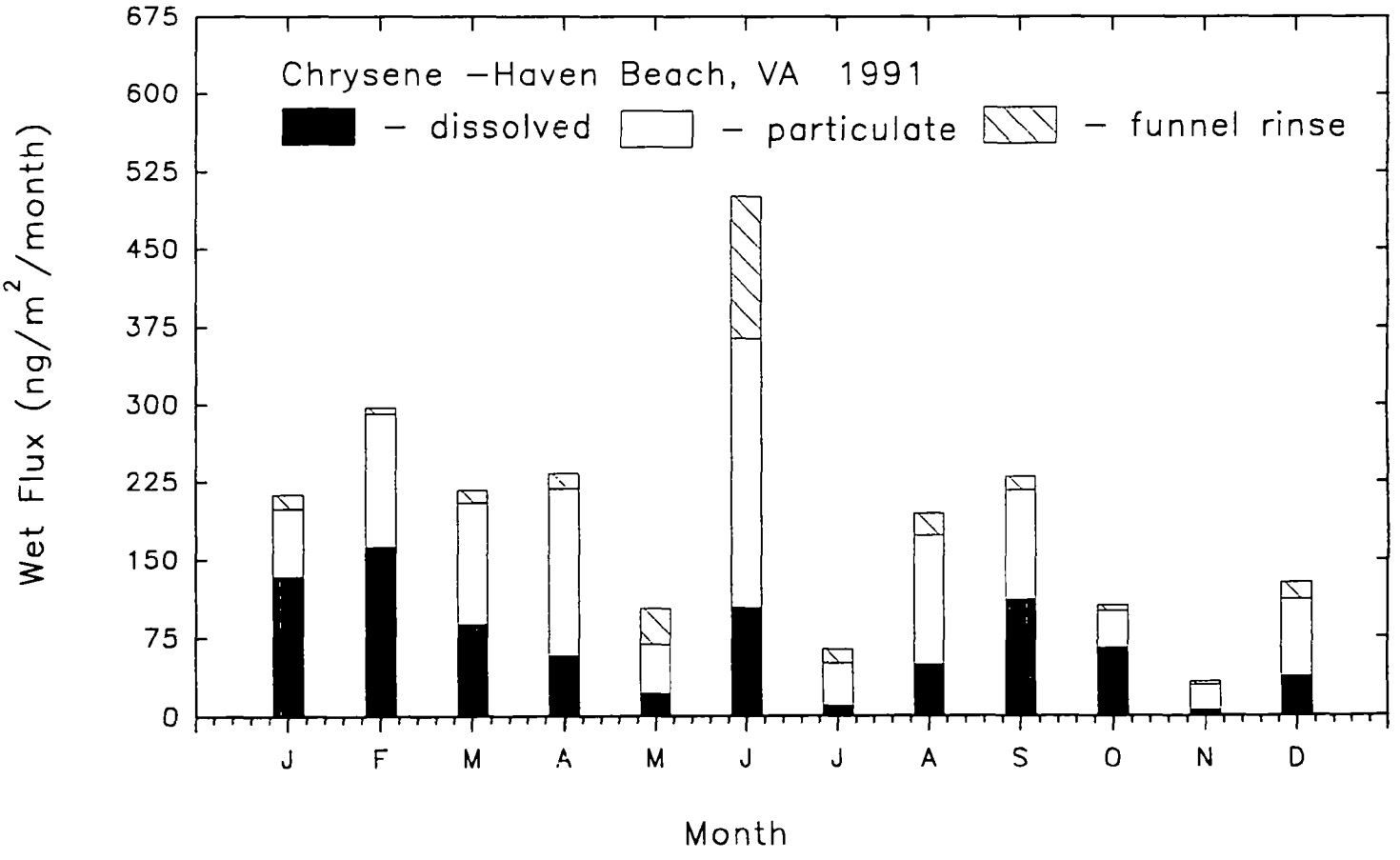

Benz[a]anthracene
Elms,1990
dissolved
particulate
funnel rinse
Wet Flux (ng/m2/month)
1200
900
600
300
6
3
2
3
-7-
Benz[a]anthracene
Elms,1991
Wet Flux (ng/m2/month)
175
150
125
100
75
50
25
1
*
*
J
F
M
A
M
J
J
A
S
O
N
D
Month

Figure IV.1.51. Chrysene wet depositional fluxes measured at the Elms and Haven Beach sites. (1=not quantif able in dissolved phase, 2=not quantifiable on filter, 3=not quantifiable in funnel, 4=not detected in dissolved phase, 5=not detected on filter, 6=not detected in funnel, 7 = sampler down, * = lost dissolved samples). Particulate fraction after June, 1991 includes funnel rinse.



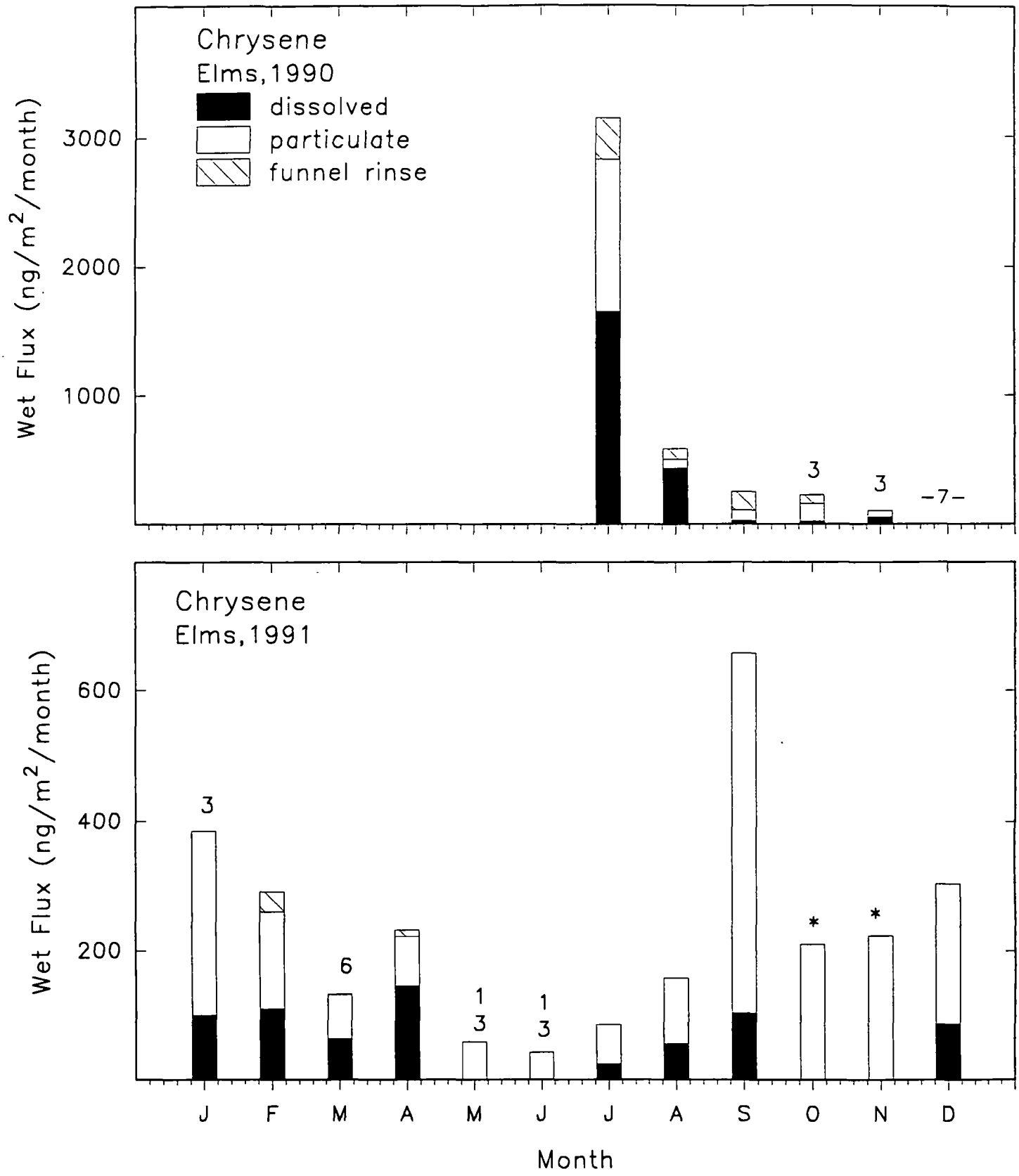
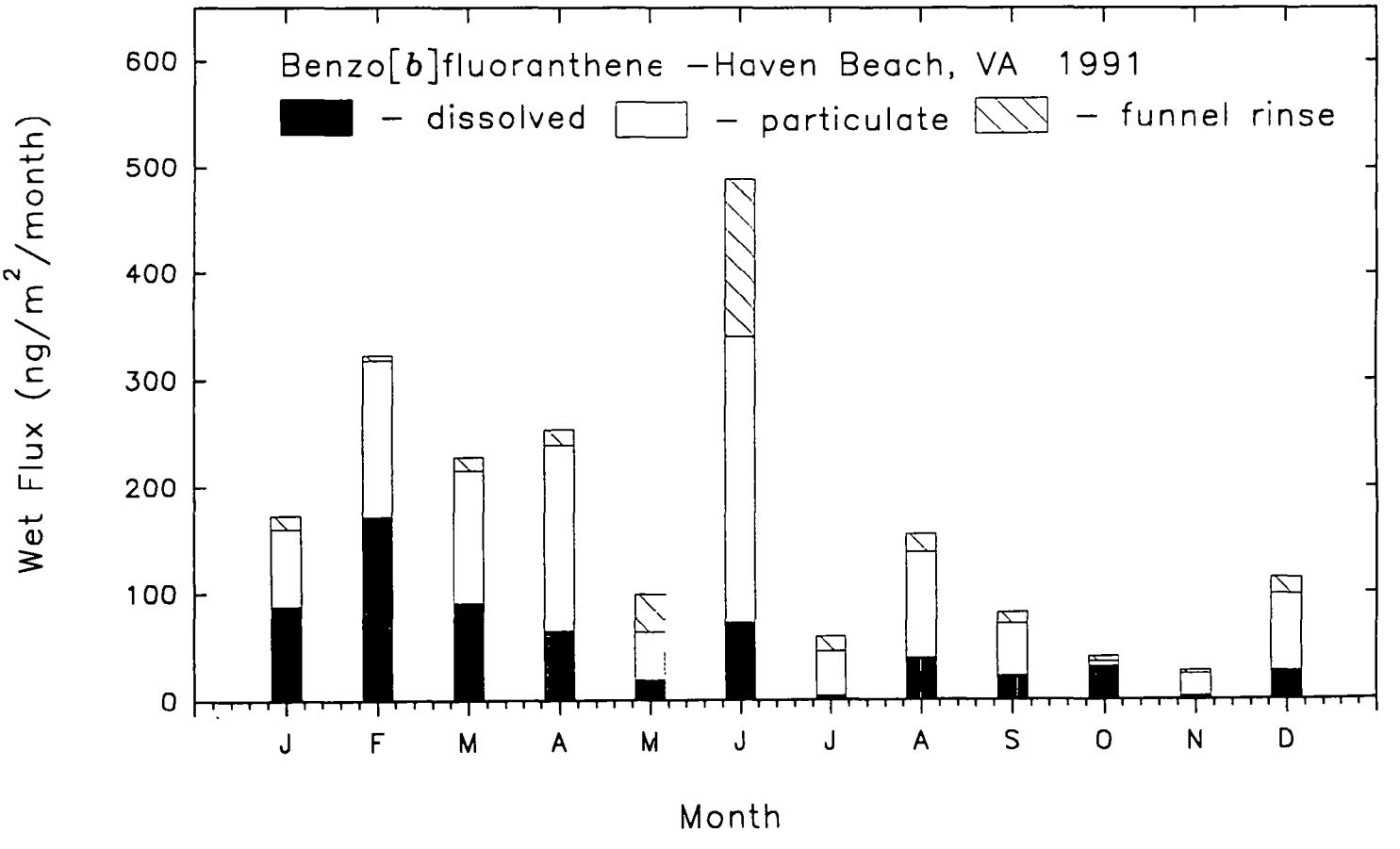

Chrysene
Elms,1990
dissolved
particulate
funnel rinse
Wet Flux (ng/m2/month)
3000
2000
1000
3
3
-7-
Chrysene
Elms,1991
Wet Flux (ng/m2/month)
600
400
200
3
6
1
3
1
3
*
*
J
F
M
A
M
J
J
A
S
O
N
D
Month

Figure IV.1.52. Benzo[*b*]fluoranthene wet depositional fluxes measured at the Elms and Haven Beach sites. (1=not quantifiable in dissolved phase, 2=not quantifiable on filter, 3=not quantifiable in funnel, 4=not detected in dissolved phase, 5=not detected on filter, 6=not detected in funnel, 7 = sampler down, * = lost dissolved samples). Particulate fraction after June, 1991 includes funnel rinse.



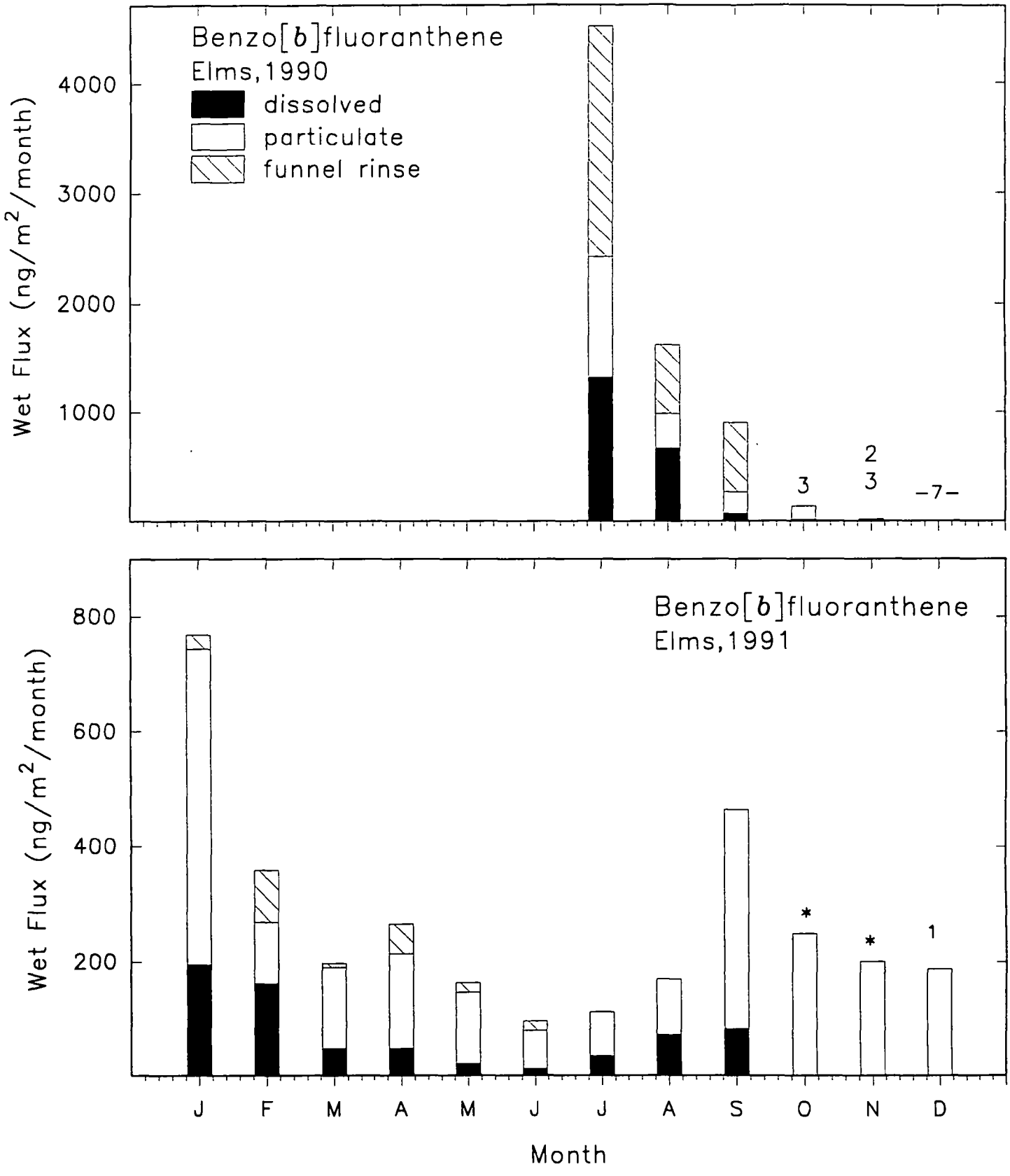
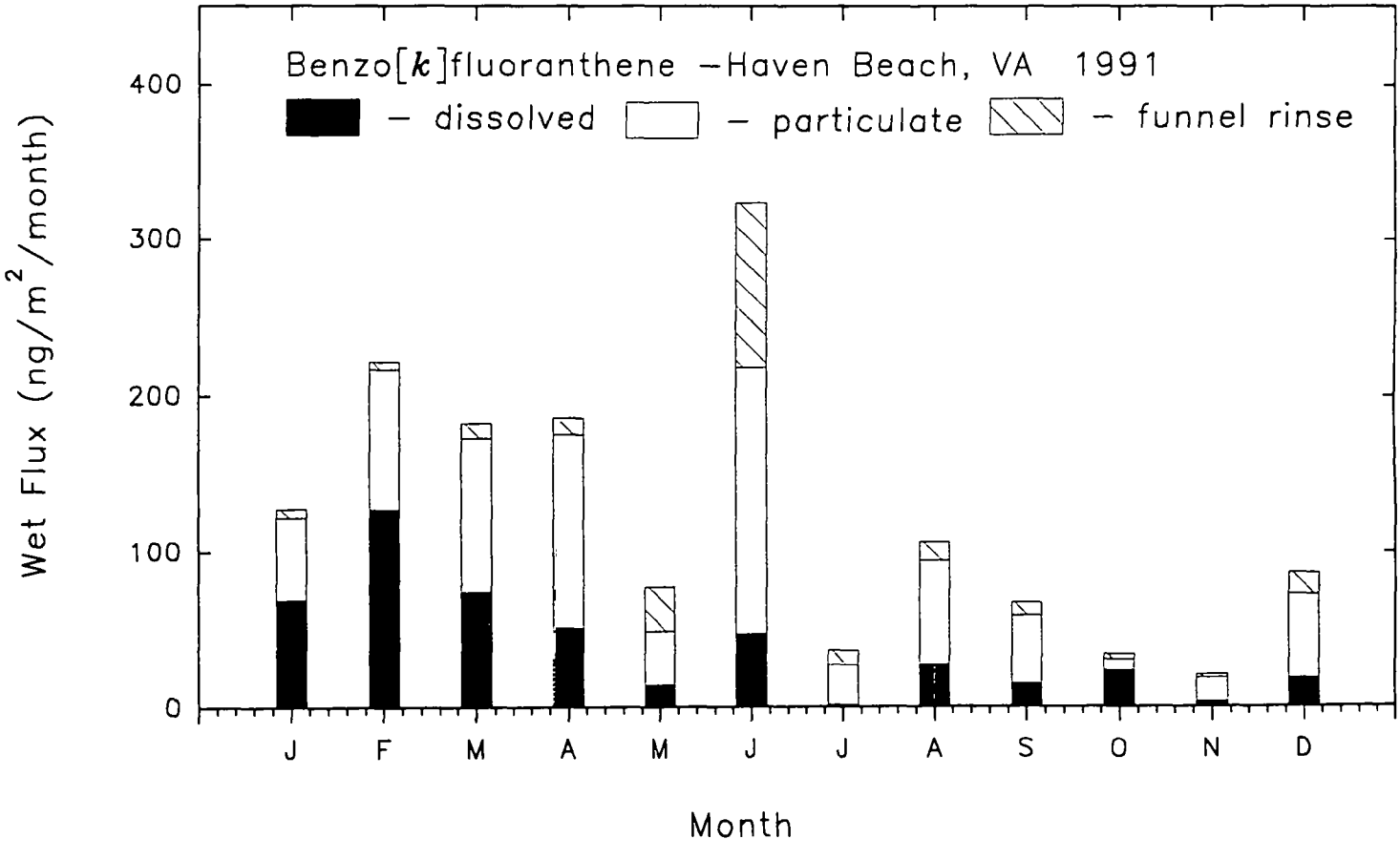

Benzo[b]fluoranthene
Elms,1990
dissolved
particulate
funnel rinse
Wet Flux (ng/m2/month)
4000
3000
2000
1000
3
2
3
-7-
Benzo[b]fluoranthene
Elms,1991
Wet Flux (ng/m2/month)
800
600
400
200
*
*
1
J
F
M
A
M
J
J
A
S
O
N
D
Month

Figure IV.1.53. Benzo[*k*]fluoranthene wet depositional fluxes measured at the Elms and Haven Beach sites. (1=not quantifiable in dissolved phase, 2=not quantifiable on filter, 3=not quantifiable in funnel, 4=not detected in dissolved phase, 5=not detected on filter, 6=not detected in funnel, 7 = lsampler down, * = lost dissolved samples). Particulate fraction after June, 1991 incluces funnel rinse.



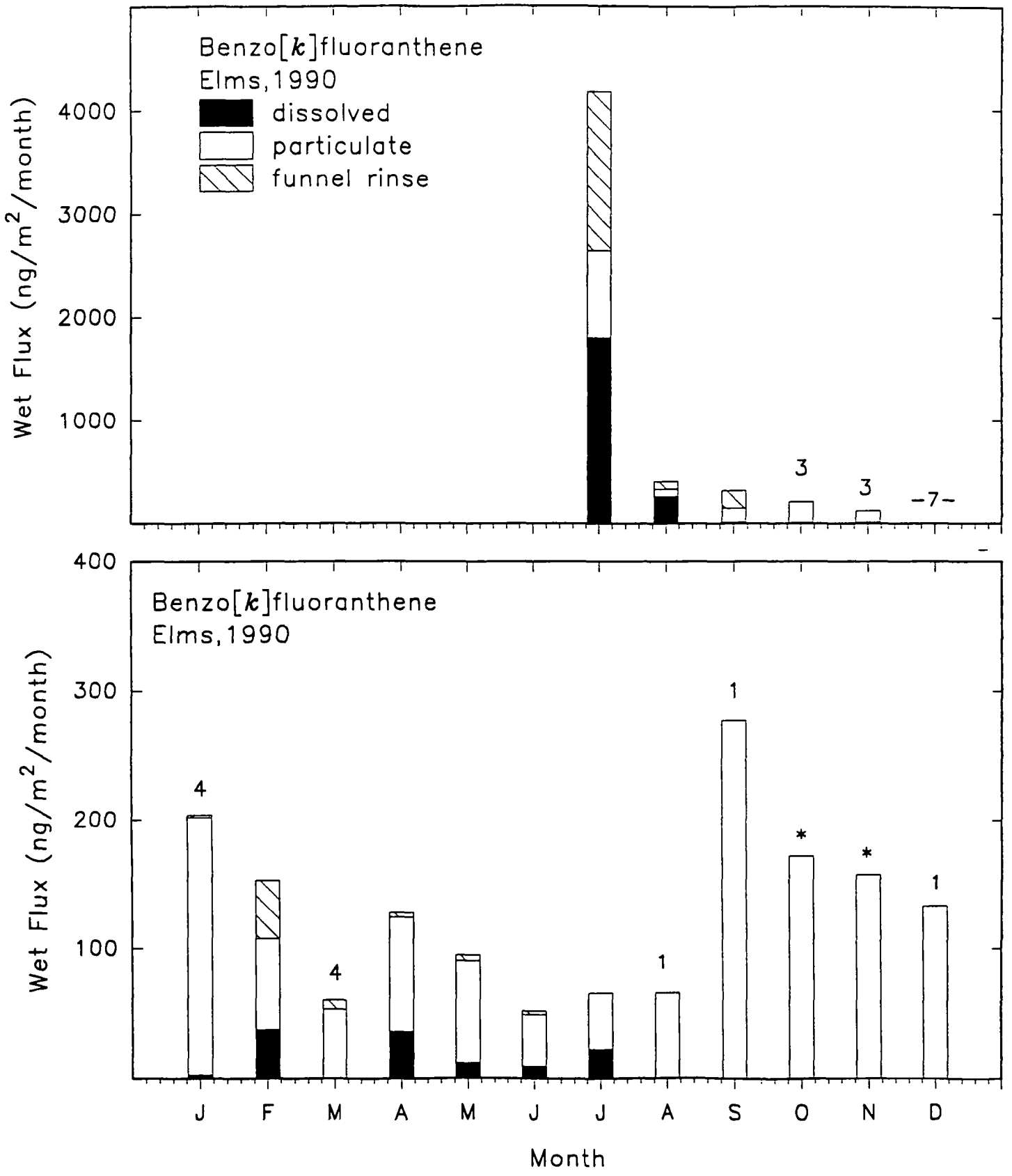
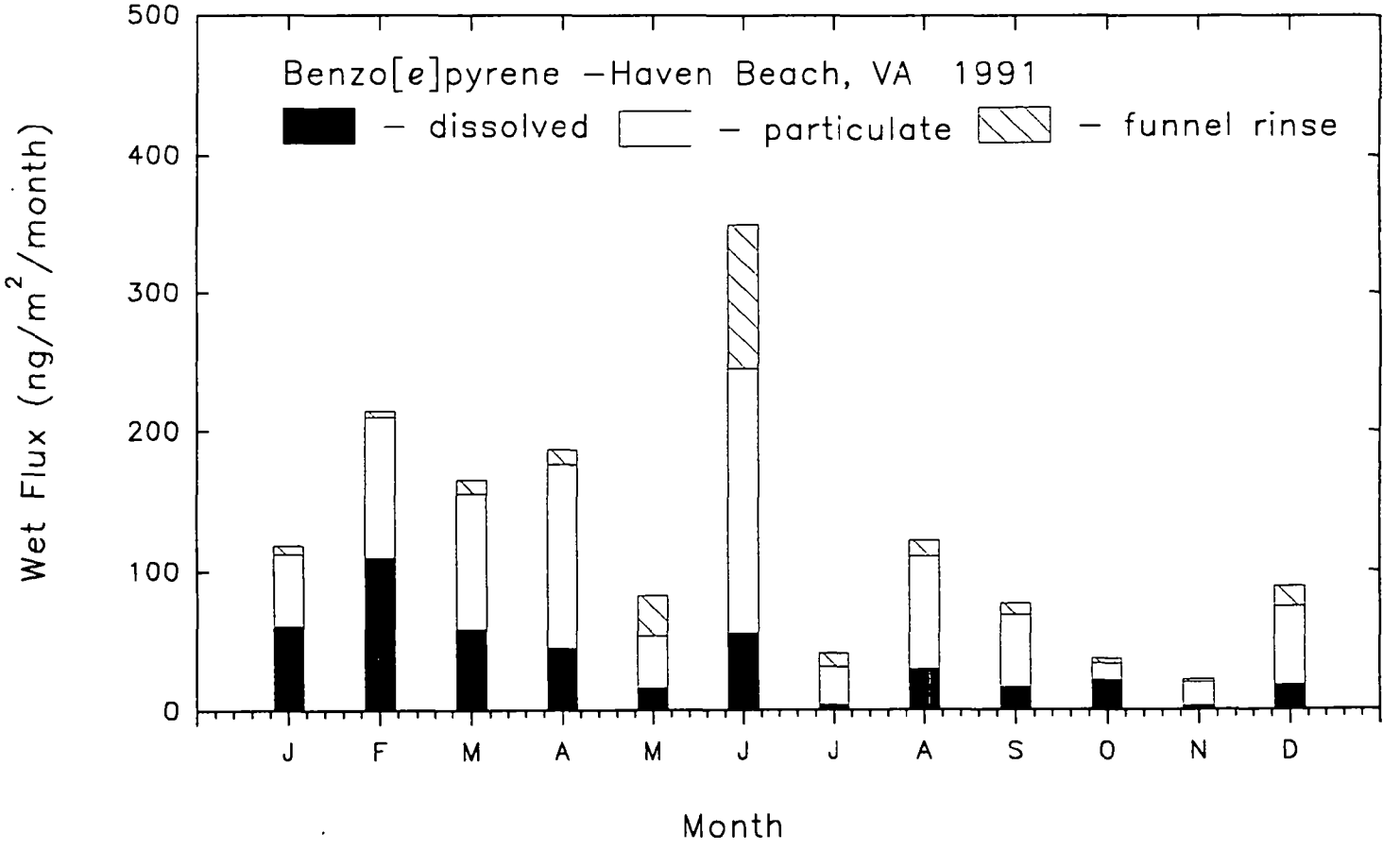

Benzo[k]fluoranthene
Elms,1990
dissolved
particulate
funnel rinse
Wet Flux (ng/m2/month)
4000
3000
2000
1000
3
3
-7-
400
300
200
100
Benzo[k]fluoranthene
Elms,1990
Wet Flux (ng/m2/month)
4
4
1
1
*
*
1
J
F
M
A
M
J
J
A
S
O
N
D
Month

Figure IV.1.54. Benzo[*e*]pyrene wet depositional fluxes measured at the Elms and Haven Beach sites. (1=not quantifiable in dissolved phase, 2=not quantifiable on filter, 3=not quantifiable in funnel, 4=not detected in dissolved phase, 5=not detected on filter, 6=not detected in funnel, 7=not analyzed, 8 = sampler down, * = lost dissolved samples). Particulate fraction after June, 1991 includes funnel rinse.



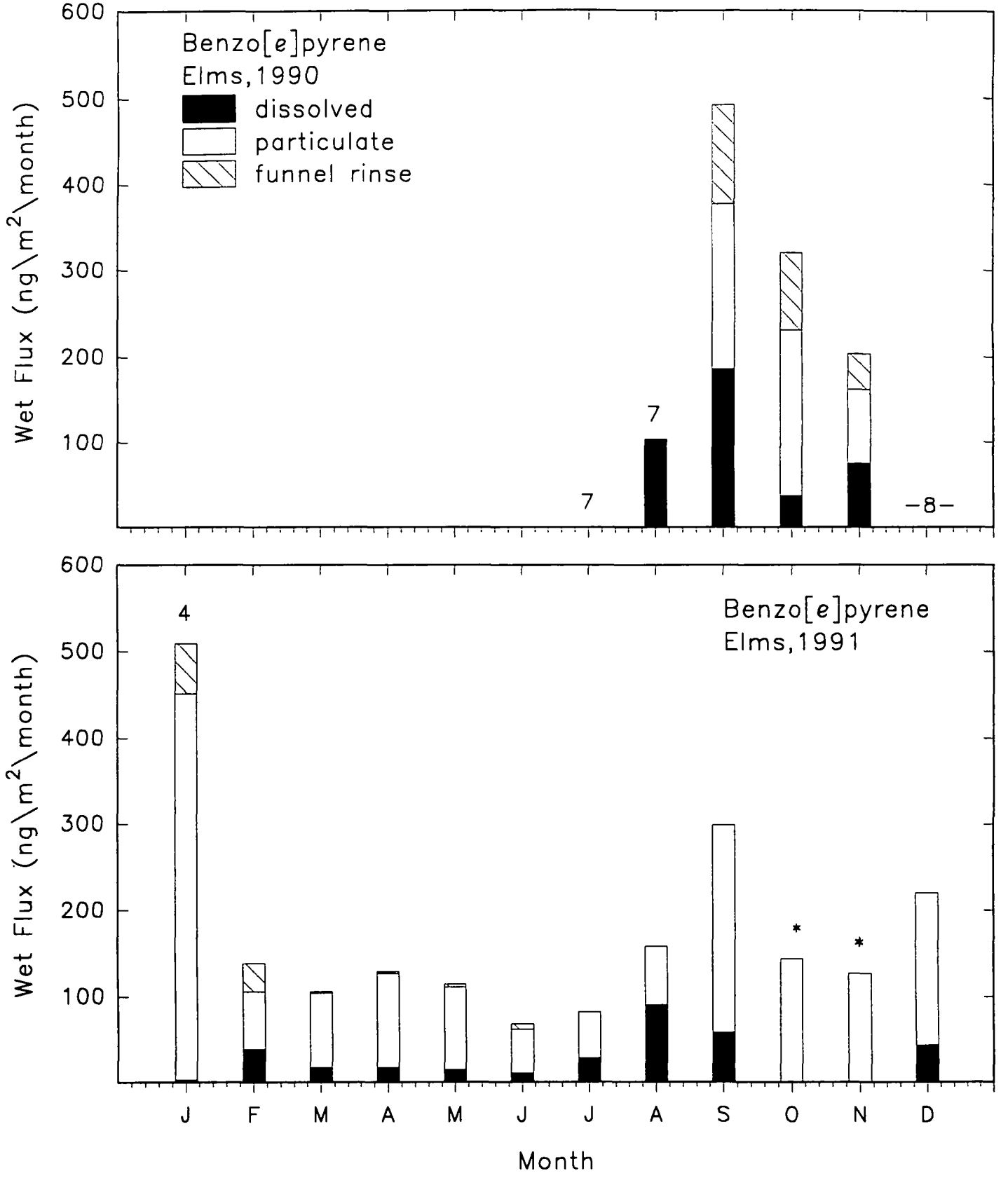
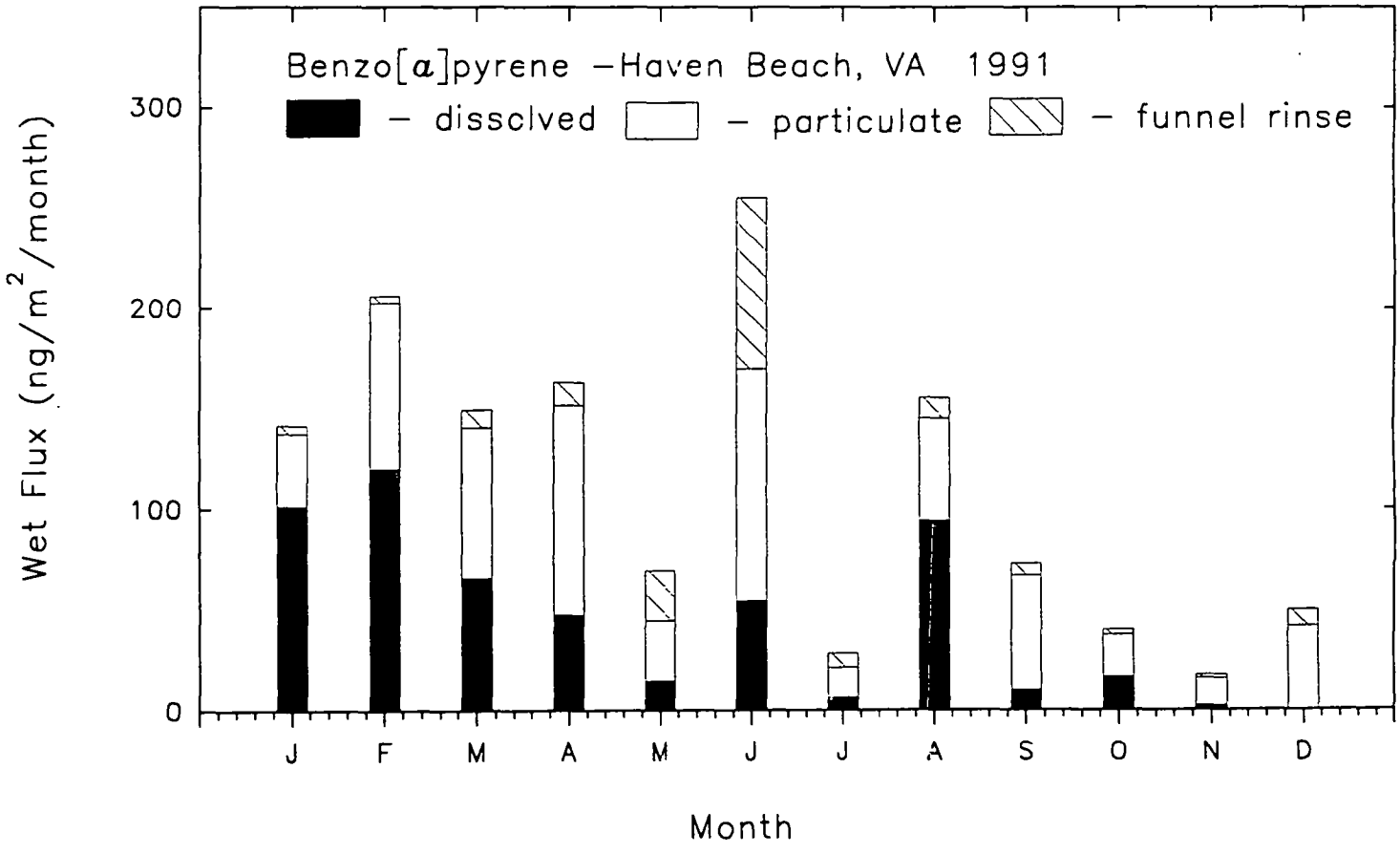

Benzo[e]pyrene
Elms,1990
dissolved
particulate
funnel rinse
Wet Flux (ng\m2\month)
600
500
400
300
200
100
7
7
-8-
Benzo[e]pyrene
Elms,1991
4
*
*
J
F
M
A
M
J
J
A
S
O
N
D
Month

Figure IV.1.55. Benzo[*a*]pyrene wet depositional fluxes measured at the Elms and Haven Beach sites. (1=not quantifiable in dissolved phase, 2=not quantifiable on filter, 3=not quantifiable in funnel, 4=not detected in dissolved phase, 5=not detected on filter, 6=not detected in funnel, 7 = lsampler down, * = lost dissolved samples). Particulate fraction after June, 1991 includes funnel rinse.



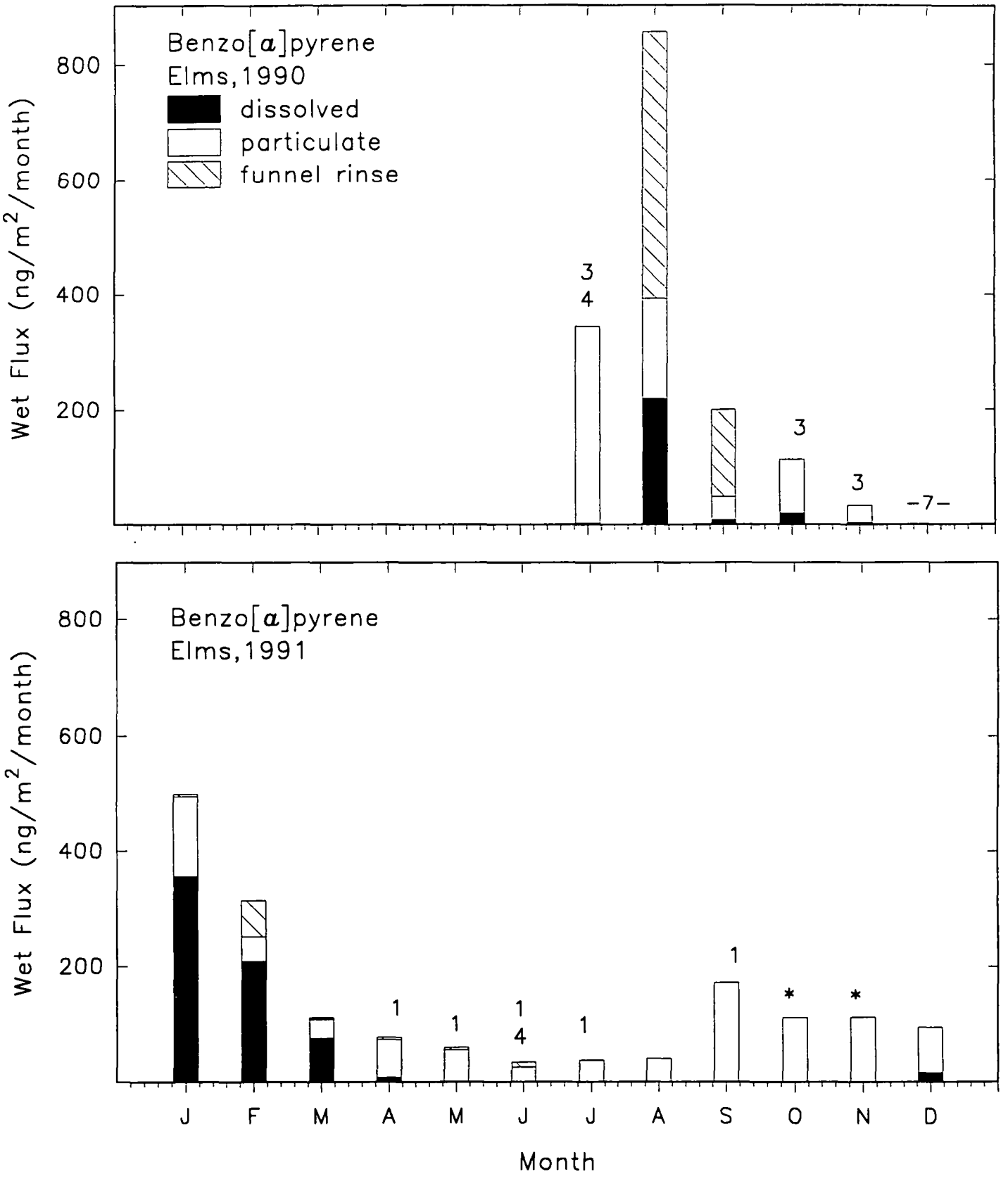
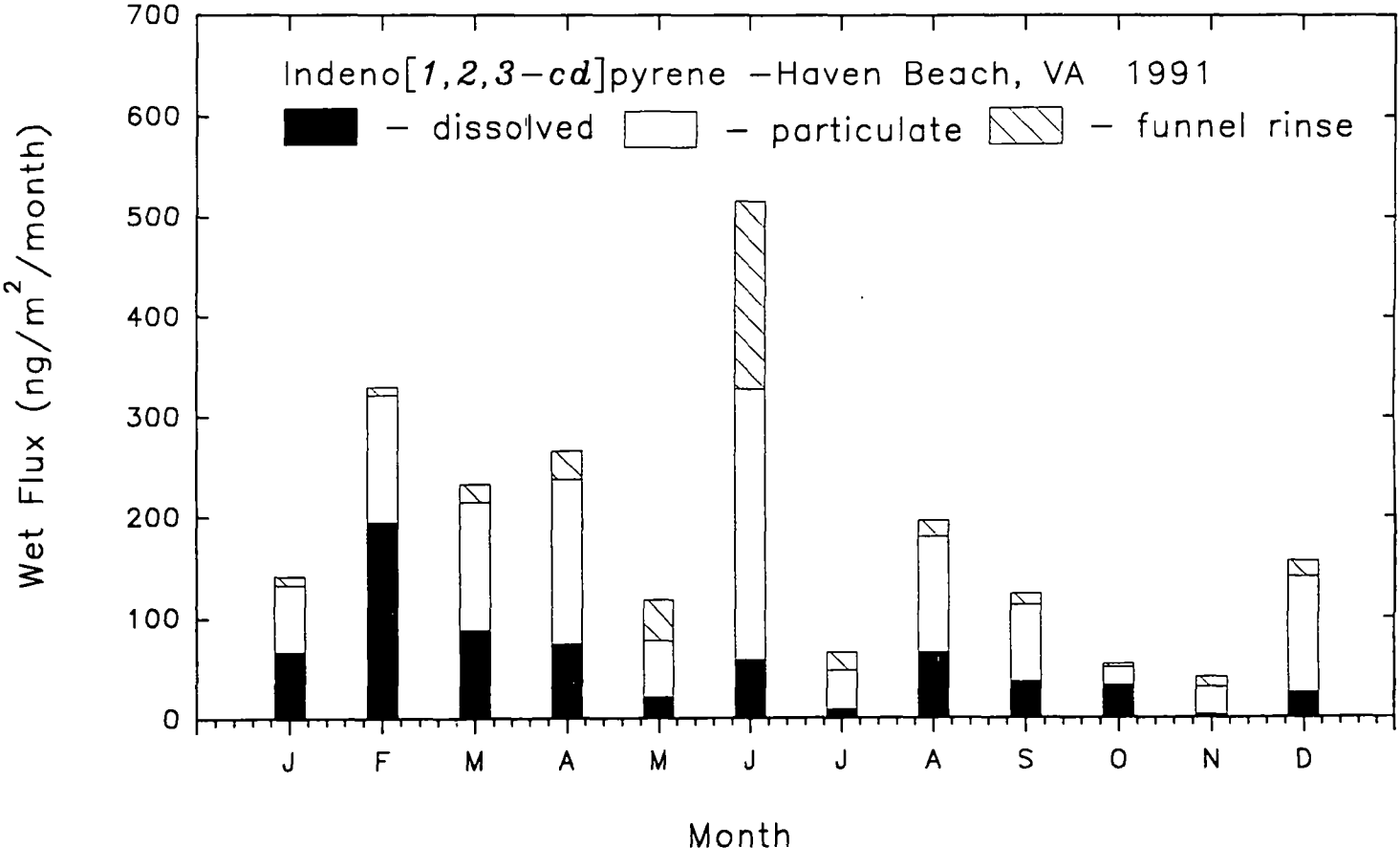

Benzo[a]pyrene
Elms,1990
dissolved
particulate
funnel rinse
Wet Flux (ng/m2/month)
800
600
400
200
3
4
3
3
-7-
Benzo[a]pyrene
Elms,1991
Wet Flux (ng/m2/month)
800
600
400
200
1
1
1
4
1
1
*
*
J
F
M
A
M
J
J
A
S
O
N
D
Month

Figure IV.1.56. Indeno[*1,2,3–cd*]pyrene wet depositional fluxes measured at the Elms and Haven Beach sites.(1=not quantifiable in dissolved phase, 2=not quantifiable on filter, 3=not quantifiable in funnel, 4=not detected in dissolved phase, 5=not detected on filter, 6=not detected in funnel, 7 = sampler down, * = lost dissolved samples). Particulate fraction after June, 1991 includes funnel rinse.



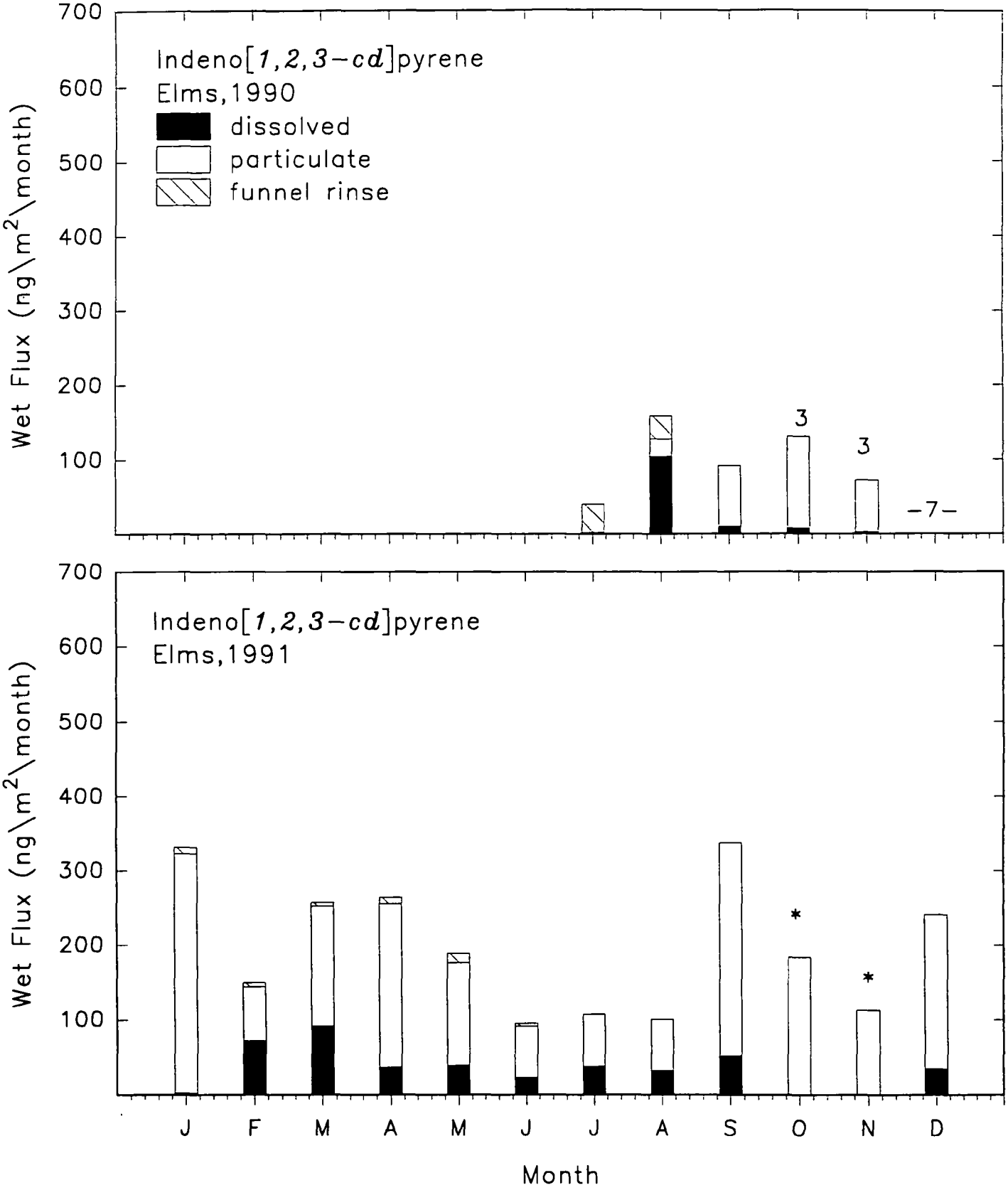
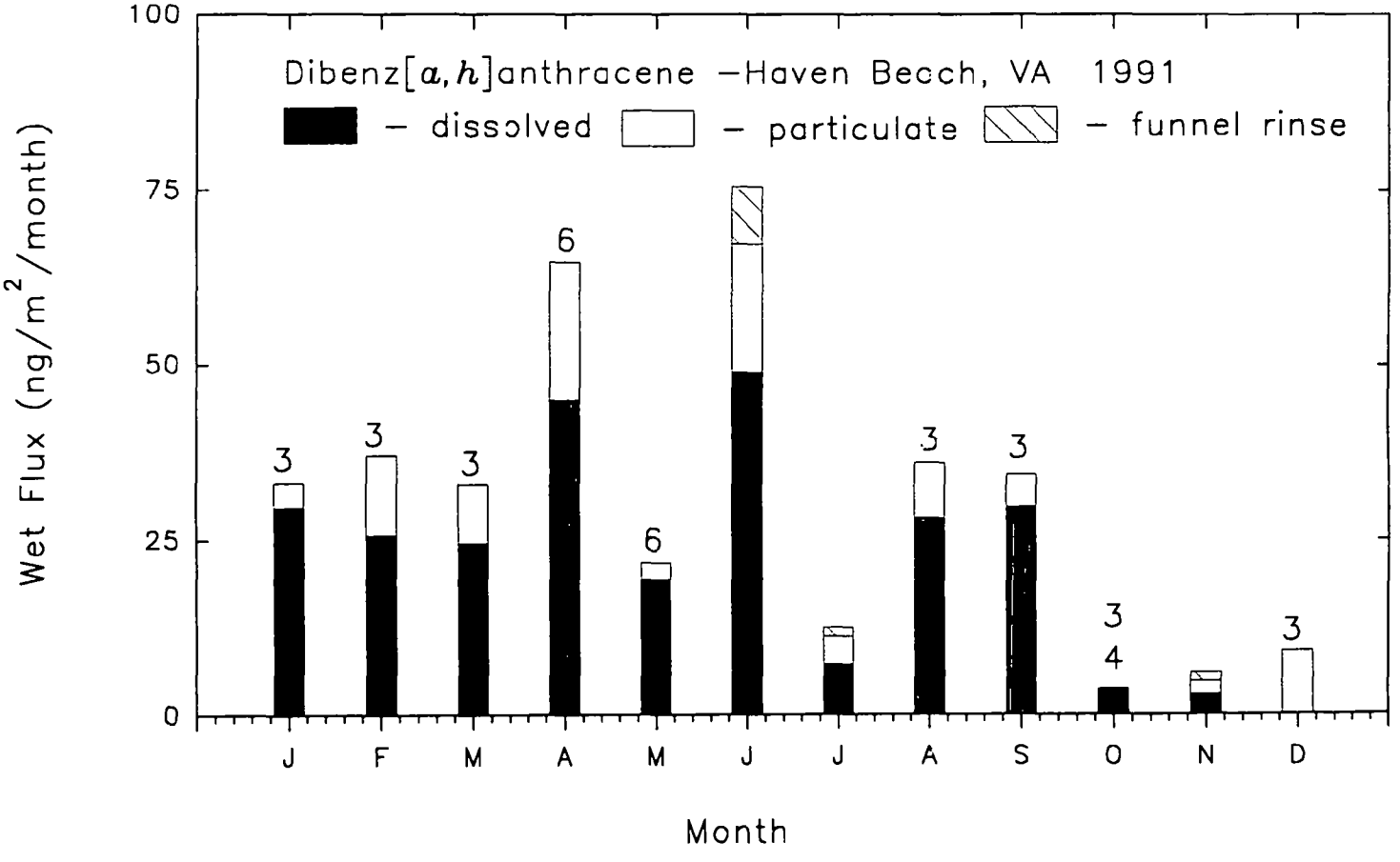

Indeno[1,2,3-cd]pyrene
Elms,1990
dissolved
particulate
funnel rinse
Wet Flux (ng\m2\month)
700
600
500
400
300
200
100
3
3
-7-
Indeno[1,2,3-cd]pyrene
Elms,1991
Wet Flux (ng\m2\month)
700
600
500
400
300
200
100
*
*
J
F
M
A
M
J
J
A
S
O
N
D
Month

Figure IV.1.57. Dibenz[*a,h*]anthracene wet depositional fluxes measured at the Elms and Haven Beach sites. (1=not quantifiable in dissolved phase, 2=not quantifiable on filter, 3=not quantifiable in funnel, 4=not detected in dissolved phase, 5=not detected on filter, 6=not detected in funnel, 7 = sampler down, * = lost dissolved samples). Particulate fraction after June, 1991 includes funnel rinse.



