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Levels and patterns of polychlorinated biphenyls in water collected from the San Francisco Bay and Estuary, 1993–95

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Abstract Levels of polychlorinated biphenyls (PCBs) were measured in water (particulate and dissolved fractions) from various locations in the San Francisco Estuary over the years 1993–1995 during six cruises. Geometric mean levels of Σ PCBs (sum of 58 congeners) in the combined dissolved and particulate fractions for the six cruises ranged from 340 ng/L to 1600 ng/L. Comparing this data to previous data from 1975 and 1980 does not reveal any significant temporal trends. The partitioning of PCBs into the dissolved/particulate fraction were correlated with total suspended solids. Using the novel chemometric technique of polytopic vector analysis (PVA) on the data from cruise 8 (April 1995), five separate PCB congener fingerprints were identified in the data. Fingerprint 1 (or end-member 1) represents a slightly degraded source of Aroclor® 1260 in the northern part of the South Bay; the end-member (EM) 2 fingerprint is related to a predominantly Aroclor® 1260 source that has been moderately-severely degraded present in the highest proportions in the Pacific Ocean sample; EM-3 is interpreted as a slightly degraded Aroclor® 1242:1254:1260 mixture in southern San Pablo Bay; end-member 4 is interpreted as a moderately degraded source of multiple Aroclors® and is present in the river samples; EM-5 is interpreted as a slightly degraded Aroclor® 1254/1260 mixture present in northern San Pablo Bay and the South Bay.

Dedicated to Professor Dr. Karlheinz Ballschmiter on the occasion of his 60th birthday

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Introduction

The San Francisco Estuary is the largest estuary on the coast of California, comprising an area of 1.24×10^9 m² [1]. Its drainage basin area is 153×103 km, with a calculated inflow of 600 m³s⁻¹, mainly from the Sacramento and San Joaquin Rivers [1]. In addition to freshwater inflow, ocean tides and winds bring ocean water into the Bay through the Golden Gate; the northern bay is a partially mixed estuary and the southern bay is a tidal lagoon [2]. This distinction results in dramatically different biogeochemical processes in the two sections of the bay [3].

The San Francisco Estuary is also a highly impacted area; 1995 population estimate of the greater bay area was 6 million people, and several areas of the bay are highly industrialized.

The possible impact of organic contaminants on the ecology of the bay and estuary has been the focus of several programs. Some of the first investigations of contaminants in the estuary began in 1969 with the determination of polychlorinated biphenyls (PCBs) and DDT compounds in shiner perch [4]. Beginning in the mid 1970s (and continuing to present day) mussel watch programs began determining levels of organochlorine (OC) contaminants in the bay [5, 6].

The first measurements of OC compounds in the water column of San Francisco Bay began in 1975 as part of a dredging operation [7]. Other measurements of OC compounds in the water column of San Francisco Bay included the work of de Lappe et al. [8], who in a study for the city and county of San Francisco, determined the baseline concentrations of organic contaminants both outside and inside the estuary prior to the construction of the Southwest Ocean Outfall. More recently, levels of OCs were determined as part of the Bay Protection and Toxic Cleanup Program [9].

The Regional Monitoring Program for San Francisco Estuary (RMP) was initiated in 1992; it is funded by the major dischargers to the bay with the objectives: (1) to obtain baseline data on contaminants (metal and organic) in

the San Francisco Estuary; (2) to determine seasonal, annual, and long term trends in chemistry and water quality; (3) to determine whether water quality and sediment quality in the estuary meets pre-defined objectives; (4) to provide a database that is compatible with other programs in the region [10].

Since its inception in 1992, data on the levels of PCBs in the estuary have been completed for seven sampling cruises over the years 1993–95. Assuming a chemical analysis of approximately 40 congeners at each site this is a data set of approximately 2,800 numbers. Determining sources and trends of PCBs from this matrix becomes a daunting task.