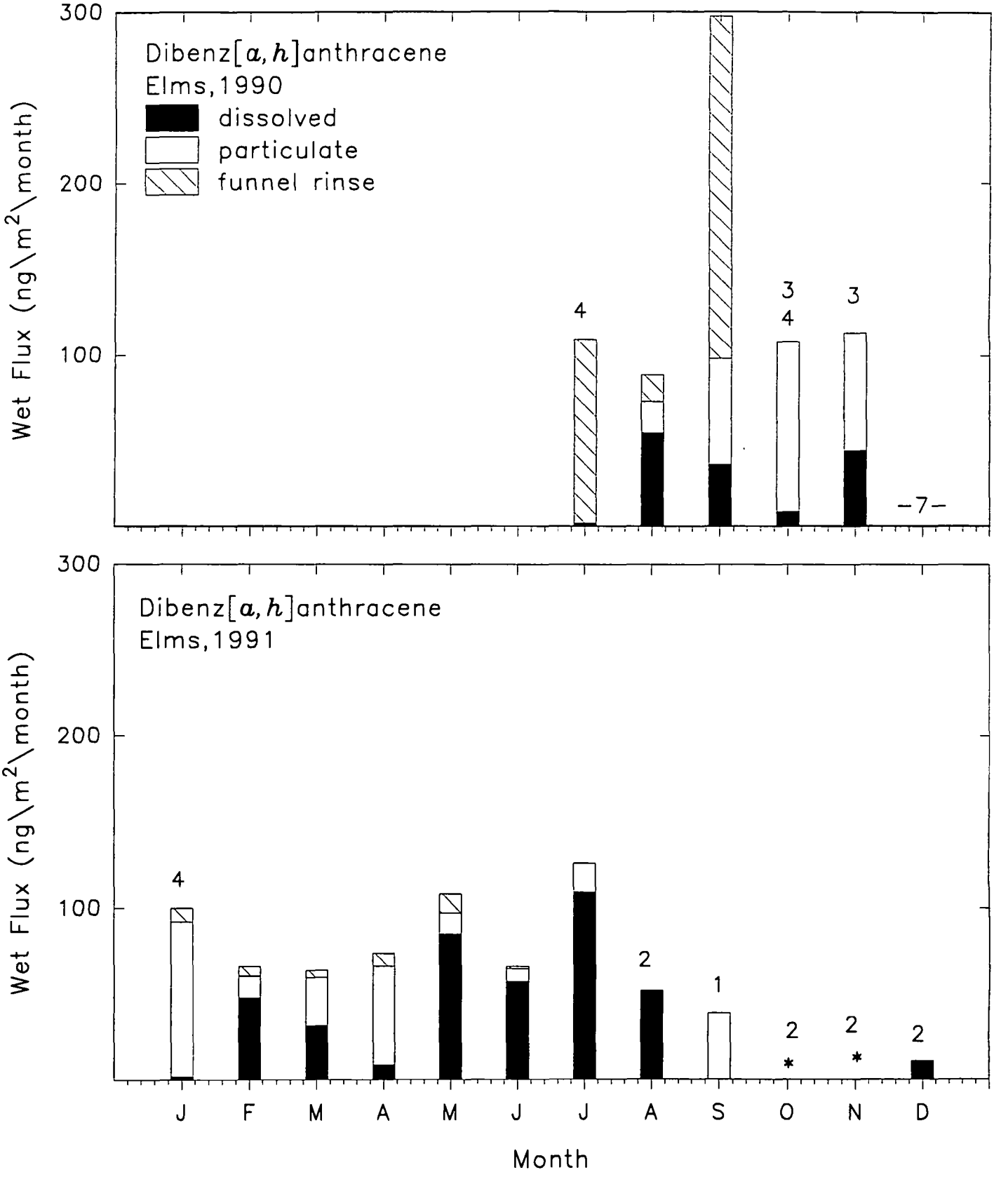
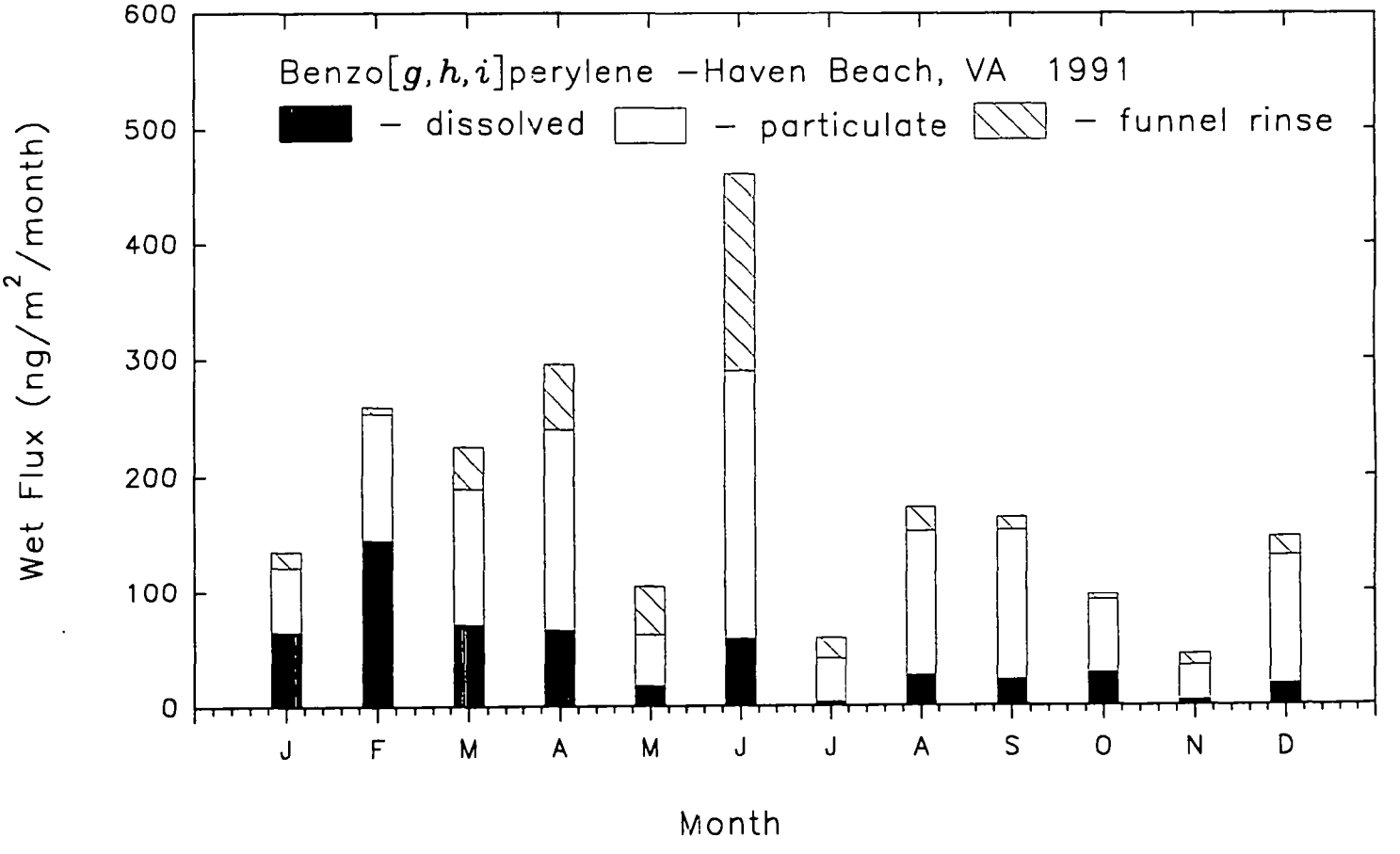

Dibenz[a,h]anthracene
Elms,1990
dissolved
particulate
funnel rinse
Wet Flux (ng\m2\month)
300
200
100
4
3
4
3
-7-
Dibenz[a,h]anthracene
Elms,1991
Wet Flux (ng\m2\month)
300
200
100
4
2
1
2
2
2
J
F
M
A
M
J
J
A
S
O
N
D
Month

Figure IV.1.58. Benzo[*g,h,i*]perylene wet depositional fluxes measured at the Elms and Haven Beach sites. (1=not quantifiable in dissolved phase, 2=not quantifiable on filter, 3=not quantifiable in funnel, 4=not detected in dissolved phase, 5=not detected on filter, 6=not detected in funnel, 7 = sampler down, * = lost dissolved samples). Particulate fraction after June, 1991 includes funnel rinse.



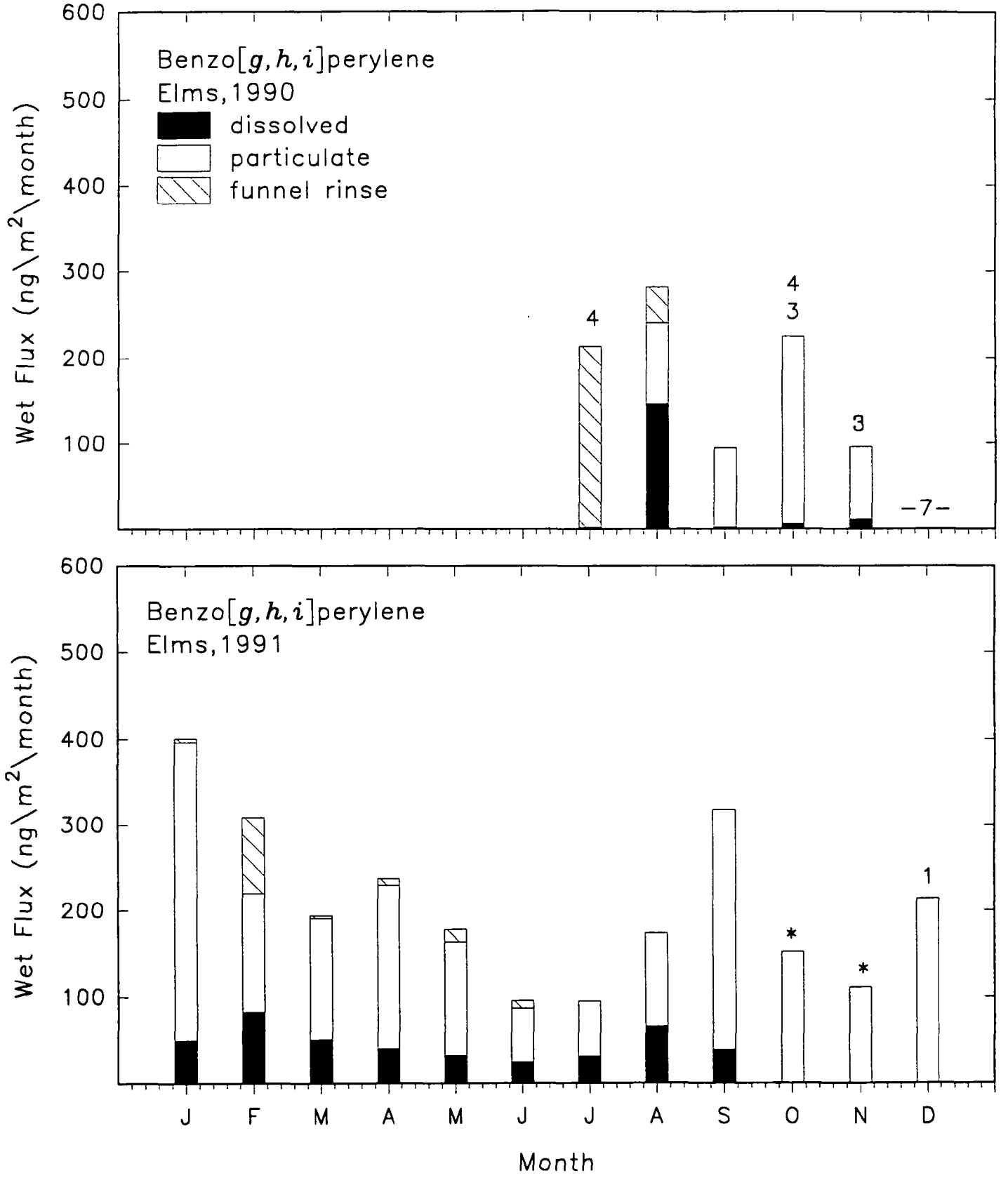
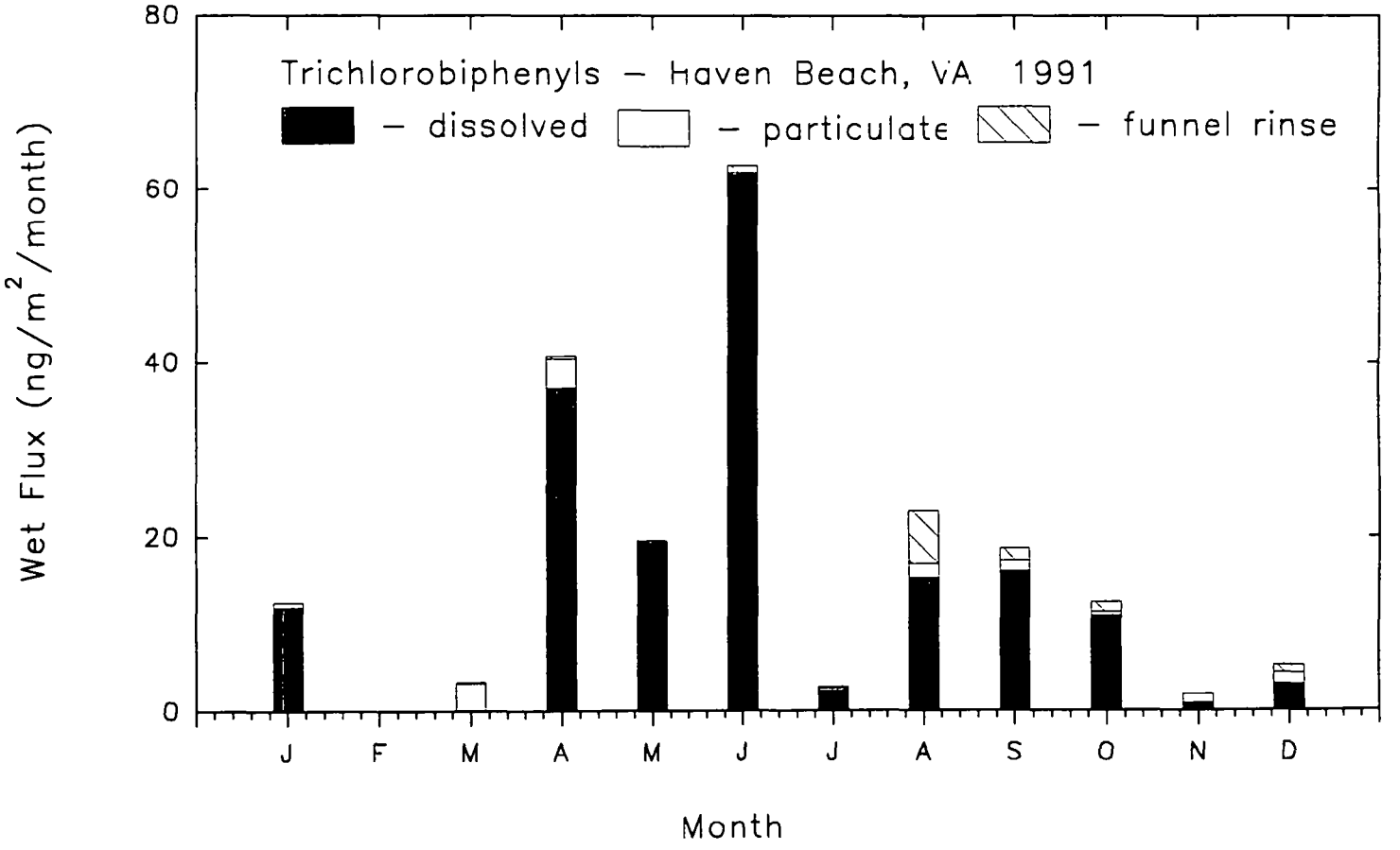

Benzo[g,h,i]perylene
Elms,1990
dissolved
particulate
funnel rinse
Wet Flux (ng\m2\month)
600
500
400
300
200
100
4
4
3
3
-7-
Benzo[g,h,i]perylene
Elms,1991
Wet Flux (ng\m2\month)
600
500
400
300
200
100
1
*
*
J
F
M
A
M
J
J
A
S
O
N
D
Month

Figure IV.1.59. Trichlorobiphenyl wet depositional fluxes measured at the Elms and Haven Beach sites. (1=not quantifiable in dissolved phase, 2=not quantifiable on filter, 3=not quantifiable in funnel, 4=not detected in dissolved phase, 5=not detected on filter, 6=not detected in funnel, 7=not analyzed, 8 = sampler down, * = lost dissolved samples). Particulate fraction after June, 1991 includes funnel rinse.



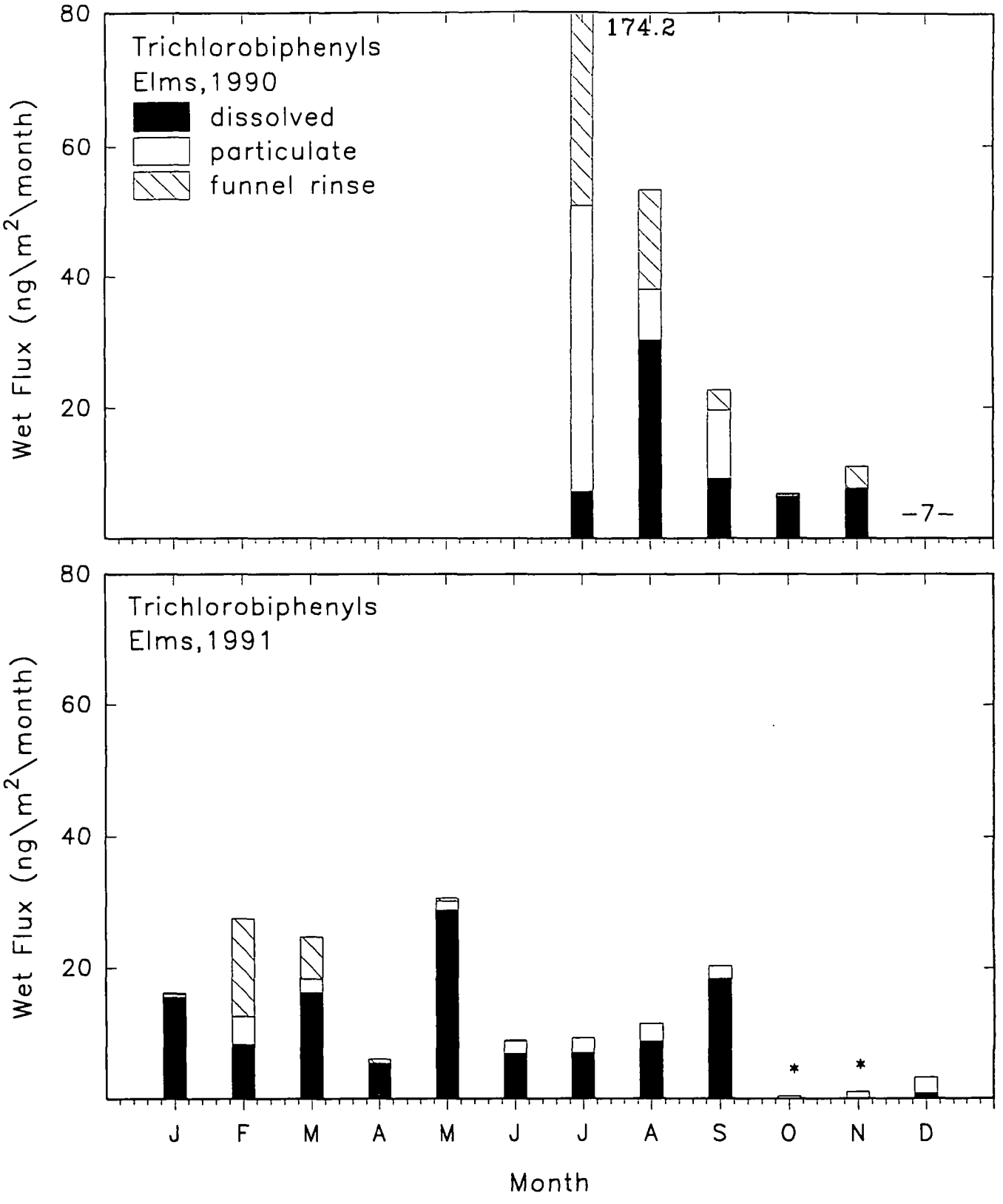
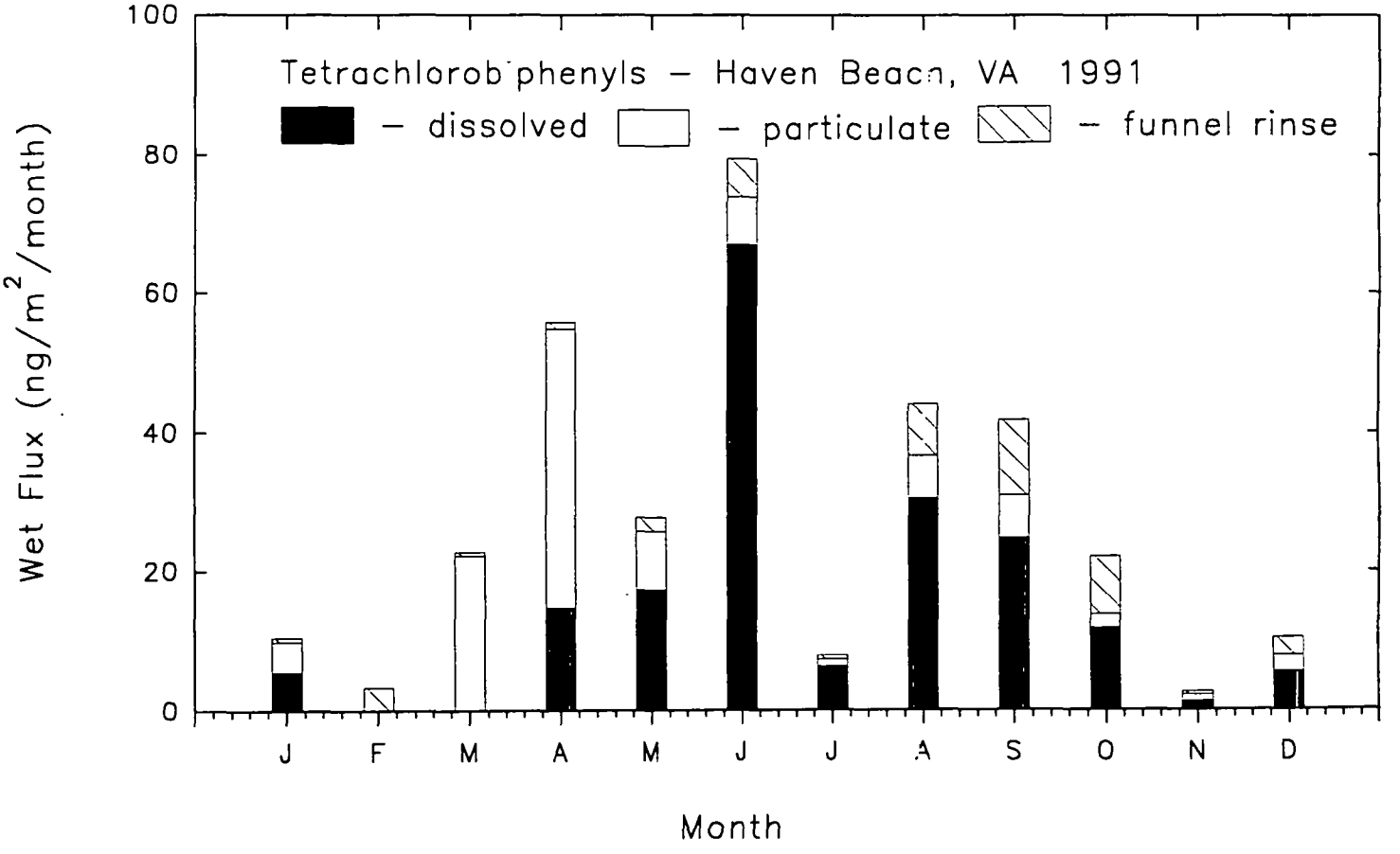

Trichlorobiphenyls
Elms,1990
dissolved
particulate
funnel rinse
174.2
-7-
Wet Flux (ng\m2\month)
80
60
40
20
Trichlorobiphenyls
Elms,1991
Wet Flux (ng\m2\month)
80
60
40
20
J
F
M
A
M
J
J
A
S
O
N
D
Month

Figure IV.1.60. Tetrachlorobiphenyl wet depositional fluxes measured at the Elms and Haven. Beach sites. (1=not quantifiable in dissolved phase, 2=not quantifiable on filter, 3=not quantifiable in funnel, 4=not detected in dissolved phase, 5=not detected on filter, 6=not detected in funnel, 7=not analyzed, 8 = sampler down, * = lost dissolved samples). Particulate fraction after June, 1991 includes funnel rinse.



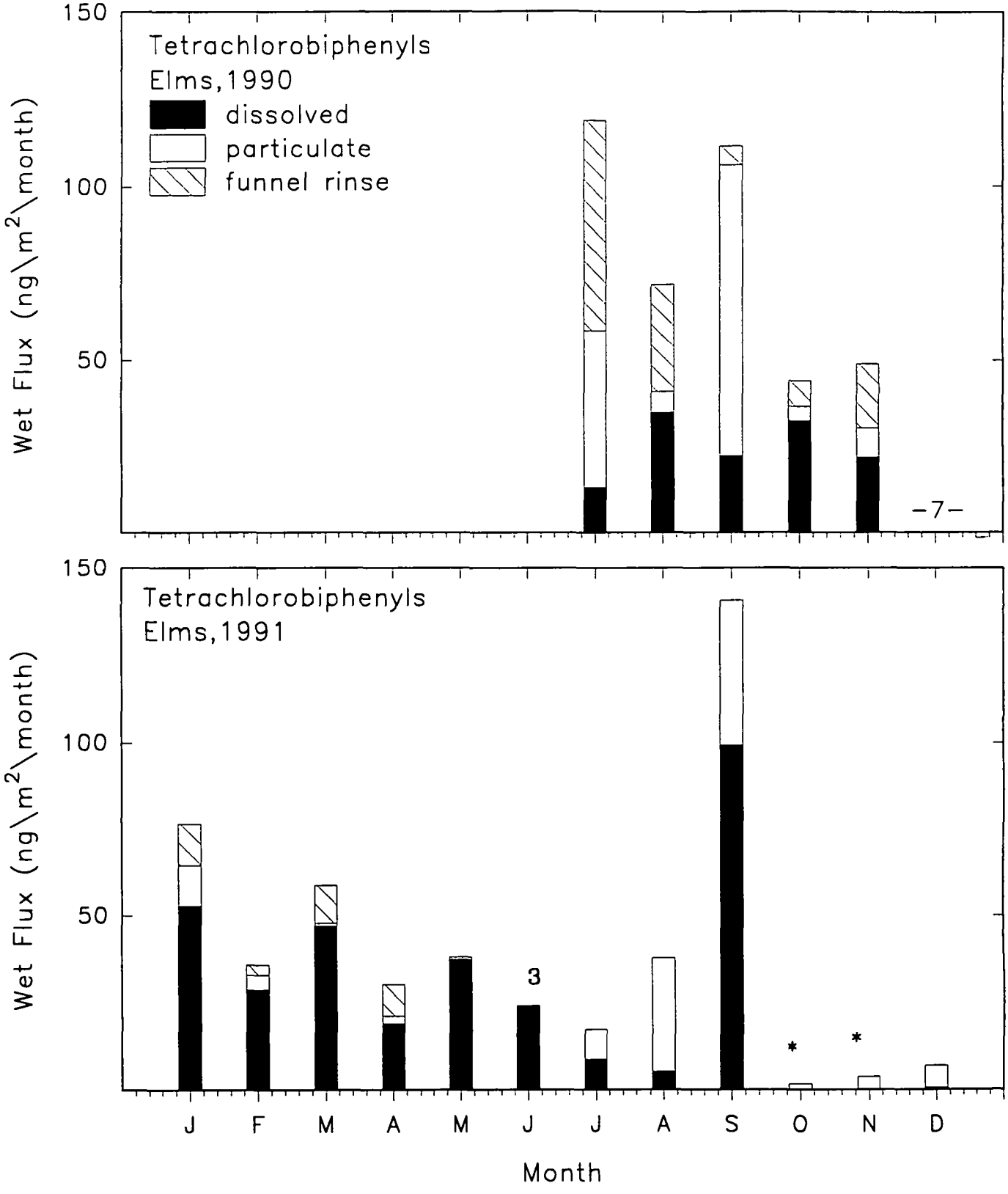
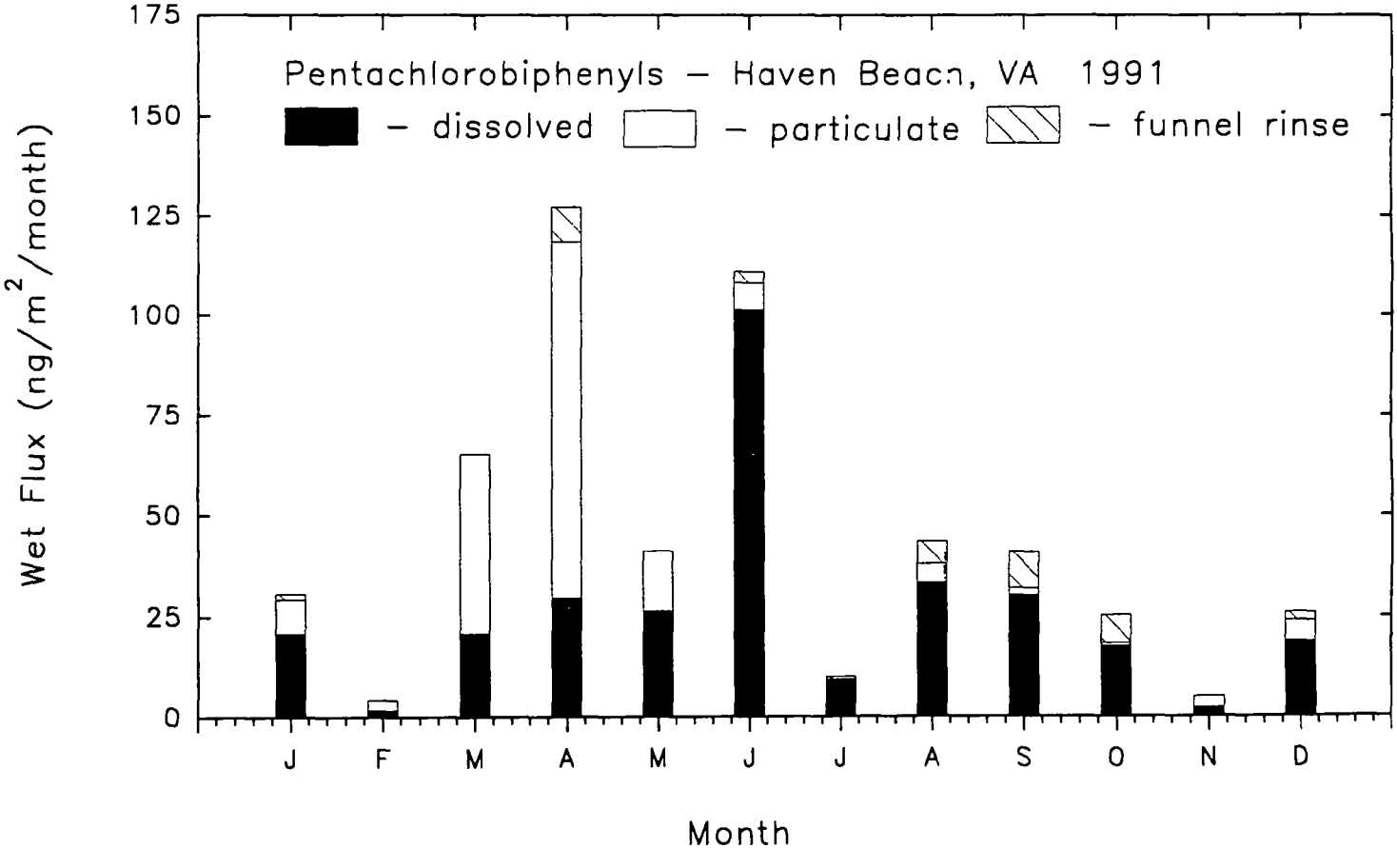

Tetrachlorobiphenyls
Elms,1990
dissolved
particulate
funnel rinse
Wet Flux (ng\m2\month)
150
100
50
-7-
Tetrachlorobiphenyls
Elms,1991
Wet Flux (ng\m2\month)
150
100
50
3
*
*
J
F
M
A
M
J
J
A
S
O
N
D
Month

Figure IV.1.61. Pentachlorobiphenyl wet depositional fluxes measured at the Elms and Haven Beach sites. (1=not quantifiable in dissolved phase, 2=not quantifiable on filter, 3=not quantifiable in funnel, 4=not detected in dissolved phase, 5=not detected on filter, 6=not detected in funnel, 7=not analyzed, 8 = sampler down, * = lost dissolved samples). Particulate fraction after June, 1991 includes funnel rinse.



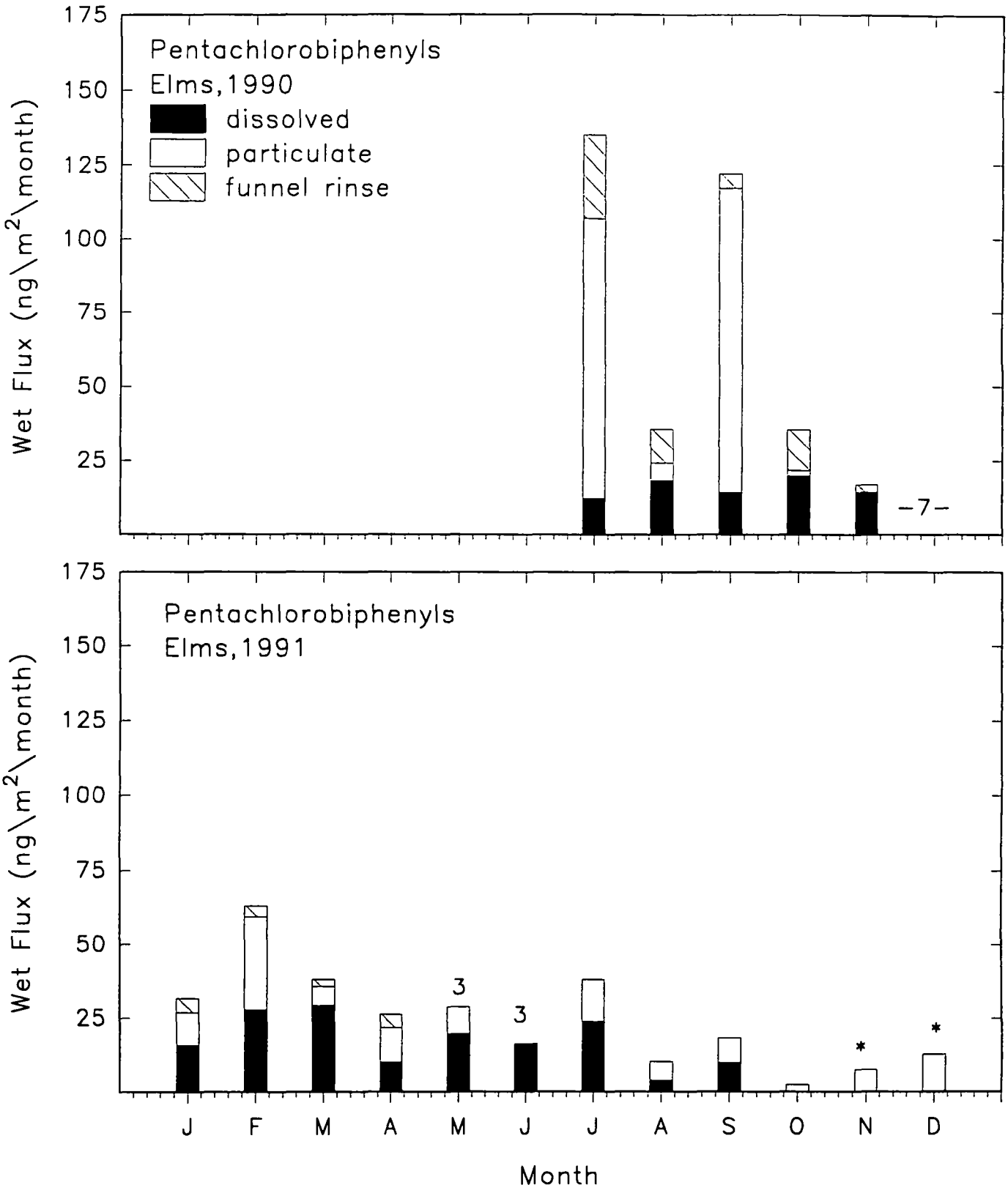
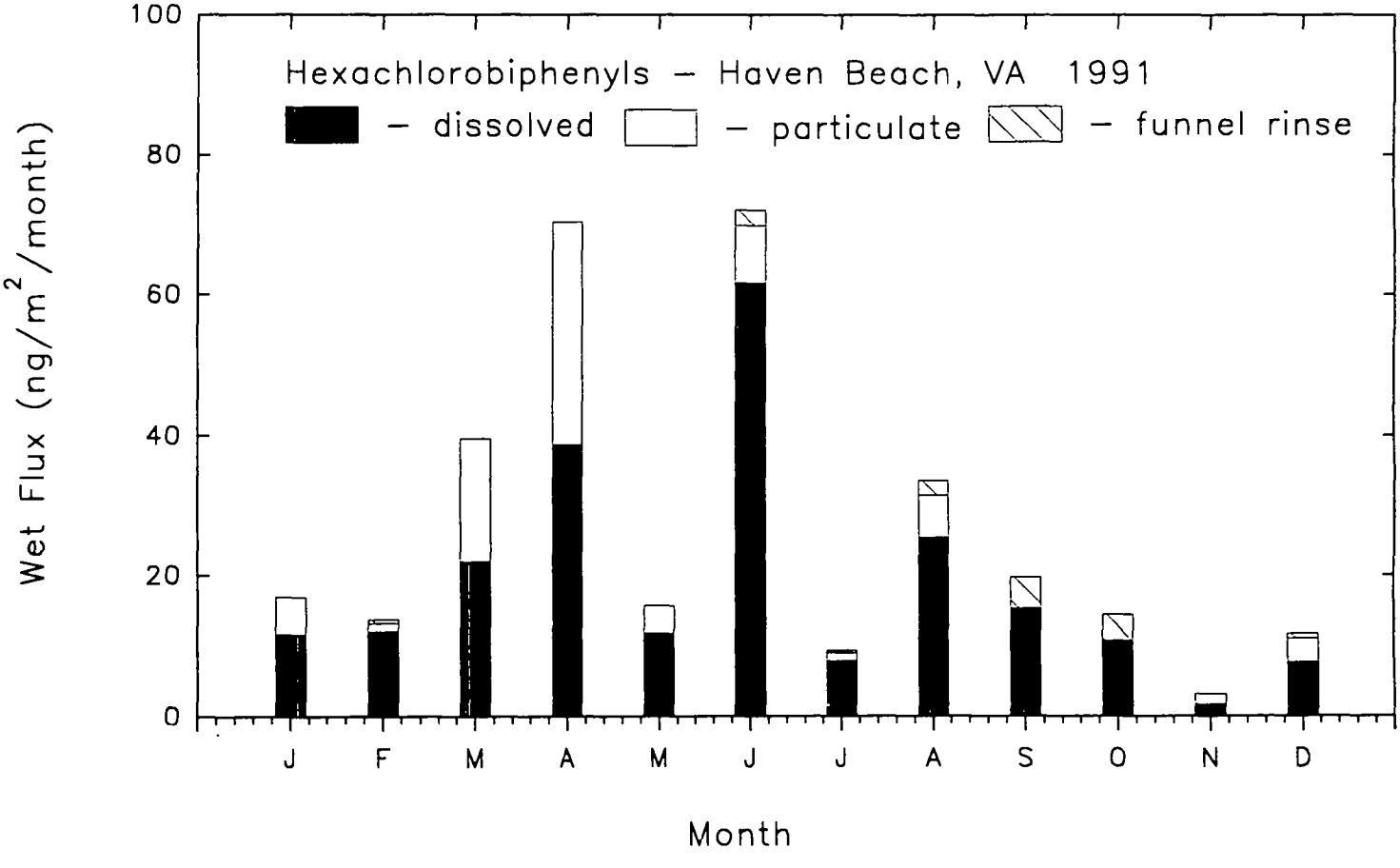

Pentachlorobiphenyls
Elms,1990
dissolved
particulate
funnel rinse
Wet Flux (ng\m2\month)
175
150
125
100
75
50
25
-7-
Pentachlorobiphenyls
Elms,1991
3
3
*
*
J
F
M
A
M
J
J
A
S
O
N
D
Month

Figure IV.1.62. Hexachlorobiphenyl wet depositional fluxes measured at the Elms and Haven Baech sites. (1=not quantifiable in dissolved phase, 2=not quantifiable on filter, 3=not quantifiable in funnel, 4=not detected in dissolved phase, 5=not detected on filter, 6=not detected in funnel, 7=not analyzed, 8 = sampler down, * = lost dissolved samples). Particulate fraction after June, 1991 includes funnel rinse.



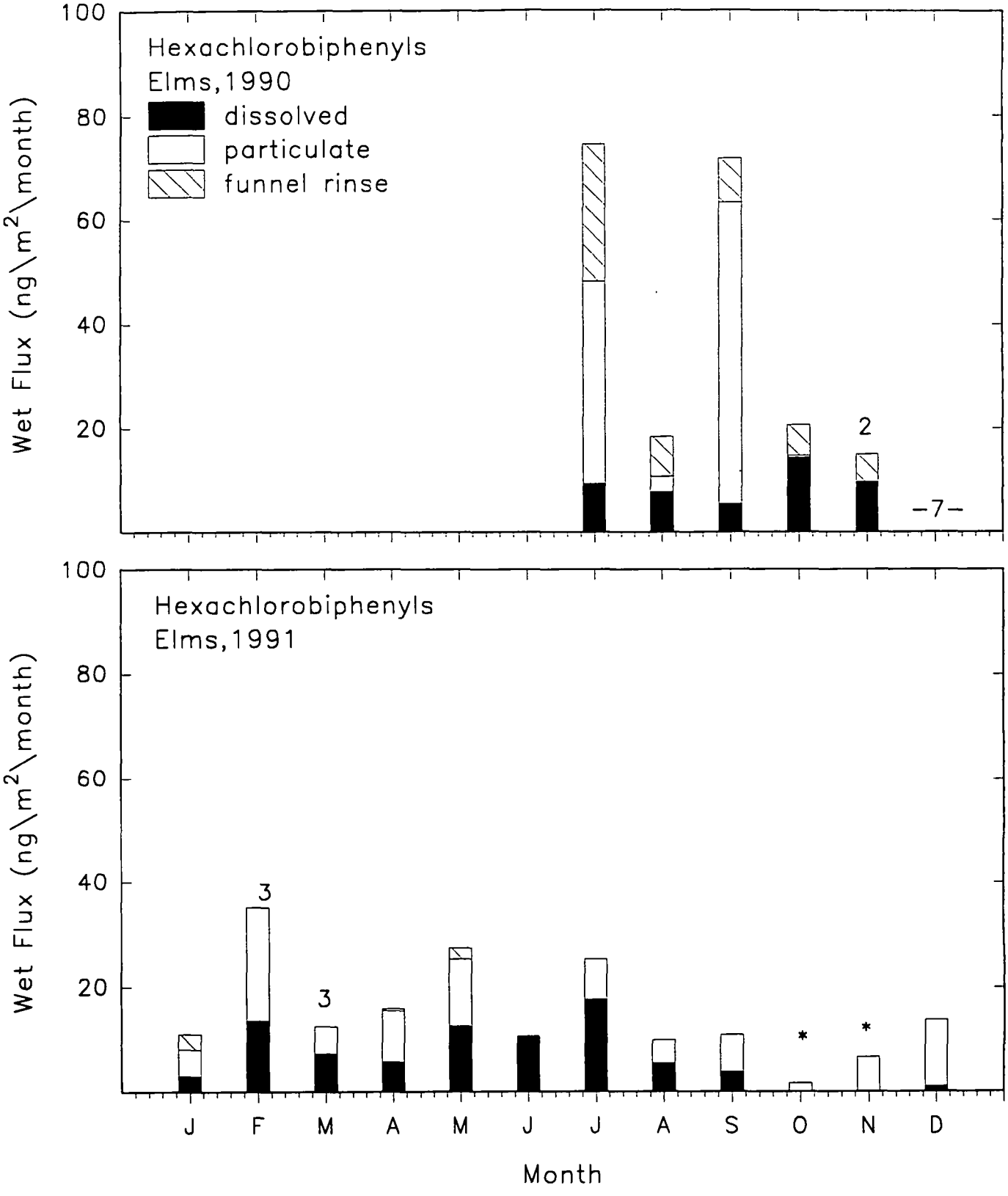
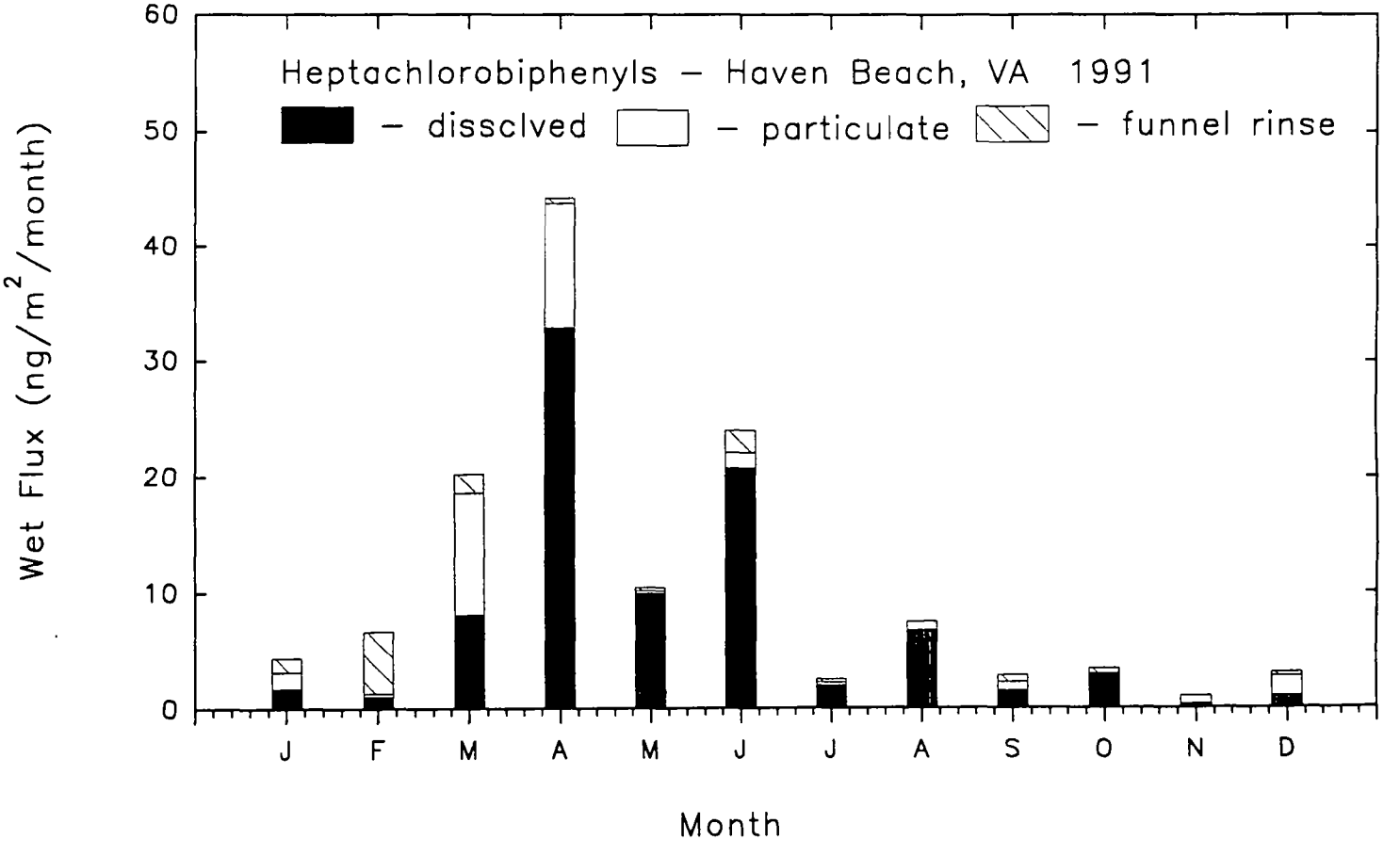

Hexachlorobiphenyls
Elms,1990
dissolved
particulate
funnel rinse
Wet Flux (ng\m2\month)
100
80
60
40
20
2
-7-
Hexachlorobiphenyls
Elms,1991
3
3
*
*
J
F
M
A
M
J
J
A
S
O
N
D
Month

Figure IV.1.63. Heptachlorobiphenyl wet depositional fluxes measured at the Elms and Haven Beach sites. (1=not quantifiable in dissolved phase, 2=not quantifiable on filter, 3=not quantifiable in funnel, 4=not detected in dissolved phase, 5=not detected on filter, 6=not detected in funnel, 7= not analyzed, 8 = sampler down, * = lost dissolved samples). Particulate fraction after June, 1991 includes funnel rinse.



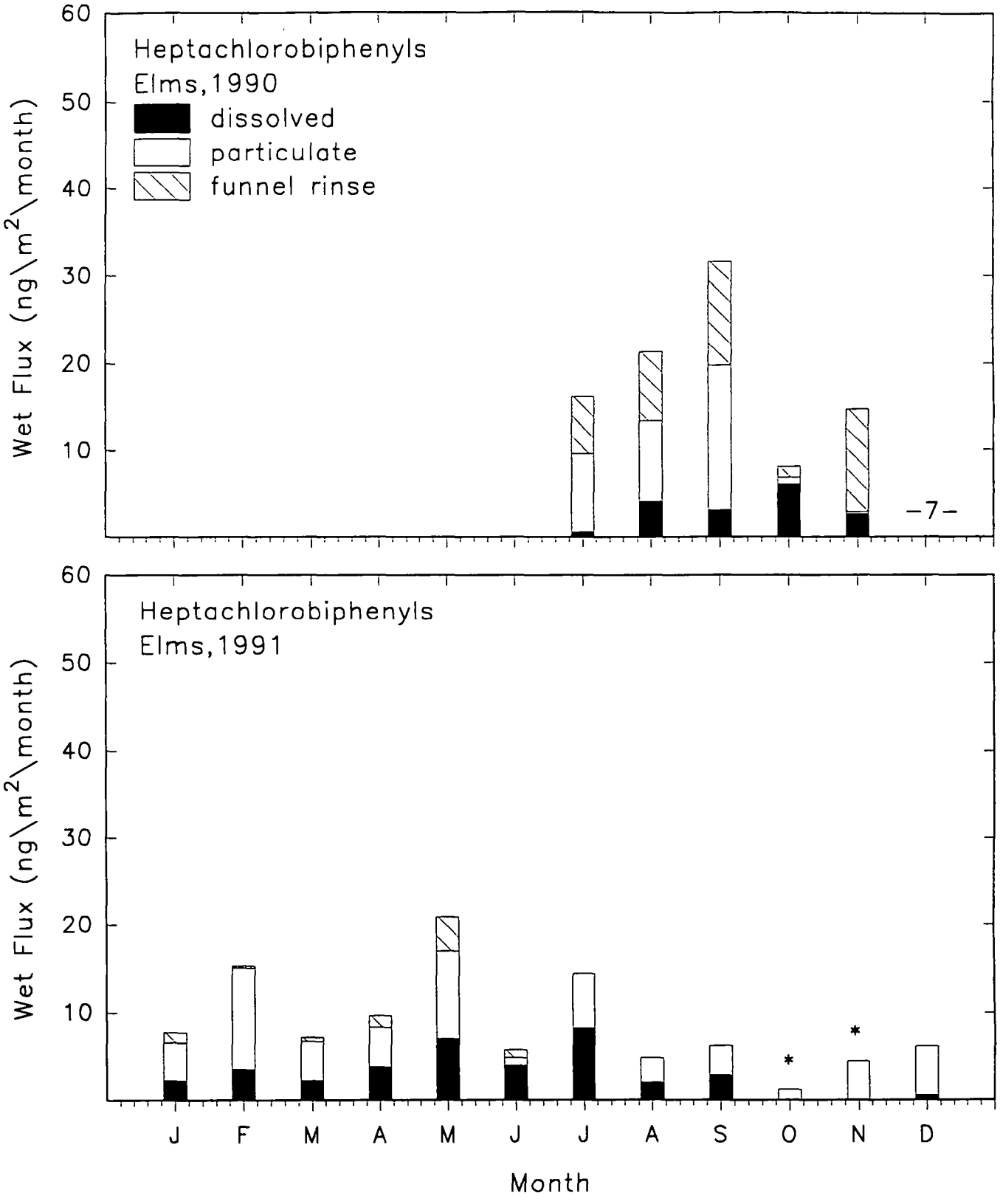
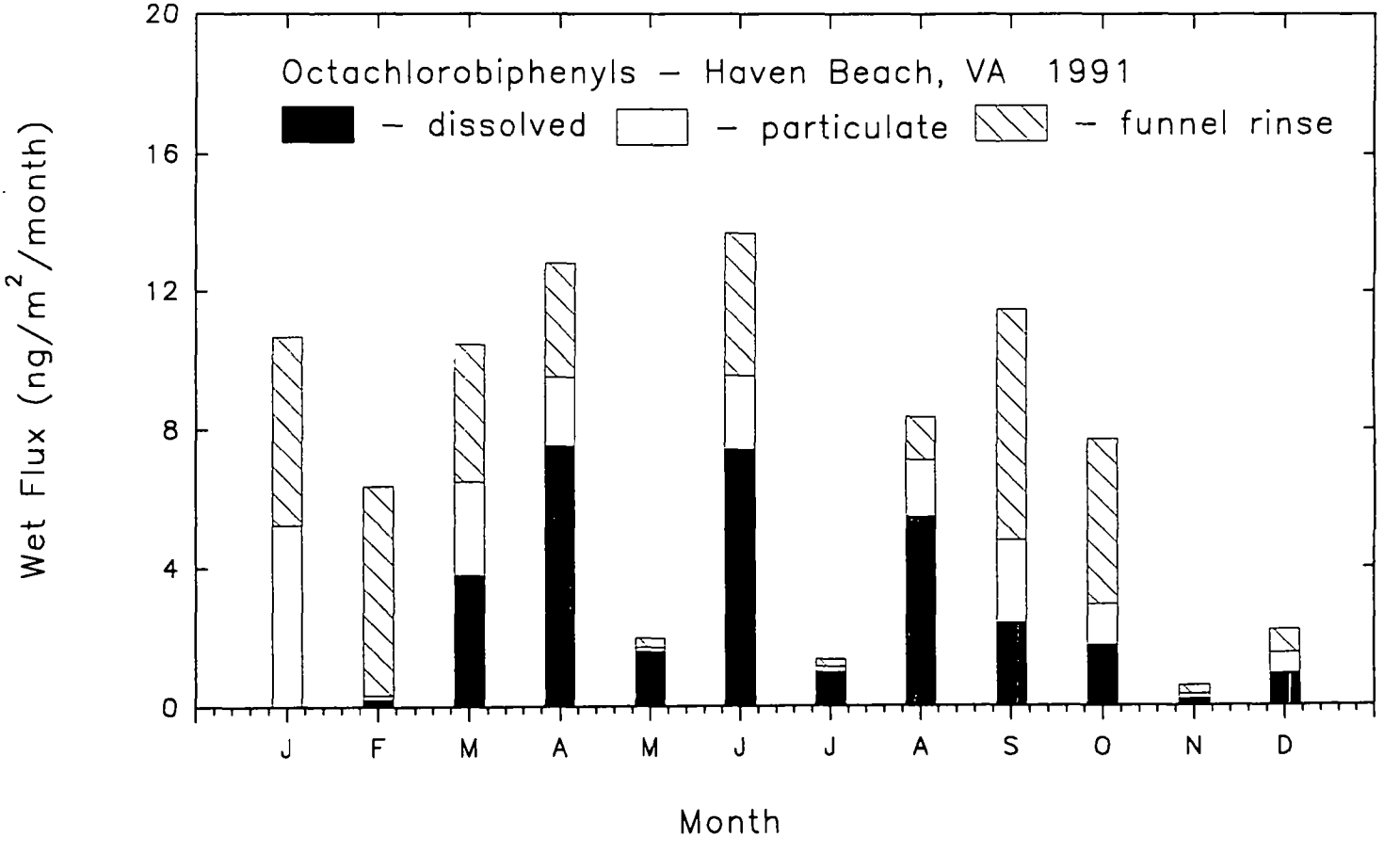

Heptachlorobiphenyls
Elms,1990
dissolved
particulate
funnel rinse
Wet Flux (ng\m2\month)
60
50
40
30
20
10
-7-
Heptachlorobiphenyls
Elms,1991
Wet Flux (ng\m2\month)
60
50
40
30
20
10
*
*
J
F
M
A
M
J
J
A
S
O
N
D
Month

Figure IV.1.64. Octachlorobiphenyl wet depositional fluxes measured at the Elms and Haven Beach sites. (1=not quantifiable in dissolved phase, 2=not quantifiable on filter, 3=not quantifiable in funnel, 4=not detected in dissolved phase, 5=not detected on filter, 6=not detected in funnel, 7=not analyzed, 8 = sampler down, * = lost dissolved samples). Particulate fraction after June, 1991 includes funnel rinse.



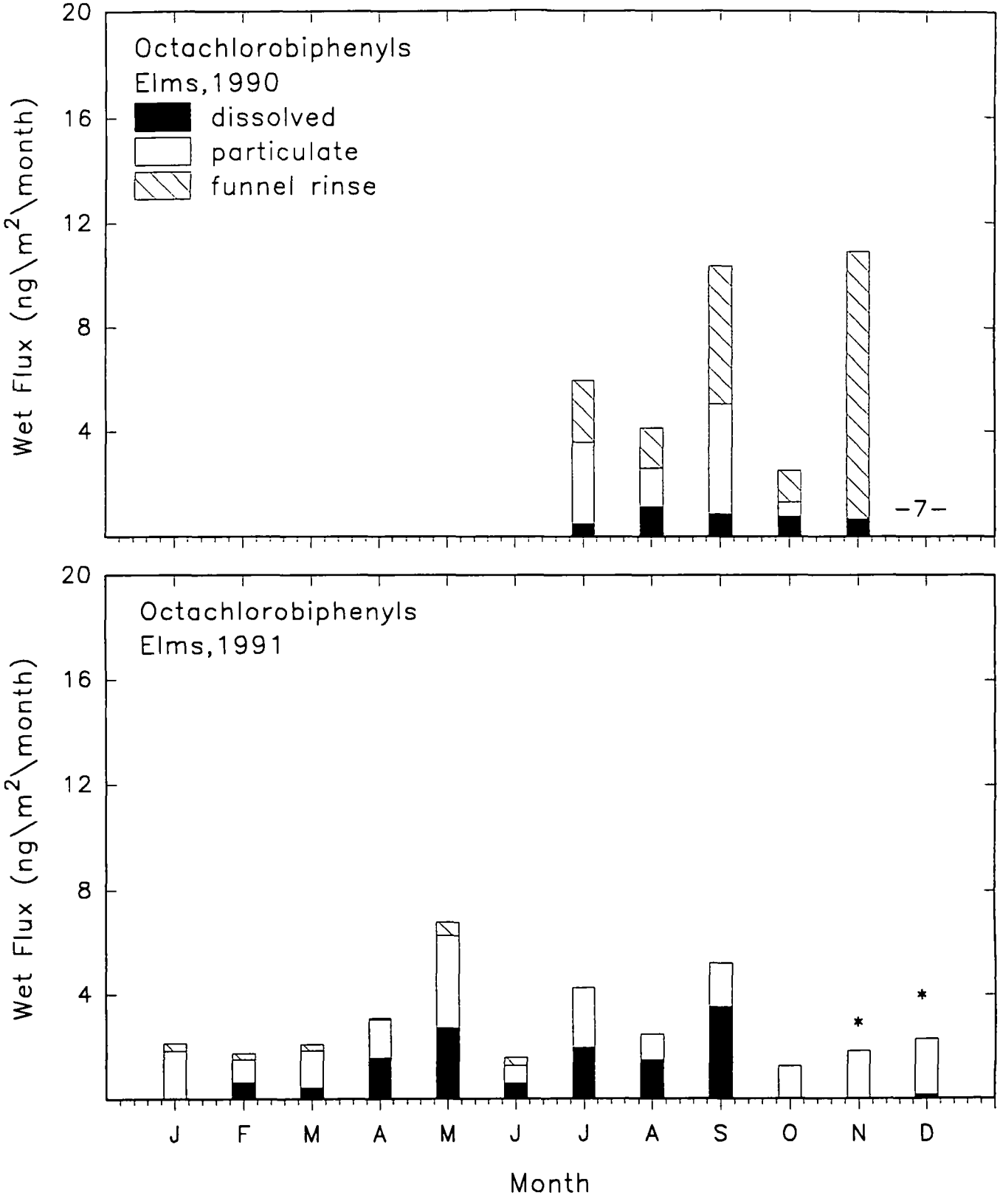
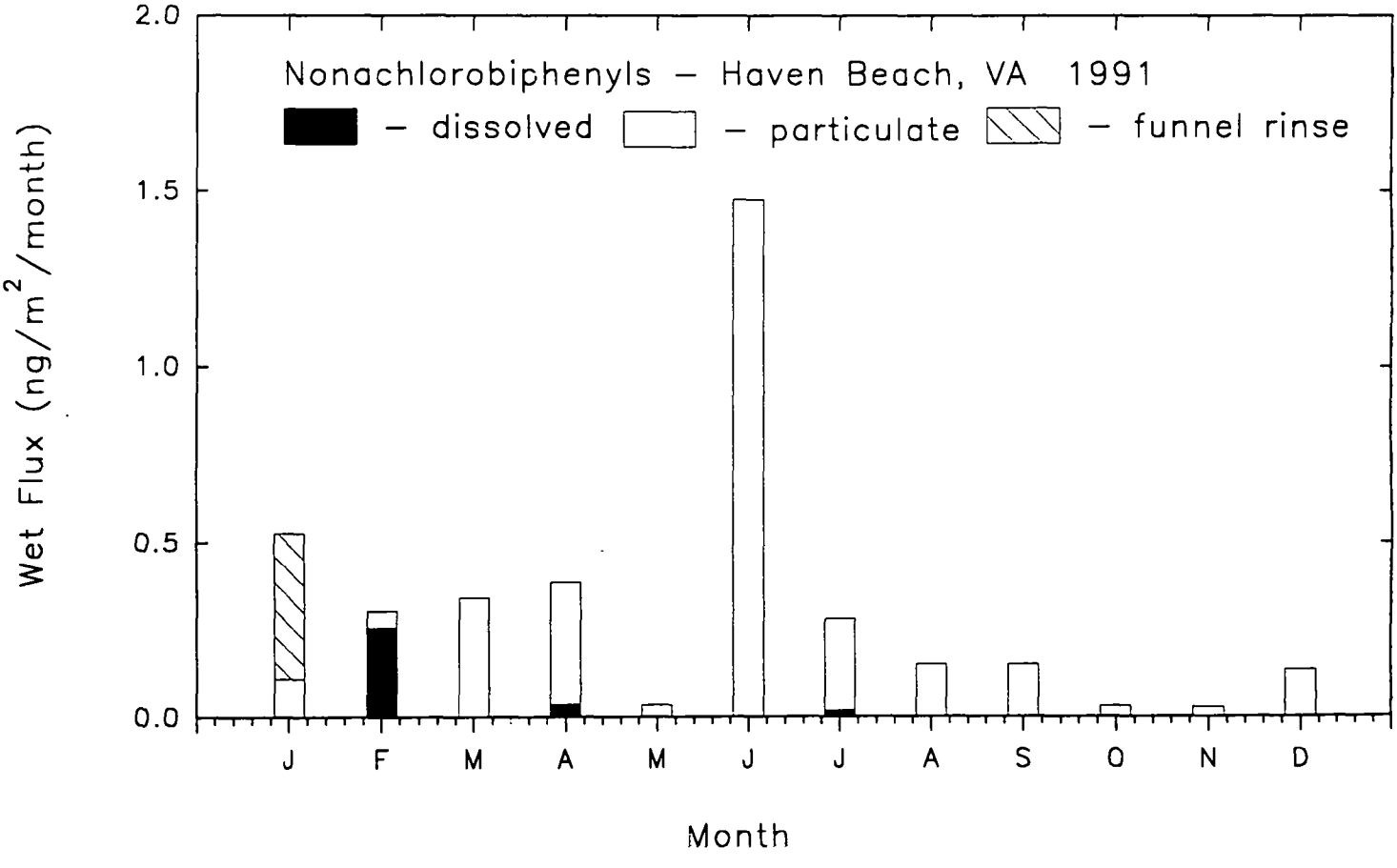

Octachlorobiphenyls
Elms,1990
dissolved
particulate
funnel rinse
Wet Flux (ng\m2\month)
20
16
12
8
4
-7-
Octachlorobiphenyls
Elms,1991
Wet Flux (ng\m2\month)
20
16
12
8
4
*
*
J
F
M
A
M
J
J
A
S
O
N
D
Month

Figure IV.1.65. Nonachlorobiphenyl wet depositional fluxes measured at the Elms and Haven Beach sites. (1=rot quantifiable in dissolved phase, 2=not ilter, 3=not quantifiable in funnel, 4=not detected in dissolved phase, 5=not detected cn filter, 6=not detected in funnel, 7=not analyzed, 8 = sampler cown, * = lost dissolved samples). Particulate fraction after June, 1991 includes funnel rinse.



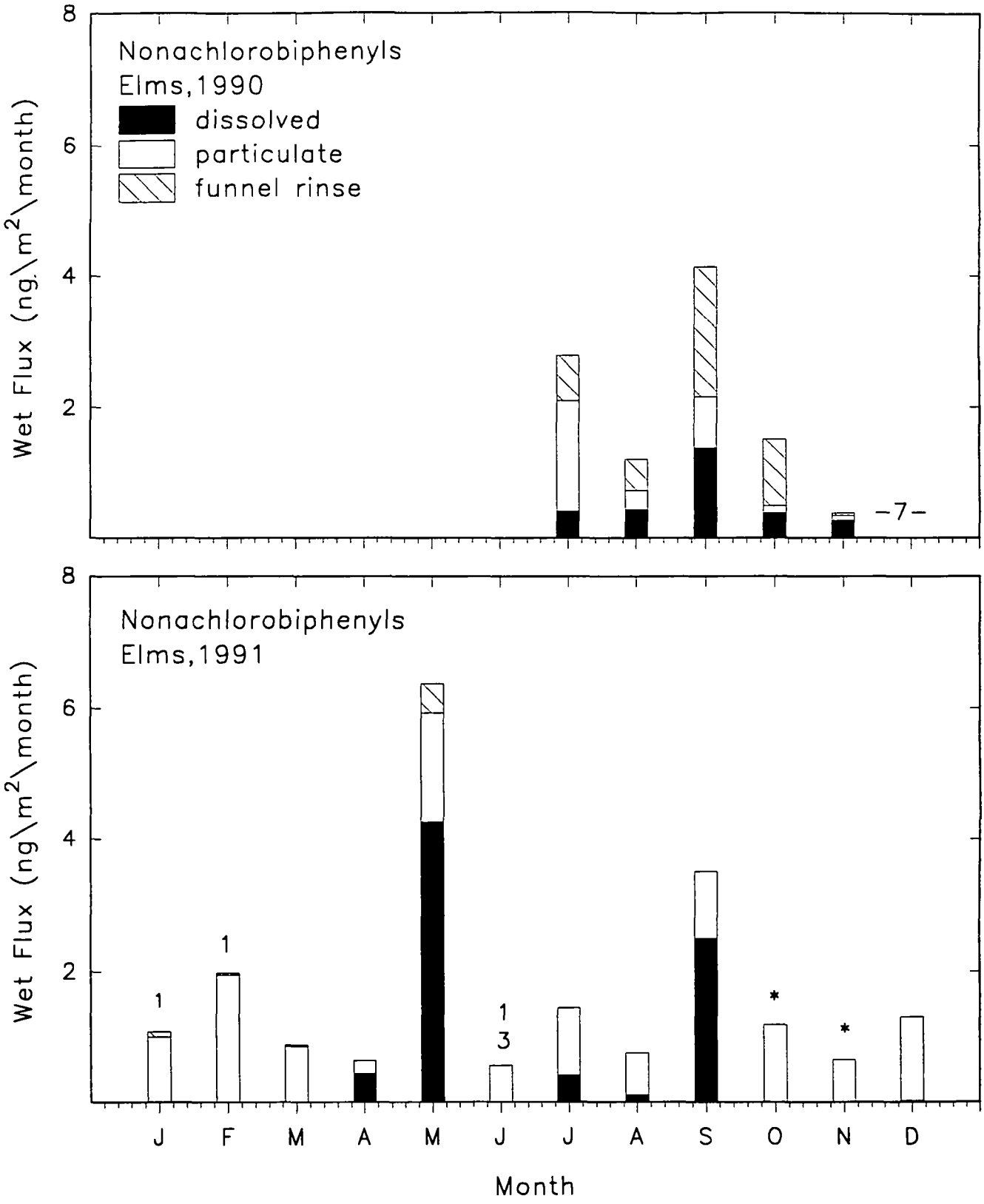
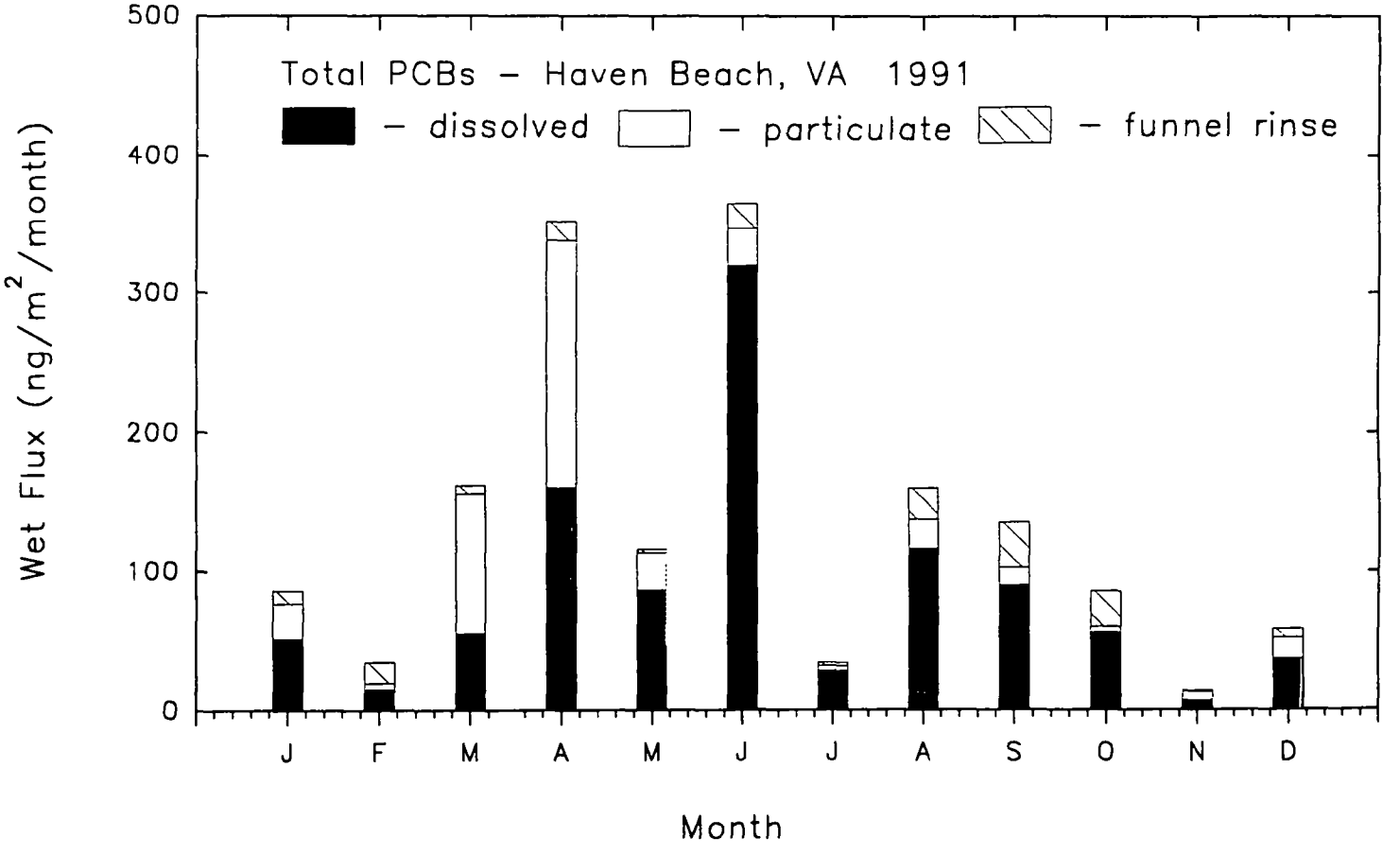
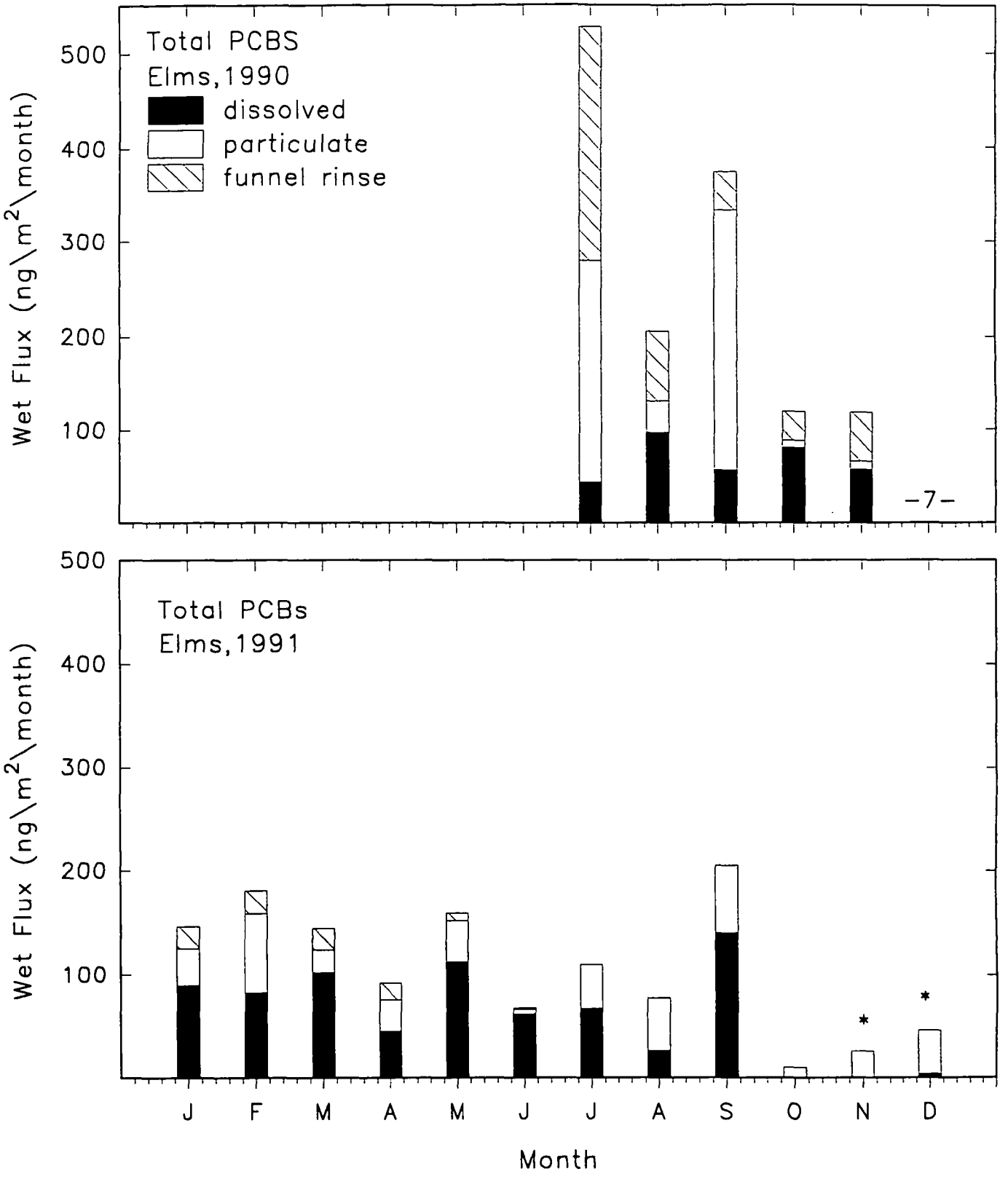

Nonachlorobiphenyls
Elms,1990
dissolved
particulate
funnel rinse
Wet Flux (ng\m2\month)
8
6
4
2
-7-
Nonachlorobiphenyls
Elms,1991
Wet Flux (ng\m2\month)
8
6
4
2
1
1
1
3
*
*
J
F
M
A
M
J
J
A
S
O
N
D
Month

Figure IV.1.66. Total PCBs wet depositional fluxes measured at the Elms and Haven Beach sites. (1=not quantifiable in dissolved phase, 2=not quantifiable on filter, 3=not quantifiable in funnel, 4=not detected in dissolved phase, 5=not detected on filter, 6=not detected in funnel, 7=not analyzed, 8 = sampler down, * = lost dissolved samples). Particulate fraction after June, 1991 includes funnel rinse.




Total PCBS
Elms,1990
dissolved
particulate
funnel rinse
Wet Flux (ng\m2\month)
500
400
300
200
100
-7-
Total PCBs
Elms,1991
Wet Flux (ng\m2\month)
500
400
300
200
100
*
*
J
F
M
A
M
J
J
A
S
O
N
D
Month

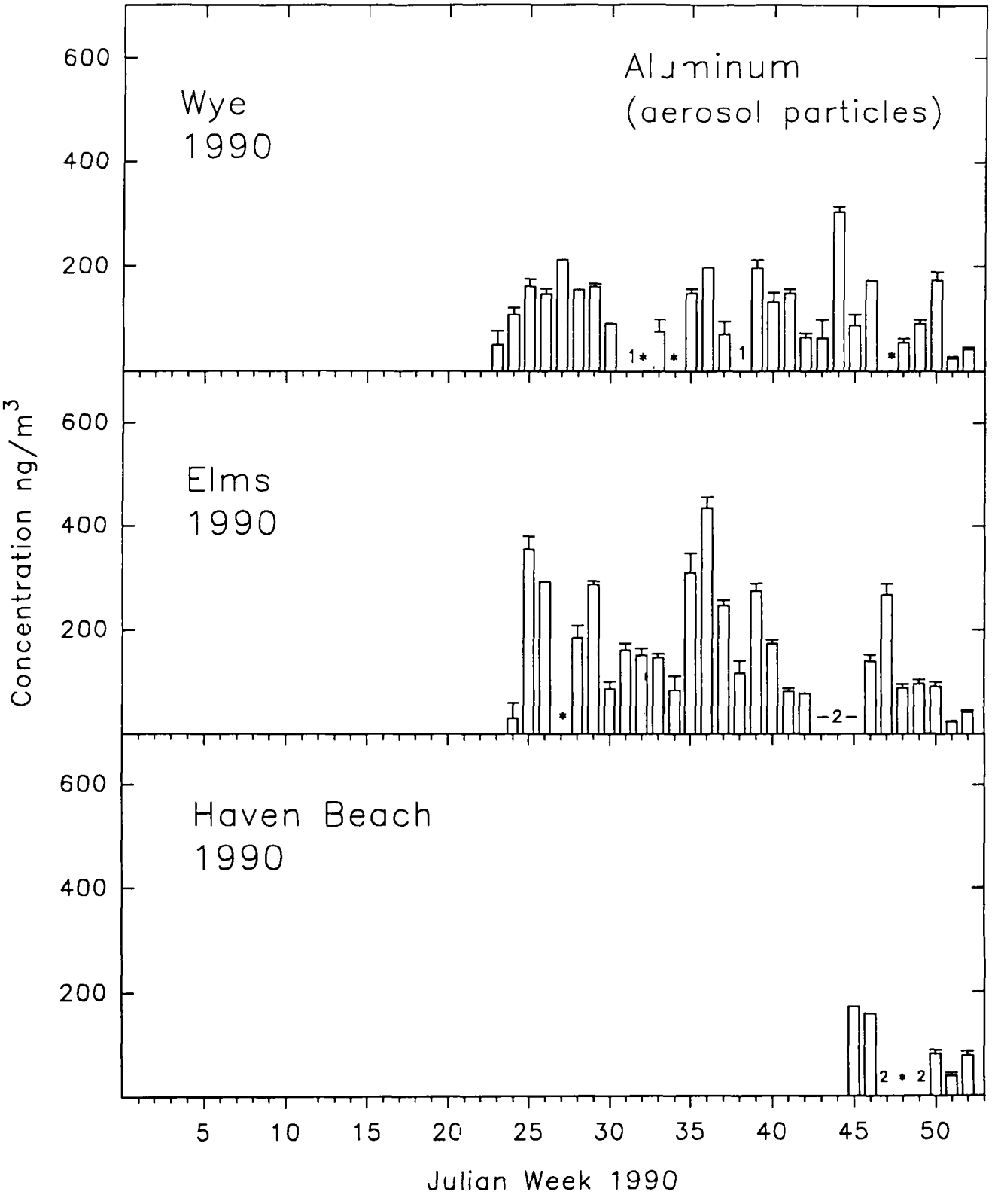


Figure IV.2.1. Aluminum concentrations on aerosol particles, integrated weekly at each CBAD site. 1 = not detected, 2 = pump down, * = outlier/no data.

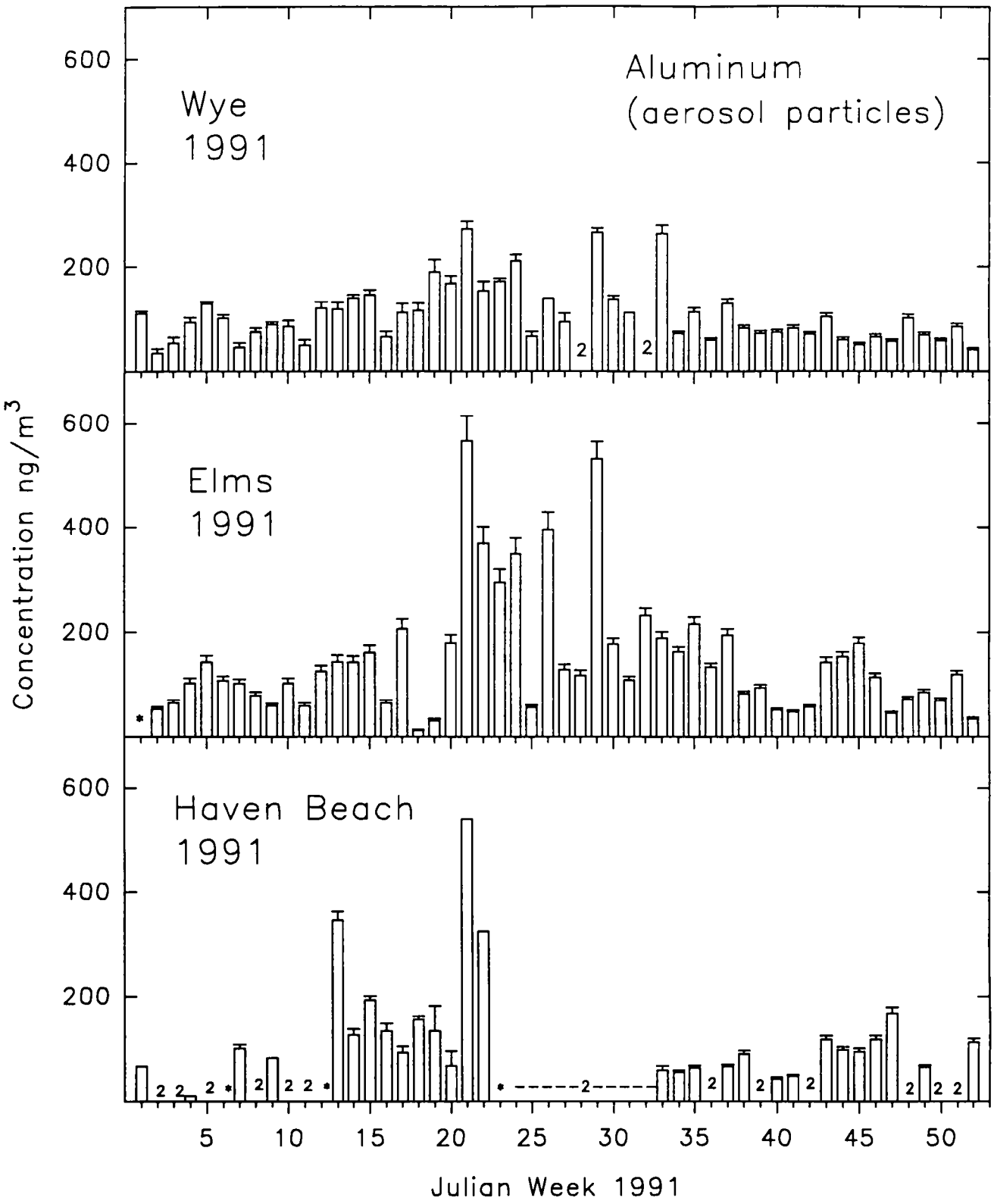


Figure IV.2.1. (Cont'd) Aluminum concentrations on aerosol particles, integrated weekly at each CBAD site. 1 = not detected, 2 = pump down, * = outlier/no data.

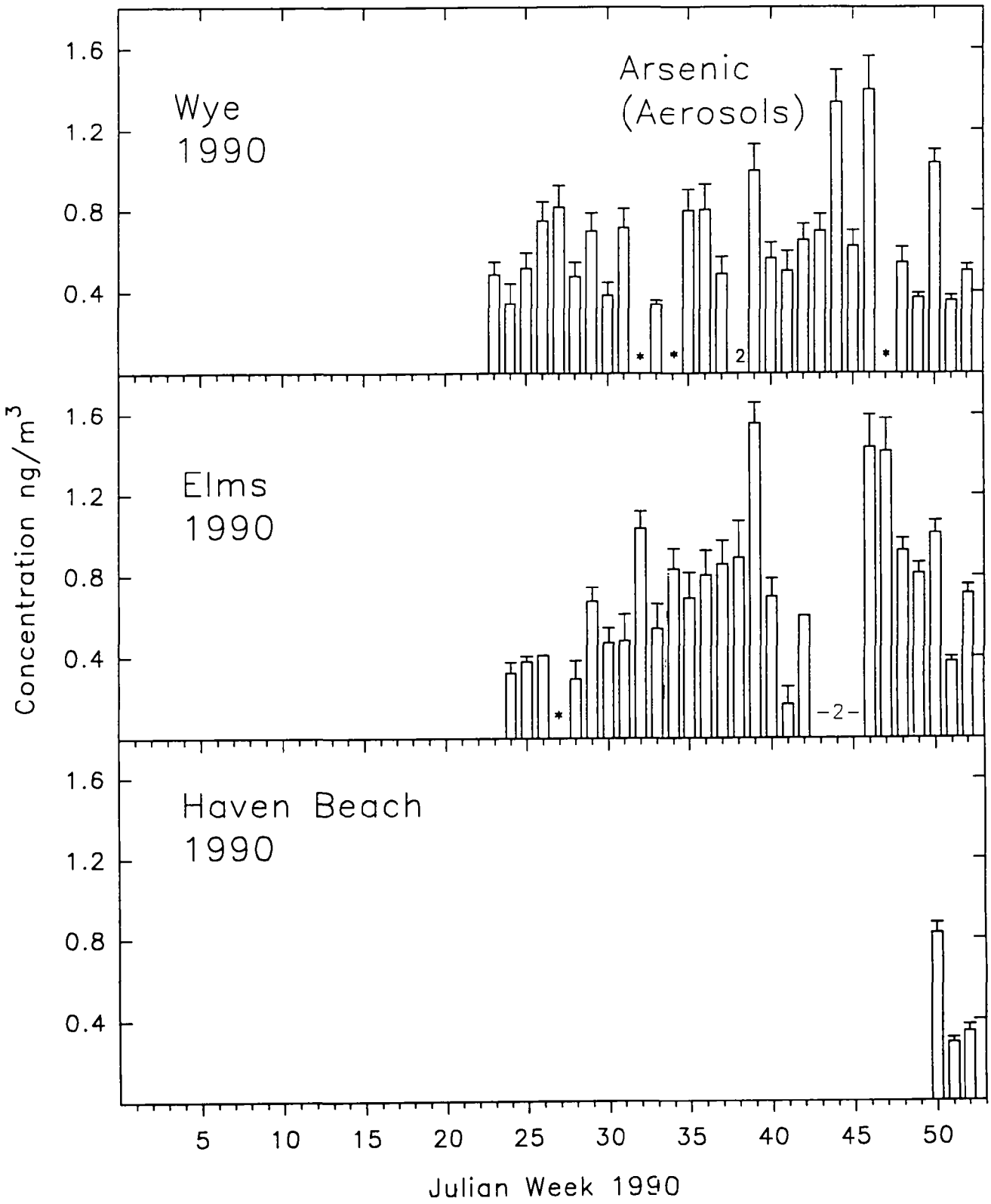


Figure IV.2.2. Arsenic concentrations on aerosols, integrated weekly at each CBAD site. 1 = not detected, 2 = pump down, * = no sample.

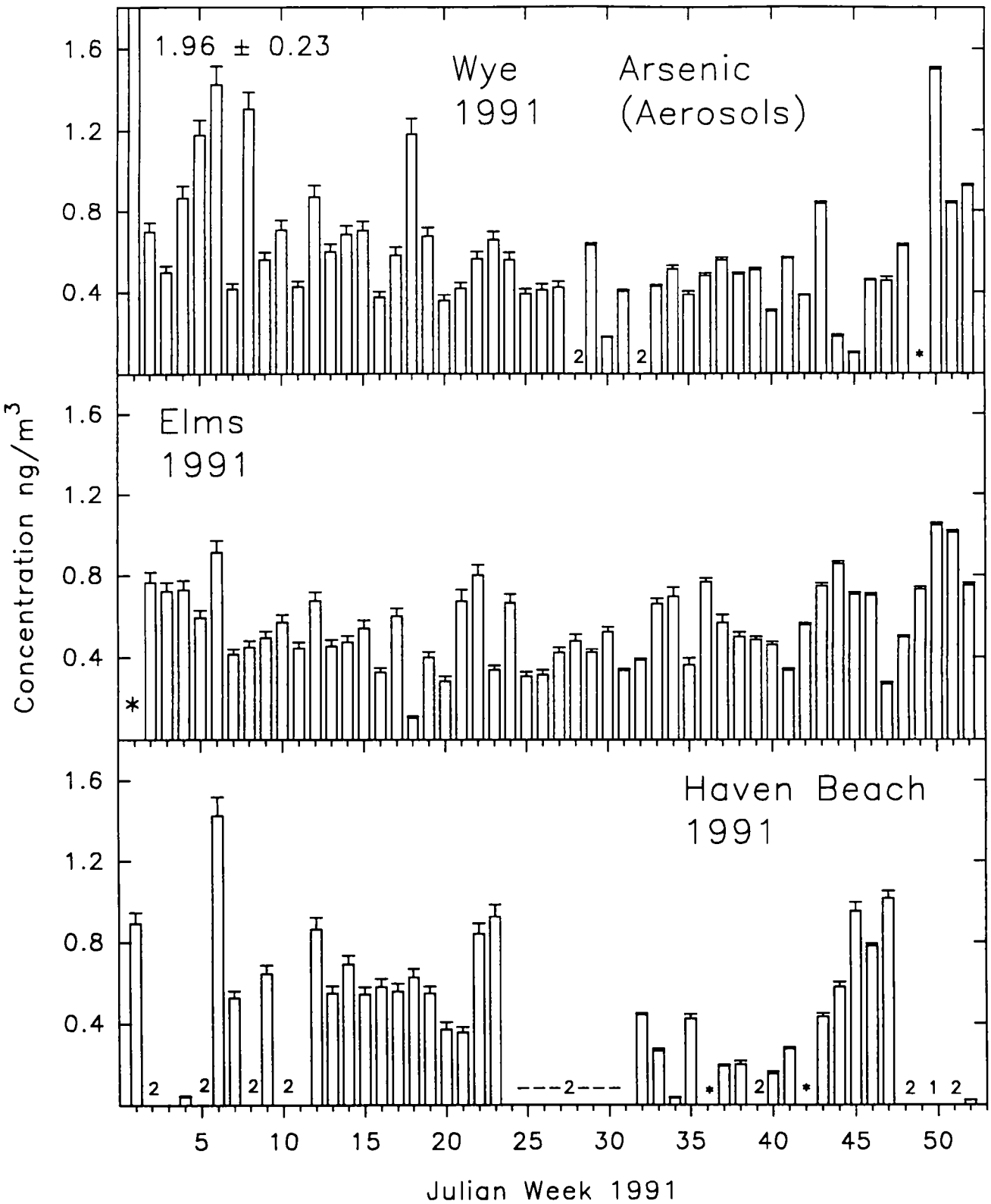


Figure IV.2.2. (Cont'd) Arsenic concentrations on aerosols, integrated weekly at each CBAD site. 1 = not detected, 2 = pump down, * = no sample.

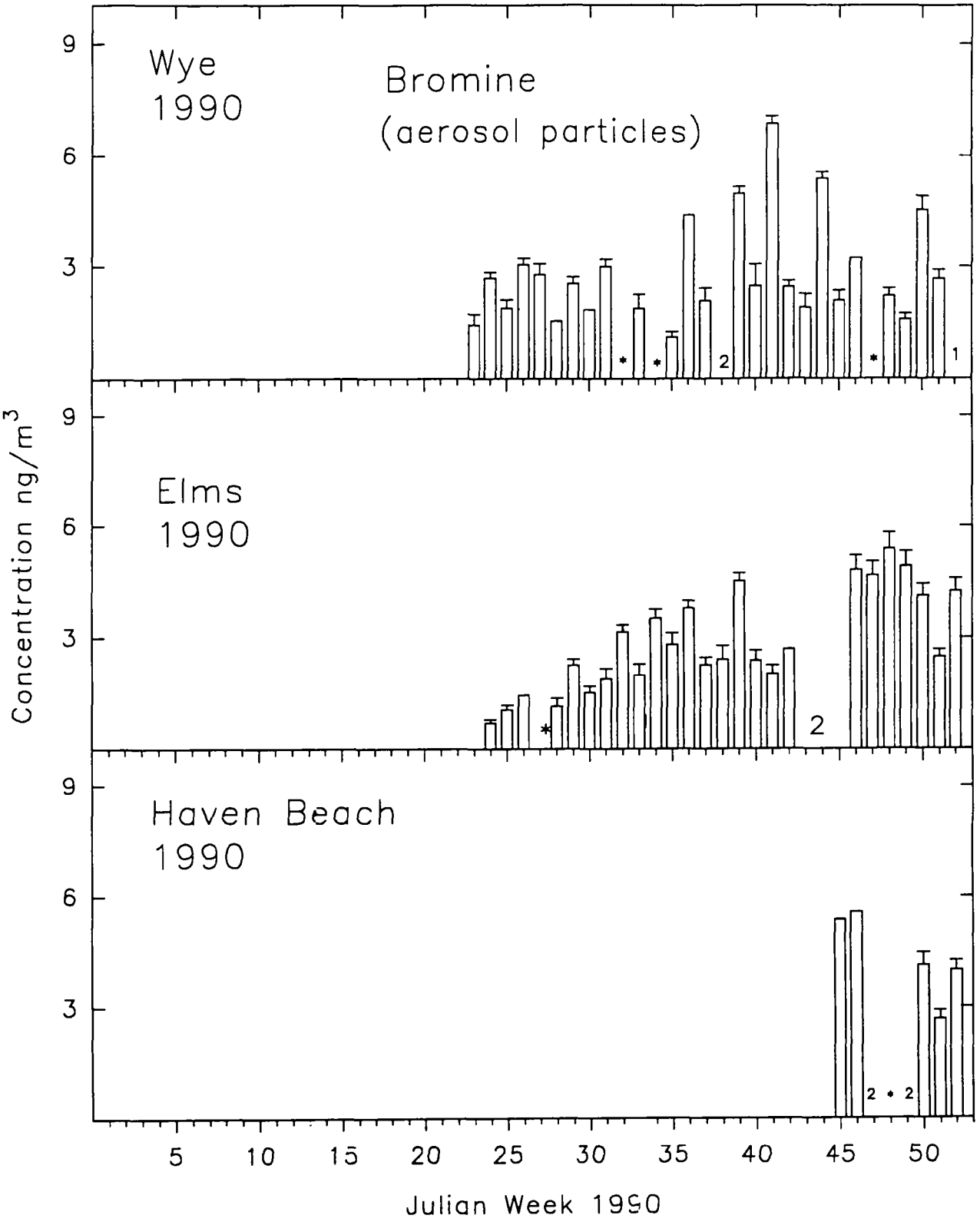


Figure IV.2.3. Bromine concentrations on aerosol particles, integrated weekly at each CBAD site. 1 = not detected, 2 = pump down, * = outlier/no data.

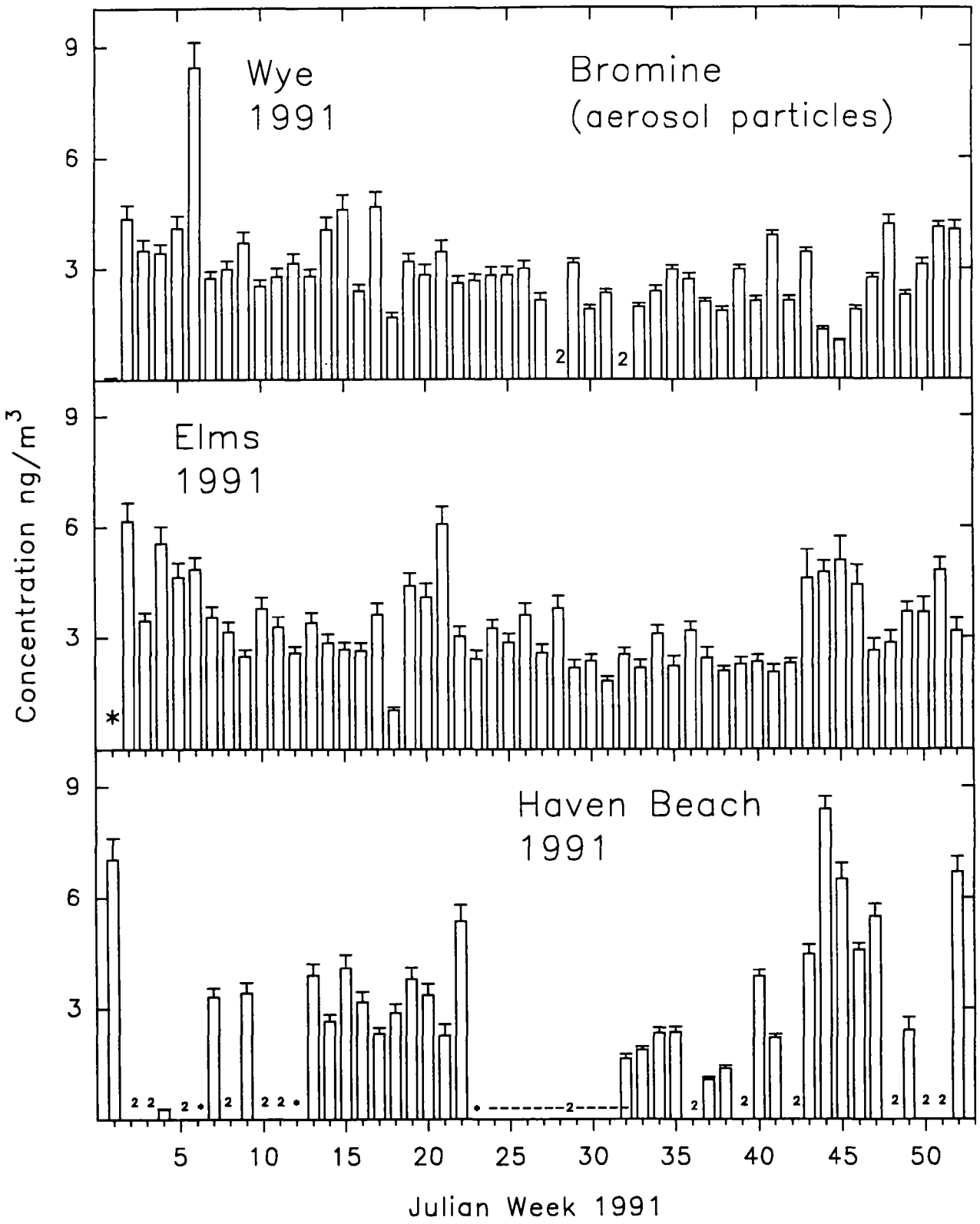


Figure IV.2.3. (Cont'd) Bromine concentrations on aerosol particles, integrated weekly at each CBAD site. 1 = not detected, 2 = pump down, * = oulier/no data.

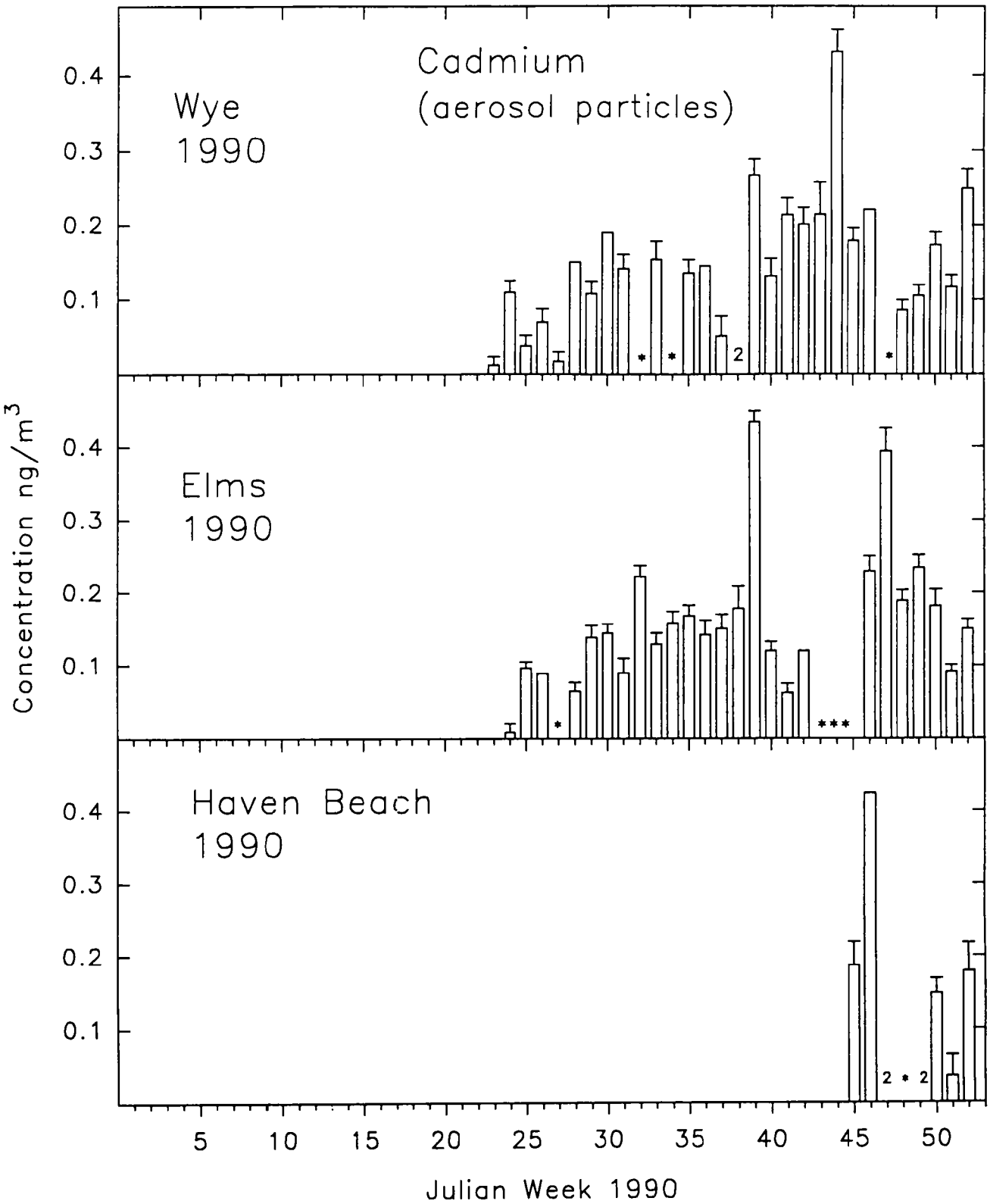


Figure IV.2.4. Cadmium concentrations on aerosol particles, integrated weekly at each CBAD site. 1 = not detected, 2 = pump down, * = outlier/no data.