Environmental chemists are increasingly turning to multivariate statistical methods to evaluate patterns of chlorinated organic compounds in the environment [11–15]. In this study we utilize a multivariate statistical technique developed in the geosciences called polytopic vector analysis (PVA) [16]. PVA was designed for analysis of mixtures in the earth sciences, and is used to determine three parameters of interest in a mixed system: (1) the number of sources (i.e., end-members or chemical fingerprints) contributing to the mixture; (2) the chemical composition of each end-member (in percent); and (3) the relative contribution of each end-member in each sample (in percent).

PVA is relatively new in the environmental and chemometric literature, but has been used extensively in the geological sciences [16–18]. PVA was chosen for this study for several reasons. First, in contrast to methods such as principal components analysis, PVA final results are reported in percentages rather than abstract scores and loadings. This makes end-member chemistry easier to interpret in a scientific context, and allows evaluation of concentration gradients by end-member mapping. Second, PVA is a “self-training classification method”; that is, no training data set of known or suspected sources is required to resolve a mixing model.

Supervised classification methods such as the PCA based method SIMCA have been used in chemometric analysis of PCBs in the environment [19, 20]. However, those studies determined that environmental PCB residues could not be described using Aroclor® formulations as the training data set. There were clearly processes (degradation, differential biological uptake, etc.) that modified original source PCB profiles. The use of a self-training classification method such as PVA allows us to make minimal *a priori* assumptions of source and degradation processes.

The purpose of this manuscript is to present levels and temporal trends of PCBs in San Francisco Bay and Estuary, and to examine the patterns of PCBs using PVA. This manuscript is intended to be the first in a series examining organic contaminants in the estuary.

Material and methods

PCB determination

Collection dates for the water samples were: cruise 2-May 1993, cruise 5-April 1994, cruise 6-August 1994, cruise 7-February 1995, cruise 8-April 1995, and cruise 9-August 1995. Water samples were collected approximately one meter below the water surface using a Teflon impeller pump; the sampling port was attached to an aluminum pole that was oriented up-current from the vessel and up-wind from equipment and personnel. The vessel was anchored and the engines turned off. Approximately 100 L were taken at each station. Sample locations are presented in Fig. 1.

Particulate and dissolved fractions of Estuary water were collected. The evolution of the trace organic sampling system has been described in a series of papers [8, 9, 21]. Water was pumped by a Teflon impeller pump with 3/4 inch Teflon tubing through a glass fiber filter (1 μm) providing a sample of particulate-associated contaminants. The water was then passed through four exhaustively cleaned polyurethane foam plugs mounted in series which adsorbed the dissolved material. The entire sampling system was thoroughly rinsed with methanol prior to sampling, and an all-Teflon-stainless steel system further minimized potential contamination. During sampling, the system was closed to outside sources of contamination, and extreme precaution was taken at other times to minimize, if not eliminate, the introduction of contaminants. Total PCBs were calculated by adding particulate and dissolved fractions.

Custom built Soxhlet extraction units were used to extract the organics from both plugs and filters; an acetone extraction was followed by hexane. Water was removed by partitioning into hexane in a separatory funnel; extracts were reduced to 1–2 mL for clean-up.

Florisil® columns were used to separate each extract into three different fractions. Prior to analysis each sample was spiked with a