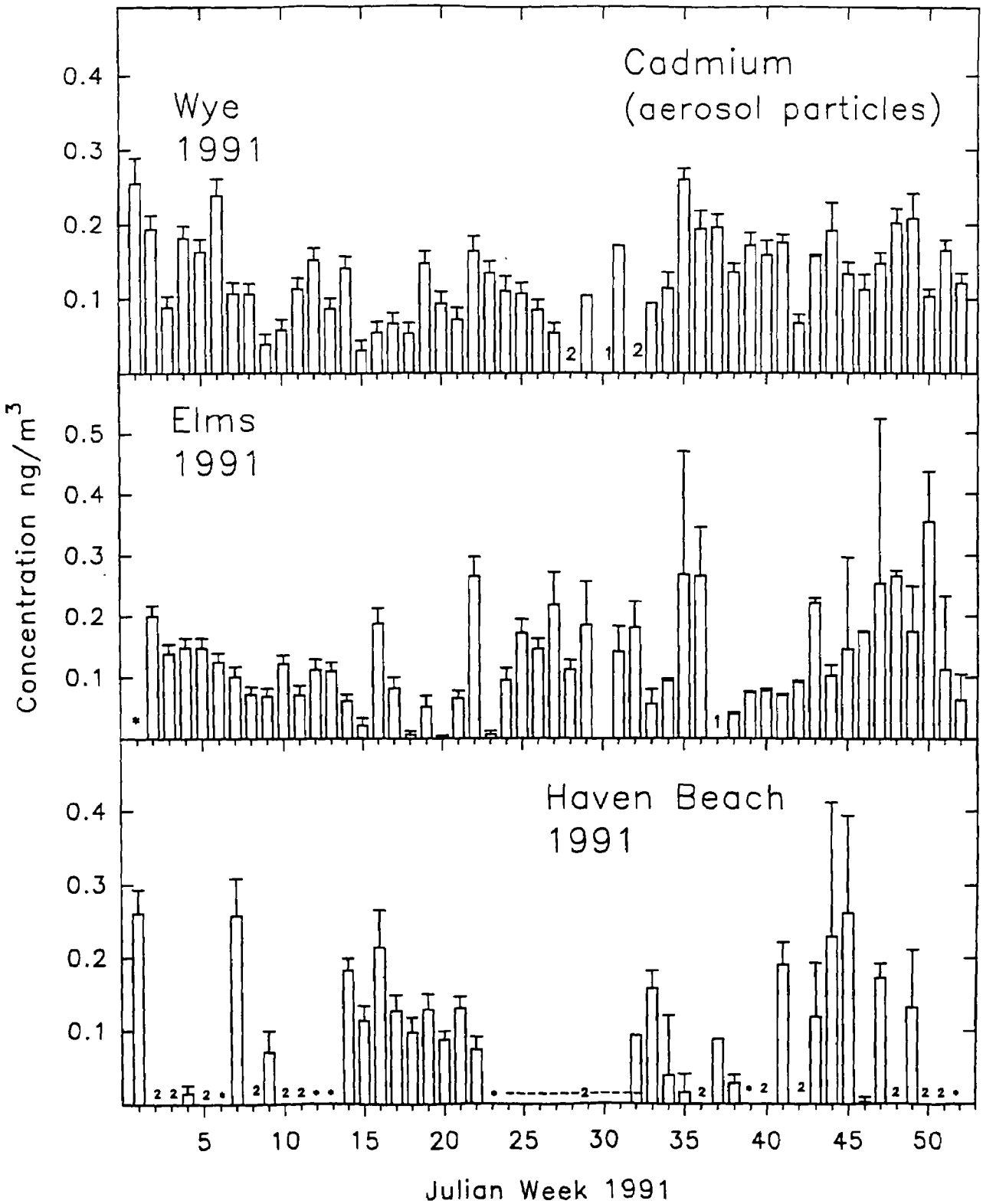


Figure IV.2.4. (Cont'd) Cadmium concentrations on aerosol particles, integrated weekly at each CBAD site. 1 = not detected, 2 = pump down, * = outlier/no data.

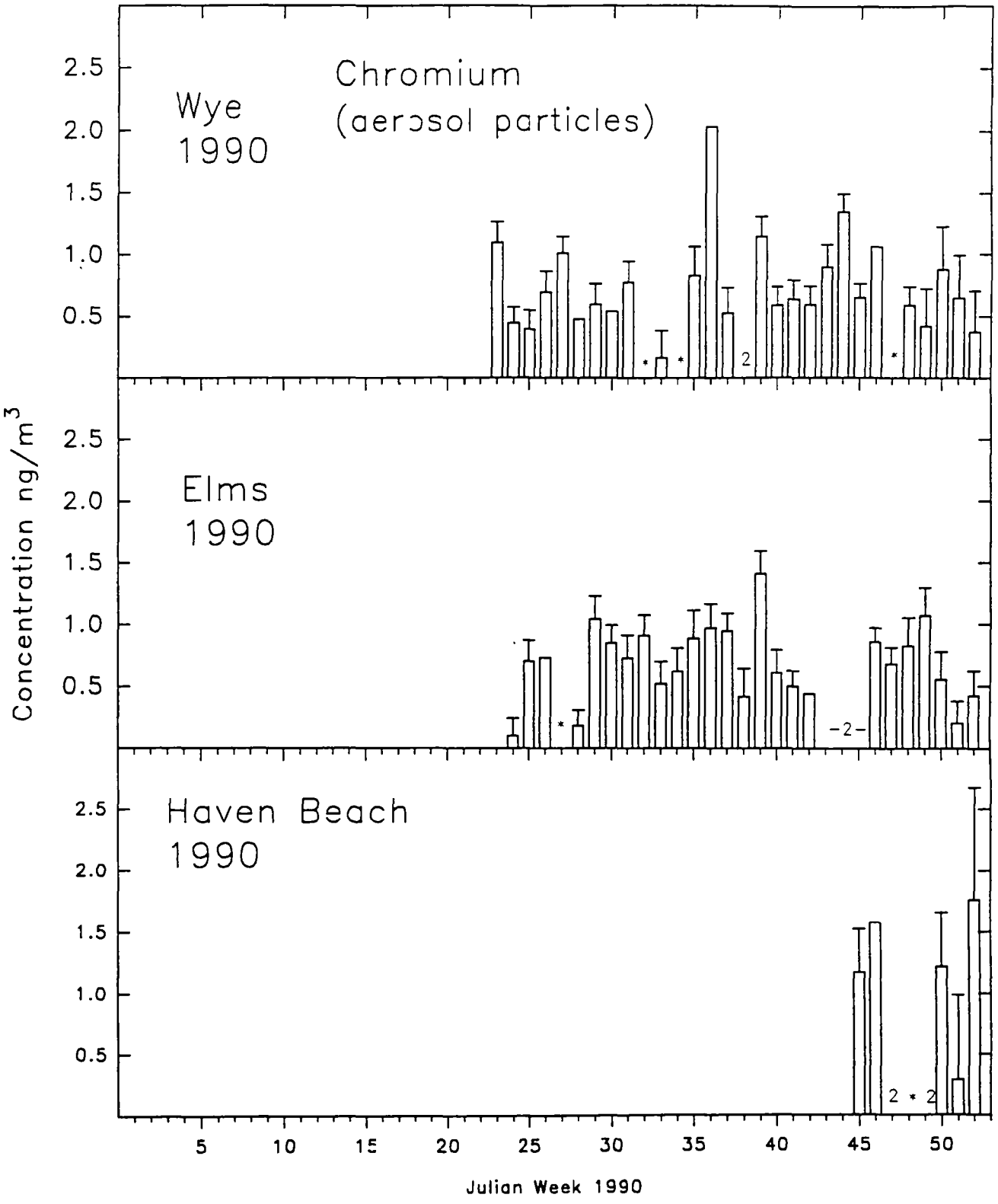


Figure IV.2.5. Chromium concentrations on aerosol particles, integrated weekly at each CBAD site. 1 = not detected, 2 = pump down, * = outlier/no data.

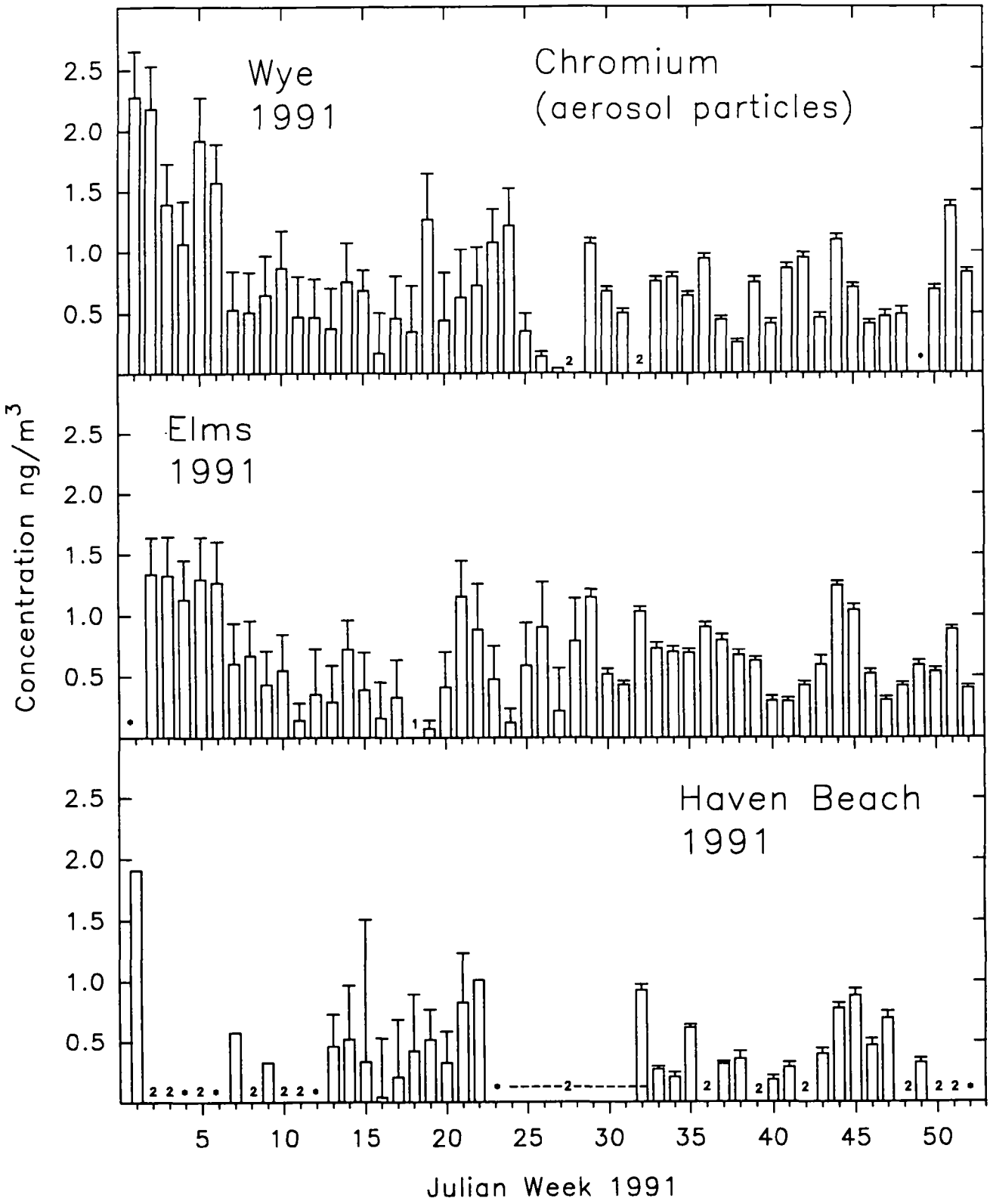


Figure IV.2.5. (Cont'd) Chromium concentrations on aerosol particles, integrated weekly at each CBAD site. 1 = not detected, 2 = pump down, * = outlier/no data.

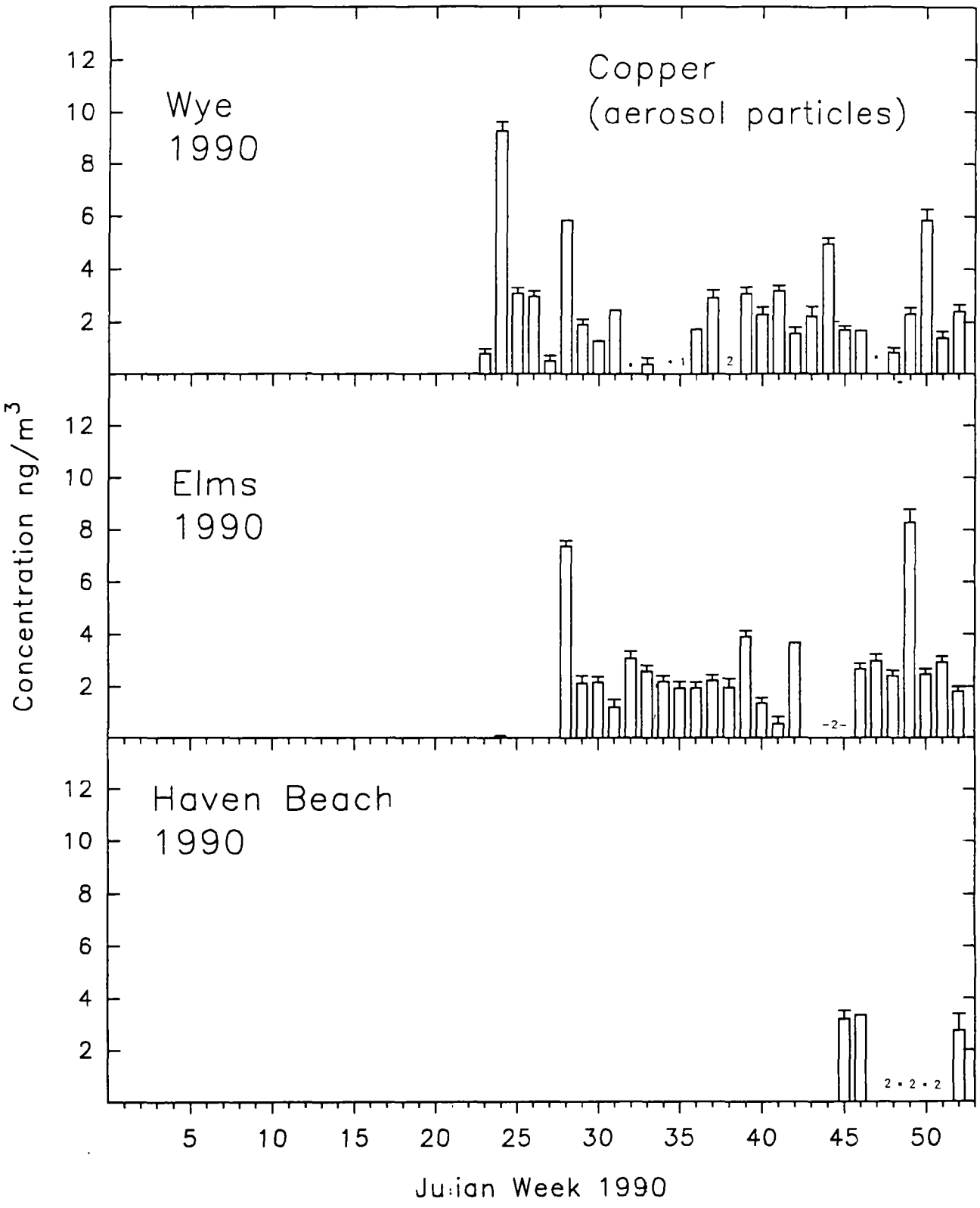


Figure IV.2.6. Copper concentrations on aerosol particles, integrated weekly at each CBAD site. 1 = not detected, 2 = pump down, * = outlier/no data.

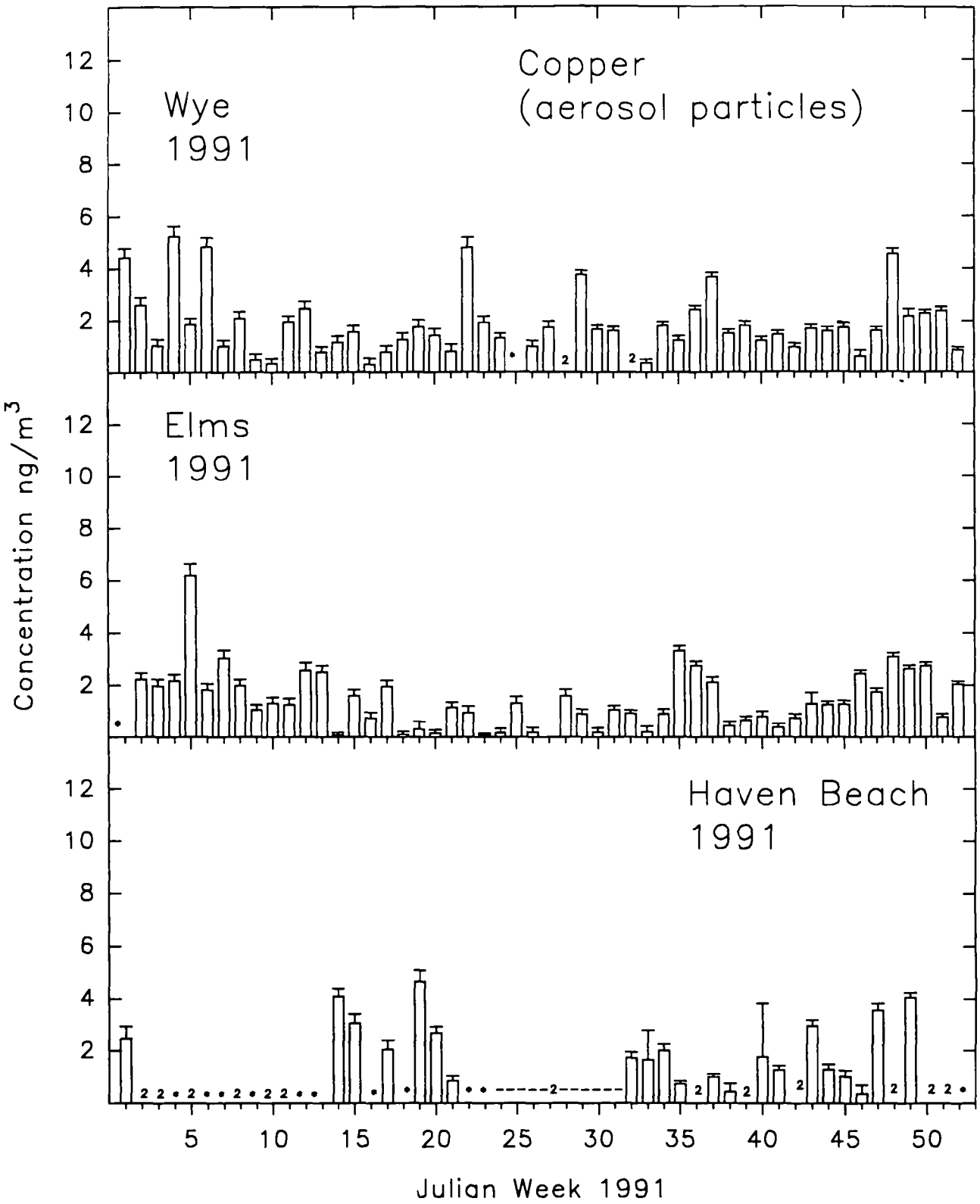


Figure IV.2.6. (Cont'd) Copper concentrations on aerosol particles, integrated weekly at each CBAD site. 1 = not detected, 2 = pump down, * = outlier/no data.

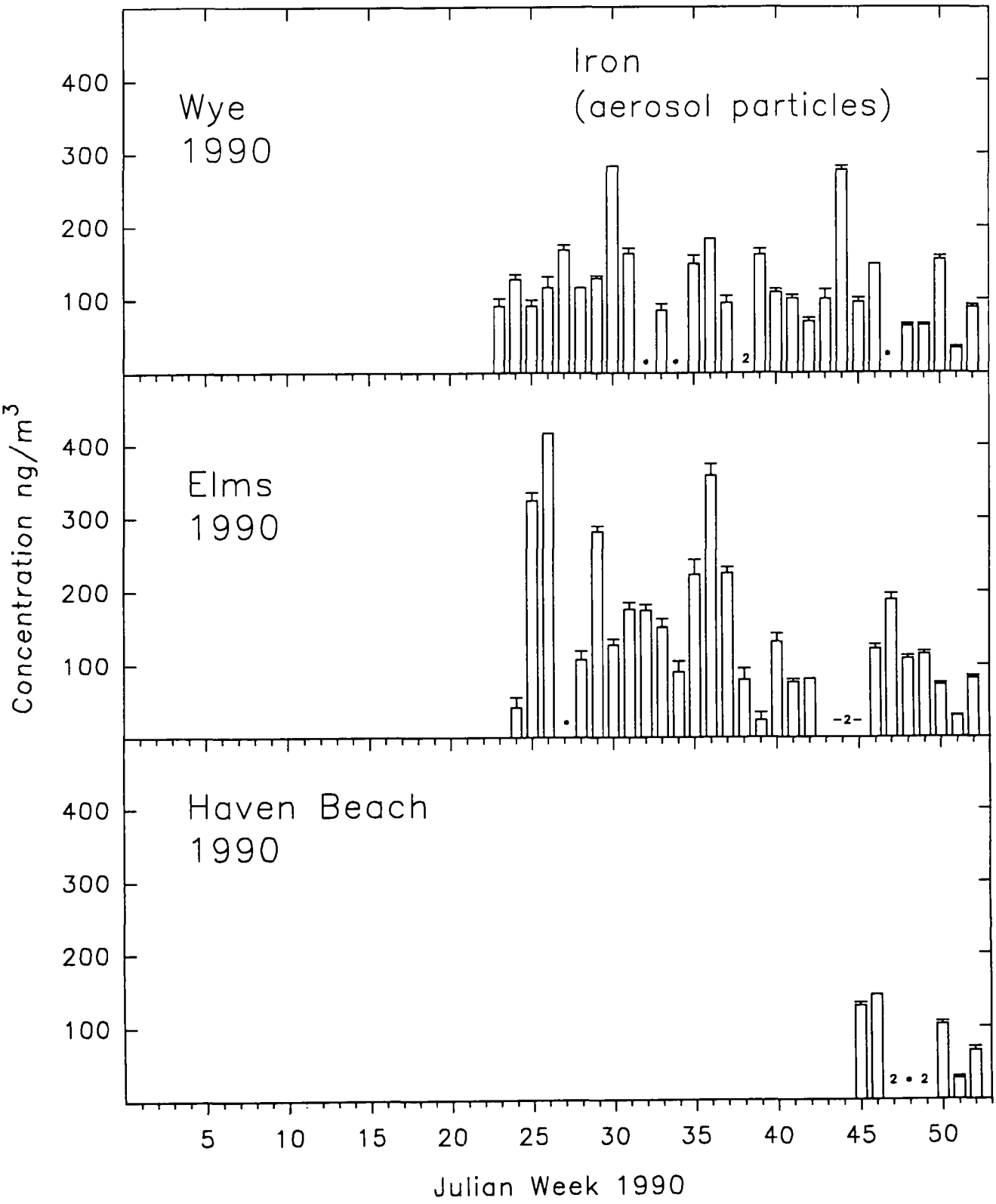


Figure IV.2.7. Iron concentrations on aerosol particles, integrated weekly at each CBAD site. 1 = not detected, 2 = pump down, * = outlier/no data.

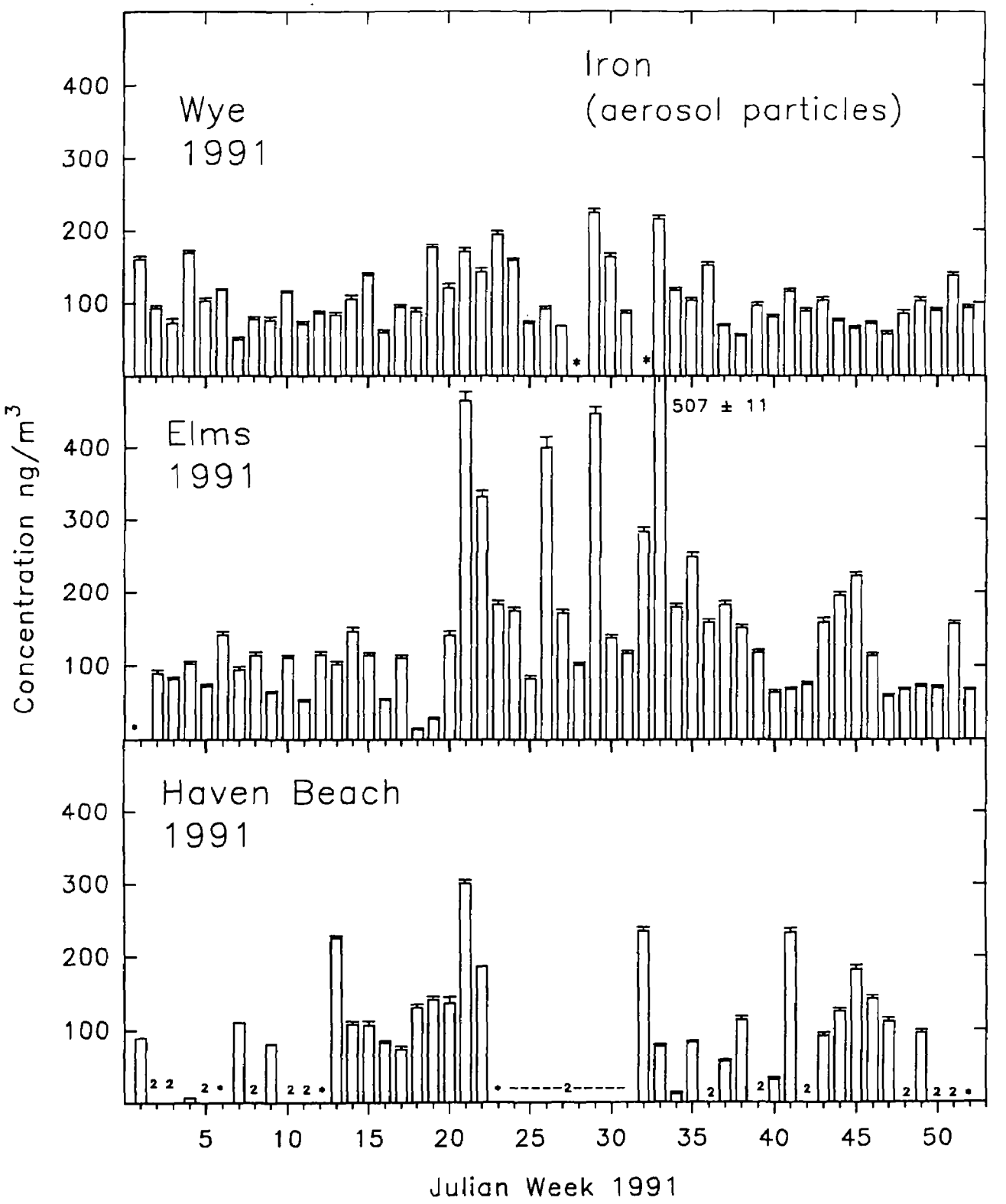


Figure IV.2.7. (Cont'd) Iron concentrations on aerosol particles, integrated weekly at each CBAD site. 1 = not detected, 2 = pump down, * = outlier/no data.

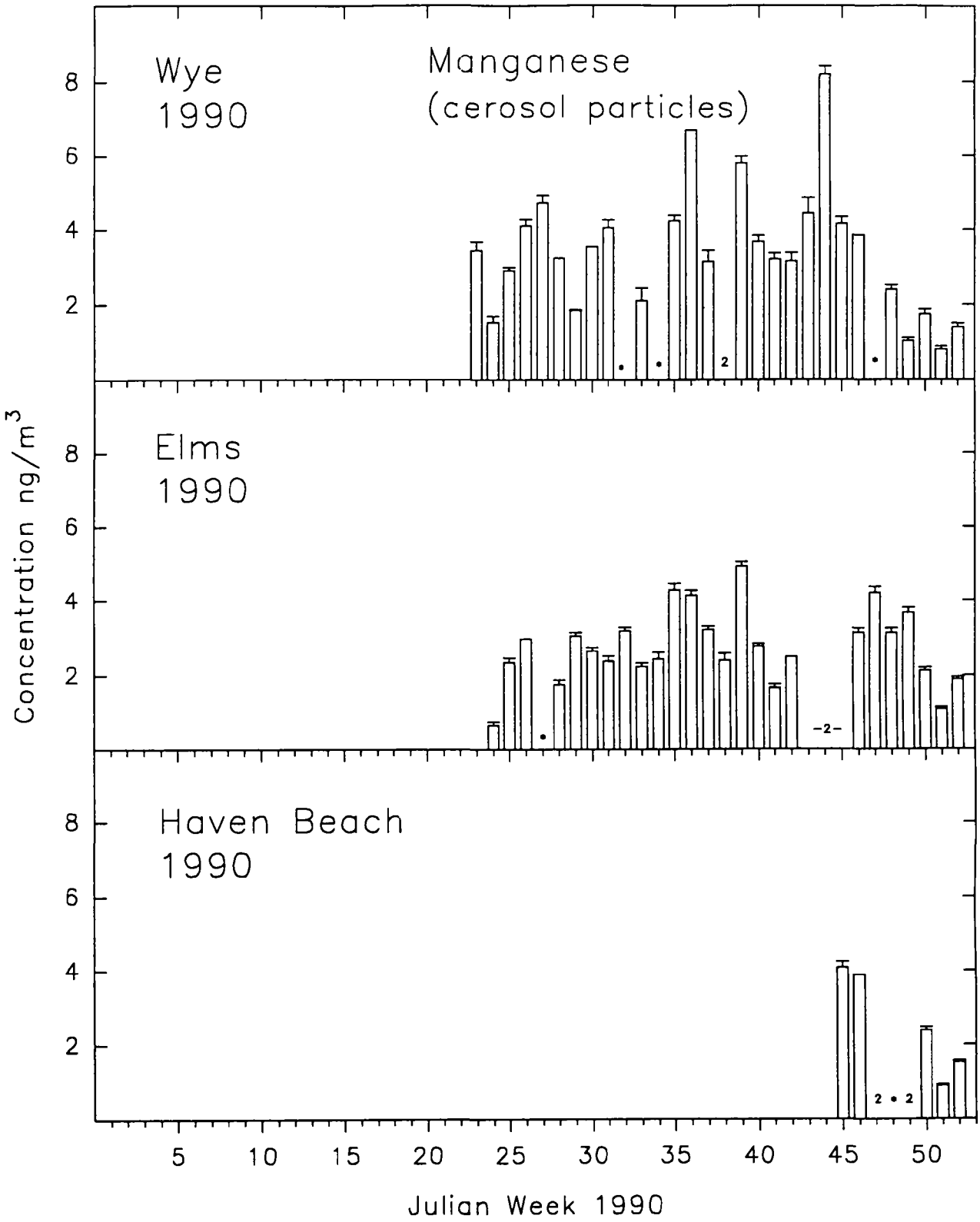


Figure IV.2.8. Manganese concentrations on aerosol particles, integrated weekly at each CBAD site. 1 = not detected, 2 = pump down, * = outlier/no data.

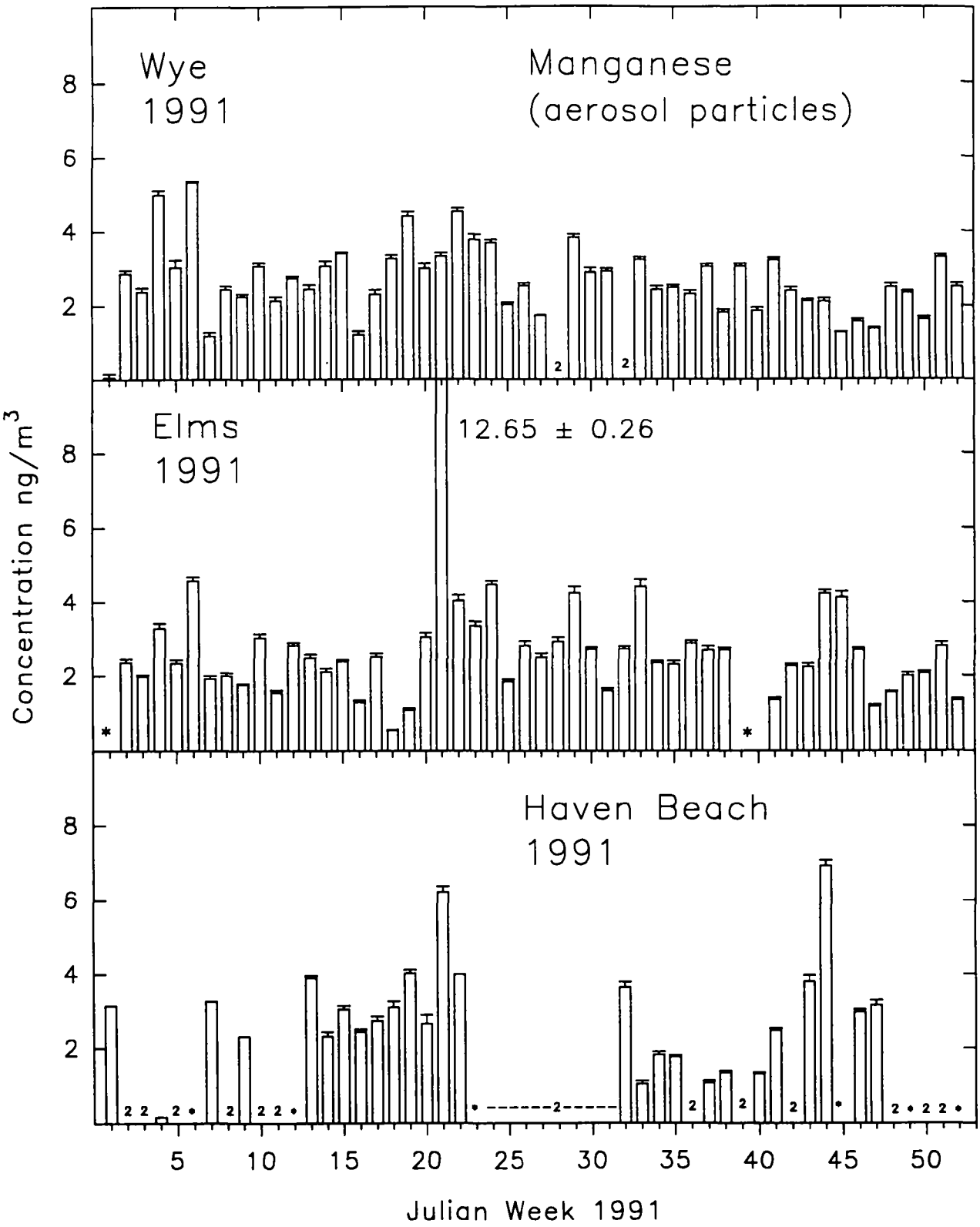


Figure IV.2.8. (Cont'd) Manganese concentrations on aerosol particles, integrated weekly at each CBAD site. 1 = not detected, 2 = pump down, * = outlier/no data.

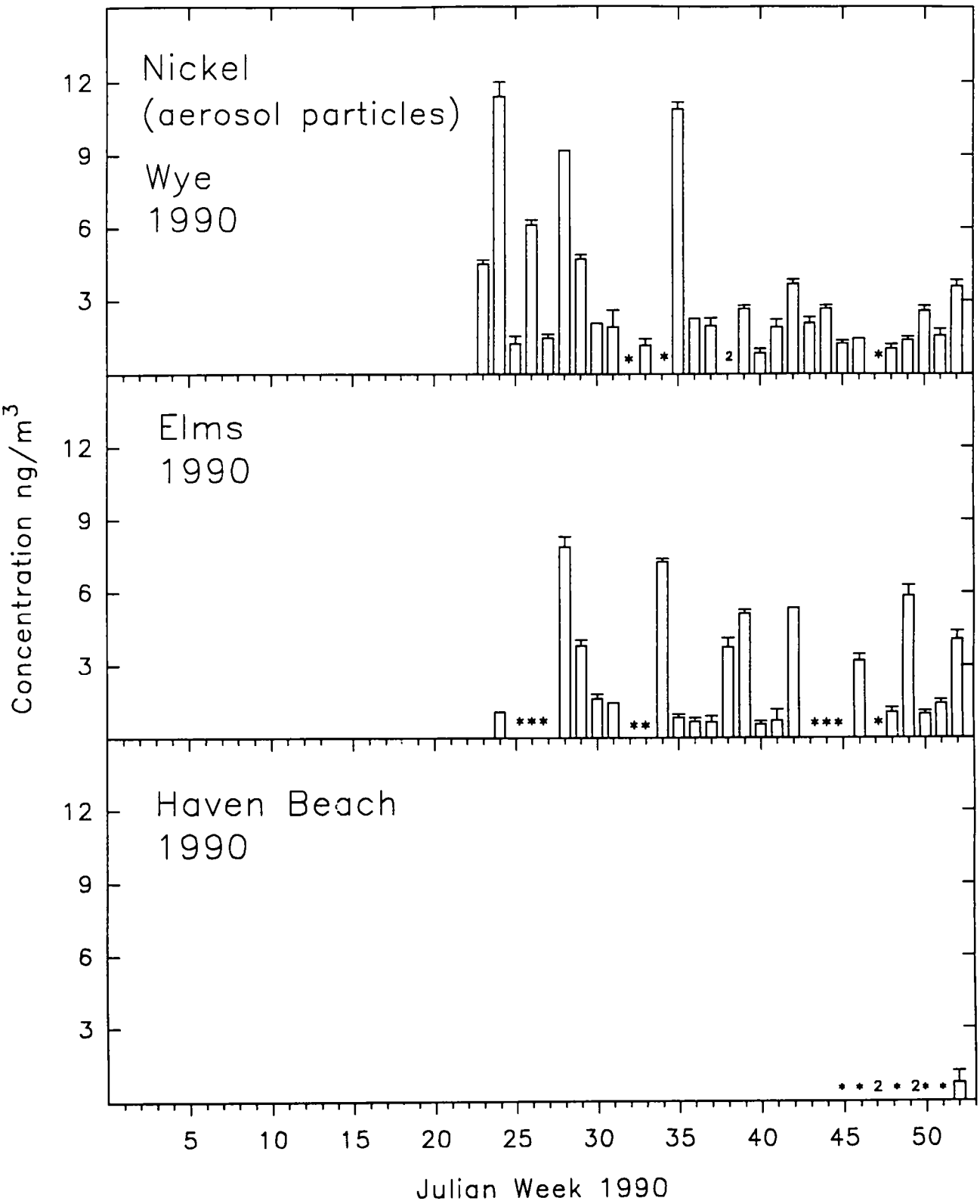


Figure IV.2.9. Nickel concentrations on aerosol particles, integrated weekly at each CBAD site. 1 = not detected, 2 = pump down, * = outlier/no data.

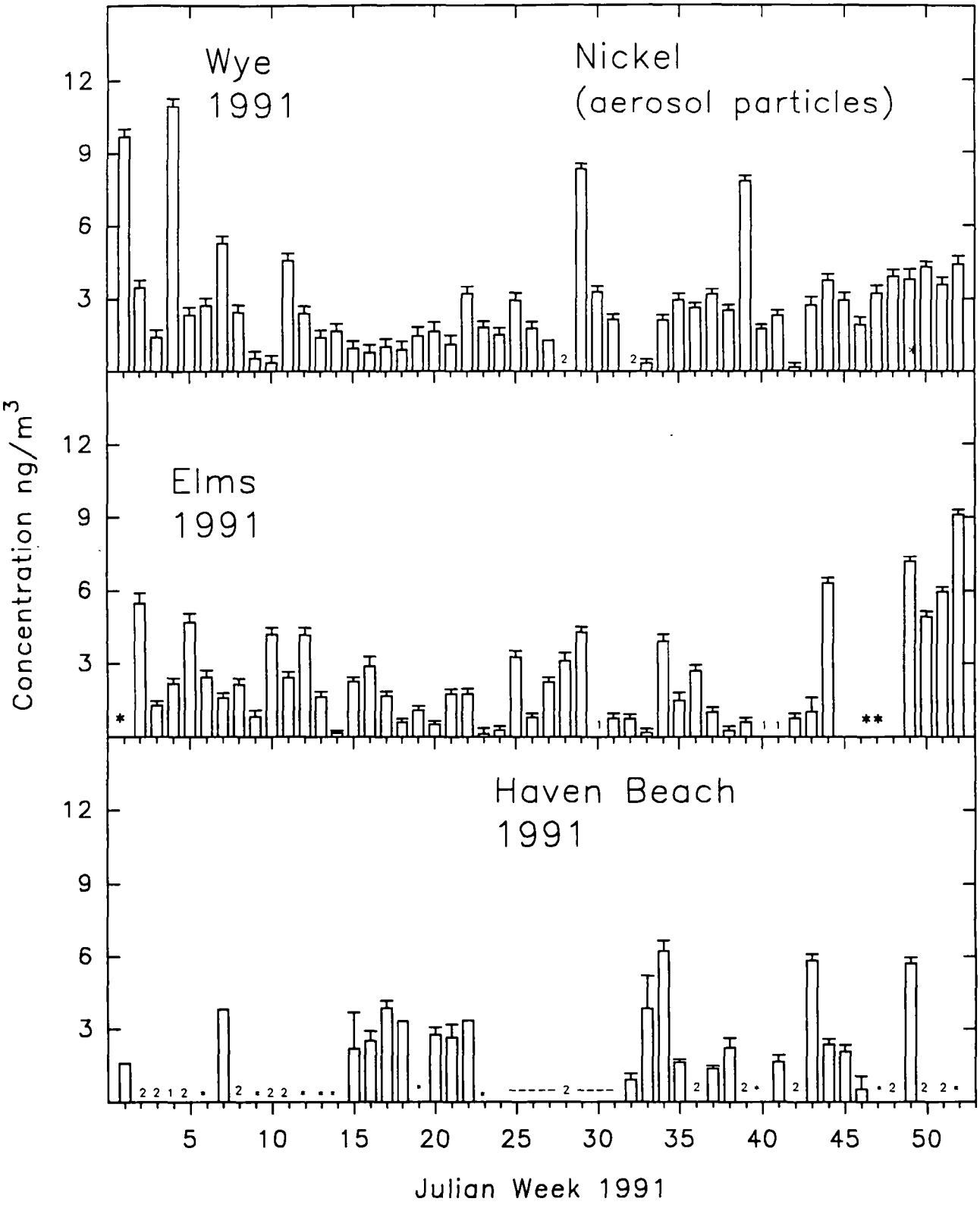


Figure IV.2.9. (Cont'd) Nickel concentrations on aerosol particles, integrated weekly at each CBAD site. 1 = not detected, 2 = pump down, * = outlier/no data.

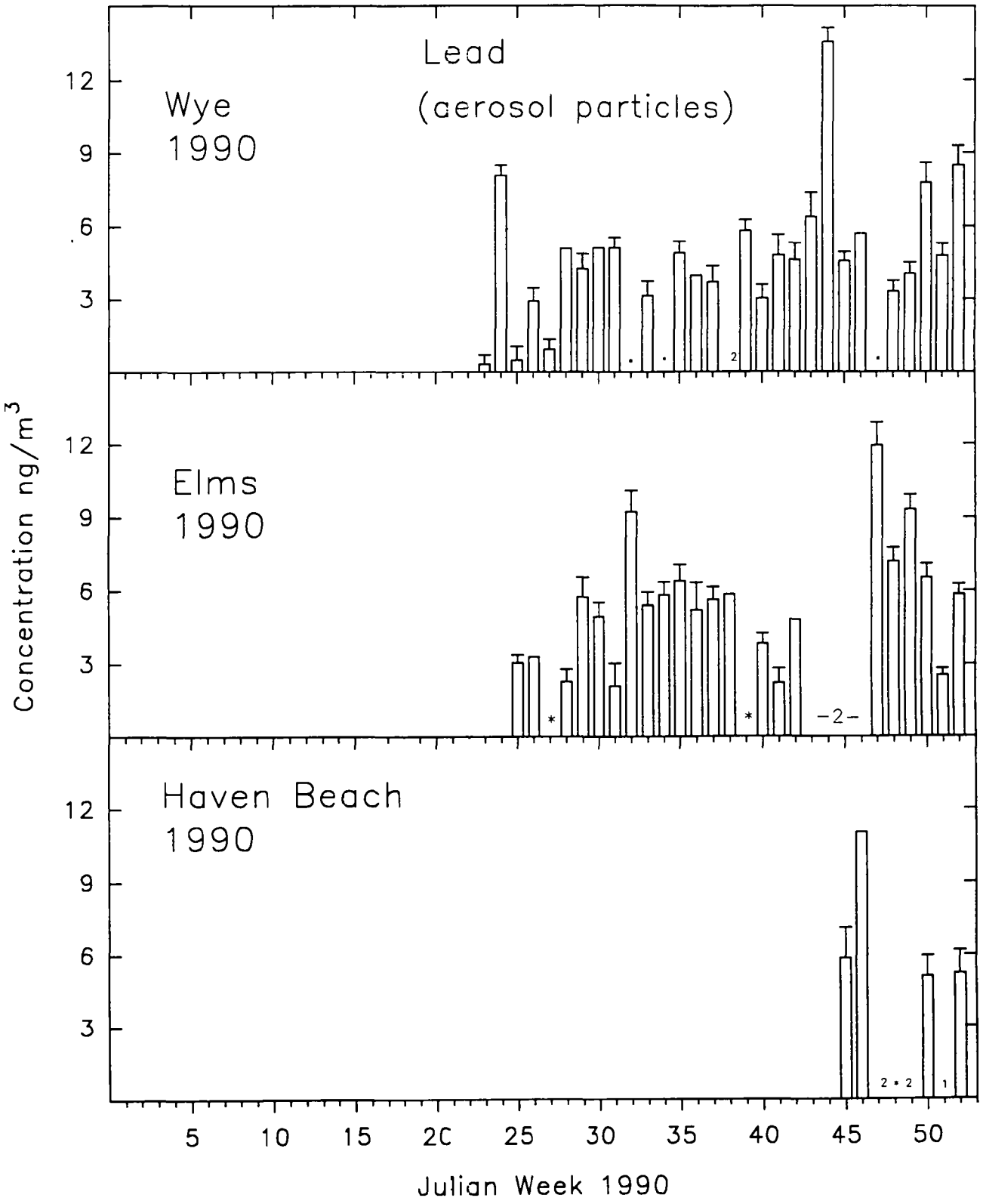


Figure IV.2.10. Lead concentrations on aerosol particles, integrated weekly at each CBAD site. 1 = not detected, 2 = pump down, * = outlier/no data.

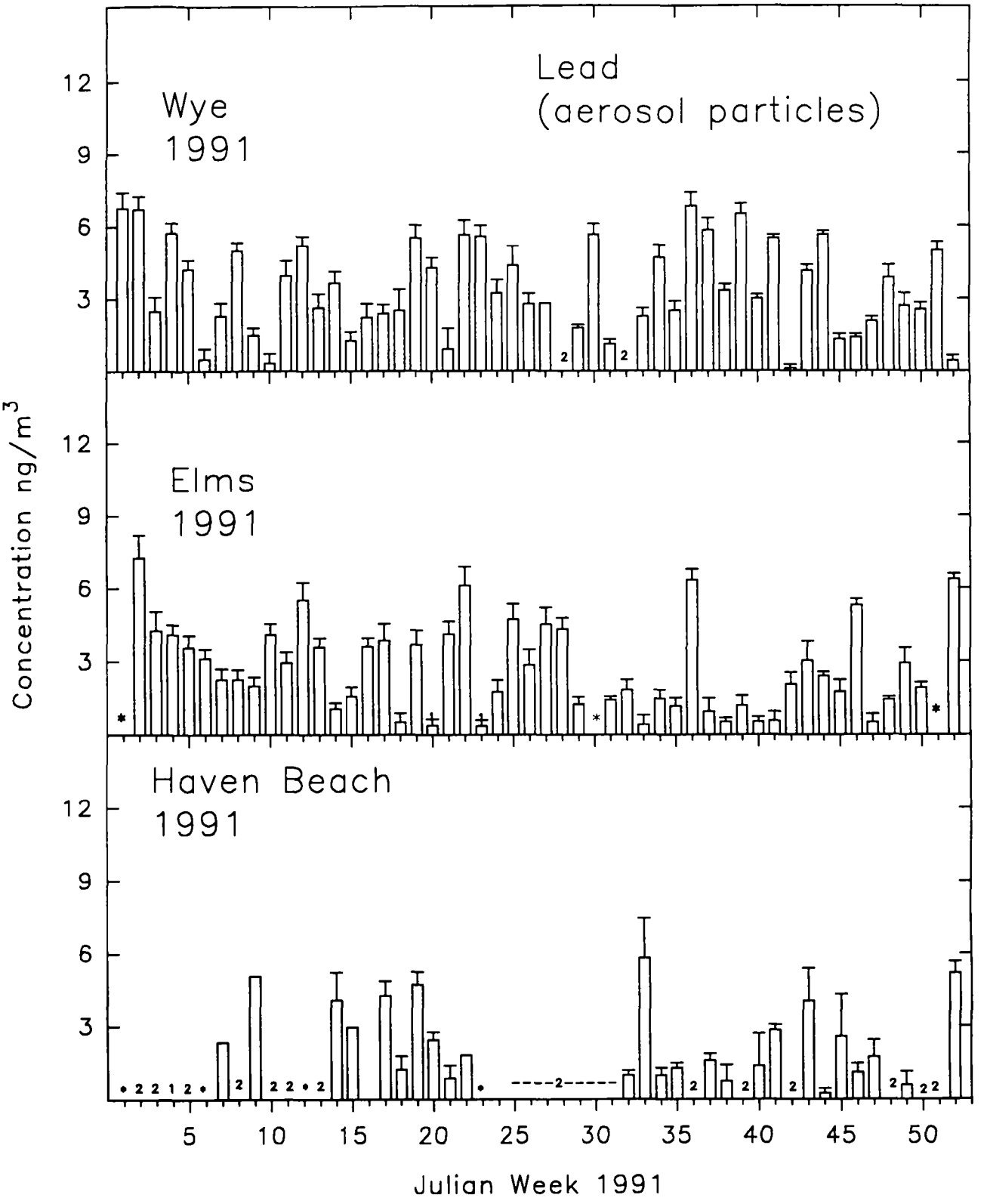


Figure IV.2.10. (Cont'd) Lead concentrations on aerosol particles, integrated weekly at each CBAD site. 1 = not detected, 2 = pump down, * = outlier/no data.

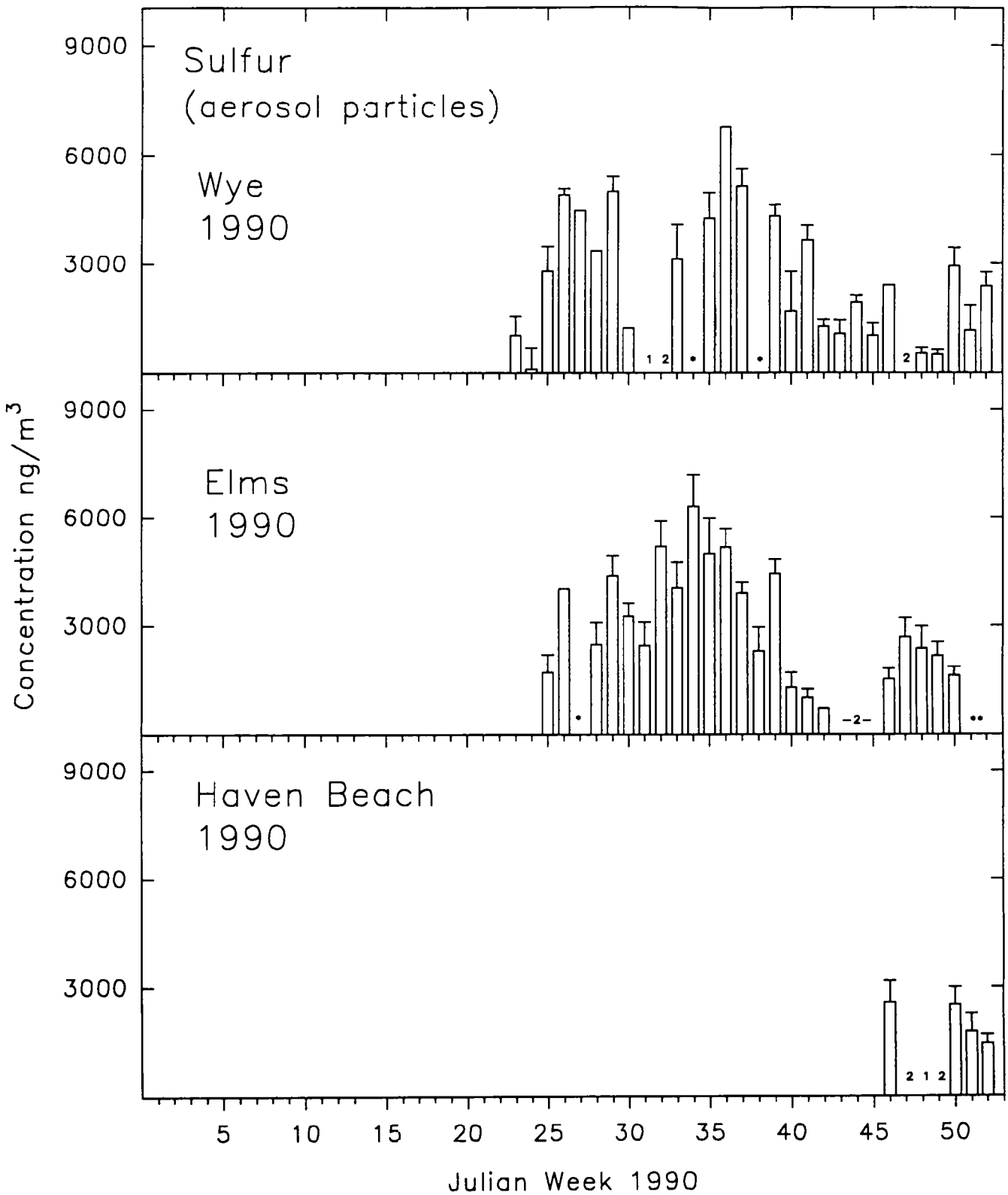


Figure IV.2.11. Sulfur concentrations on aerosol particles, integrated weekly at each CBAD site. 1 = not detected, 2 = pump down, * = outlier/no data.