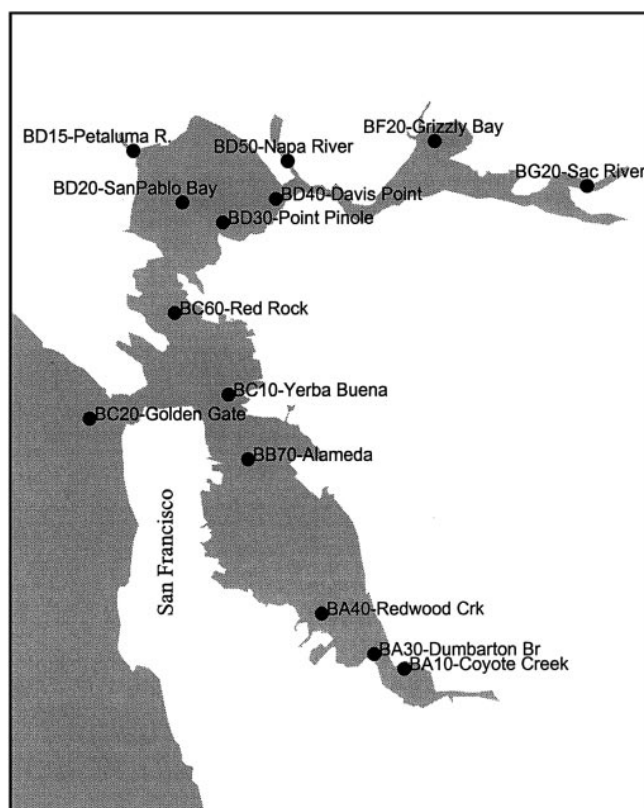


Fig. 1 Water sample collection locations and site codes in the San Francisco Estuary

gas chromatography internal standard (GCI standard) to account for volume differences among samples. Fractions were analyzed on a Hewlett-Packard (HP) 5890 series II gas chromatograph (GC) equipped with a ^{63}Ni electron-capture detector and an HP 7673A automatic sampler. Two 60 m, 0.25 mm i.d., 0.25 mm (film thickness), DB-5 and DB-17 columns (J&W Scientific) were used to provide dual column confirmation. Only PCB values are reported in this paper. ΣPCBs (sum polychlorinated biphenyls) was calculated from the sum of 58 individual congeners [22].

Statistical analysis

Matrix adjustments. Cruise 2 was deleted from the data set because it had different congeners analyzed than cruises 5–9. Initial exploratory data analysis was accomplished by analyzing data sets composed of different combinations of samples (e.g., all samples from all cruises, particulate samples only, samples from a single cruise only, etc.). These initial analyses resulted in the following observations:

There is a strong compositional difference between the particulate analyses and the dissolved analyses. For example, particulate samples from different cruises were generally more similar to each other than dissolved samples from the same location and the same cruise.

There is a strong compositional difference between cruises. Even when the dissolved and particulate data were run as separate data sets, these cruise-to-cruise differences were observed. The cruise-to-cruise difference was also identified through analysis of variance as described in the PCB levels section of this paper.

On account of these observations, we achieved best resolution of PCB patterns and their geographic gradients in the estuary by separating the data into particulate and dissolved data sets, and developing separate models for each cruise. Of the five cruises, cruise 8 had the best and largest data set in terms of non-detects and minimal missing data values. For clarity and brevity, only the PVA results from cruise 8 are presented. PVA models for other data sets will be presented in subsequent papers.

Prior to implementation of the PVA algorithm, several matrix adjustments were required. The original data matrix for cruise 8 particulates was 14 samples by 58 congeners. This original matrix contained a number of elements with missing data or data reported below method detection limits ("non-detects"). In order to have a robust data set for statistical analysis, it was necessary to reduce this matrix. Given the small number of samples, we chose to delete variables from the data set rather than samples. As such we removed all variables with missing data, and all variables with more than one non-detect. This resulted in a final matrix of 14 samples and 32 congeners.

Prior to PVA, three data transformations are performed. The data are first normalized as constant row-sum sample vectors (i.e., concentrations are expressed as percent of total concentration). PVA is most useful and interpretable when homogeneity of variance may be assumed among the variables. However, variance is typically proportional to the mean. Accordingly, a second transformation is performed to ensure that the variance across all variables is independent of the mean. We typically use a range transformation [23] that fixes the value of each variable between values of 0 and 1. We prefer the range transform because it does not force the data to conform to a theoretical data distribution that might not be applicable. A final transformation is performed to force each of the sample vectors to have equal Euclidean length [23].