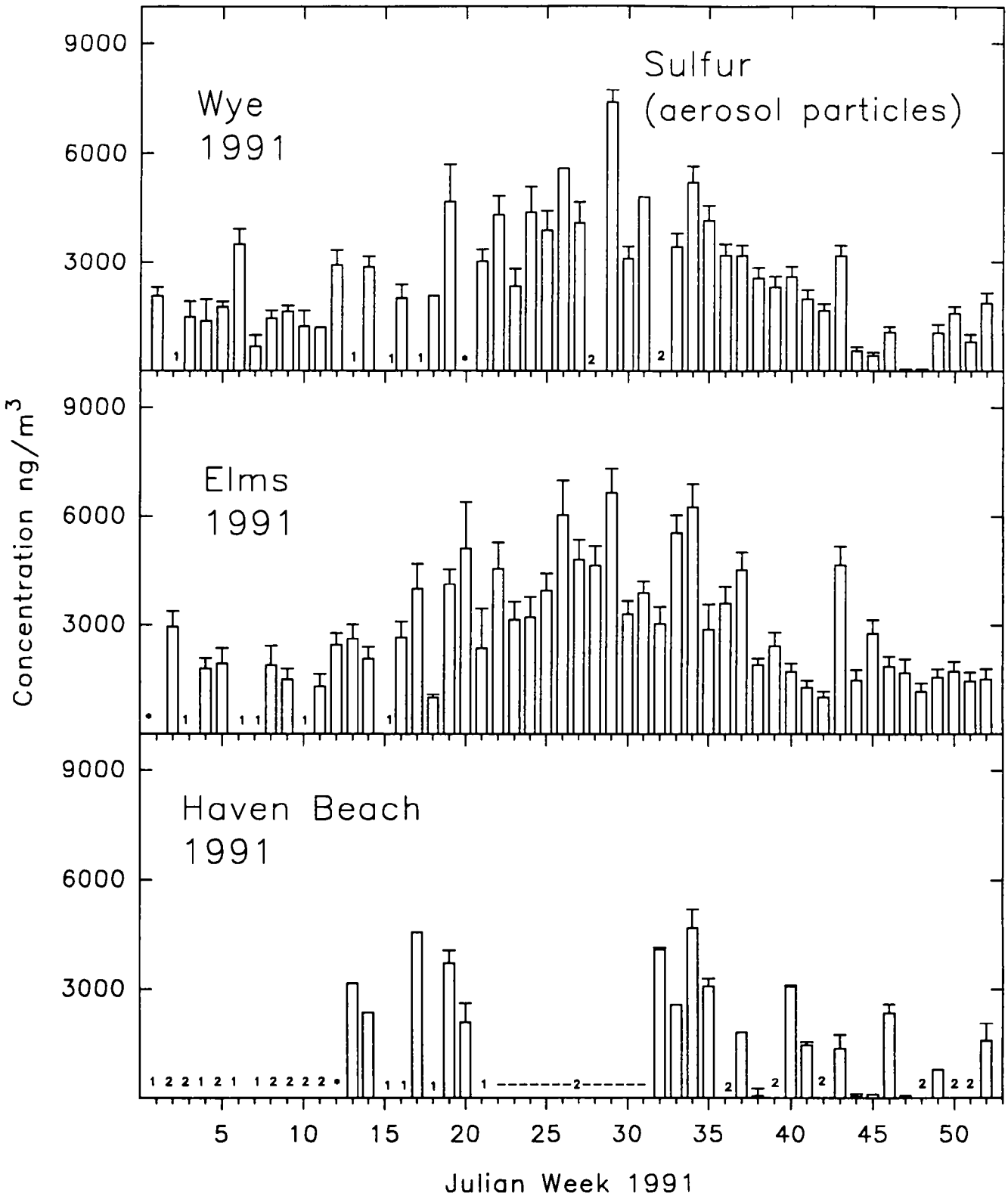


Figure IV.2.11. (Cont'd) Sulfur concentrations on aerosol particles, integrated weekly at each CBAD site. 1 = not detected, 2 = pump down, * = outlier/no data.

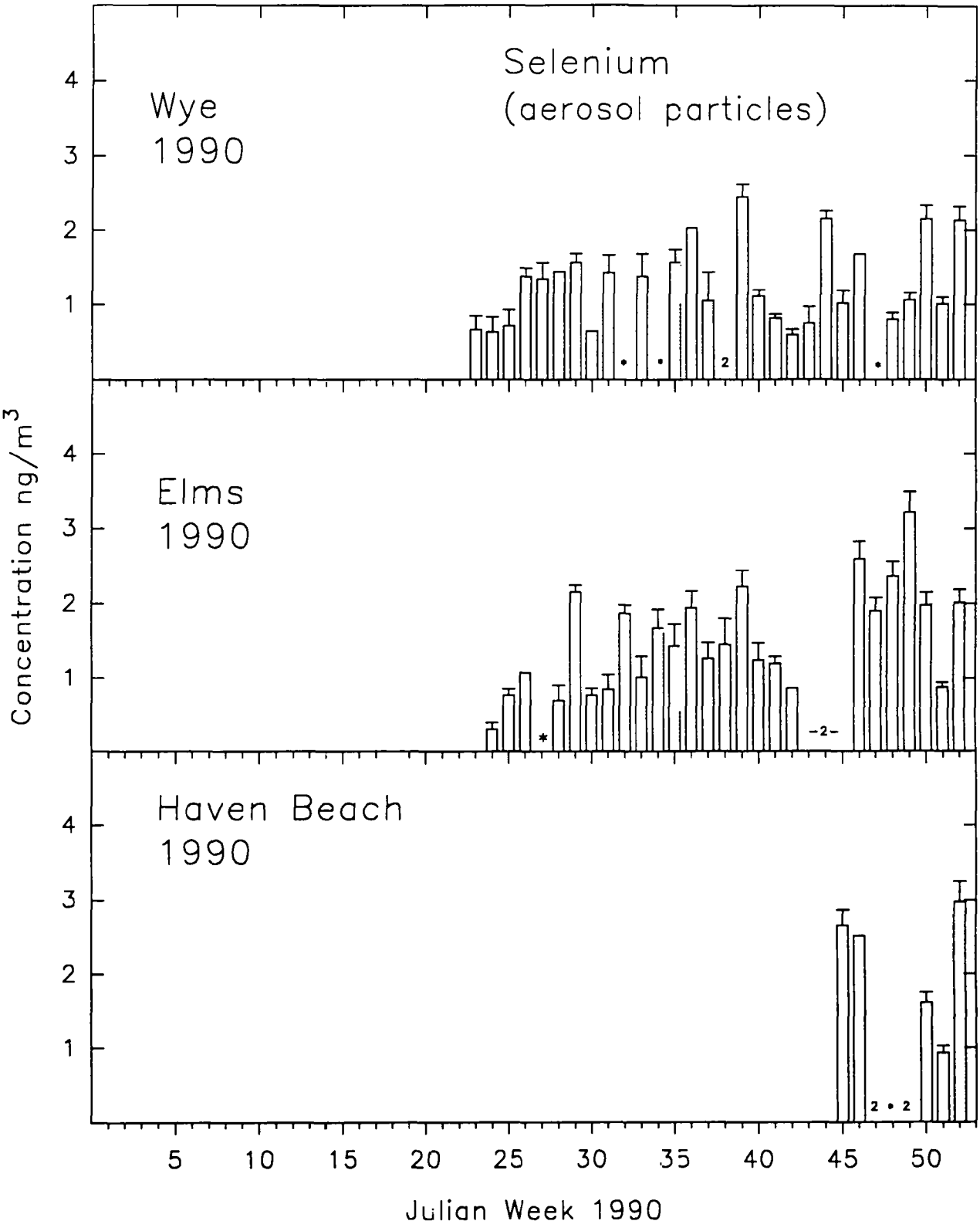


Figure IV.2.12. Selenium concentrations on aerosol particles, integrated weekly at each CBAD site. 1 = not detected, 2 = pump down, * = outlier/no data.

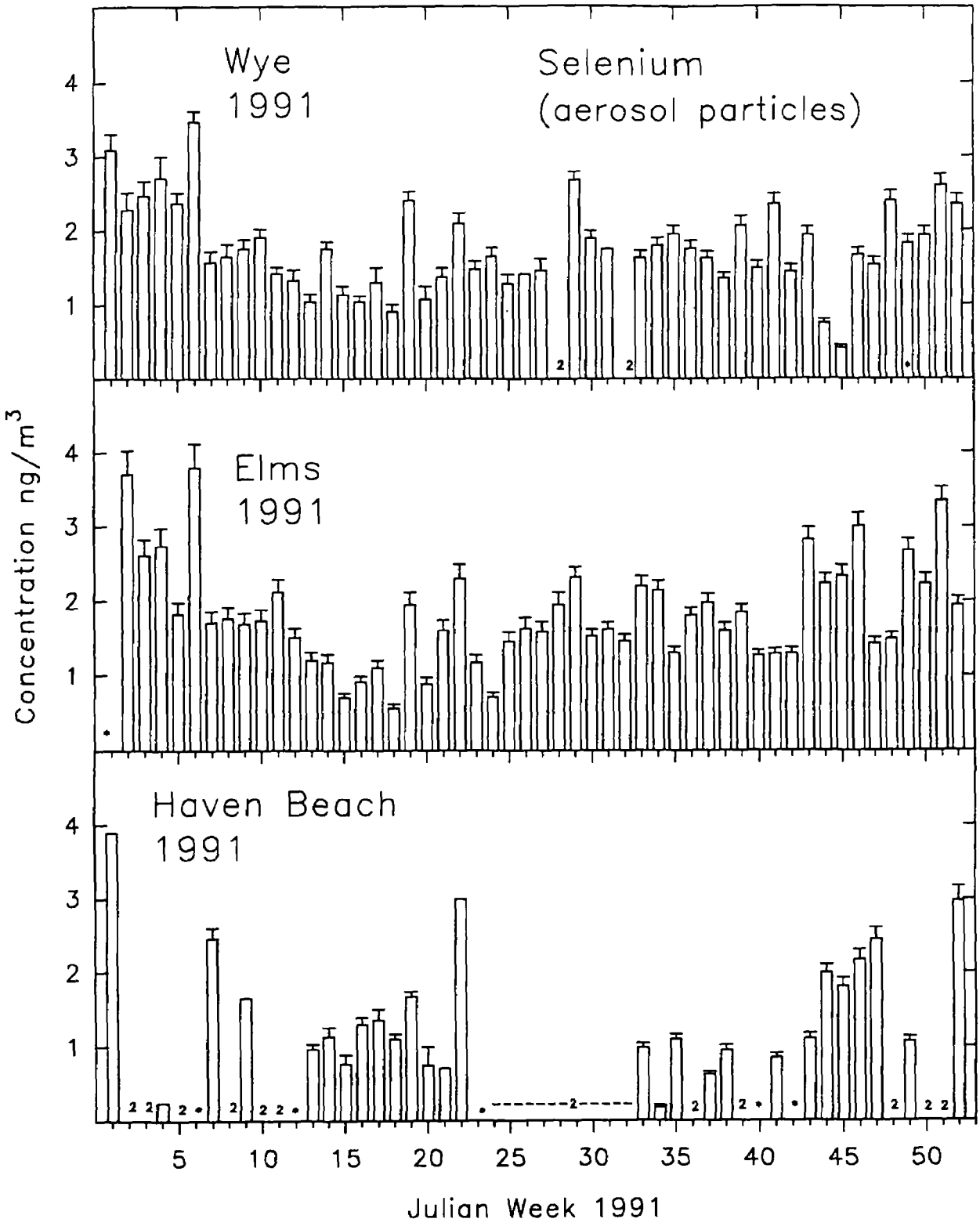


Figure IV.2.12. (Cont'd) Selenium concentrations on aerosol particles, integrated weekly at each CBAD site. 1 = not detected, 2 = pump down, * = outlier/no data.

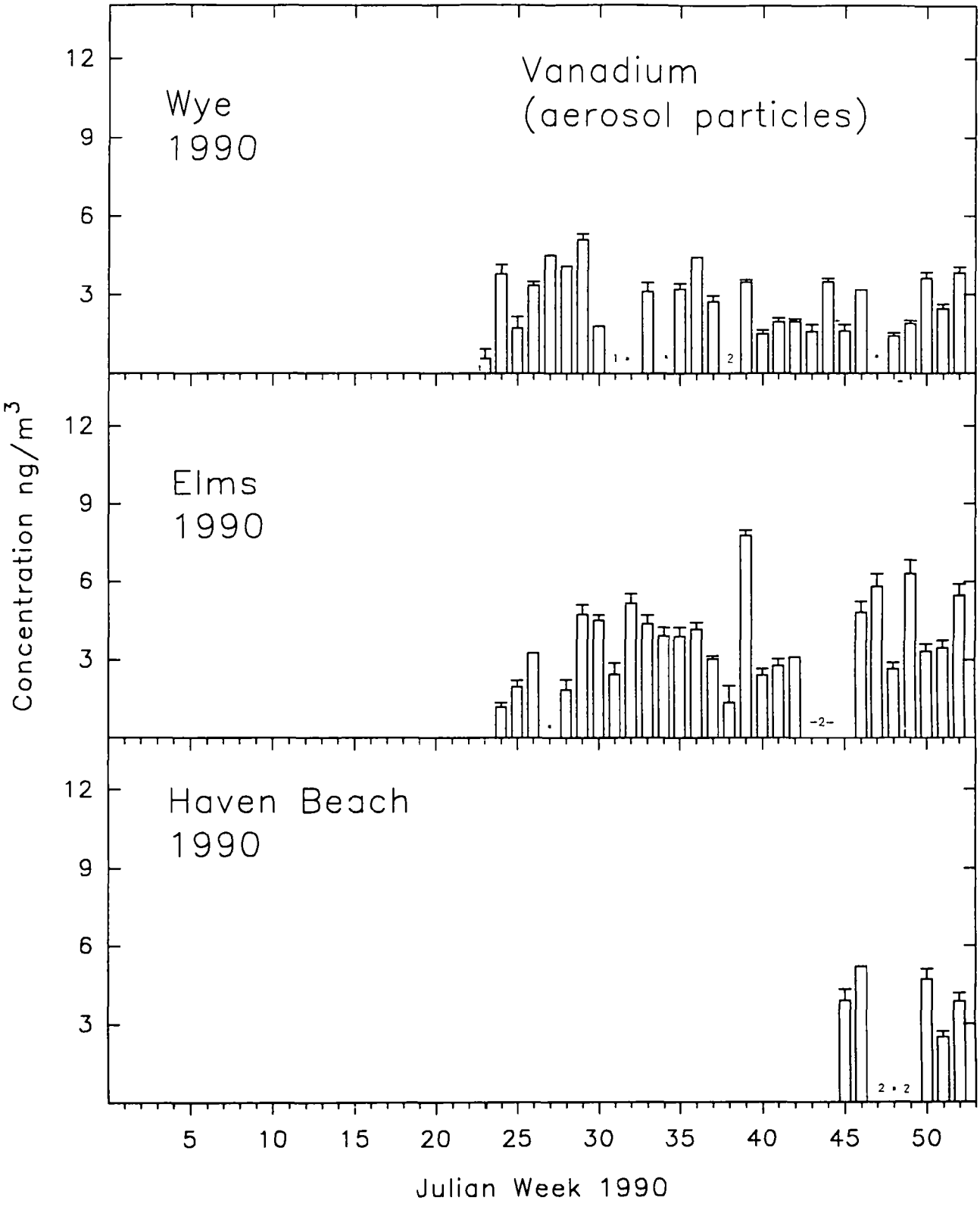


Figure IV.2.13. Vanadium concentrations on aerosol particles, integrated weekly at each CBAD site. 1 = not detected, 2 = pump down, * = outlier/no data.

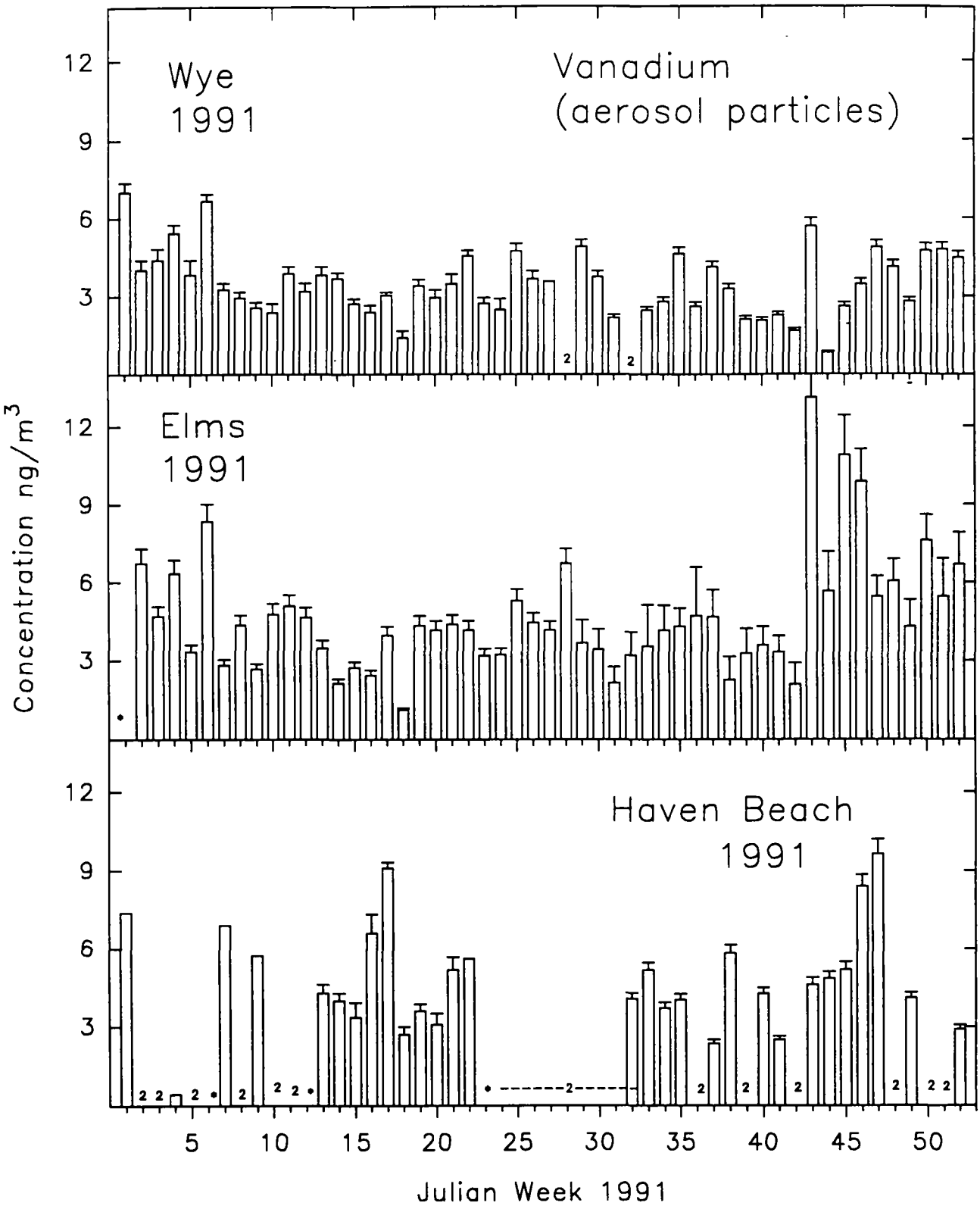


Figure IV.2.13. (Cont'd) Vanadium concentrations on aerosol particles, integrated weekly at each CBAD site. 1 = not detected, 2 = pump down, * = outlier/no data.

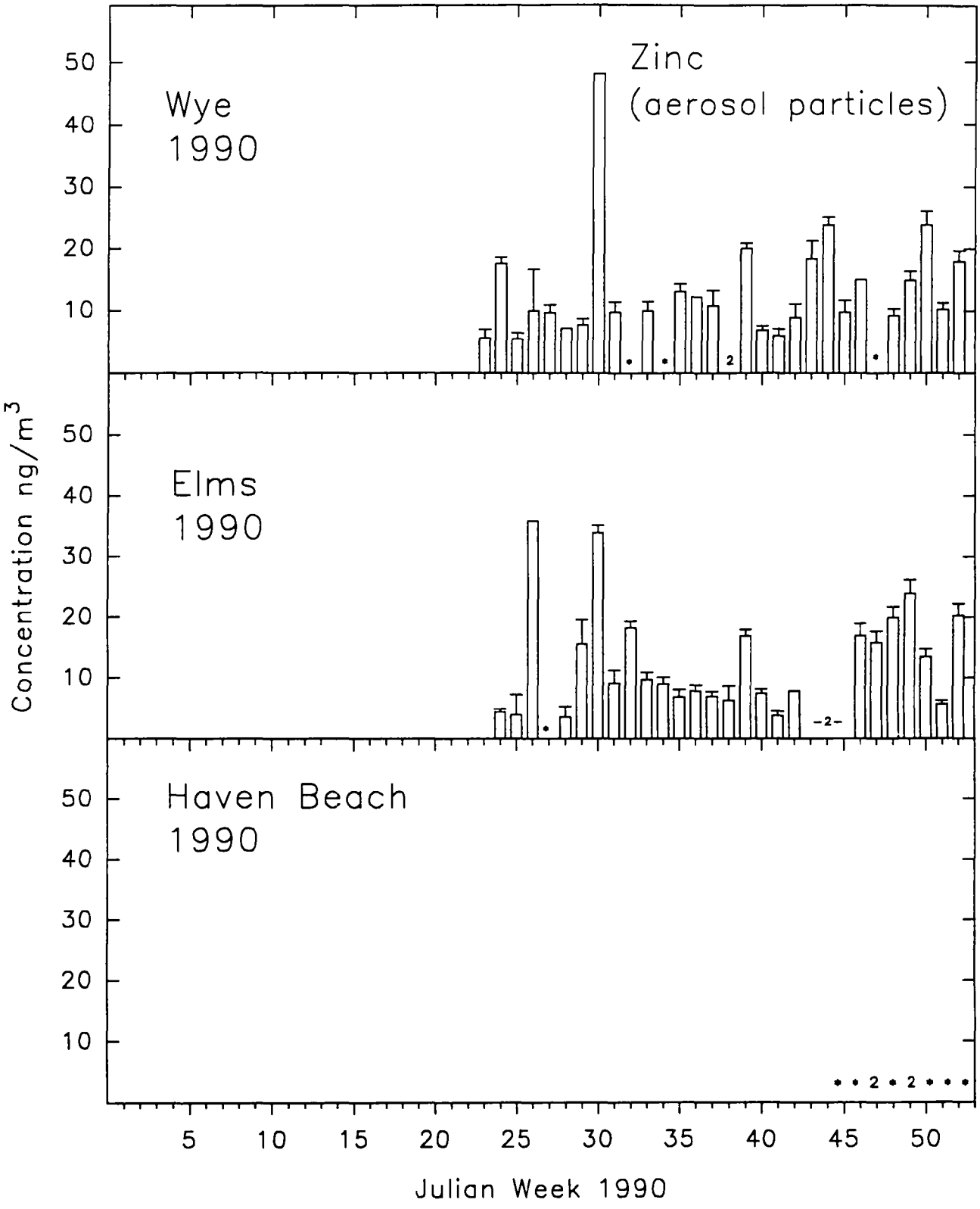


Figure IV.2.14. Zinc concentrations on aerosol particles, integrated weekly at each CBAD site. 1 = not detected, 2 = pump down, * = outlier/no data.

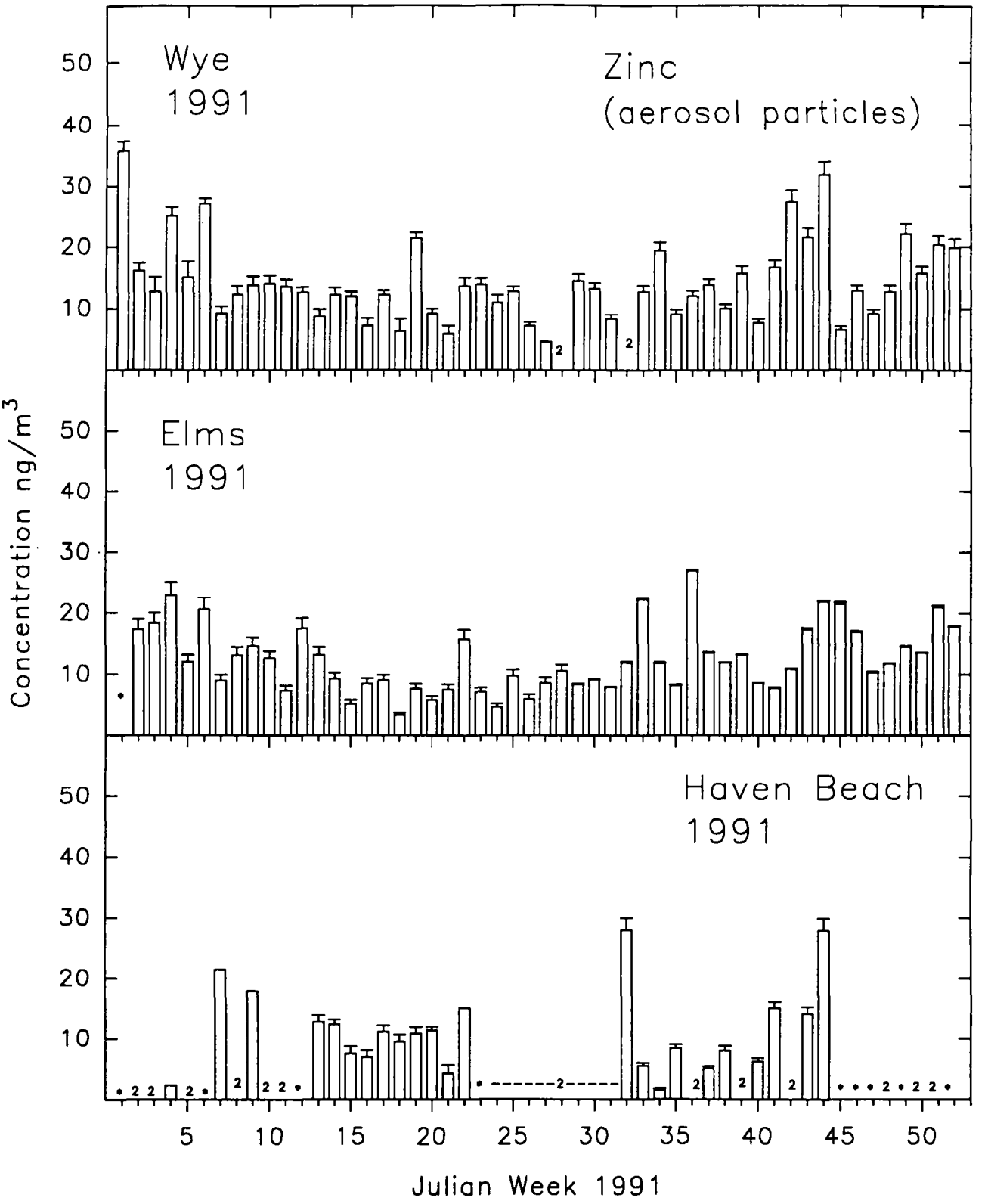


Figure IV.2.14. (Cont'd) Zinc concentrations on aerosol particles integrated weekly at each CBAD site. 1 = not detected, 2 = pump down, * = outlier/no data.

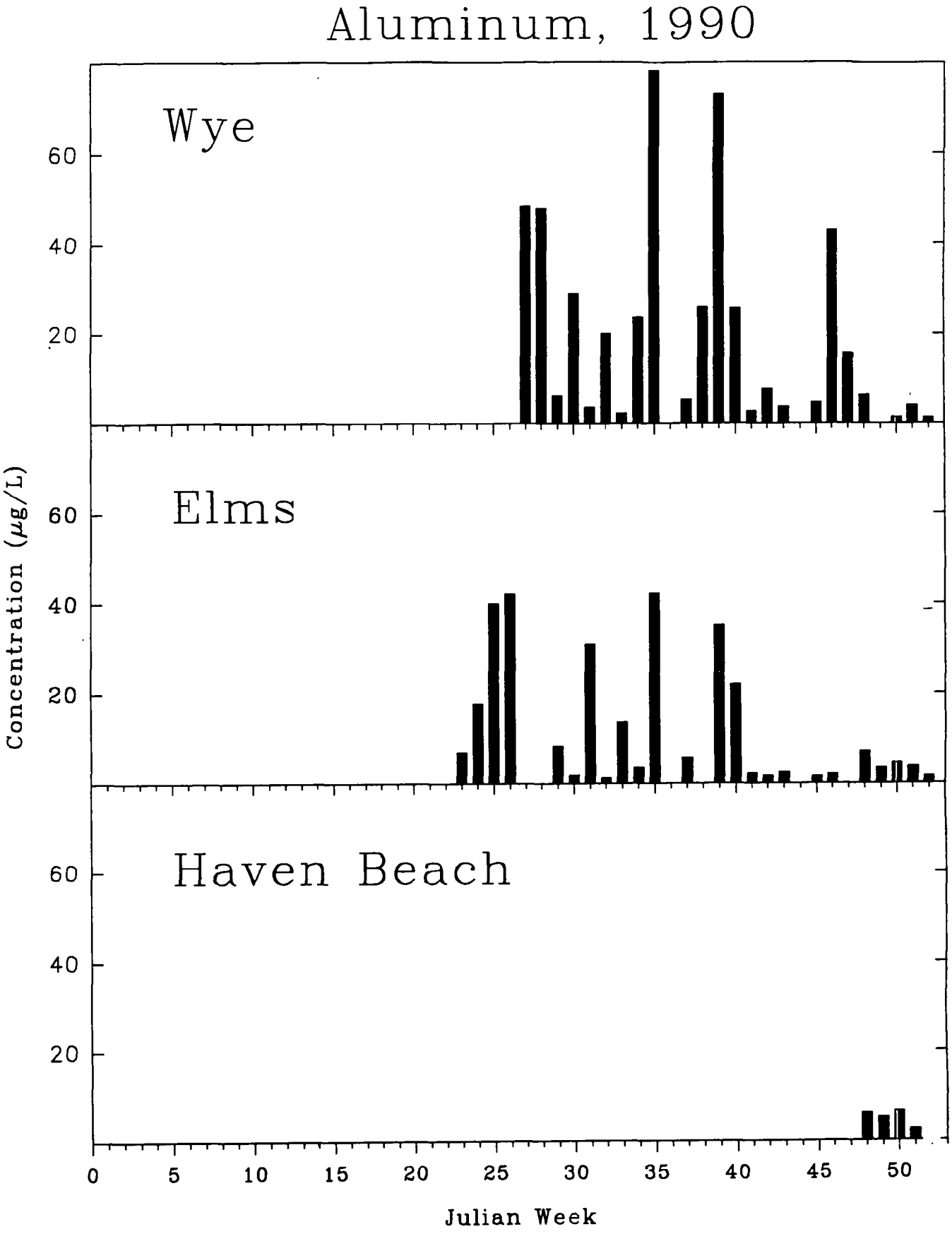


Figure IV.3.1. Aluminum concentrations in precipitation, integrated weekly at each CBAD site.

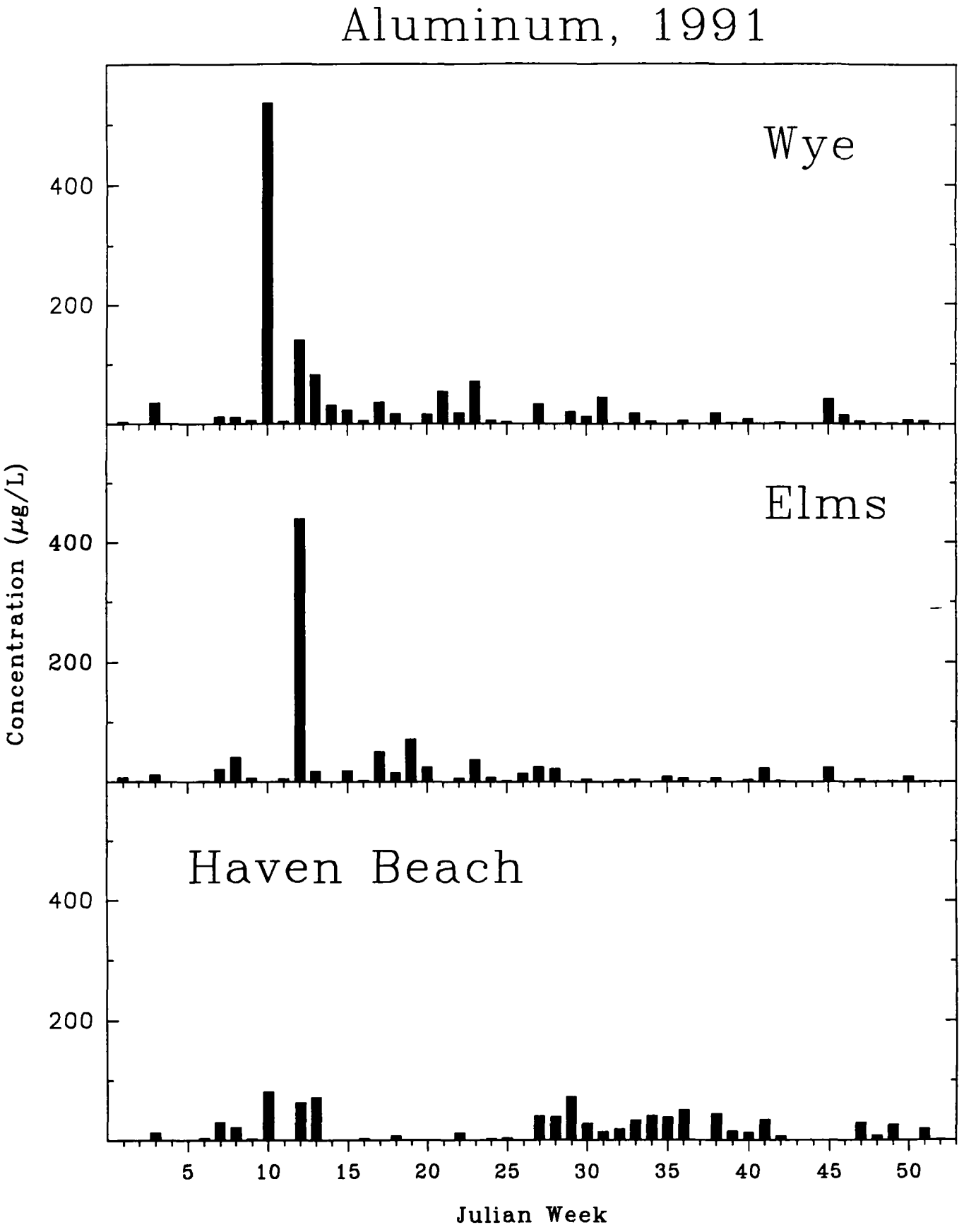


Figure IV.3.1 (Cont'd) Aluminum concentrations in precipitation, integrated weekly at each CBAD site.

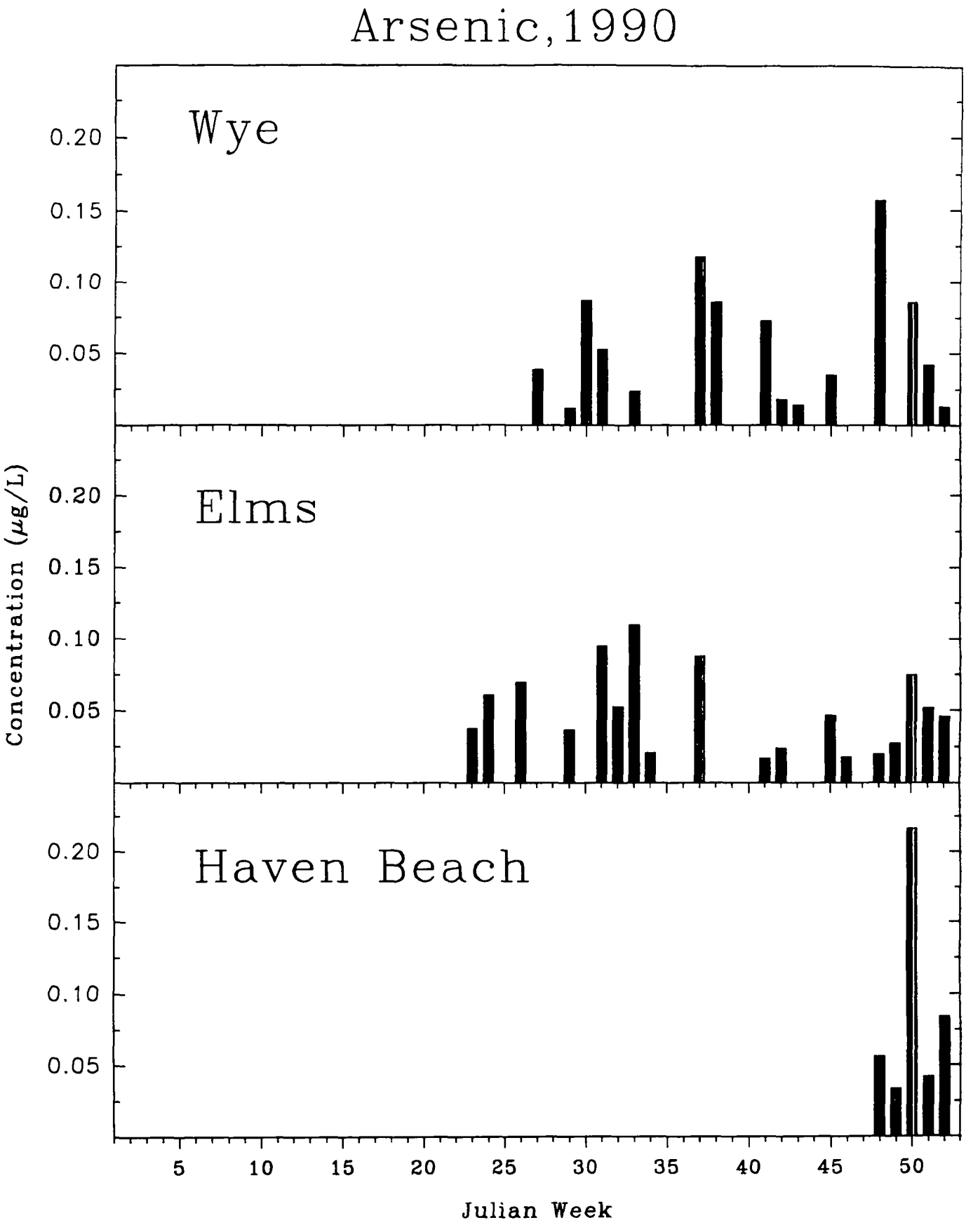


Figure IV.3.2. Arsenic concentrations in precipitation, integrated weekly at each CBAD site.

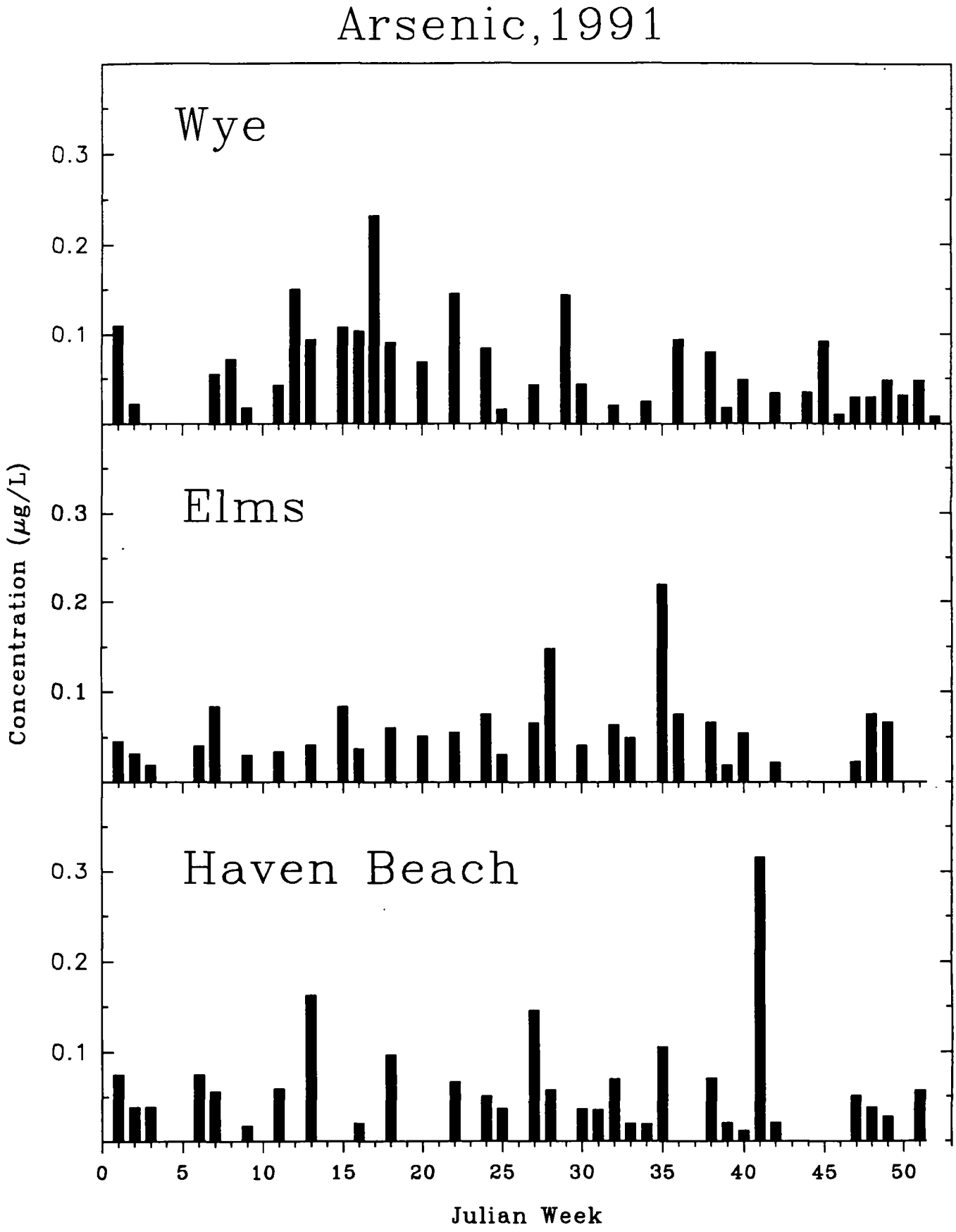


Figure IV.3.2 (Cont'd) Arsenic concentrations in precipitation, integrated weekly at each CBAD site.

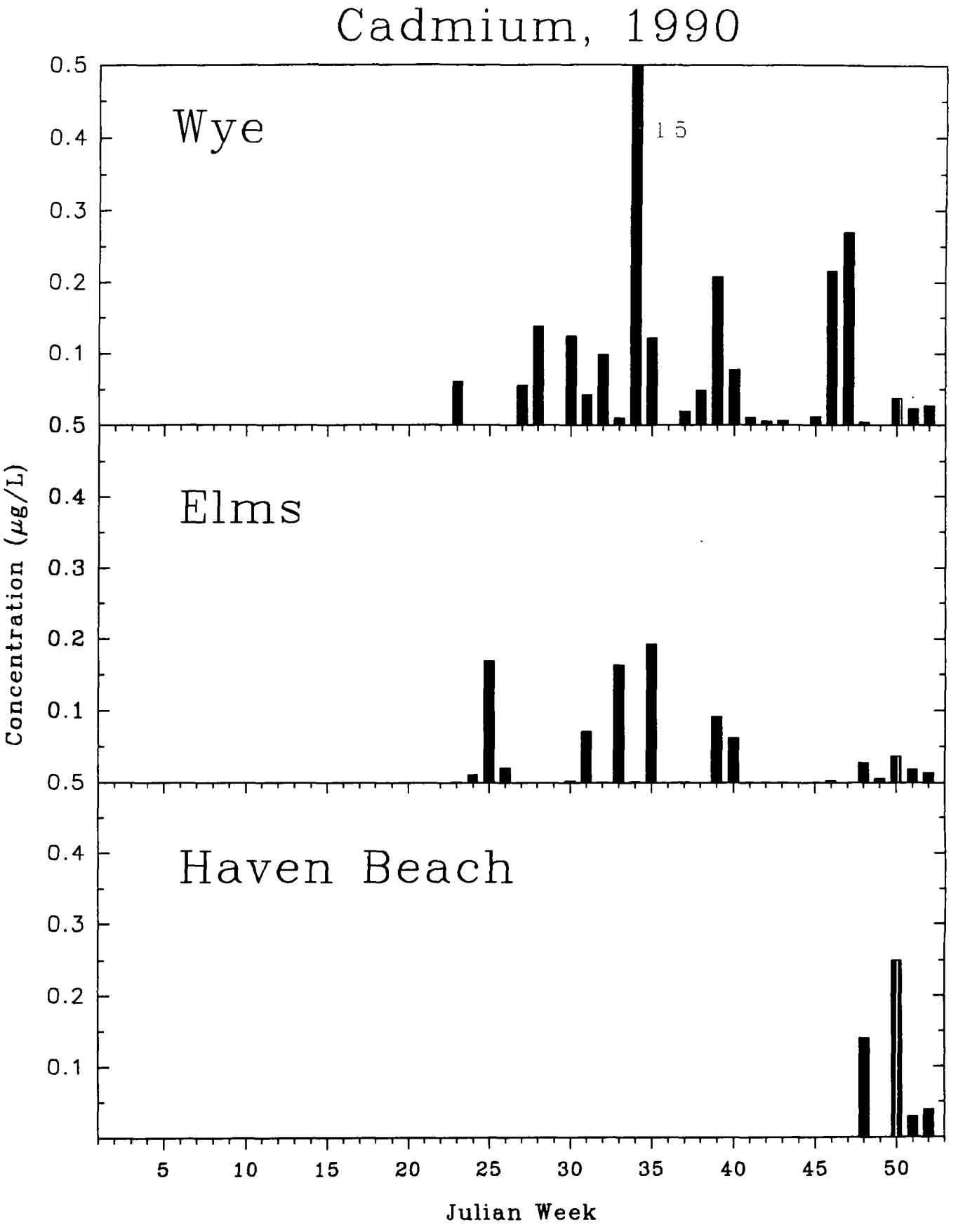


Figure IV.3.3. Cadmium concentrations in precipitation, integrated weekly at each CBAD site.

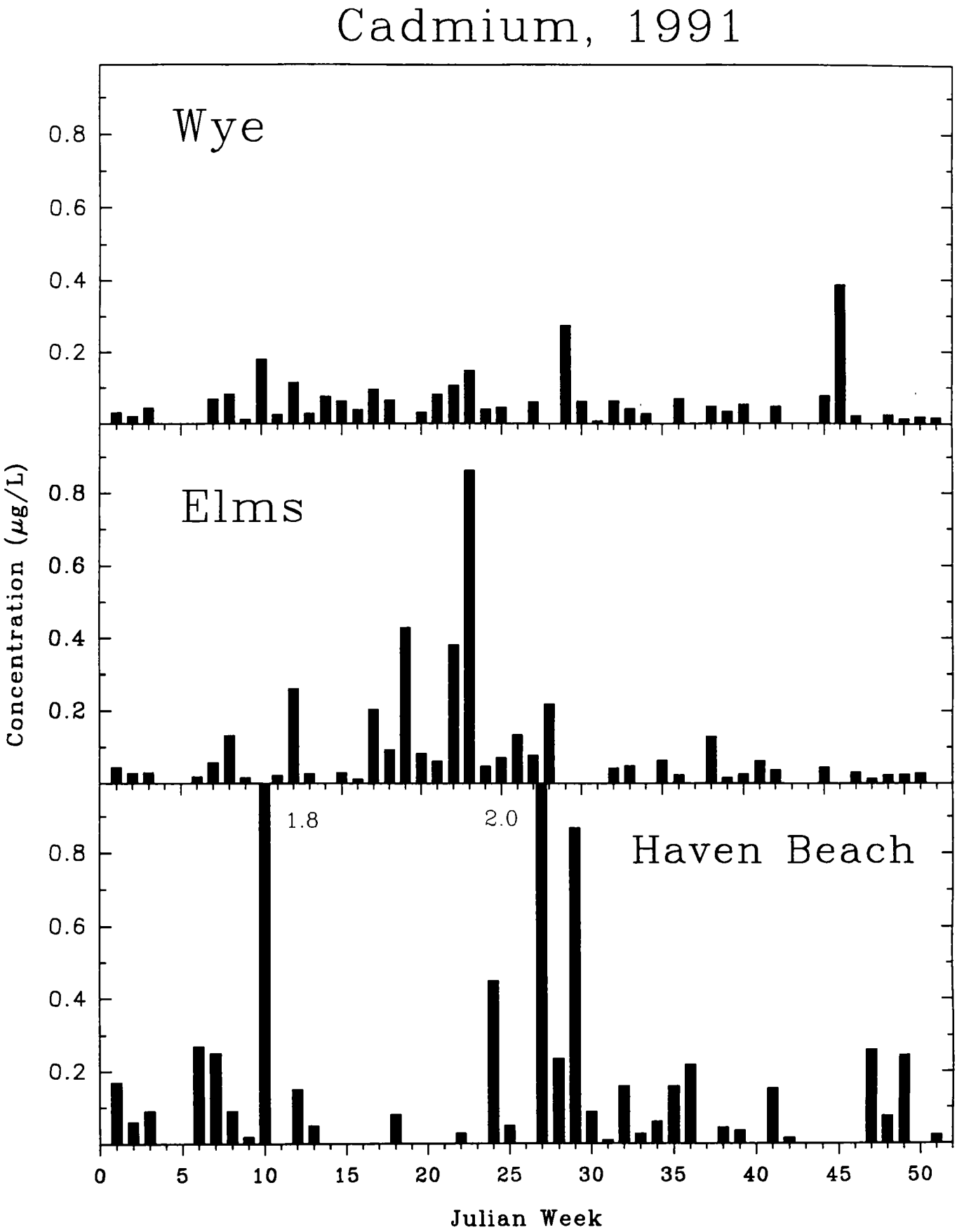


Figure IV.3.3 (Cont'd) Cadmium concentrations in precipitation, integrated weekly at each CBAD site.

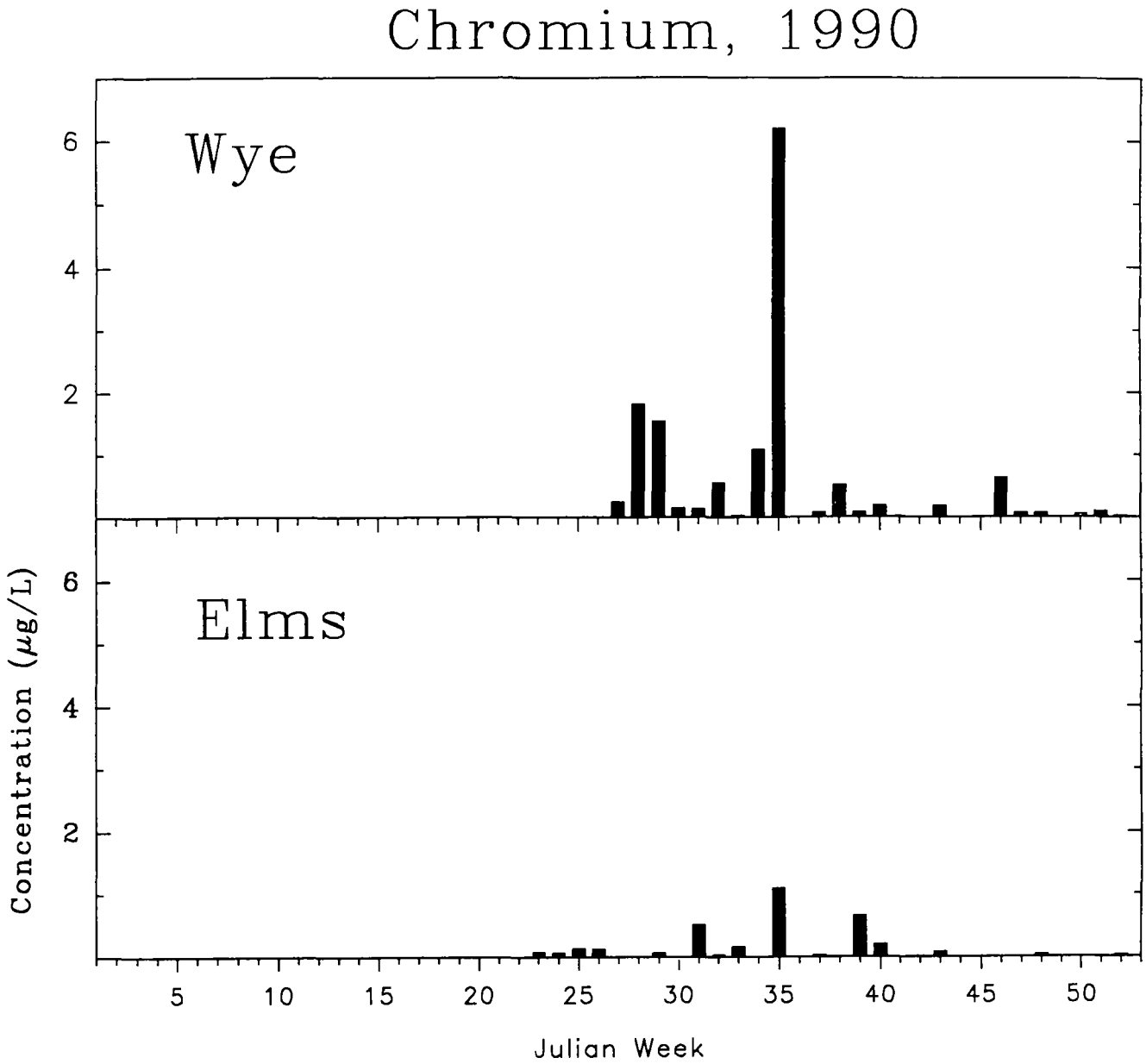


Figure IV.3.4. Chromium concentrations in precipitation, integrated weekly at each CBAD site.