Polypotic vector analysis. PVA was performed using software coded in the MATLAB high-level programming language. The software was written based on the original FORTRAN algorithms of Klován and Miesch [24] and Full et al. [25, 26]. The software has been modified to include graphical goodness-of-fit diagnostics and output. PVA is performed in two steps. The Klován and Miesch [24] algorithm is used to determine the number of end-members and to evaluate outliers. This algorithm involves singular

value decomposition of the input matrix and evaluation of significant eigenvectors. The number of significant eigenvectors is equal to the number of end-members in the model, and is evaluated using (1) the variable-by-variable goodness-of-fit criteria of Miesch [24]; (2) the loadings index of Ehrlich and Full [16]. The second step in PVA modeling involves an iterative algorithm [26] that determines the chemical composition of the end-members and the relative proportions of each end-member in each sample. The range and Euclidean length transforms are undone at the conclusion of the analysis such that final results are reported in constant-sum (percent) metric [23].

Results and discussion

PCB levels

As has been noted in previous RMP annual reports, the particle loadings in aquatic environments are related to the dissolved/particulate ($> 1 \mu\text{m}$ in the RMP) partitioning of lipophilic organic contaminants [27, 28]; that is, the more particulates there are in the water the greater percentage of the contaminants will be associated with the particulate fraction. Since in the RMP total suspended solids (TSS) has been measured in every sampling cruise, this allows a test of the relationship between dissolved and particulate fractions.

The ratio of the concentration of the dissolved ΣPCBs to the concentration of the particulate ΣPCBs for each station in each of all of the cruises (2,5–9) was compared to the TSS for the corresponding site. This relationship was not statistically significant; however, one data point (Cruise 2 BC20, Golden Gate) seemed exceptionally high. The ratio of the concentration of ΣPCBs dissolved to particulate is more than an order of magnitude different in this station than the ratio for any of the other cruises. When this data point is removed, there is a statistical correlation between TSS and dissolved/particulate ΣPCBs ($p < 0.05$).

The concentration of the total water (sum of particulate and dissolved) ΣPCBs (the sum of the concentrations of

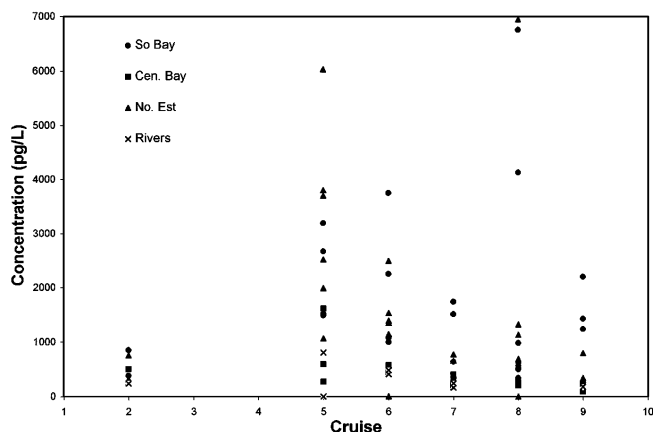


Fig. 2 Levels of ΣPCBs (pg/L) in the combined particulate and dissolved phase of seawater, by region and cruise, in the San Francisco Estuary, 1993–1995

all the congeners) for each station by region (South Bay, Central Bay, Northern Estuary, Rivers, [10]) and cruises (2,5–9) is presented in Fig. 2. The patterns reveal several things: there is a large range of values both within and between cruises. Also, it is apparent that cruises 2, 7–9 are similar, and cruises 5, 6, and 8 are similar. These are not seasonal groupings, e.g., cruise 2 is a spring cruise, 7 is winter, and 9 is summer. It is important to note that the data of cruise 2 does not include as many stations as the other cruises, and more importantly does not include data from Coyote Creek (BA10), which is consistently one of the most contaminated sites. From this data set there are no clear trends, however, more cruises over time may clarify this.