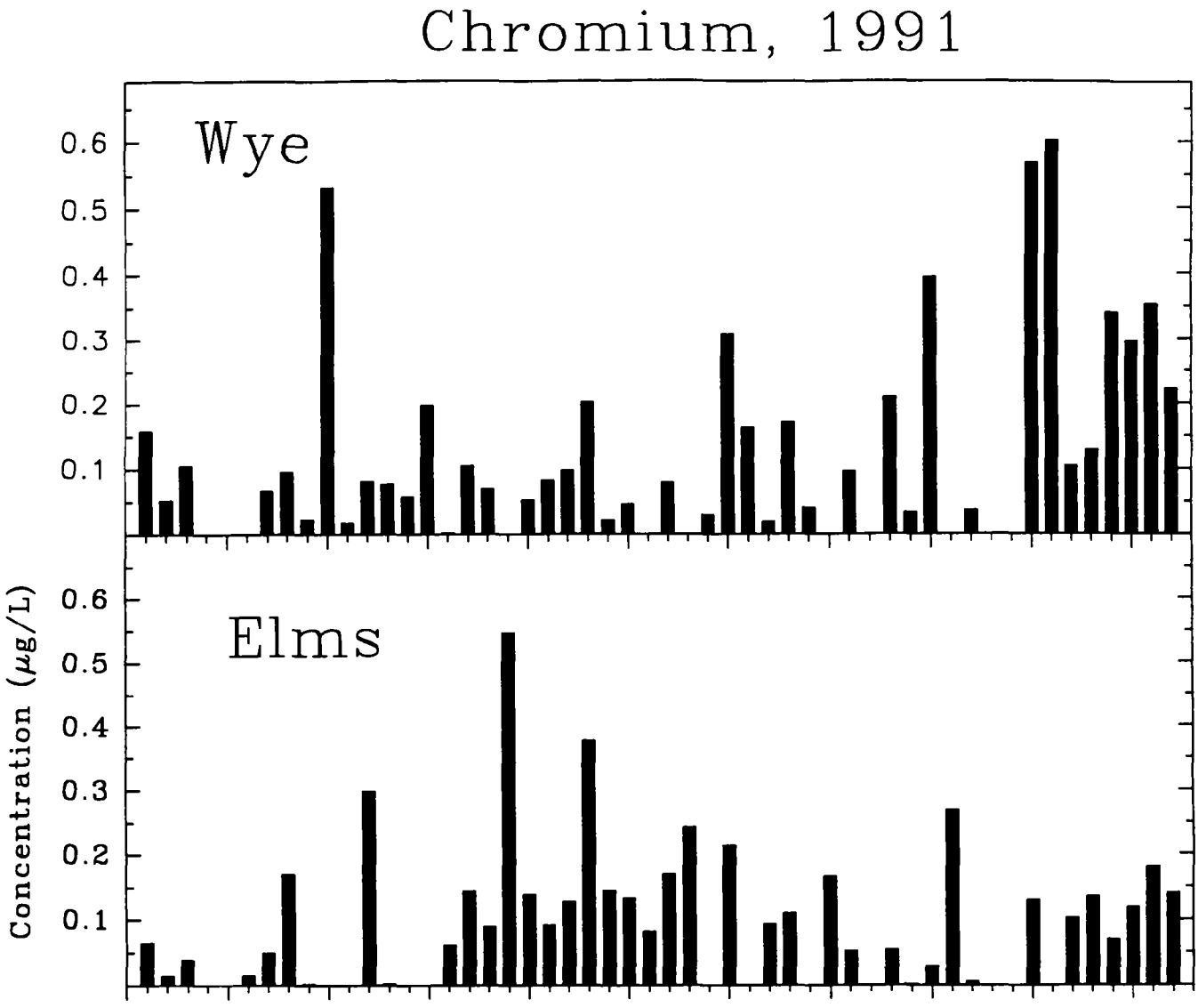


Figure IV.3.4. (Cont'd) Chromium concentrations in precipitation, integrated weekly at each CBAD site.

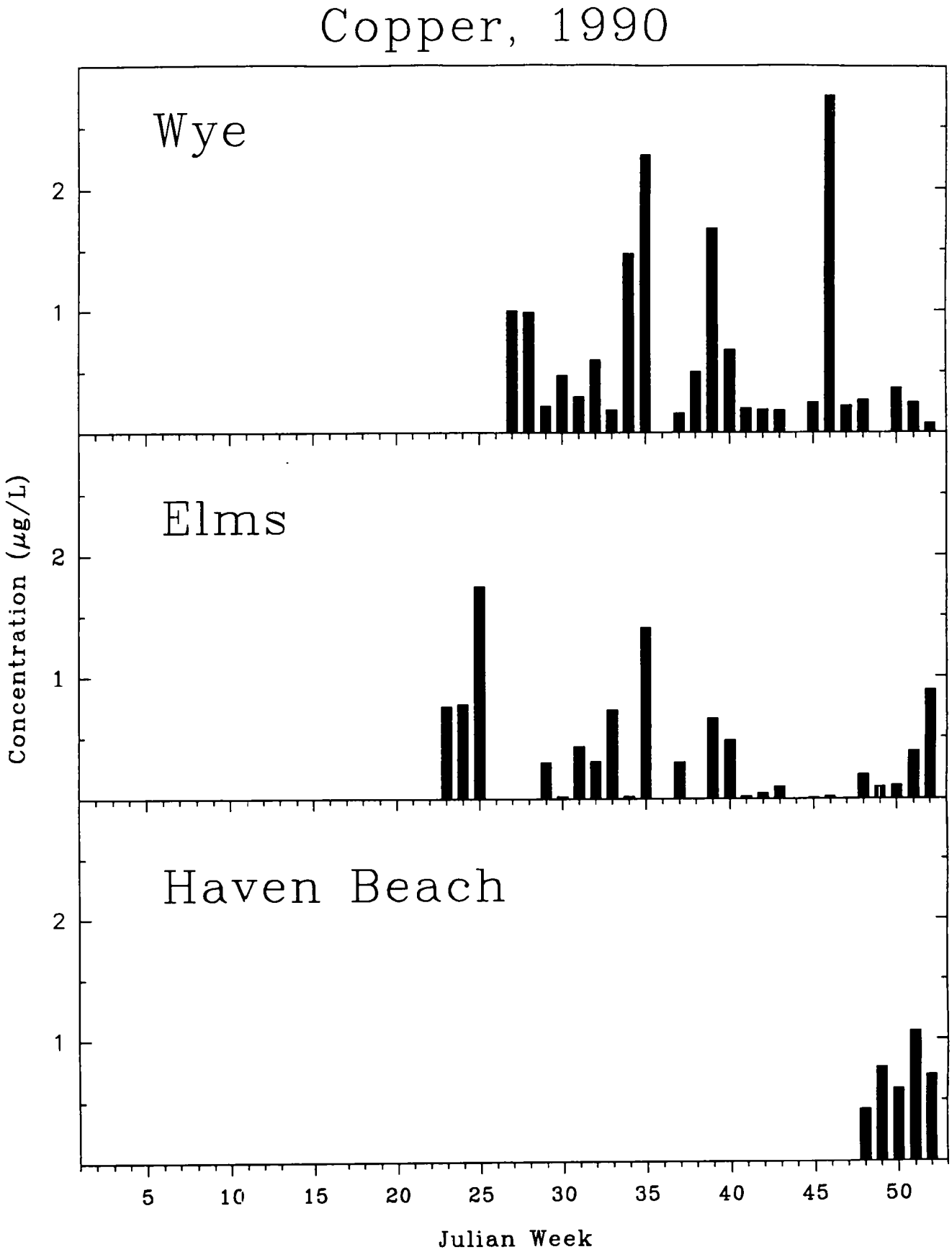


Figure IV.3.5. Copper concentrations in precipitation, integrated weekly at each CBAD site.

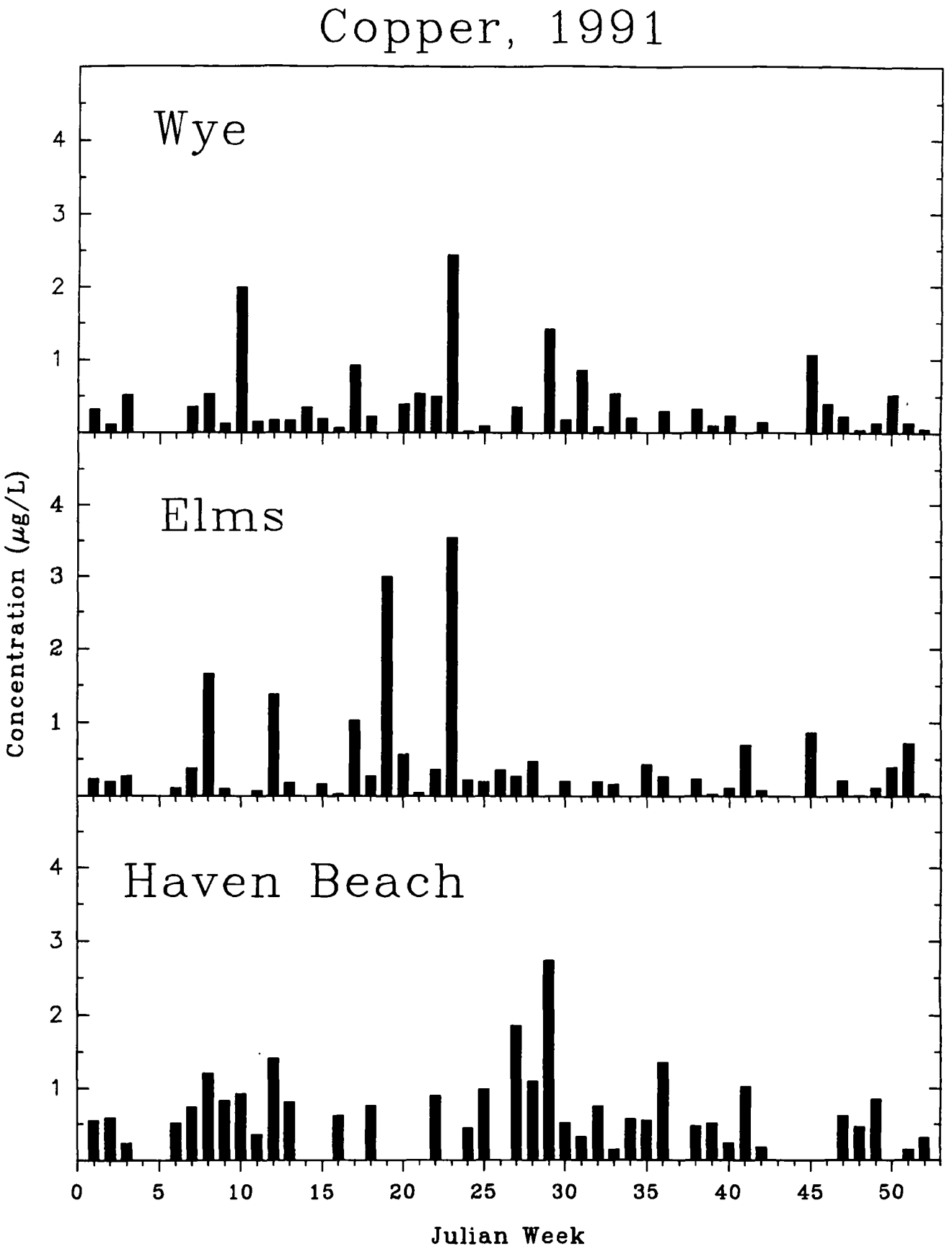


Figure IV.3.5. (Cont'd) Copper concentrations in precipitation, integrated weekly at each CBAD site.

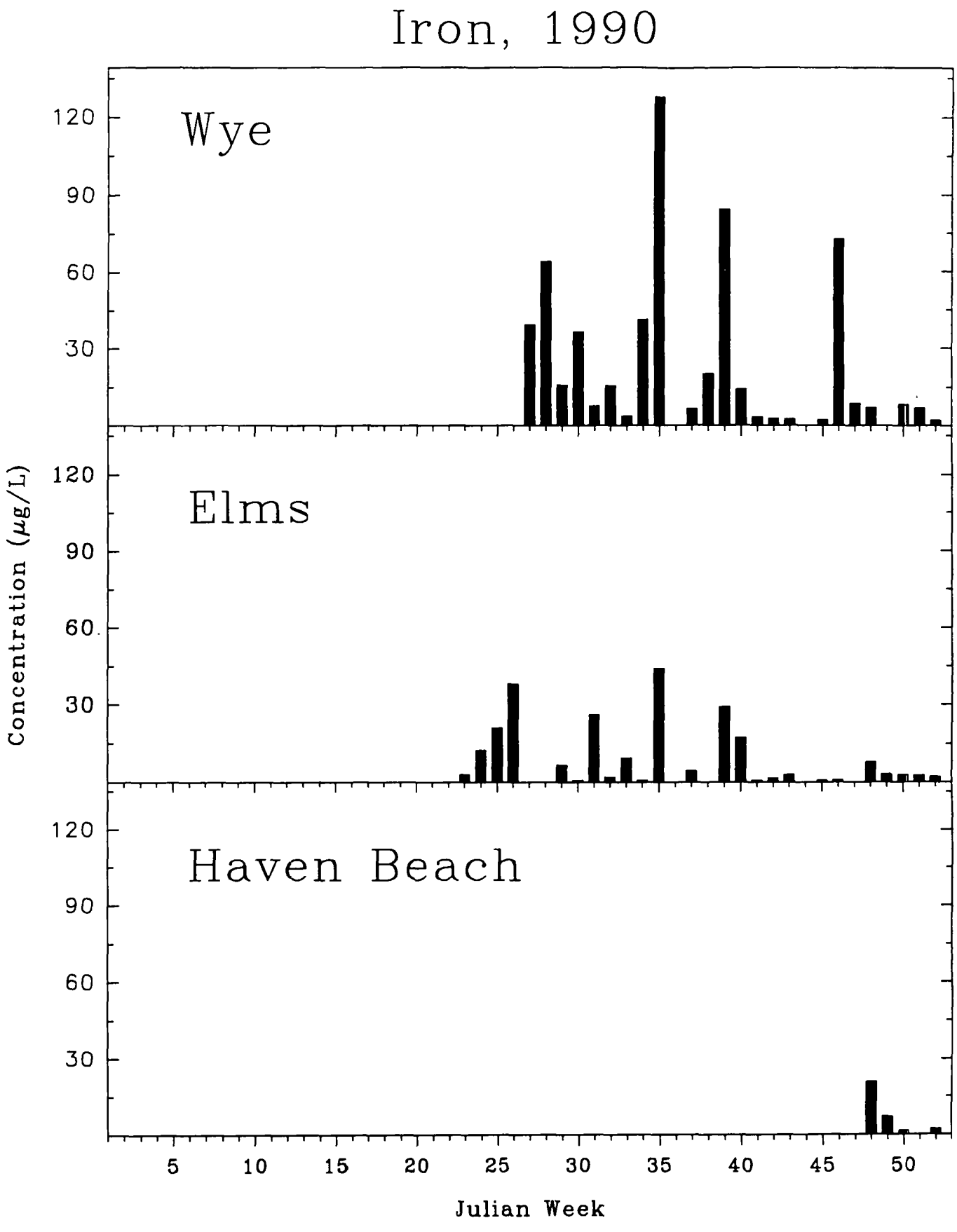


Figure IV.3.6. Iron concentrations in precipitation, integrated weekly at each CBAD site.

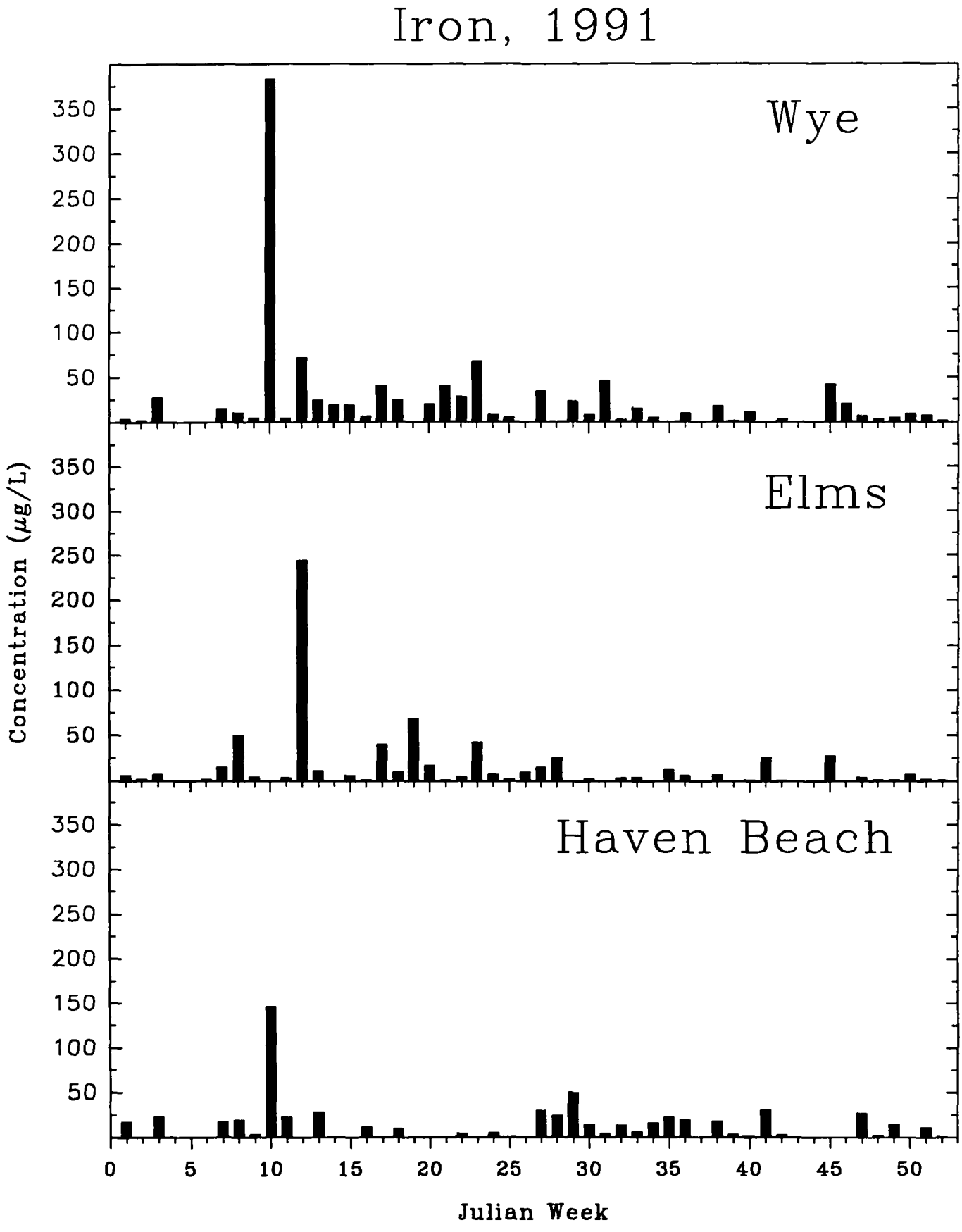


Figure IV.3.6. (Cont'd) Iron concentrations in precipitation, integrated weekly at each CBAD site.

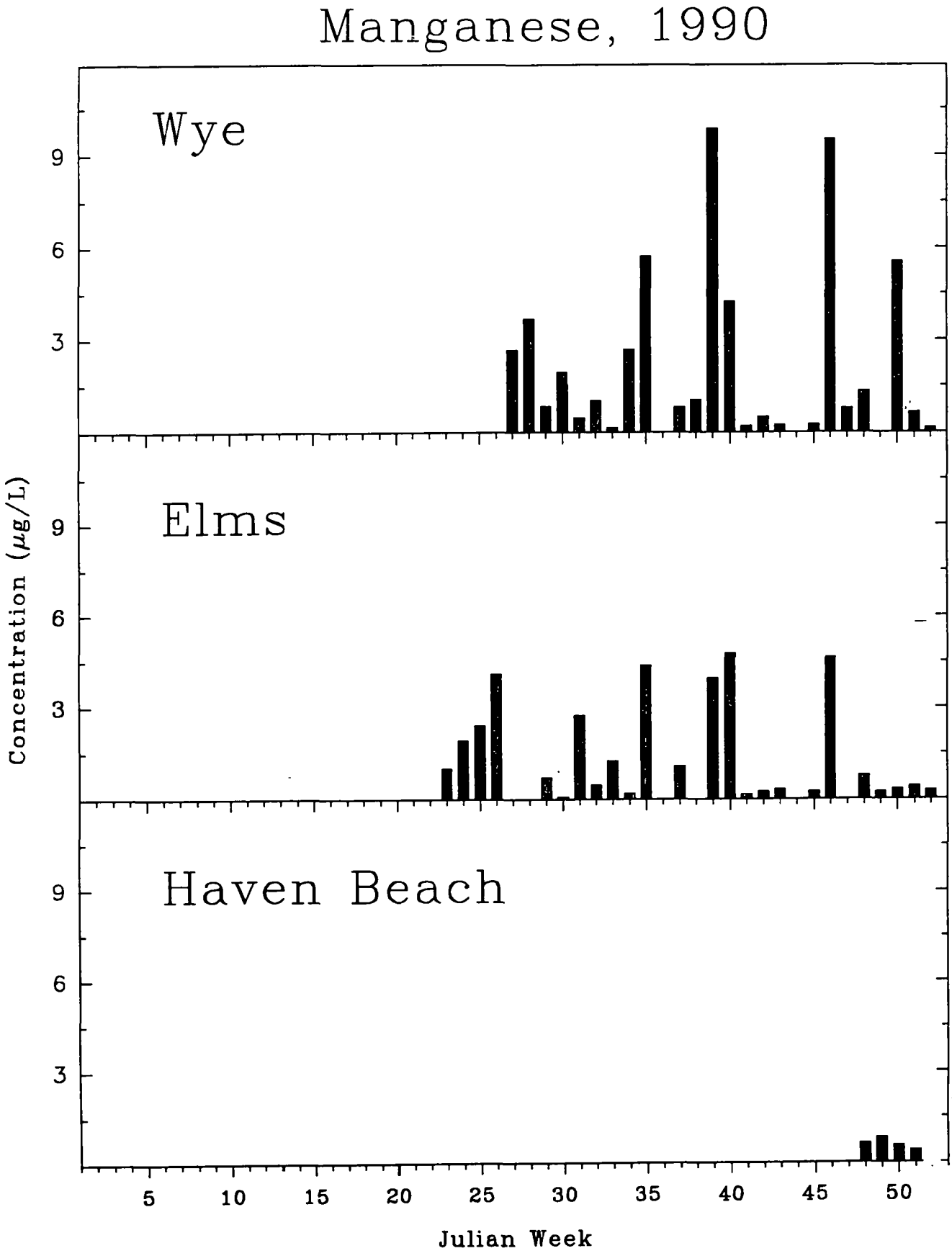


Figure IV.3.7. Manganese concentrations in precipitation, integrated weekly at each CBAD site.

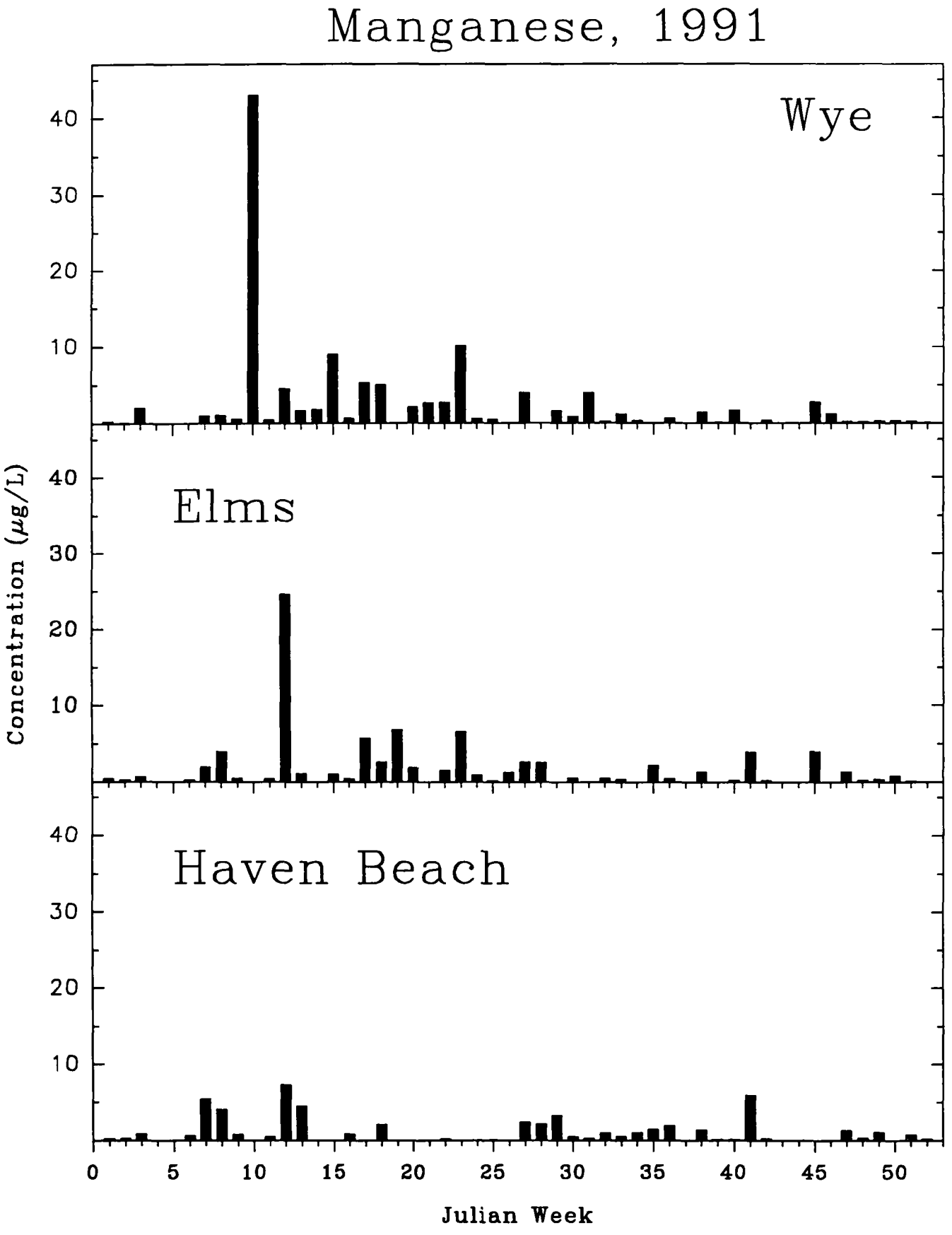


Figure IV.3.7. (Cont'd) Manganese concentrations in precipitation, integrated weekly at each CBAD site.

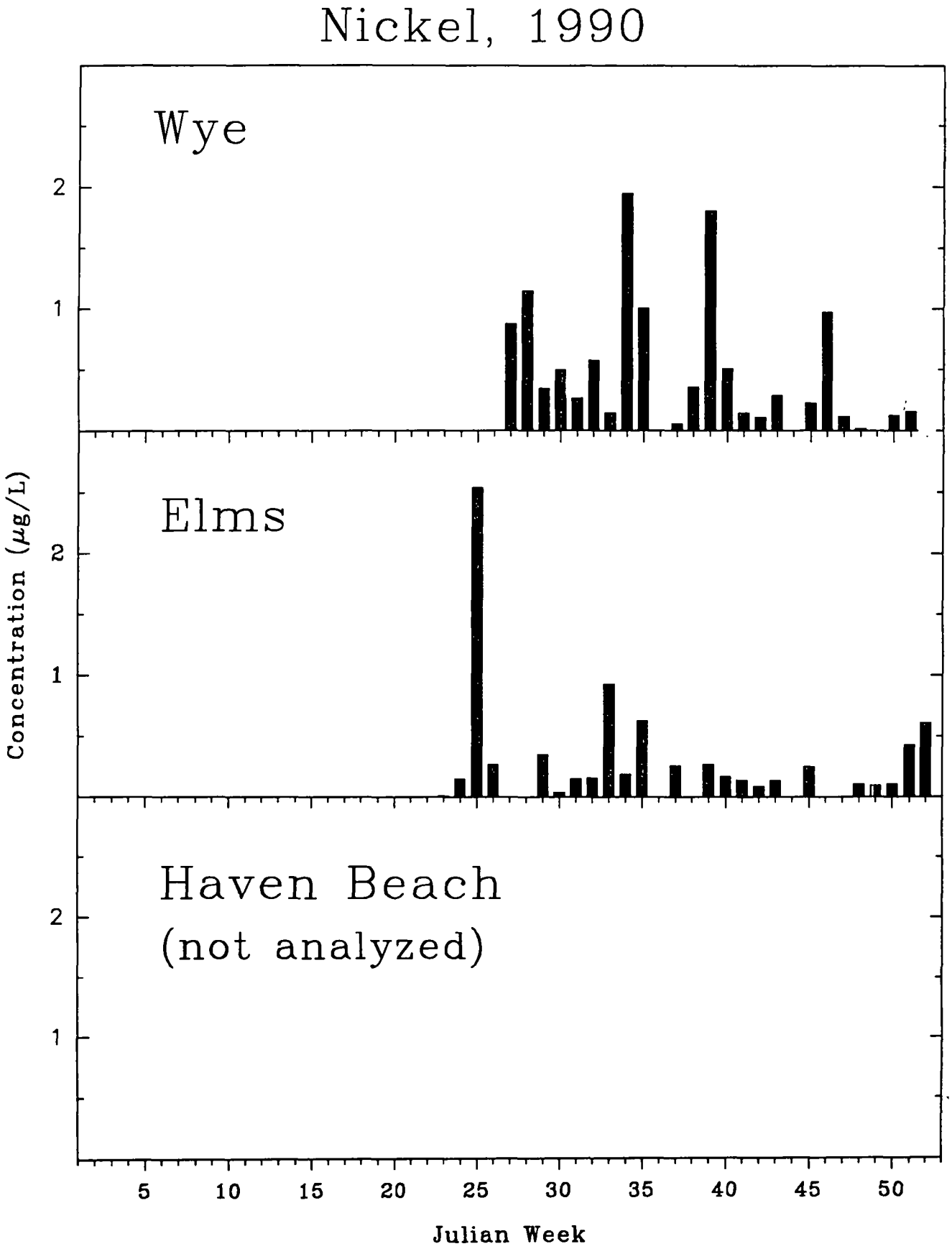


Figure IV.3.8. Nickel concentrations in precipitation, integrated weekly at each CBAD site.

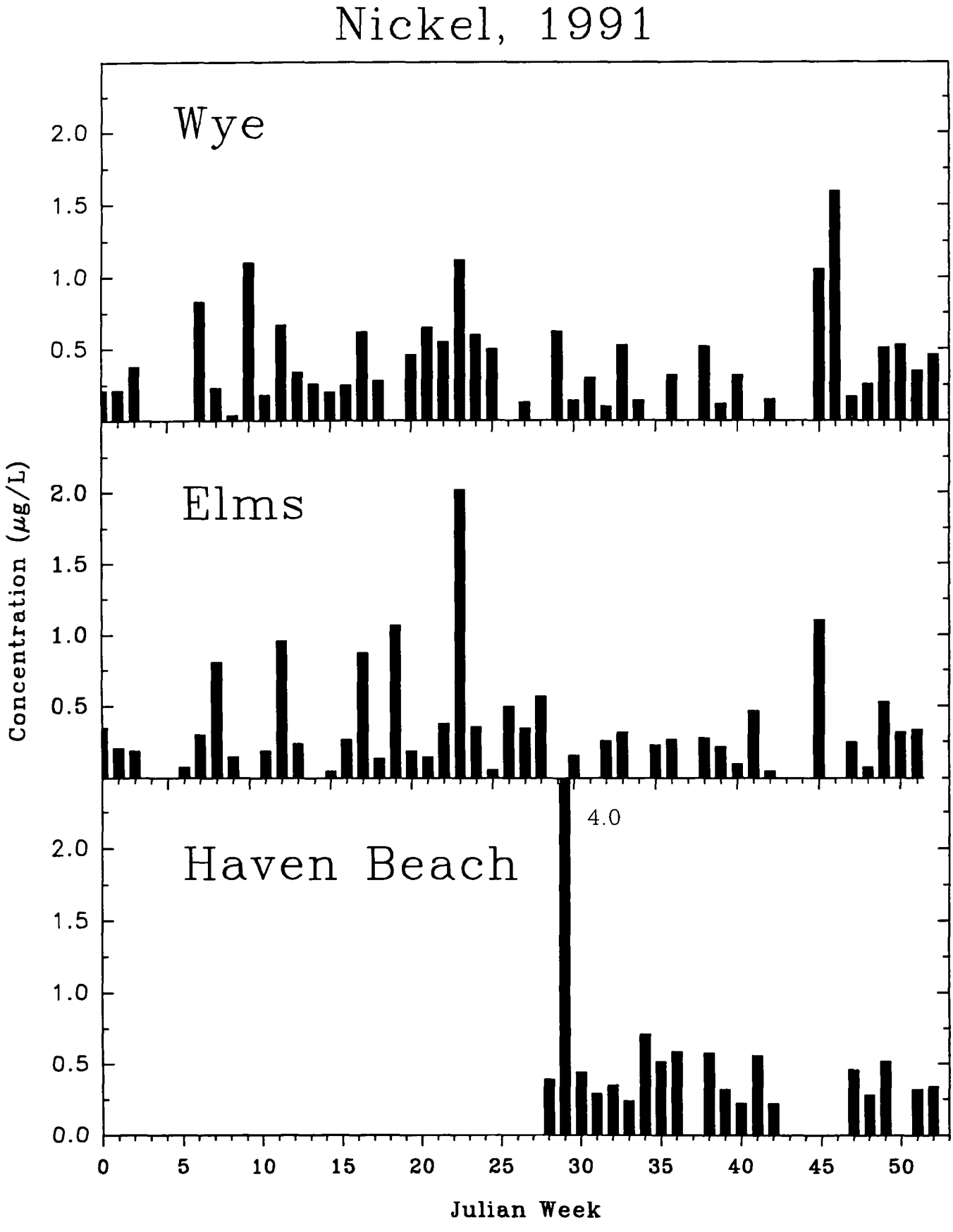


Figure IV.3.8. (Cont'd) Nickel concentrations in precipitation, integrated weekly at each CBAD site.

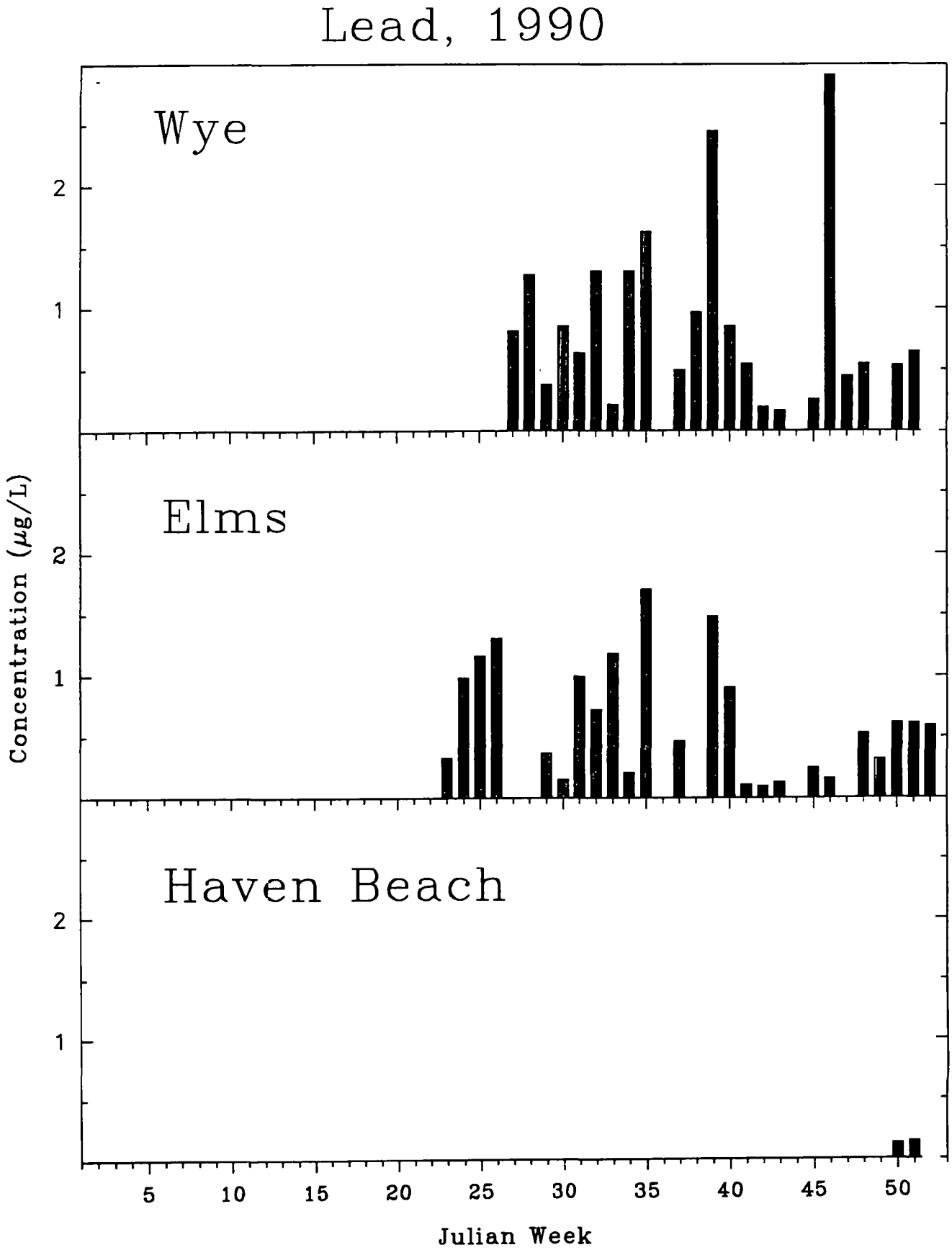


Figure IV.3.9. Lead concentrations in precipitation, integrated weekly at each CBAD site.

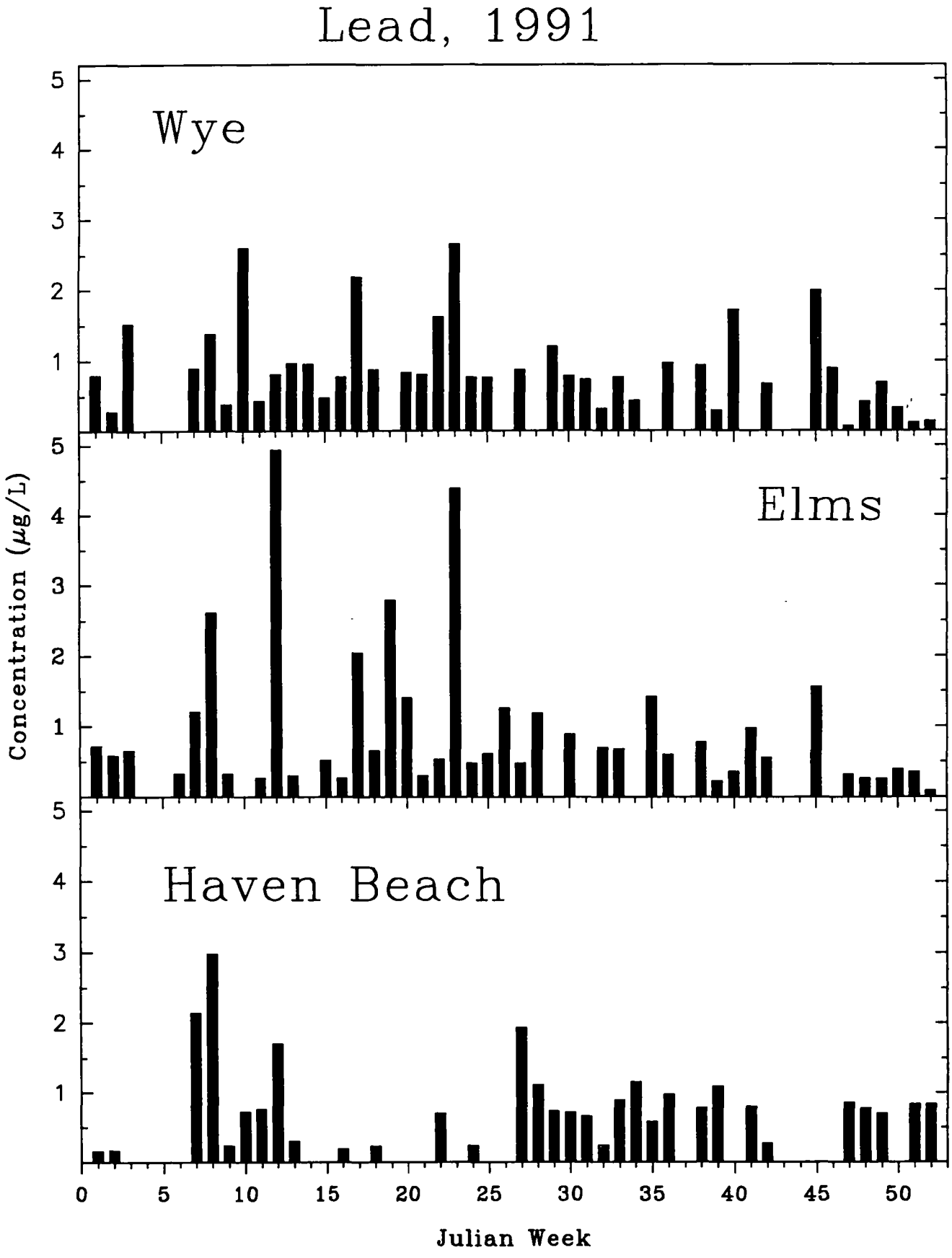


Figure IV.3.9. (Cont'd.) Lead concentrations in precipitation, integrated weekly at each CBAD site.

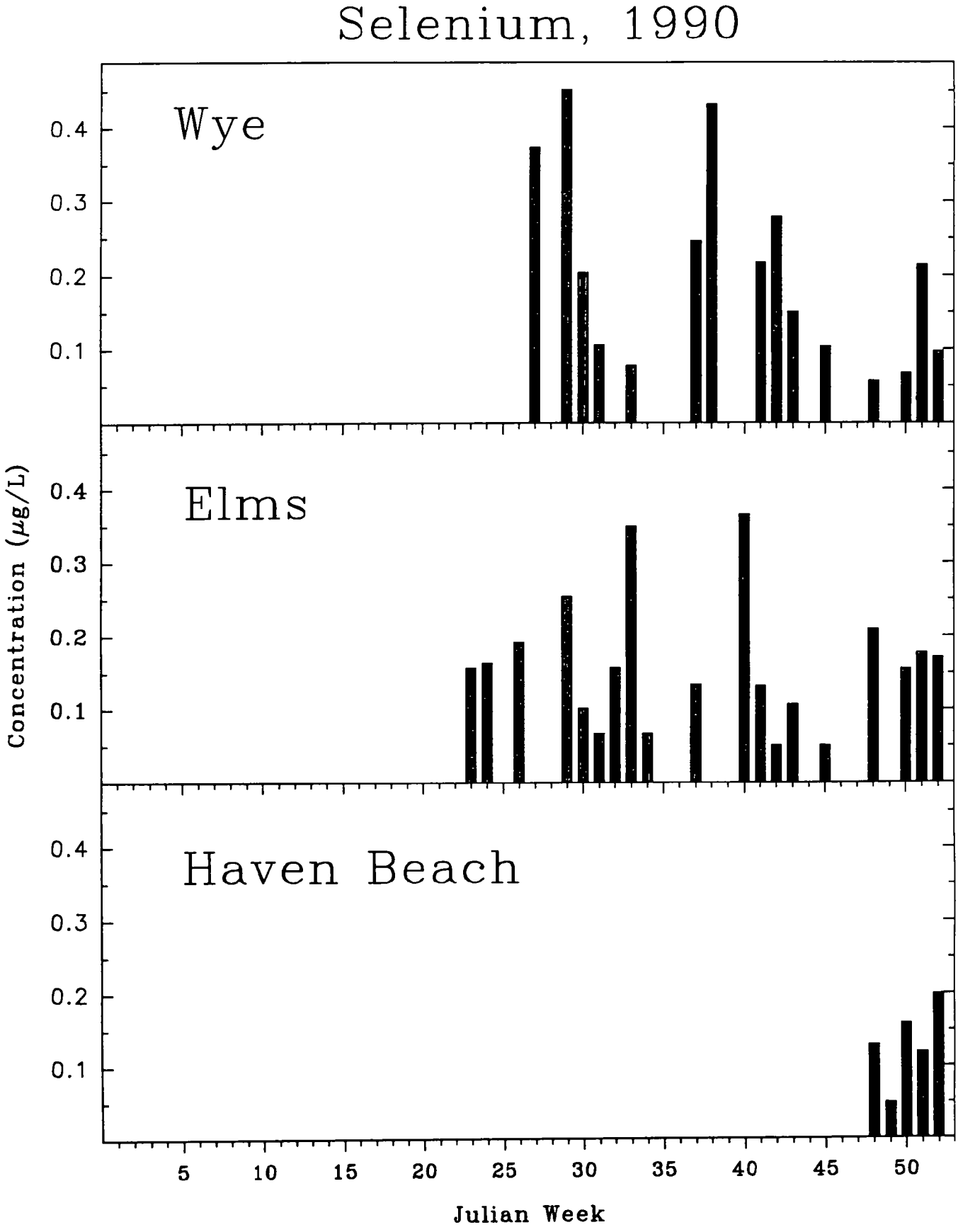


Figure IV.3.10. Selenium concentrations in precipitation, integrated weekly at each CBAD site.

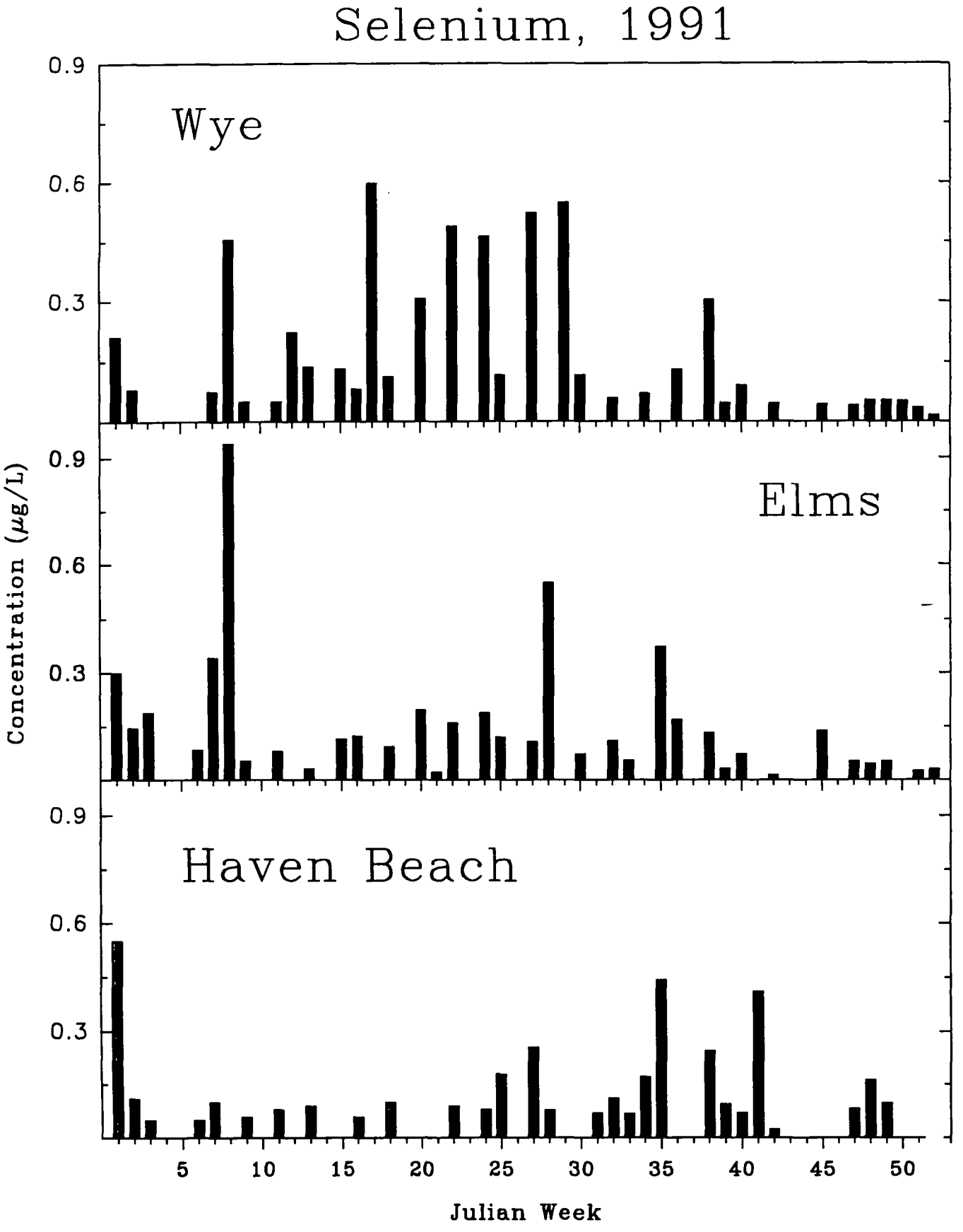


Figure IV.3.10. (Cont'd) Selenium concentrations in precipitation, integrated weekly at each CBAD site.

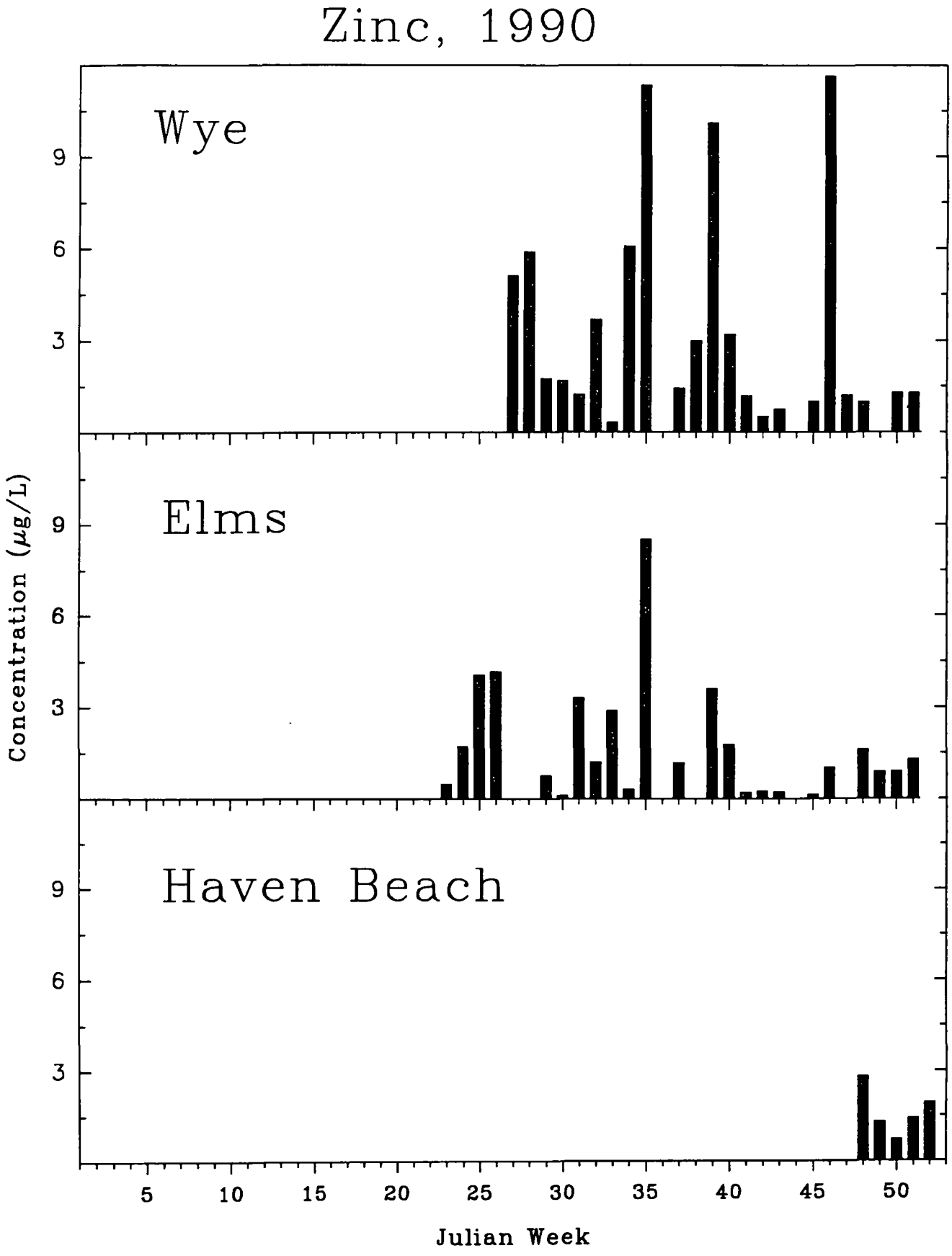


Figure IV.3.11. Zinc concentrations in precipitation, integrated weekly at each CBAD site.

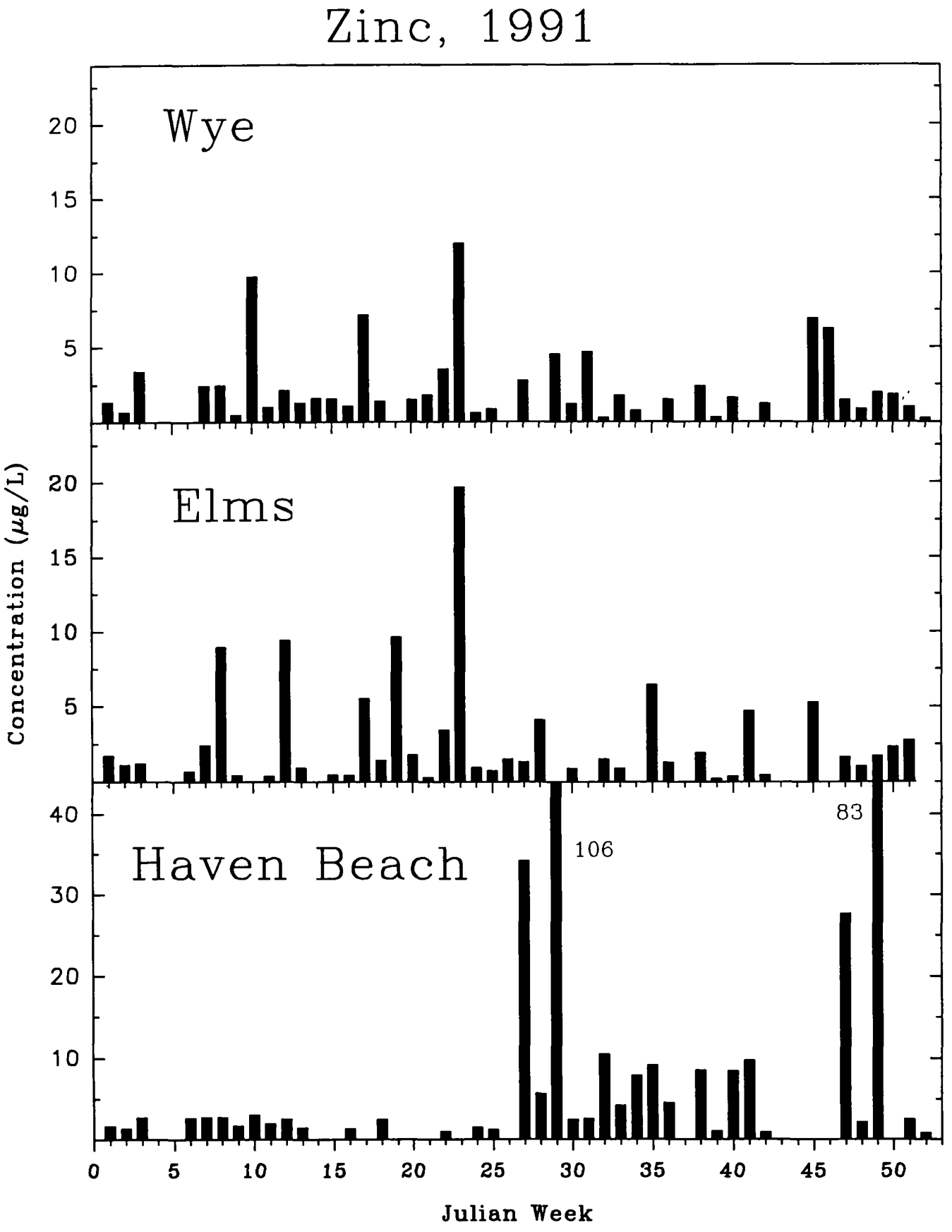


Figure IV.3.11. (Cont'd) Zinc concentrations in precipitation, integrated weekly at each CBAD site.

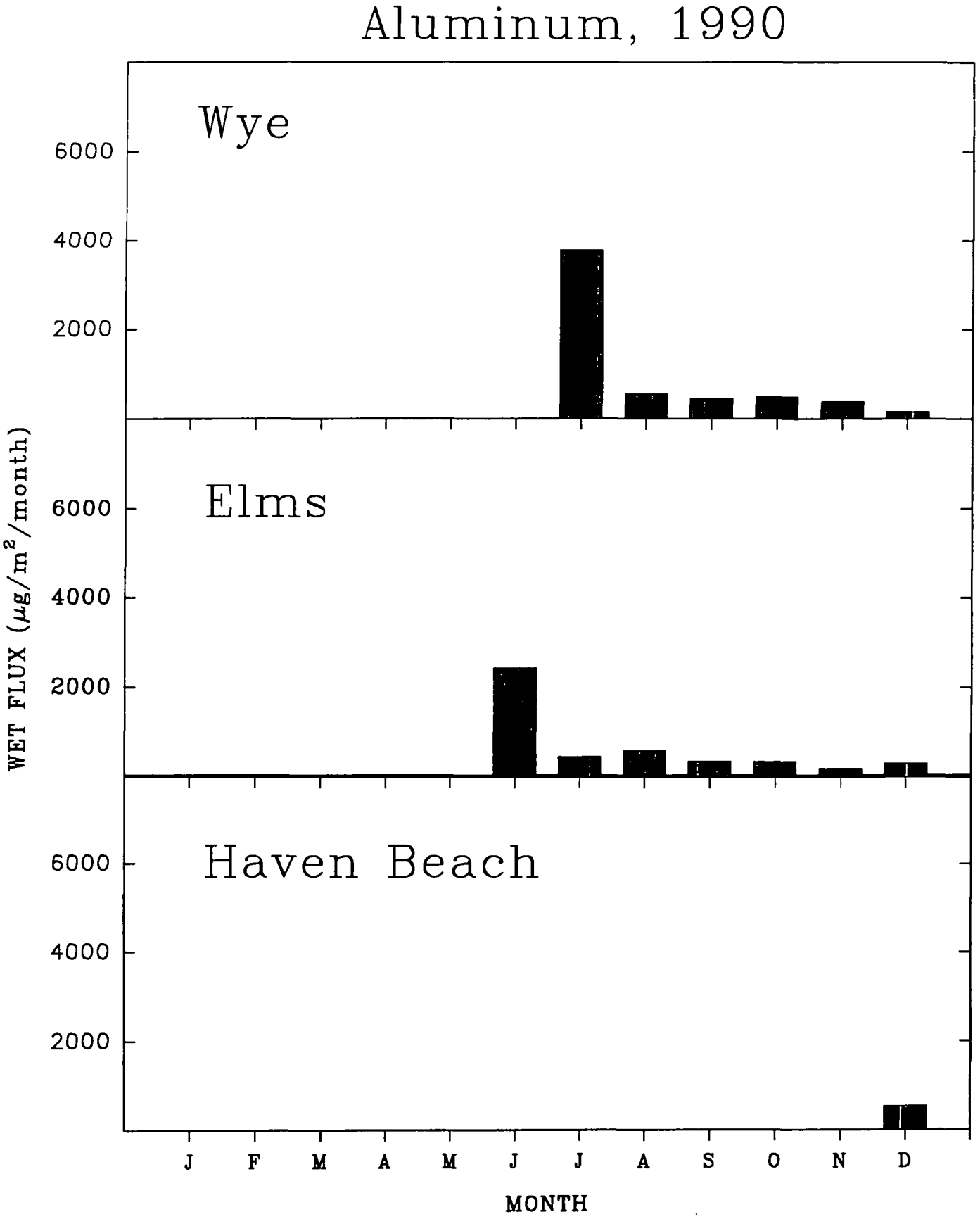


Figure IV.3.12. Monthly integrated wet deposition of Aluminium at each CBAD site.

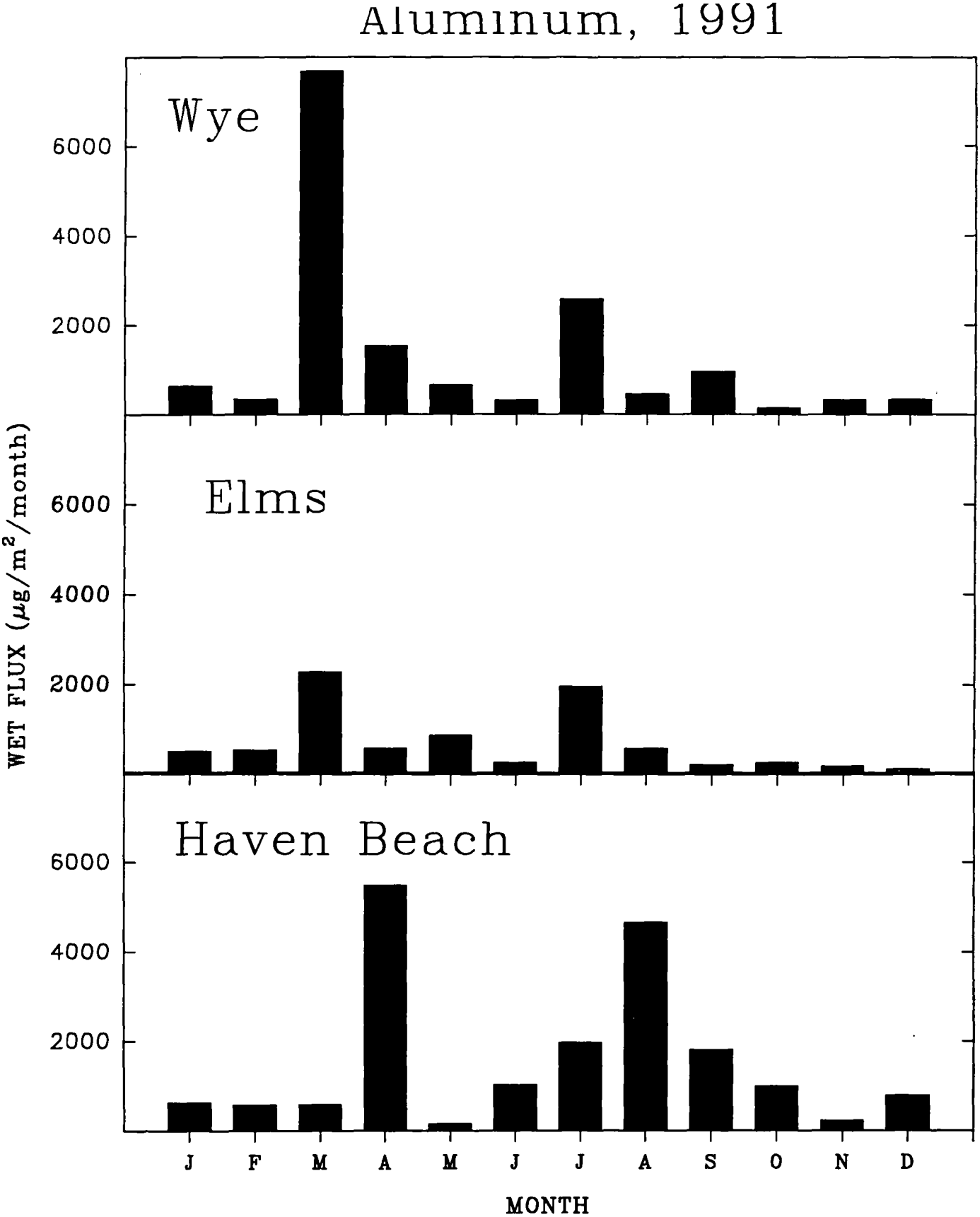


Figure IV.3.12 (Cont'd) Monthly integrated wet deposition of Aluminium at each CBAD site.

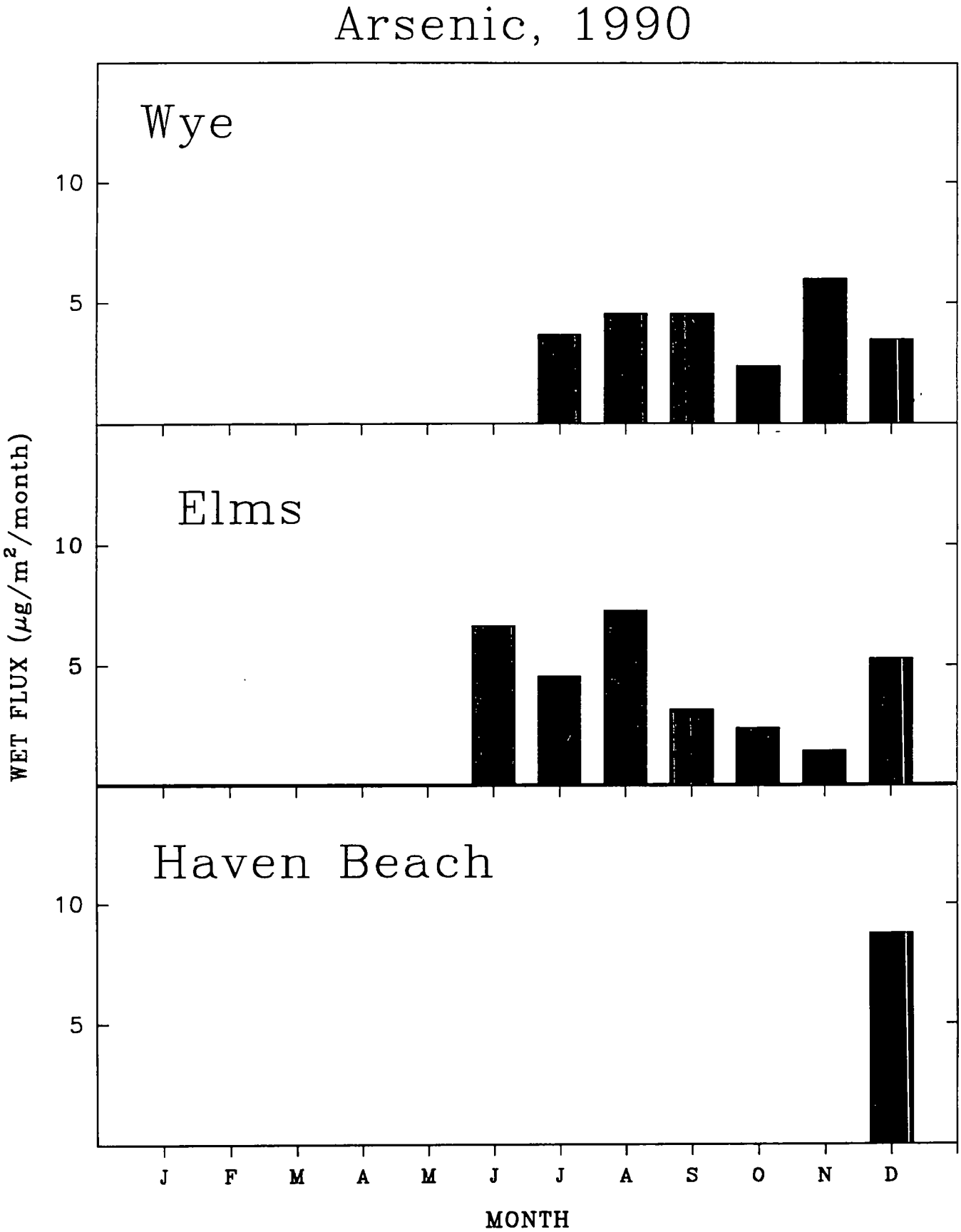


Figure IV.3.13. Monthly integrated wet deposition of Arsenic at each CBAD site.

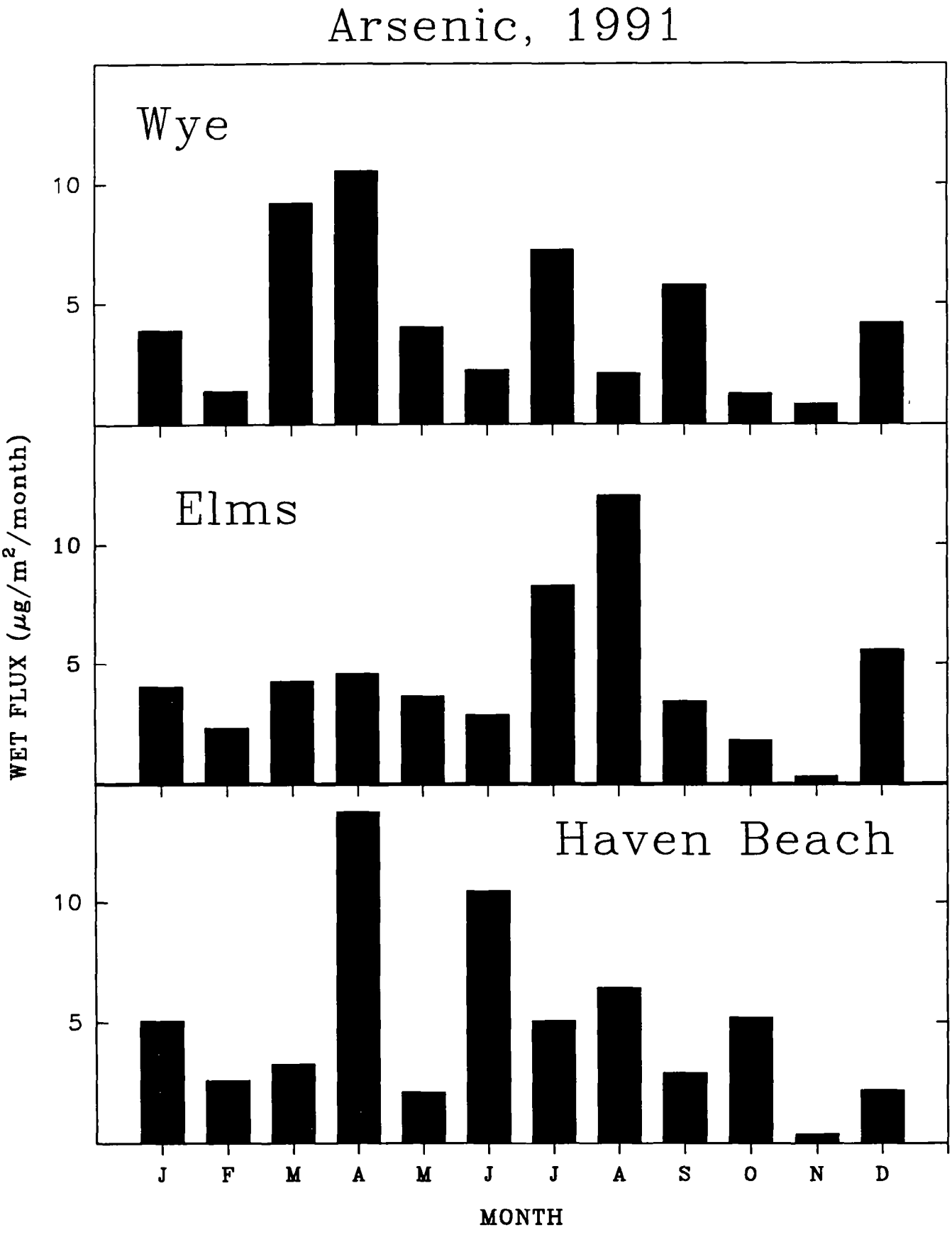


Figure IV.3.13. (Cont'd) Monthly integrated wet deposition of Arsenic at each CBAD site.

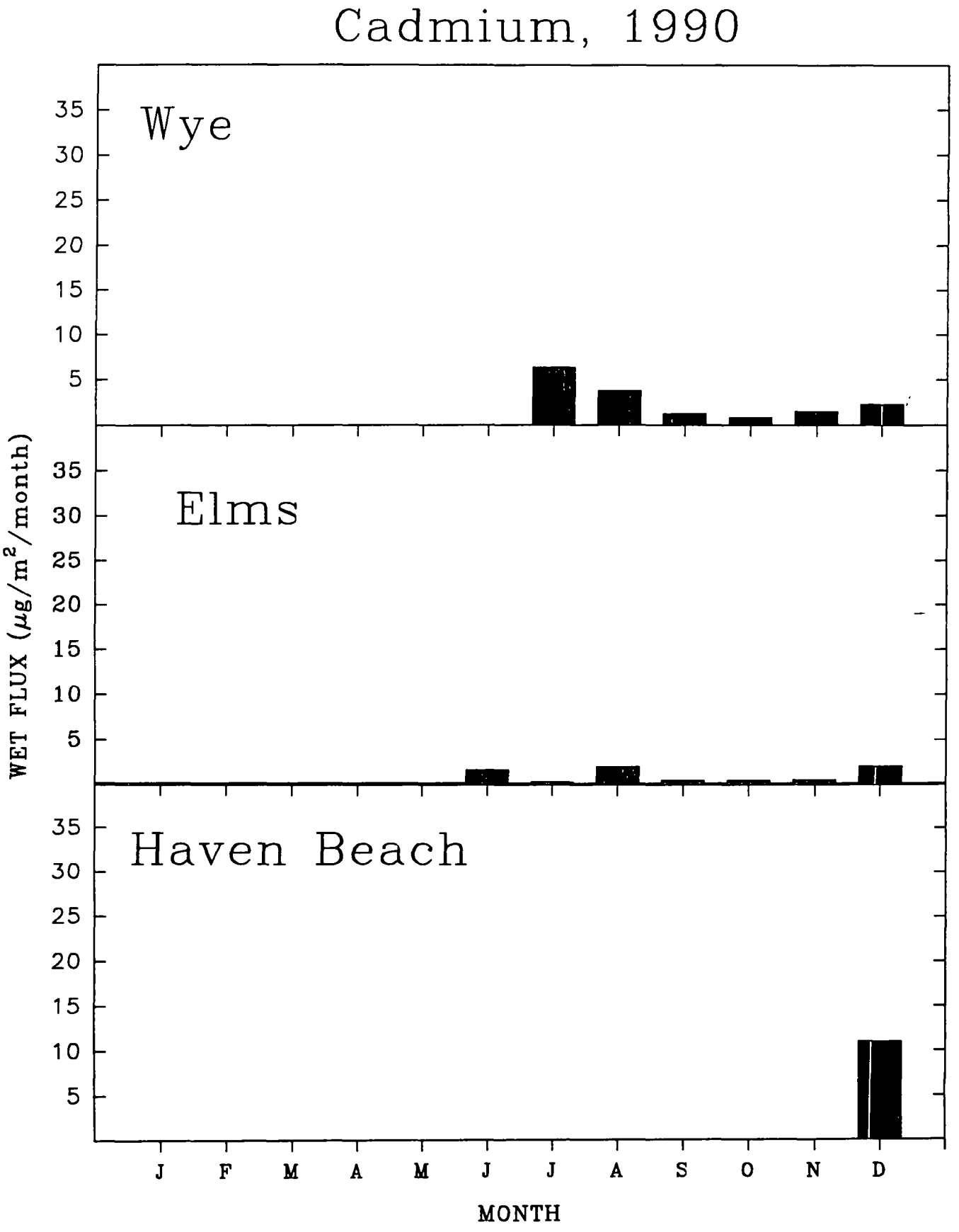


Figure IV.3.14. Monthly integrated wet deposition of Cadmium at each CBAD site.

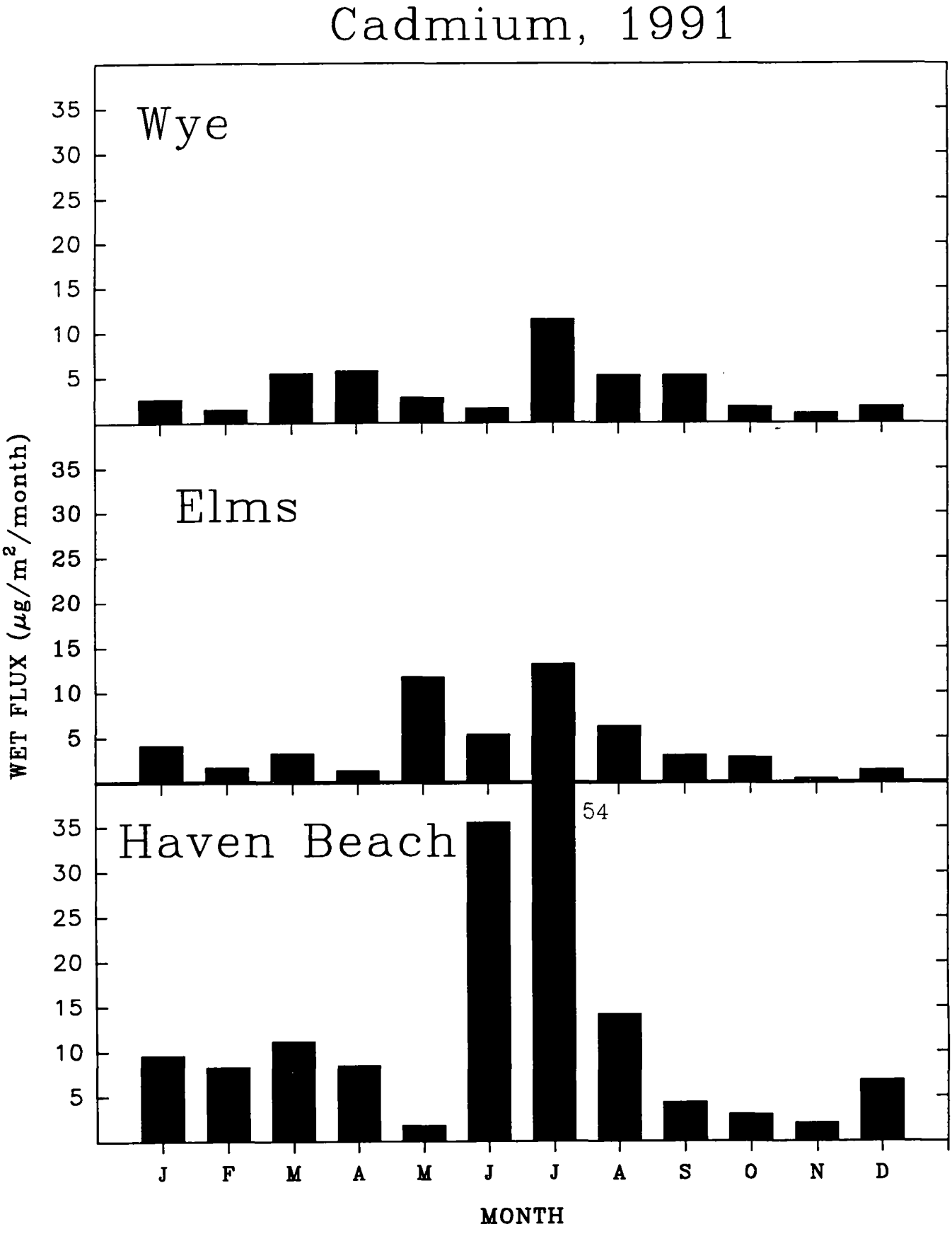


Figure IV.3.14. (Cont'd) Monthly integrated wet deposition of Cadmium at each CBAD site.

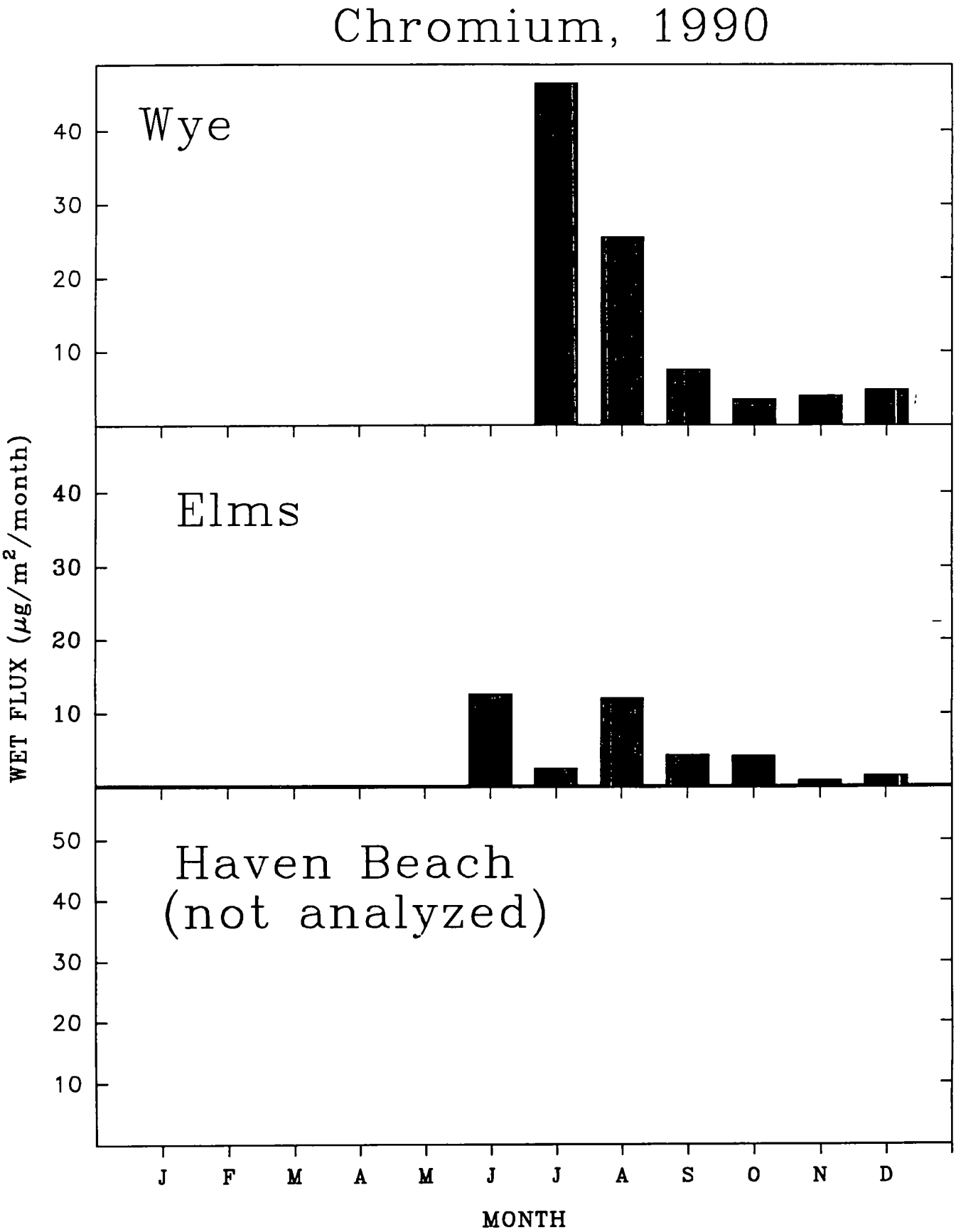


Figure IV.3.15. Monthly integrated wet deposition of Chromium at each CBAD site.

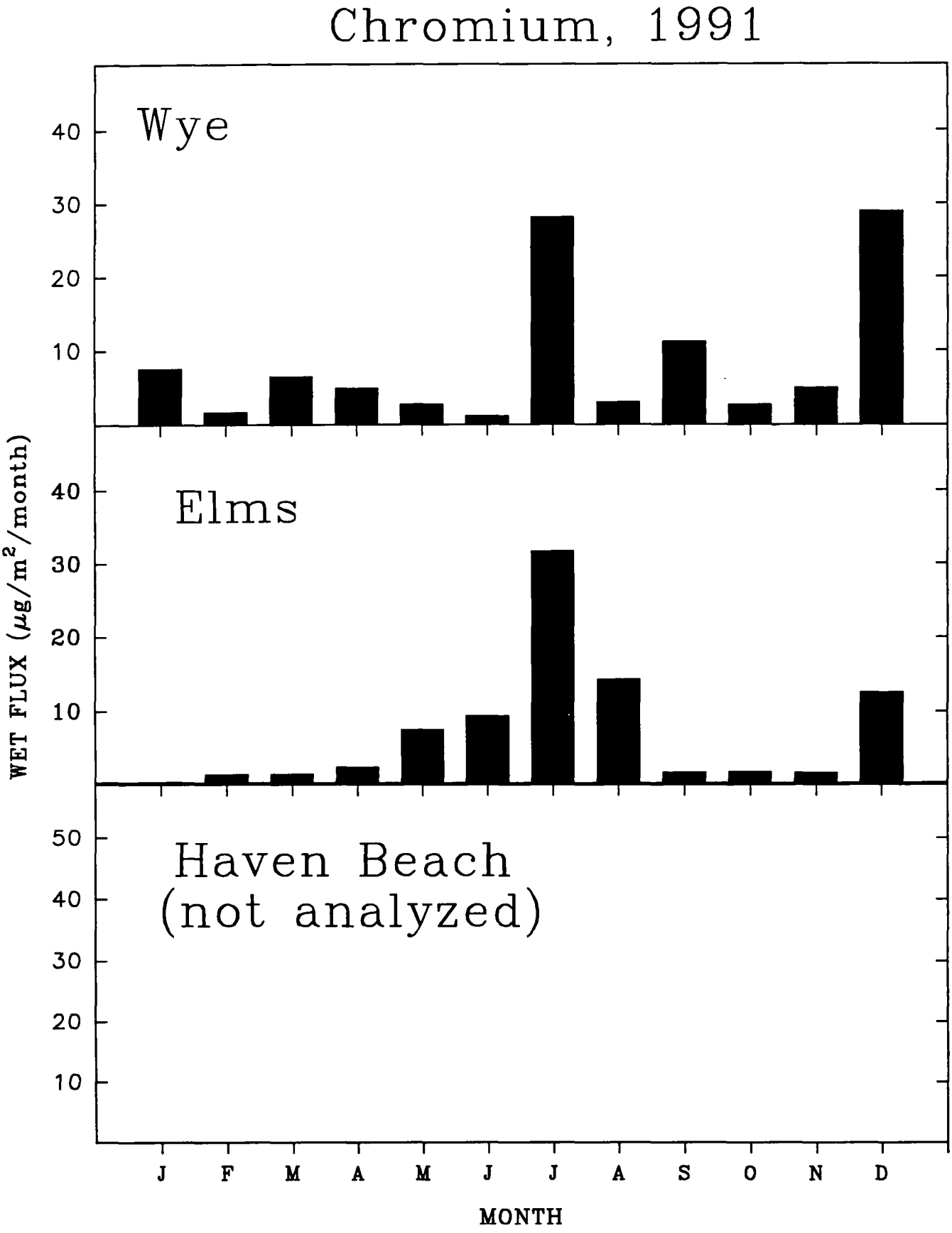


Figure IV.3.15. (Cont'd) Monthly integrated wet deposition of Chromium at each CBAD site.

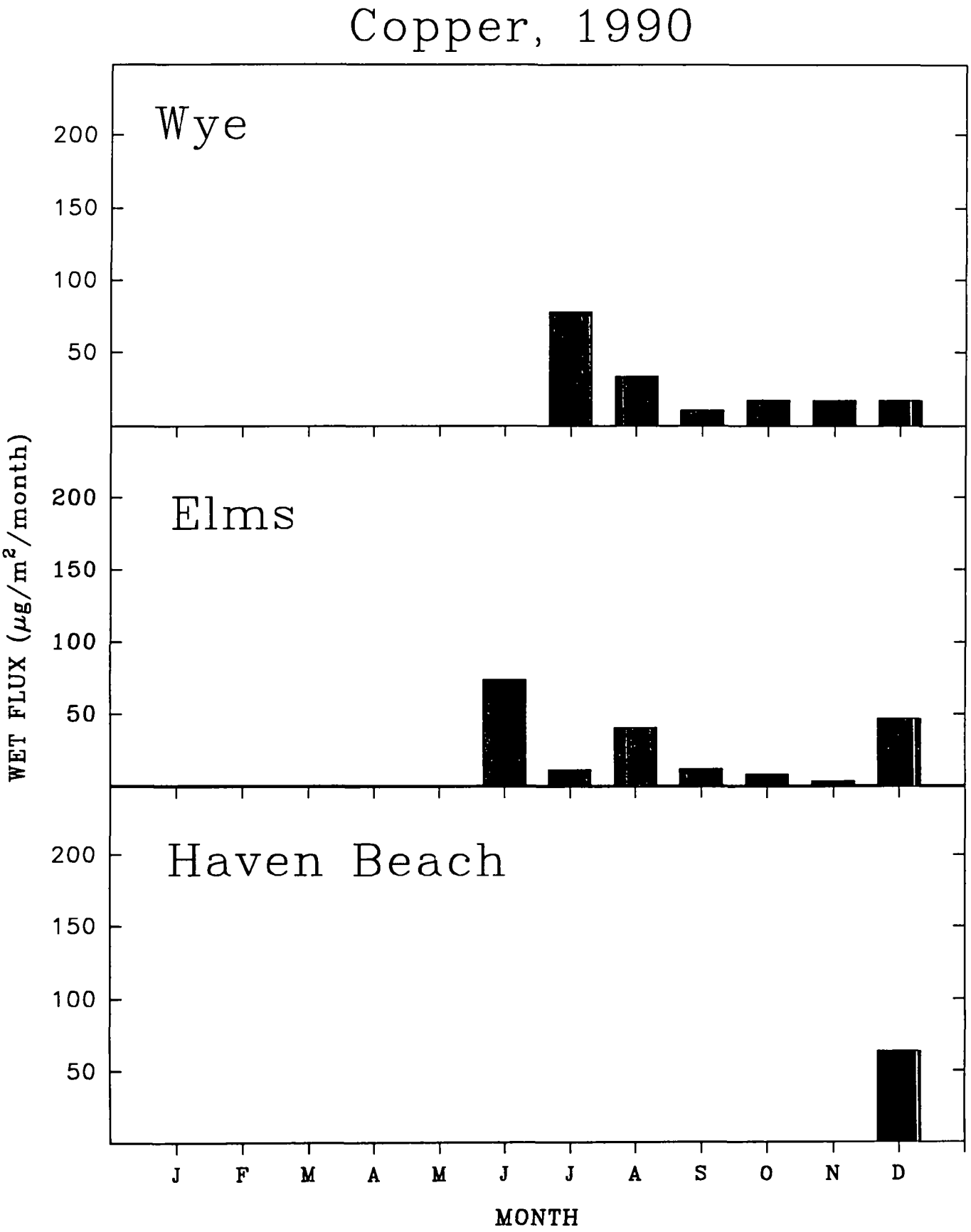


Figure IV.3.16. Monthly integrated wet deposition of Copper at each CBAD site.

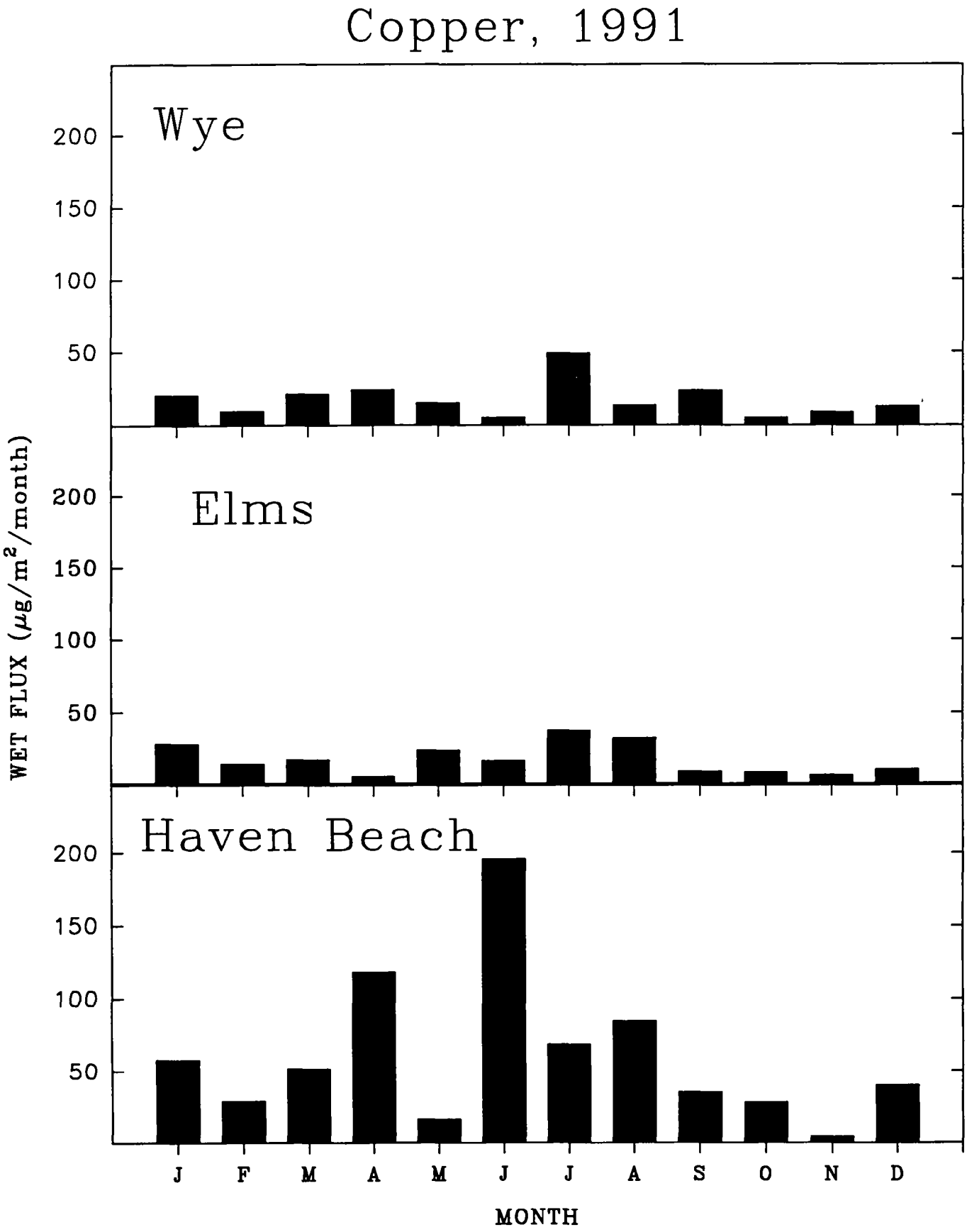


Figure IV.3.16. (Cont'd) Monthly integrated wet deposition of Copper at each CBAD site.

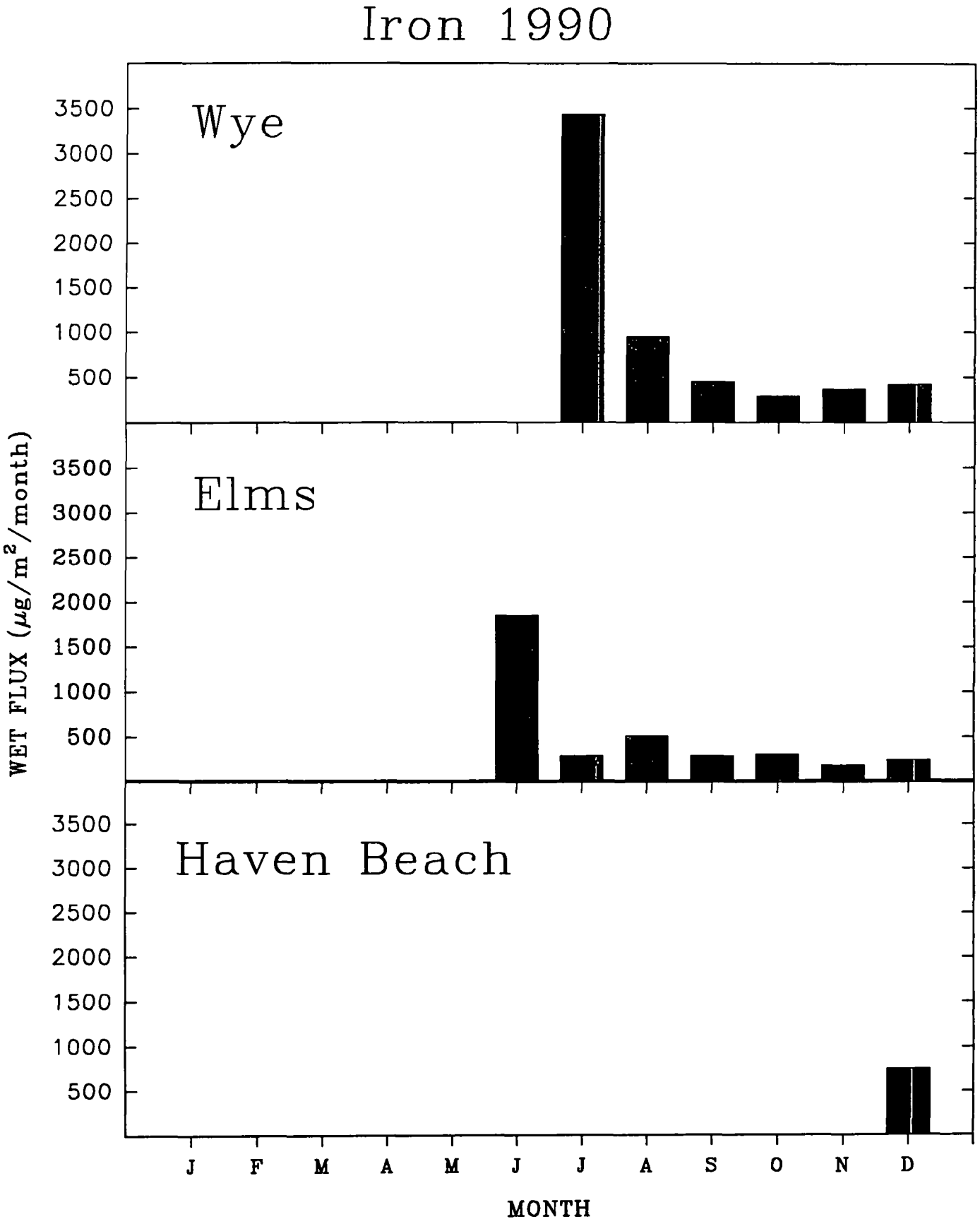


Figure IV.3.17. Monthly integrated wet deposition of Iron at each CBAD site.

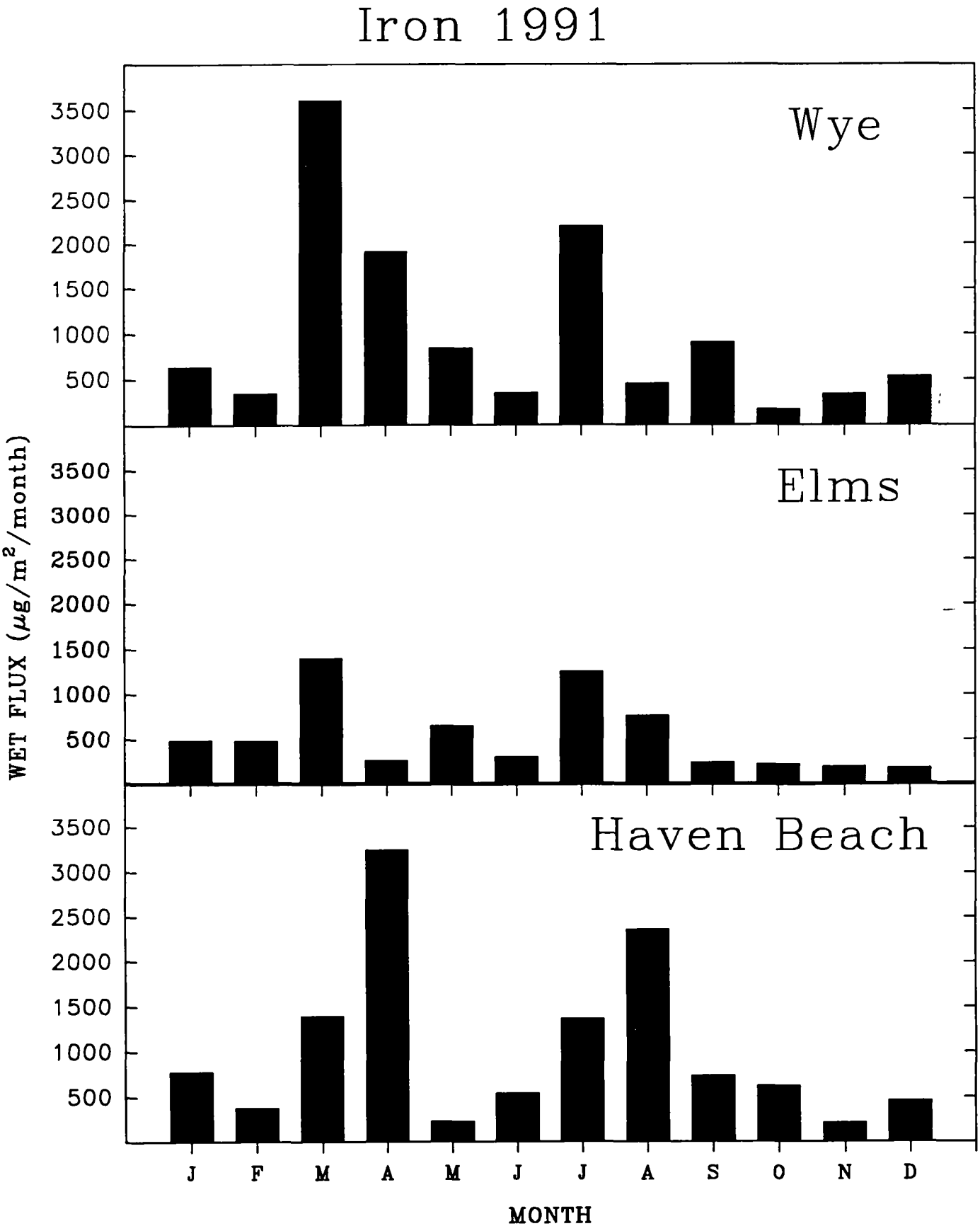


Figure IV.3.17. (Cont'd) Monthly integrated wet deposition of Iron at each CBAD site.

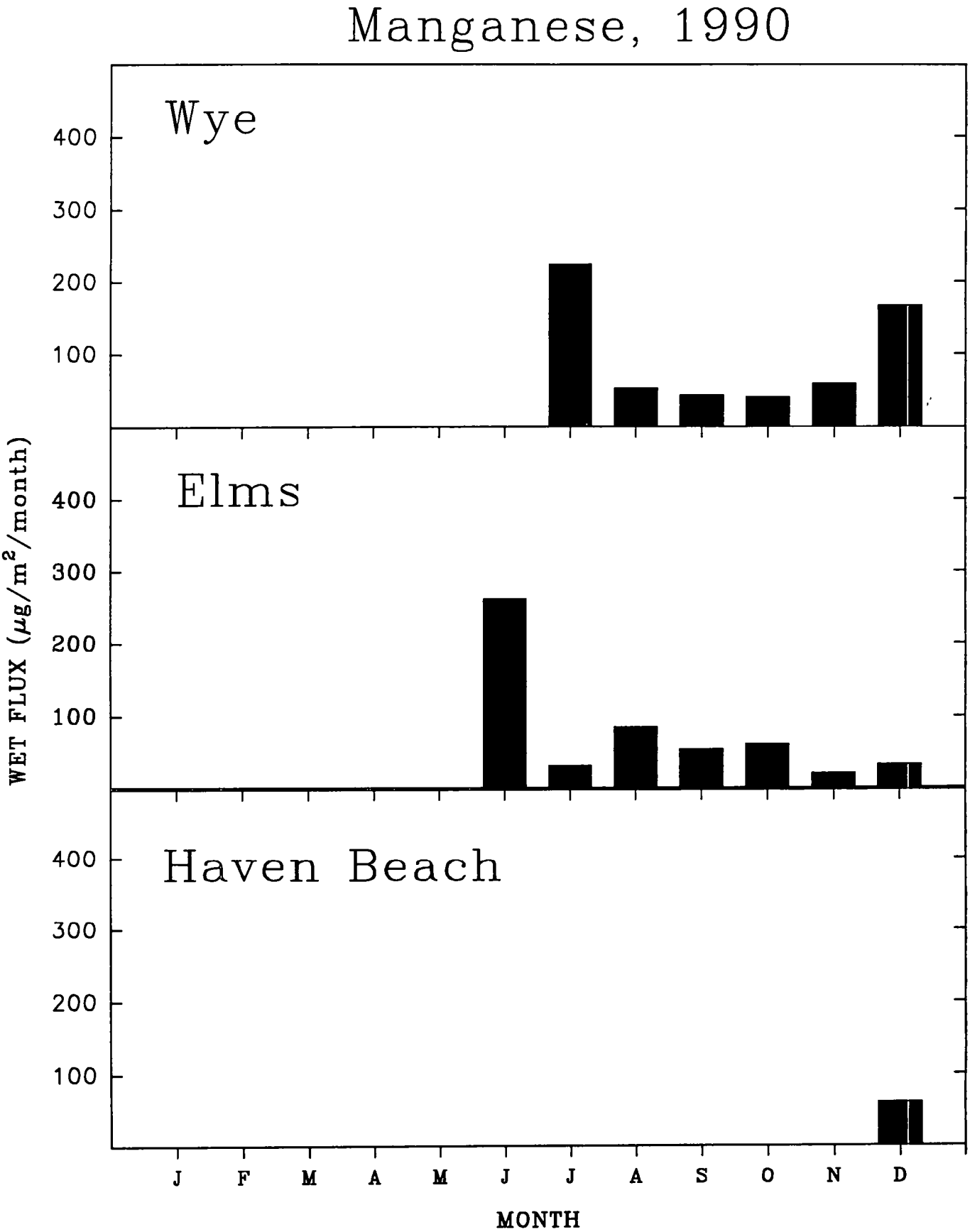


Figure IV.3.18. Monthly integrated wet deposition of Manganese at each CBAD site.

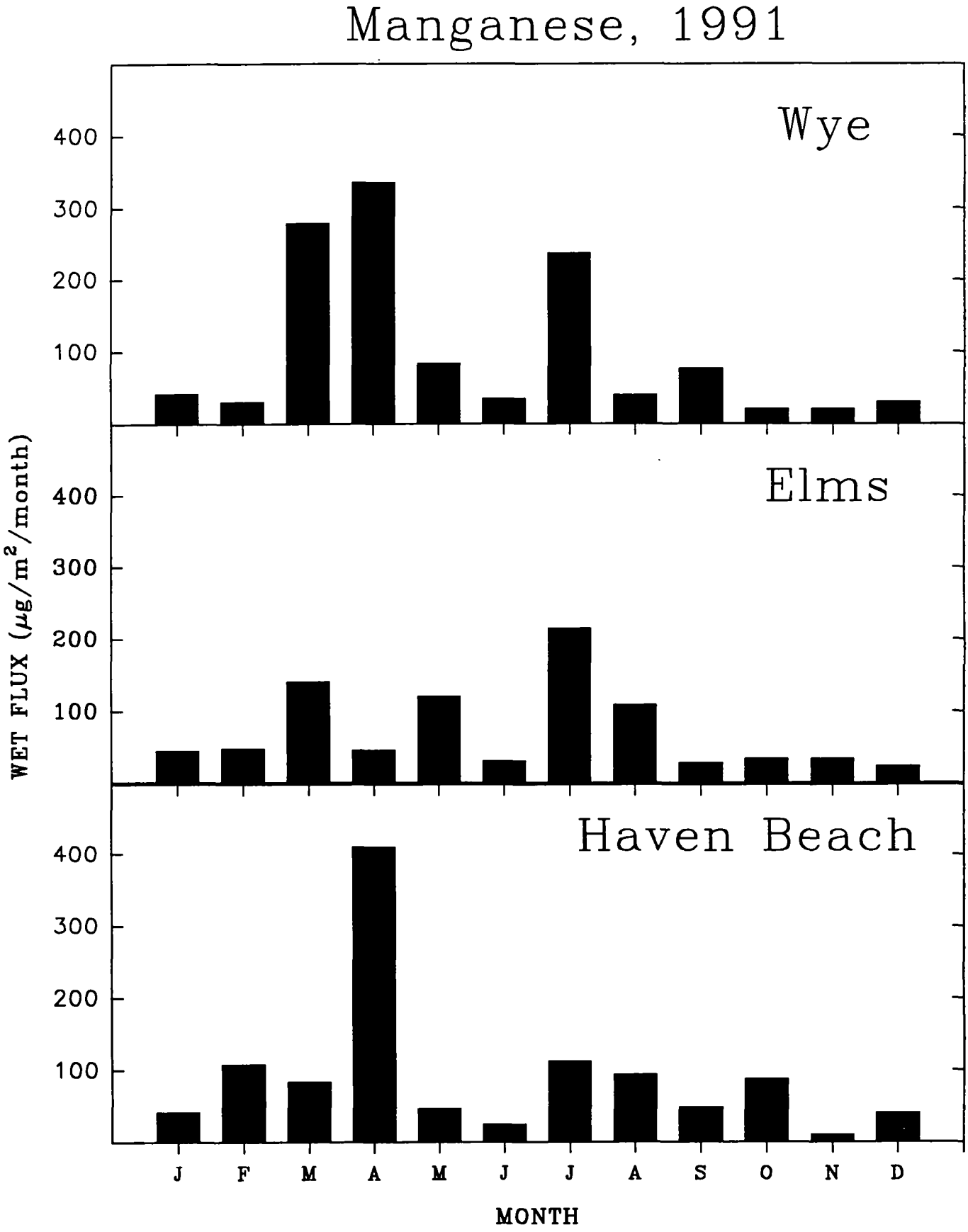


Figure IV.3.18. (Cont'd) Monthly integrated wet deposition of Manganese at each CBAD site.

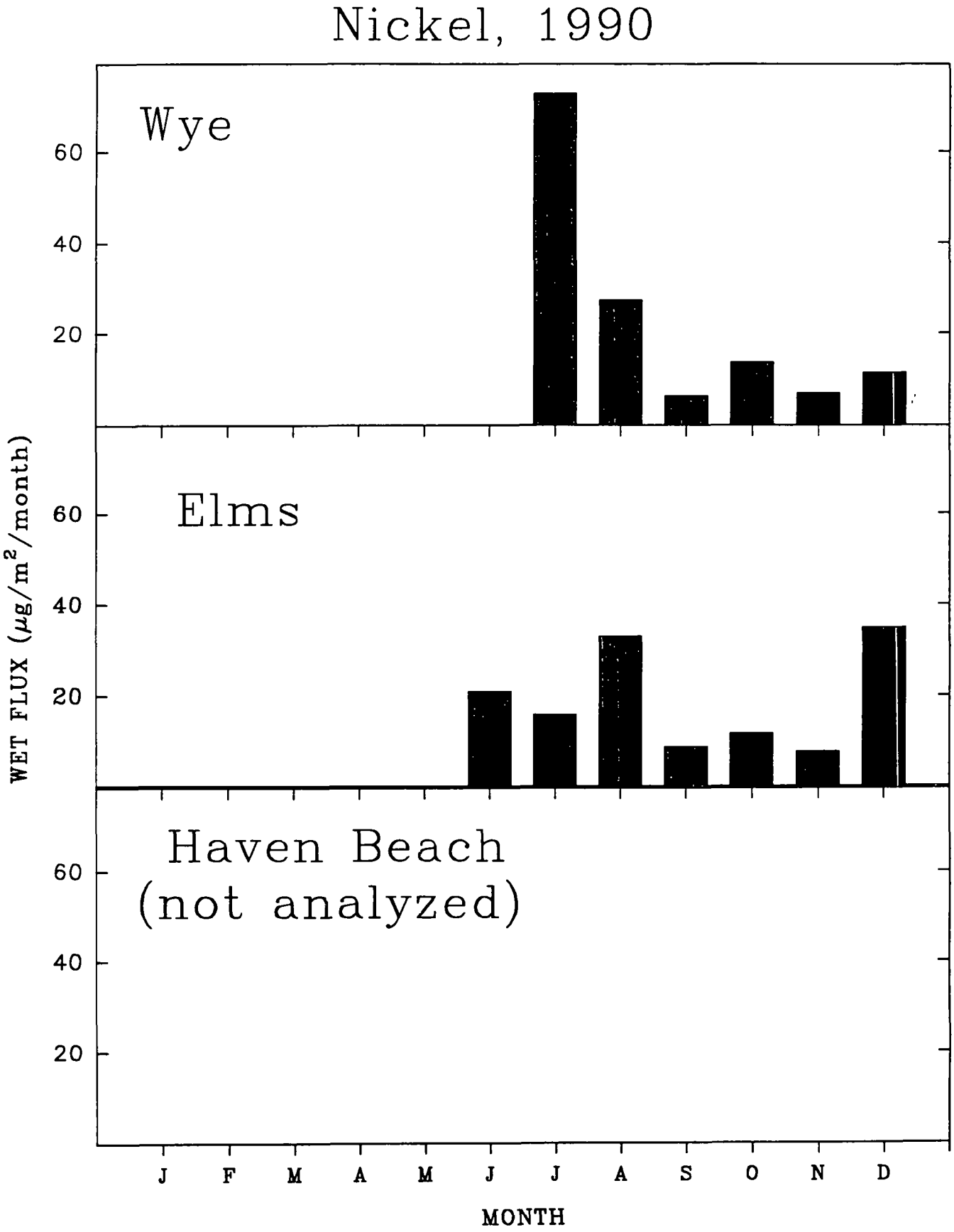


Figure IV.3.19. Monthly integrated wet deposition of Nickel at each CBAD site.

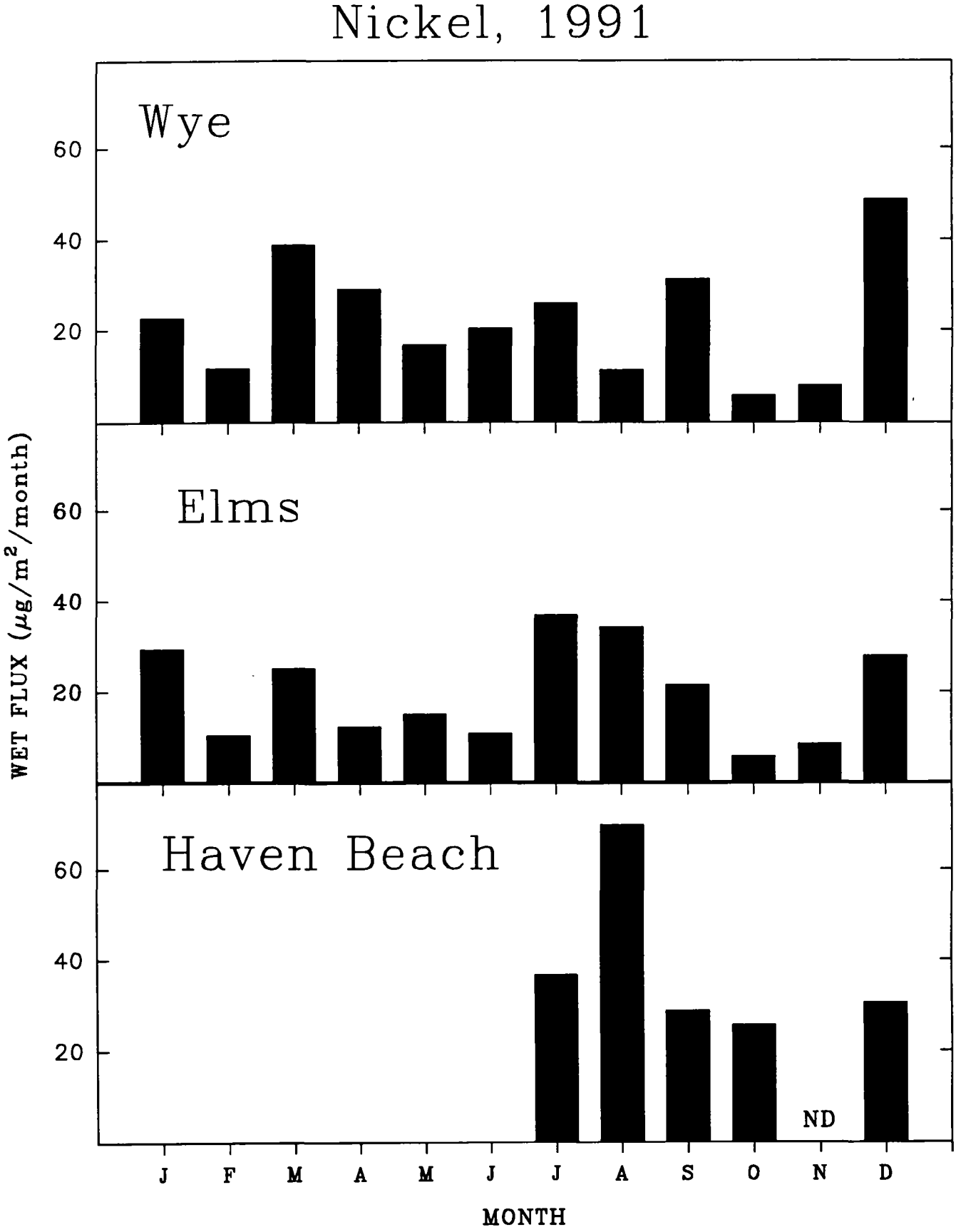


Figure IV.3.19. (Cont'd) Monthly integrated wet deposition of Nickel at each CBAD site.

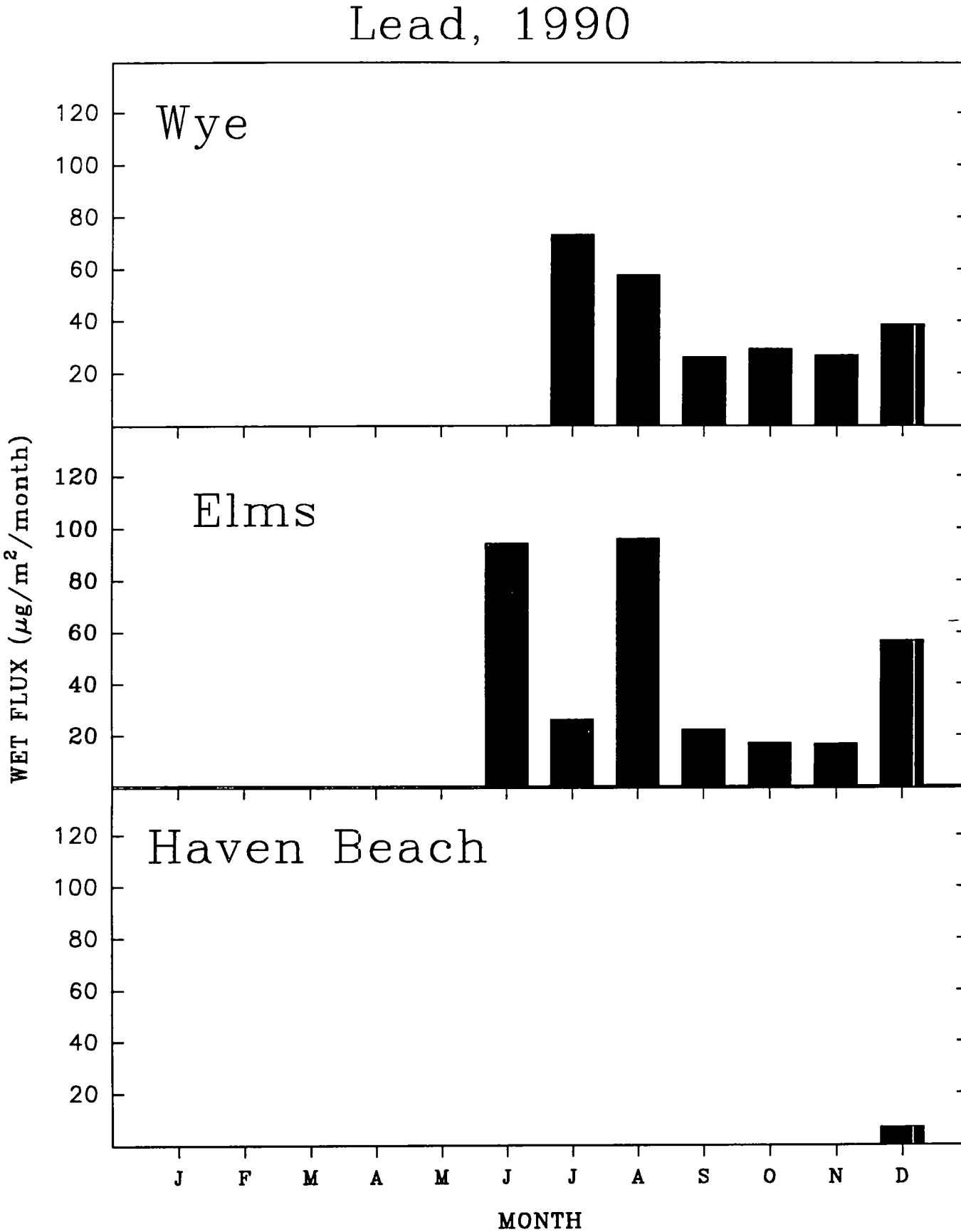


Figure IV.3.20. Monthly integrated wet deposition of Lead at each CBAD site.

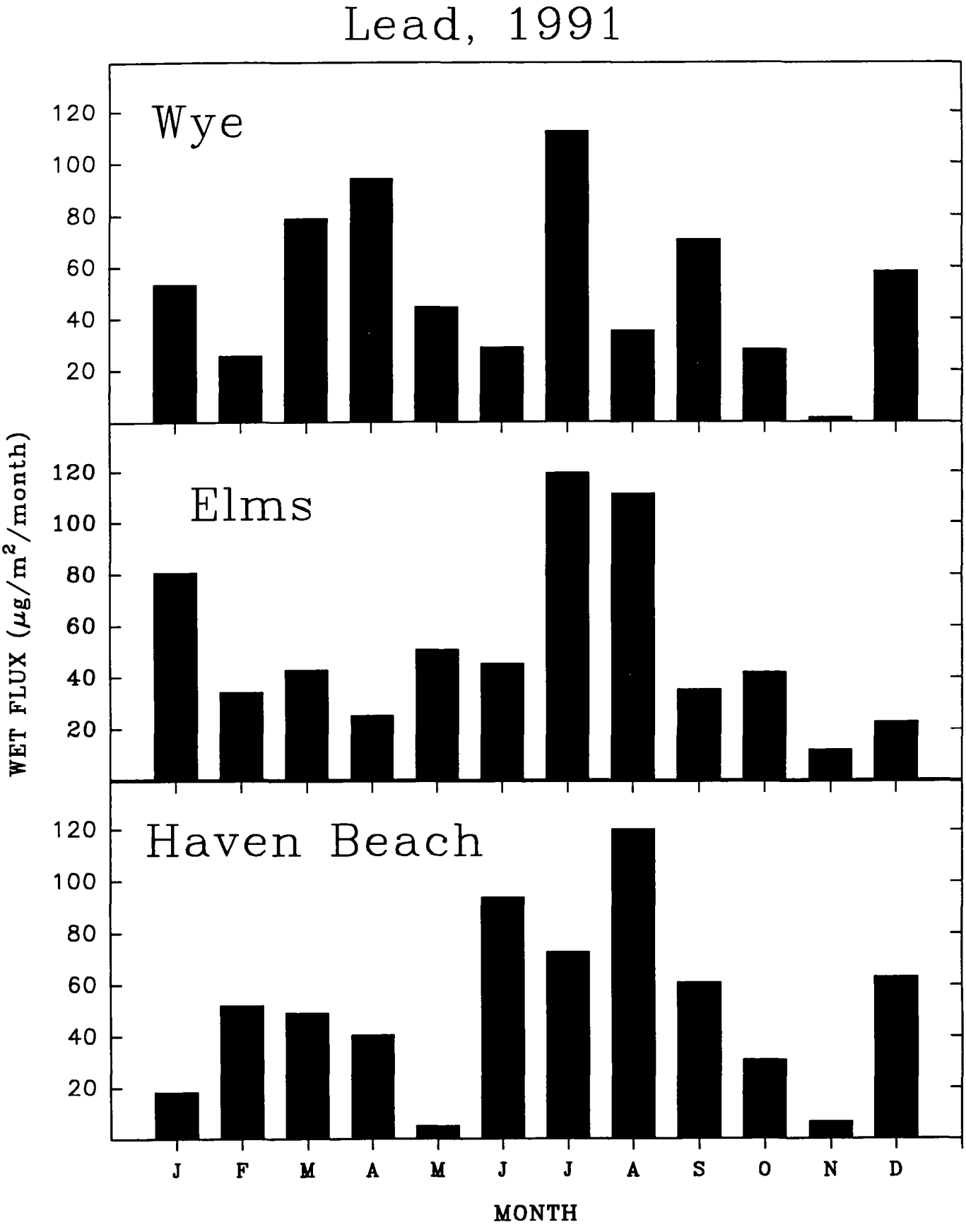


Figure IV.3.20. (Cont'd) Monthly integrated wet deposition of Lead at each CBAD site.

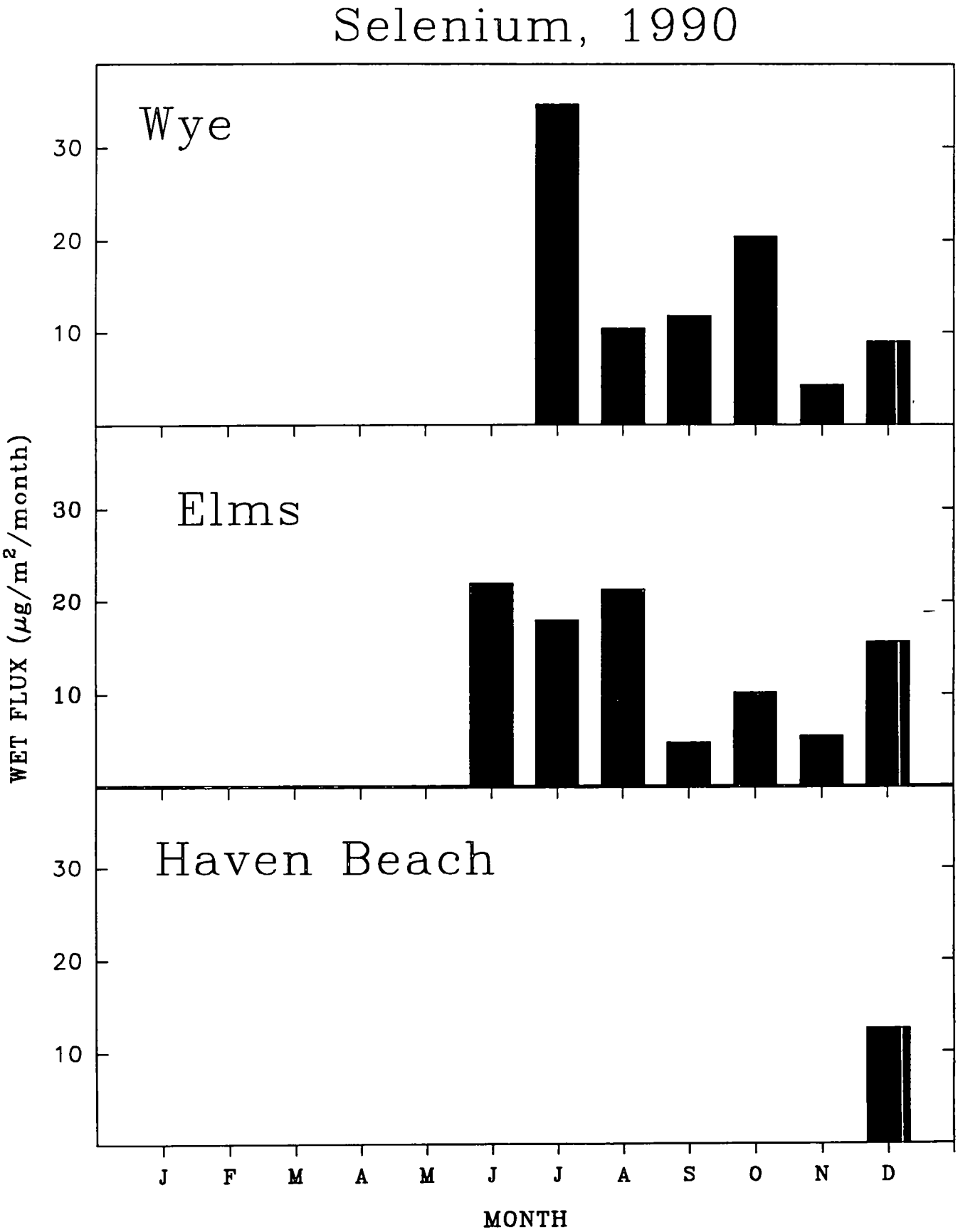


Figure IV.3.21. Monthly integrated wet deposition of Selenium at each CBAD site.

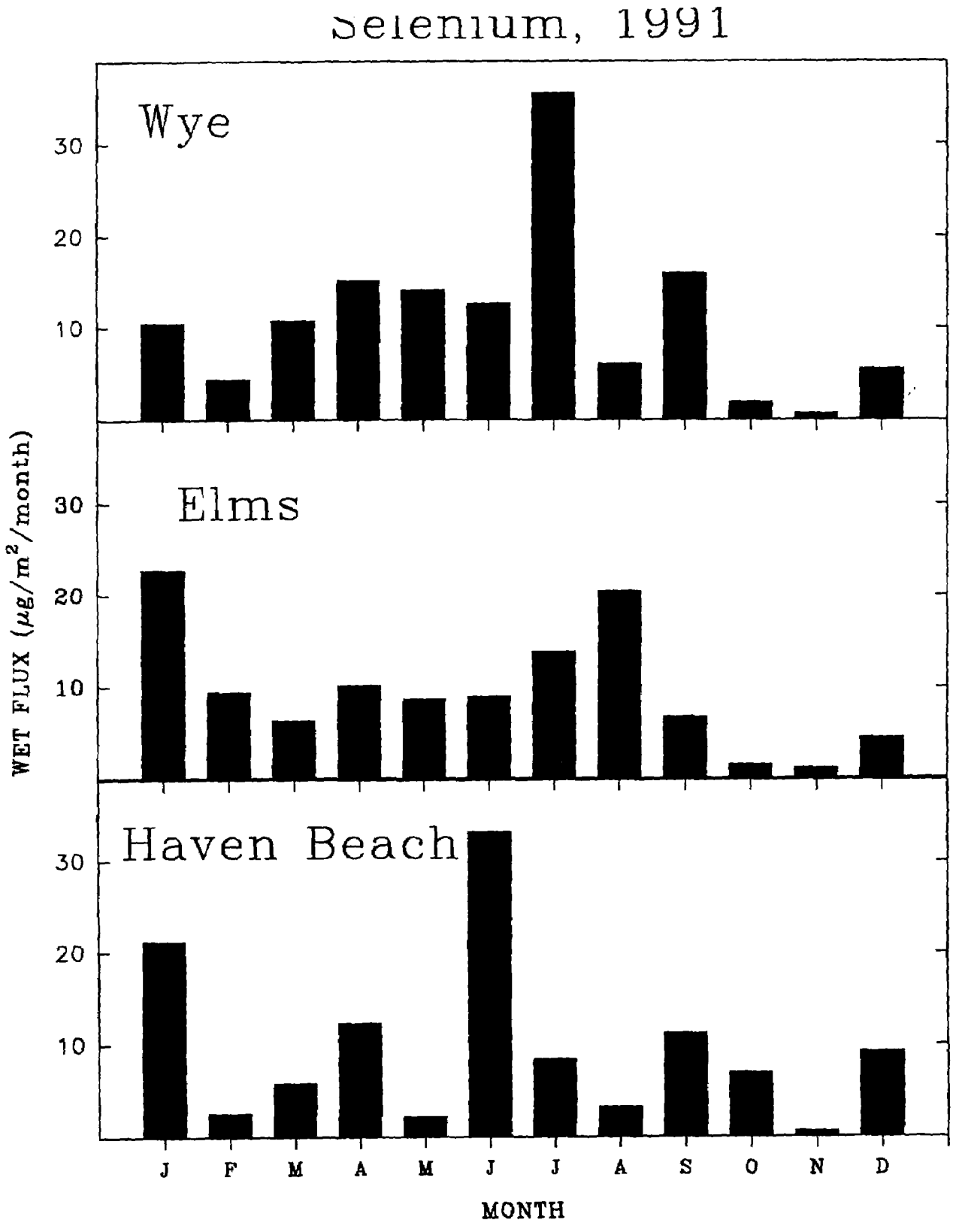


Figure IV.3.21 (Cont'd) Monthly integrated wet deposition of Selenium at each CBAD site.

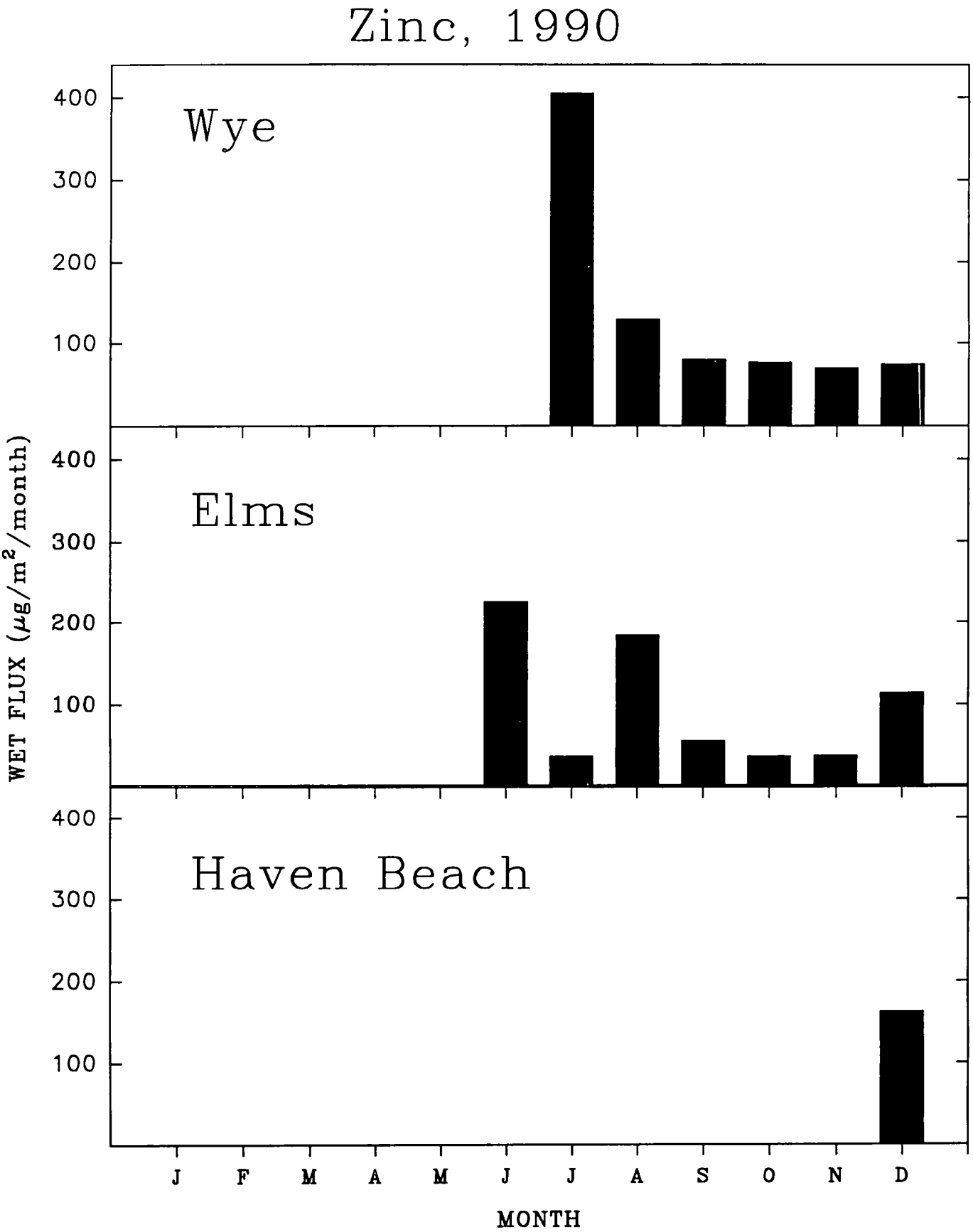


Figure IV.3.22. Monthly integrated wet deposition of Zinc at each CBAD site.

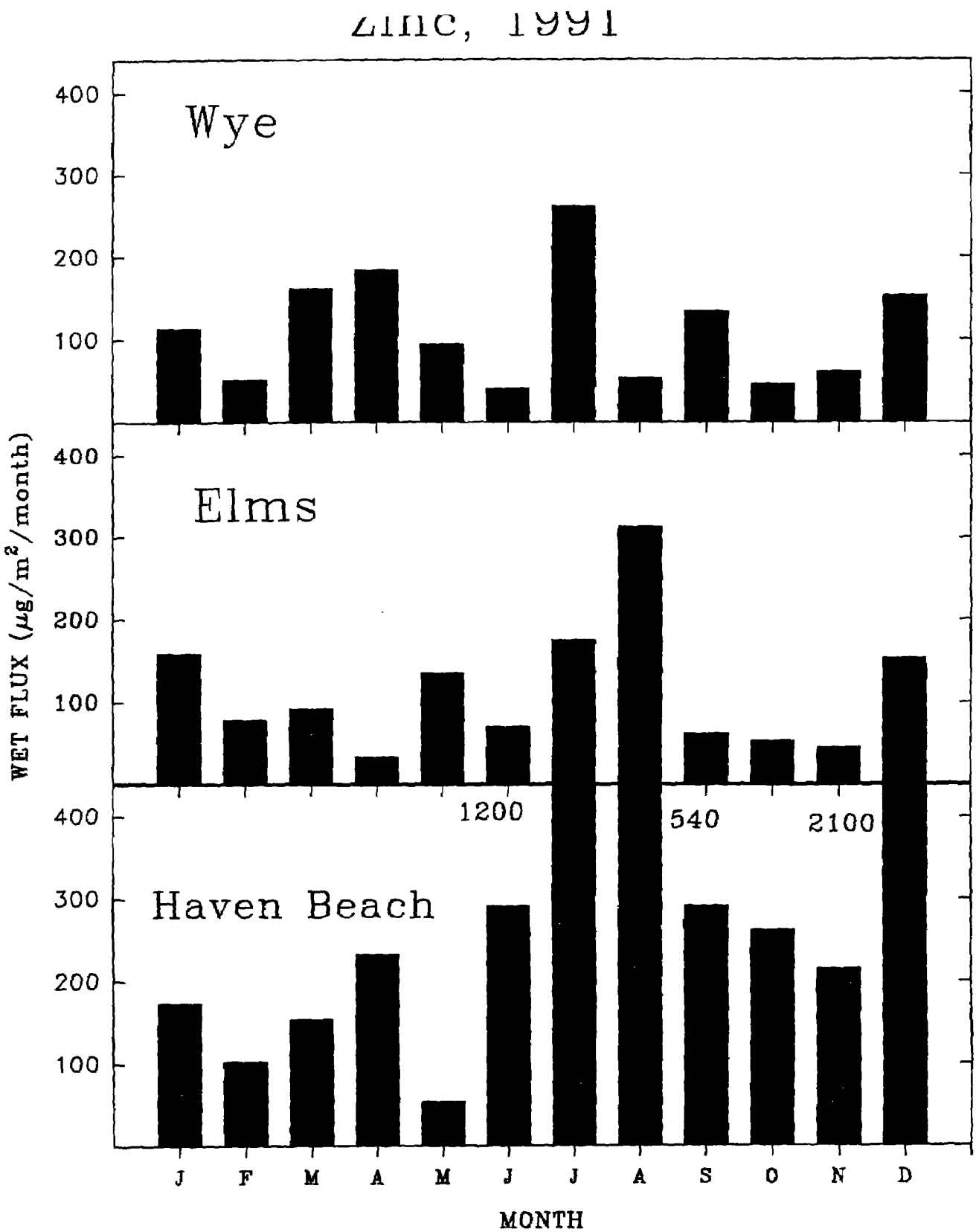


Figure IV.3.22. (Cont'd) Monthly integrated wet deposition of Zinc at each CBAD site.

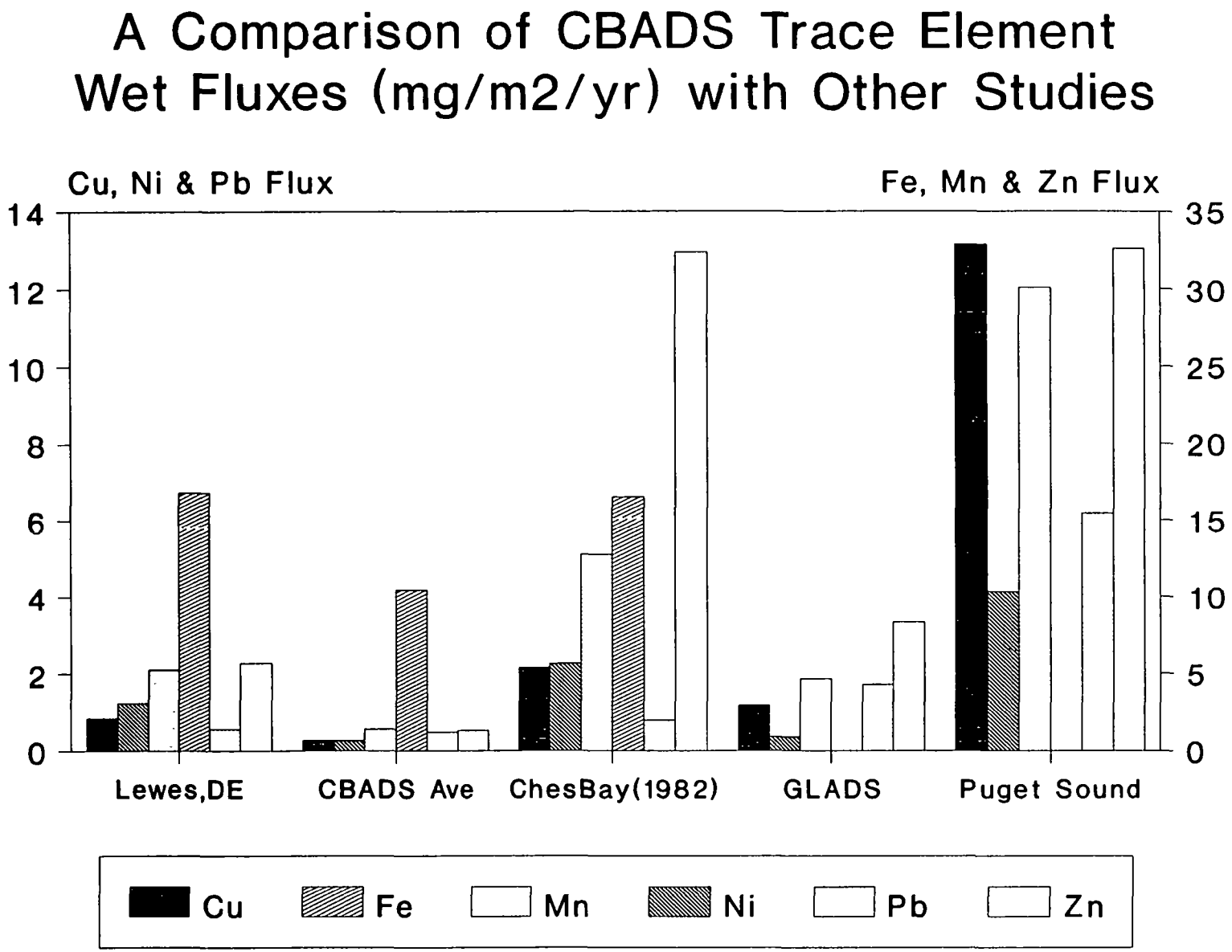


Figure IV.3.23. A comparison of the CBADS trace element wet fluxes with other studies.

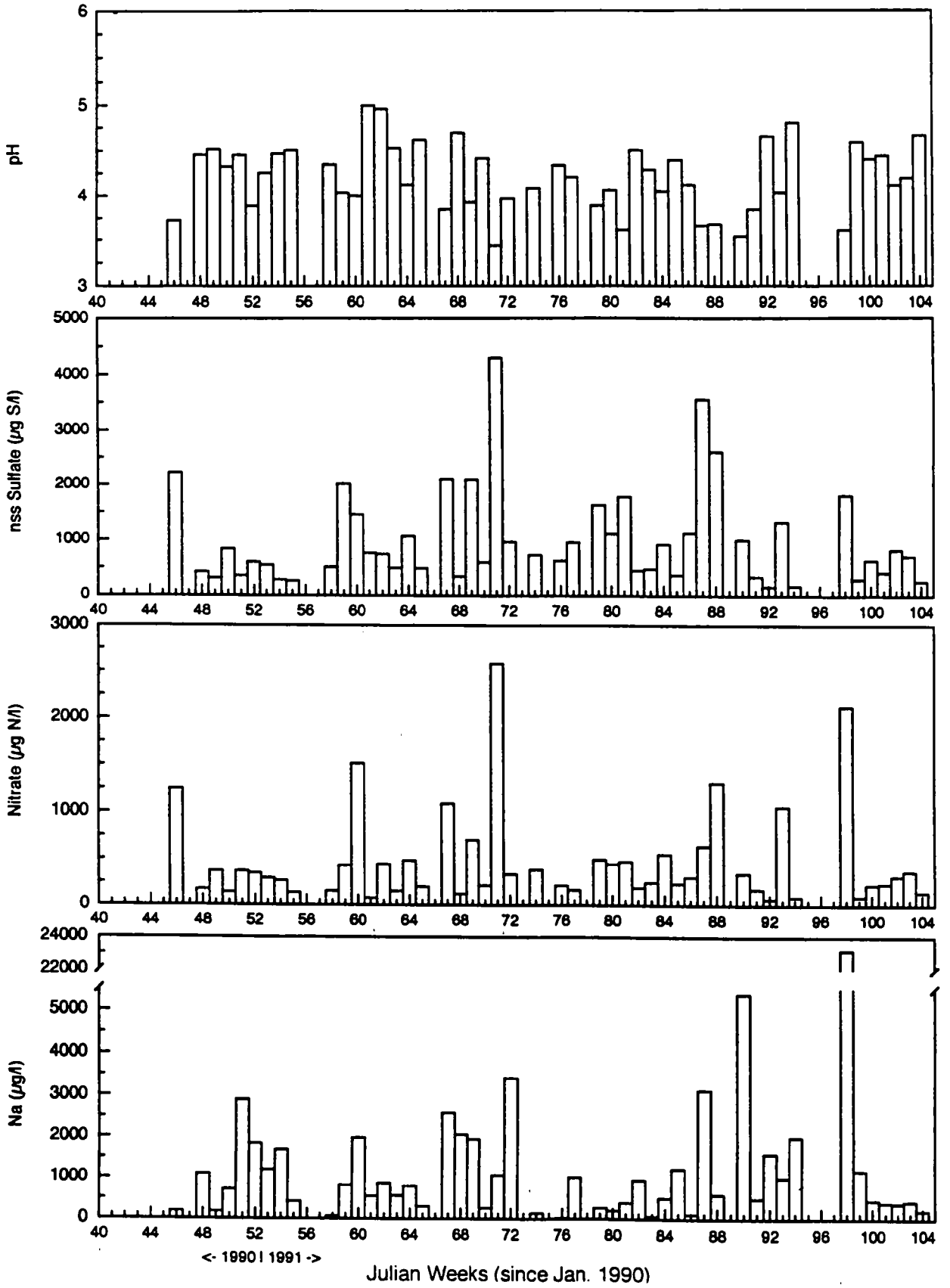


Figure IV.4.1.1. Concentrations of major ions in precipitation collected at Haven Beach. Concentrations are from weekly samples.

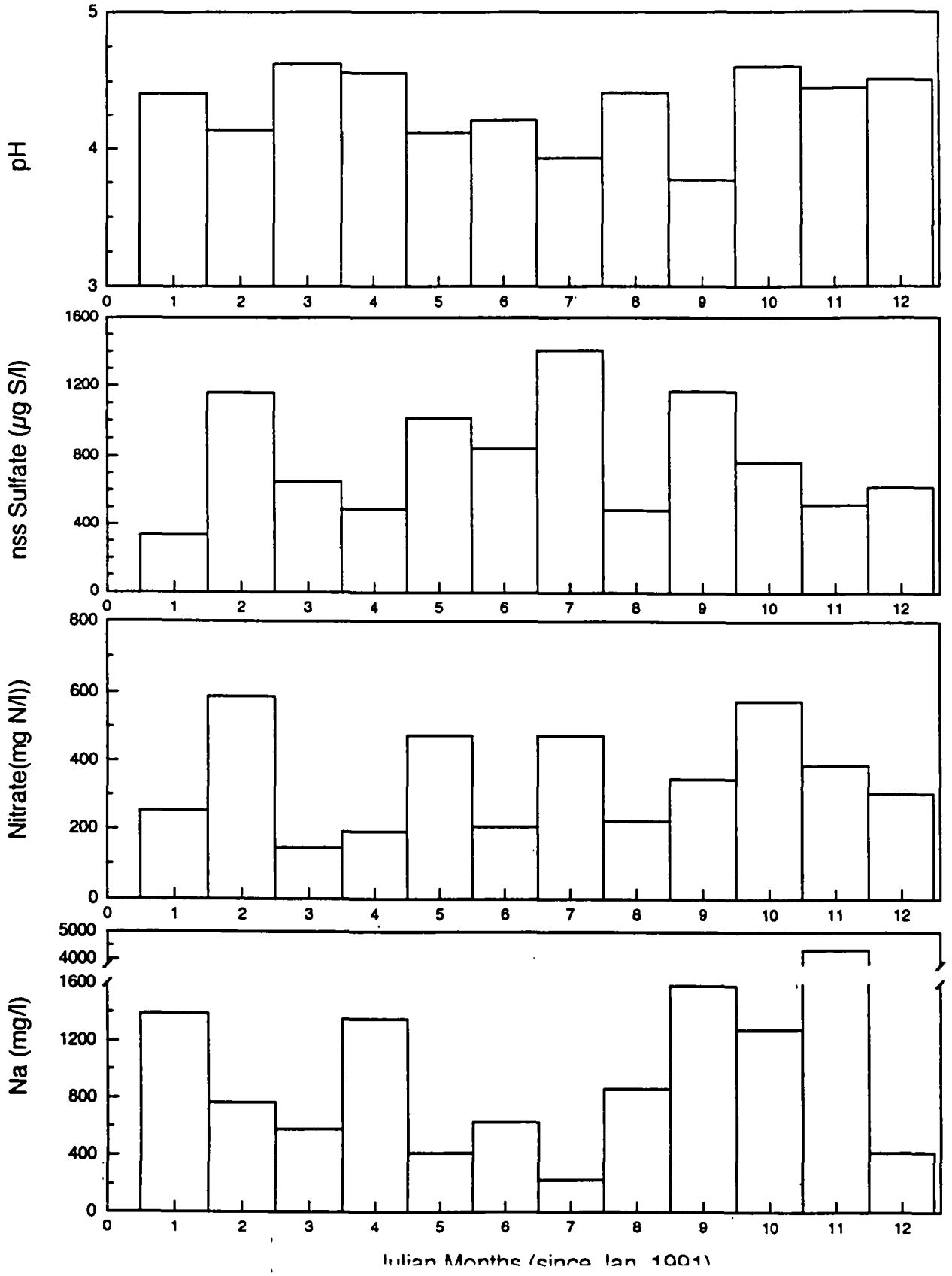


Figure IV.4.1.2. Volume weighted monthly concentrations of major ions in precipitation collected at Haven Beach.

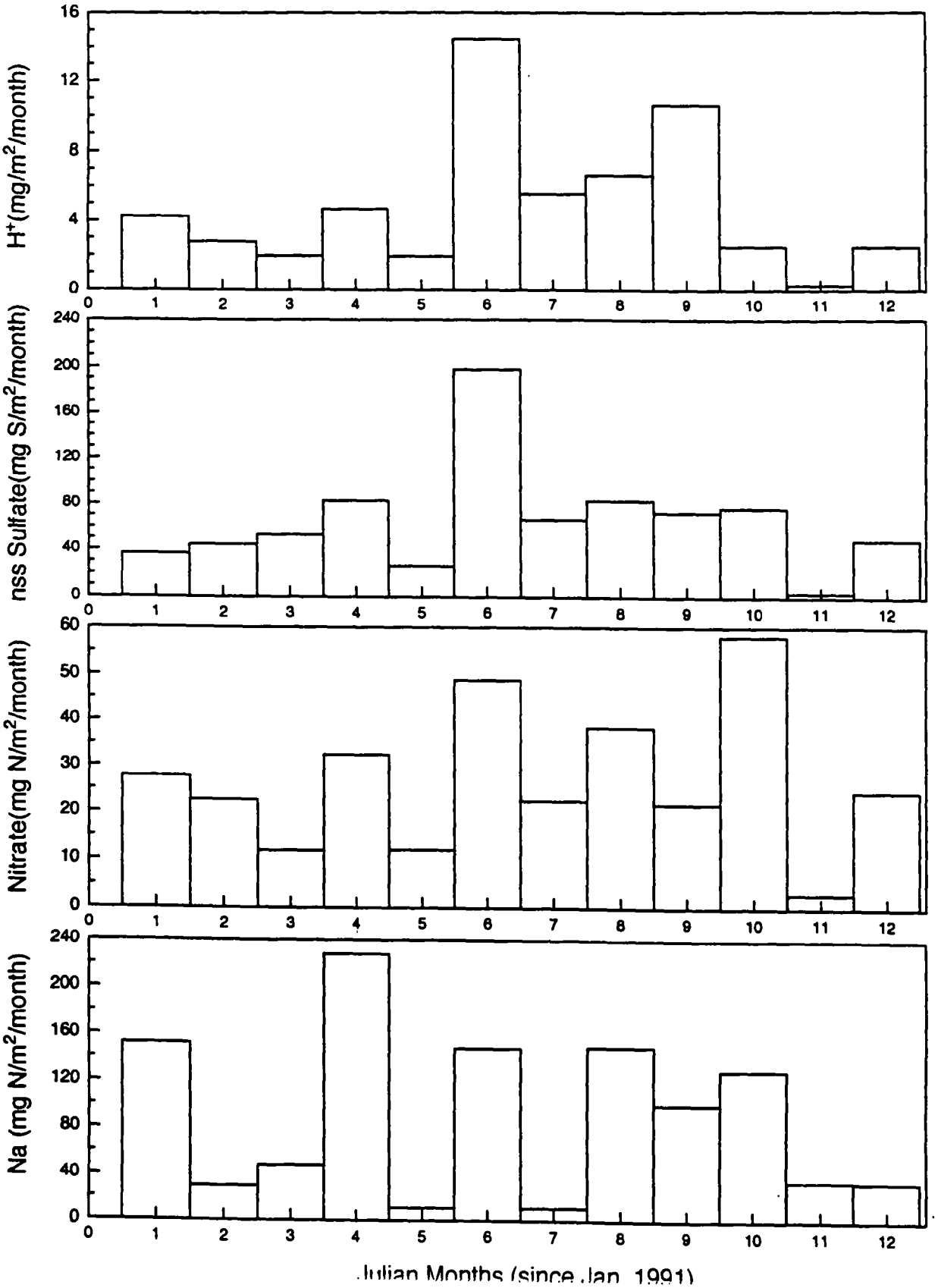


Figure IV.4.1.3. Monthly fluxes of major ions in precipitation collected at Haven Beach.

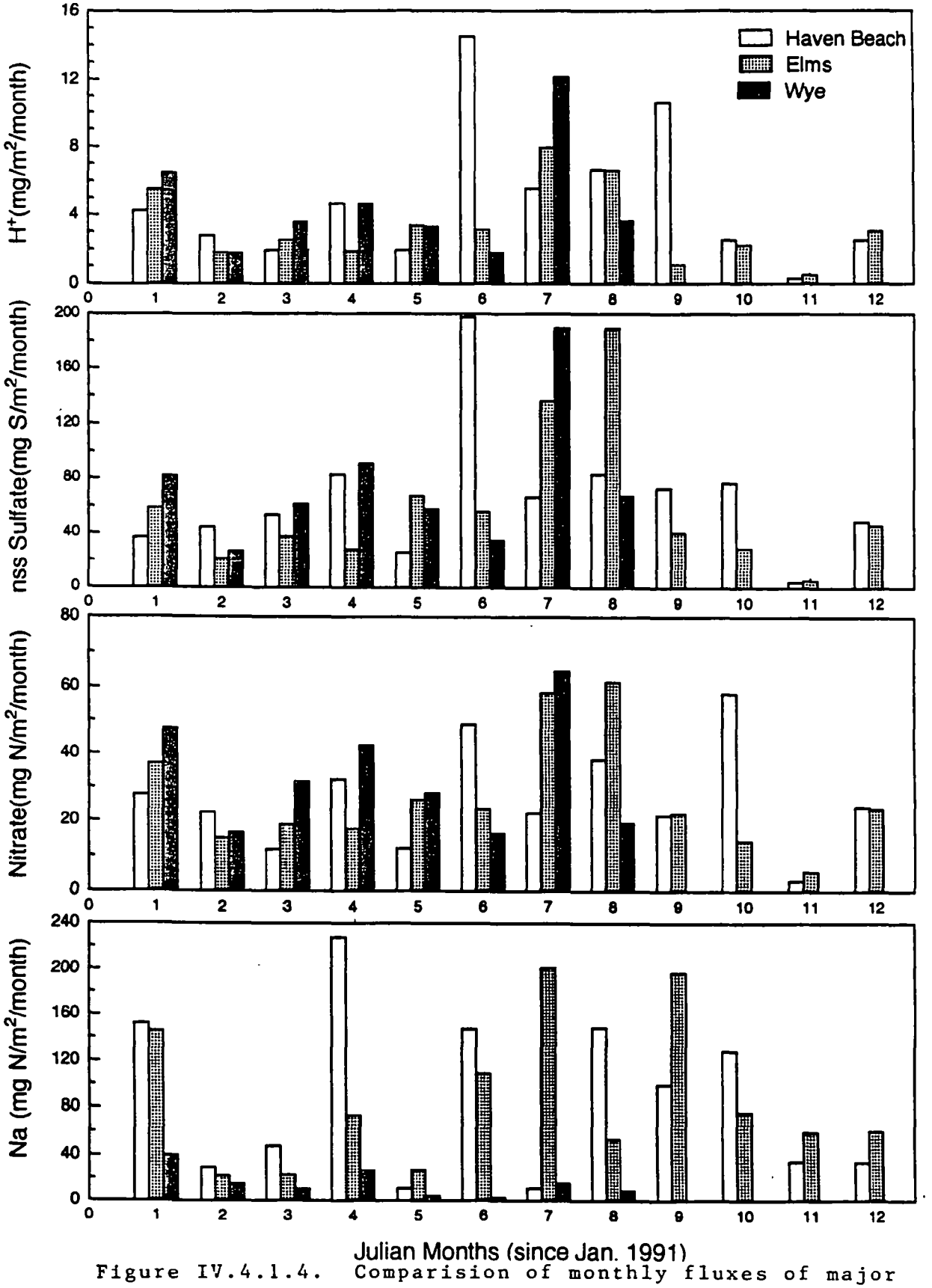


Figure IV.4.1.4. Comparision of monthly fluxes of major ions in precipitation collected at the three CBAD sites.