The only other comparable data sets that can be used for comparisons of PCBs in the water of the Estuary are those of [8] and [7]. Anderlini et al. [7], in a pre and post dredging sampling east of Angel Island, San Francisco Bay in 1975, found levels of total PCBs of 880 and 950 pg/L (geometric mean levels of 11 and 8 sites, respectively). de Lappe et al. [8] examined, in a study for the city and county of San Francisco, the baseline concentrations of organic contaminants prior to the construction of the Southwest Ocean Outfall both outside and inside the estuary. Of particular relevance are the stations “vicinity of Angel Island” and Golden Gate Channel sampled for PCBs in August 1980. Using sampling equipment roughly comparable to that currently used in the RMP (glass fibre particulate filter and polyurethane foam) they reported levels of PCBs at the Golden Gate in the dissolved fraction at 75 and 82 pg/L in two serial foam columns, respectively, 490 pg/L in the particulate fraction, and 850 pg/L in the whole water (liquid/liquid extraction) sample. In the Angel Island station levels of PCBs were reported to be 220 and 4 pg/L in two serial foam columns, respectively, and 440 pg/L in the particulate fraction [8].

For comparison, the average value of Σ PCBs in the Central Bay for RMP cruises 2, 5–9 was 420 pg/L (with a standard deviation of 370). In wildlife samples, “old” PCB quantitations (i.e., not congener specific) can overestimate the PCB levels by a factor of two or more when compared to the Σ PCB (sum of individual congeners) values in the same sample [29]; however, it is not known if this is true in water samples. Despite both variations in sampling and analytical methodology these data may indicate that PCB levels have not declined over the period 1975 through 1995.

Pattern of PCBs-polytopic vector analysis

Determination of end-members

The number of end-members was evaluated based on goodness-of-fit criteria outlined by Miesch [24] and Ehrlich and Full [16]. These criteria indicated that a minimum of 5 end-members were required to accurately reproduce the original data matrix. Coefficients of determination (CDs) for the five end-member model exceeded

0.60 for all 32 congeners, and exceeded 0.82 for all but three congeners.

End-member chemical composition and sample-by-sample mixing proportions were resolved for a five end-member model using the DENEG algorithm of Full et al. [26]. End-member compositions are presented in Fig. 3. End-member mixing proportions are shown on Fig. 4.

End-Member 1. End-member 1 represents a slightly degraded source of Aroclor® 1260 in the northern part of the South Bay. This end-member is characterized by high proportions of PCBs 153, 138, and 180; one pattern is similar to pure Aroclor® 1260. This pattern varies from a pure Aroclor® 1260 source, primarily in that there are higher proportions of the persistent congener PCB 138. Previous reports [30, 31] indicate that PCB 138 is also in high proportions in sea water, suggesting that EM-1 may represent a slightly degraded Aroclor® 1260 source, or that the partitioning of PCB congeners into the particulate phase is dependent on structure.

EM-1 is observed in highest proportions in sample BB70 (65% at Alameda sampling station), and has decreasing contributions in samples to the north and south of BB70 (Fig. 4). Risebrough [32] reported that one of the major historical discharges of PCBs into the bay was by the East Bay Municipal Discharge (EBMUD) plant located near Oakland (east of BB70); this source was characterized primarily by Aroclor® 1260, and discharge was estimated to be 2 kg/day in 1970.

End-Member 2. This fingerprint is related to a predominantly Aroclor® 1260 source that has been moderately-severely degraded. It has a similar pattern as EM-1 (Fig. 3), but with much higher proportions of the resistant congener PCB 138. The notable peak for PCB 153 and the low contribution of low chlorinated congeners support a 1260 source (Fig. 3). EM-2 is present in highest proportions in the Pacific Ocean sample (78% of BC20-Golden Gate, Fig. 4). Secondary contributions from this fingerprint are observed in samples just inside the Golden Gate.

End-Member 3. EM-3 is interpreted as a slightly degraded Aroclor® 1242:1254:1260 mixture. As for EM-5, this fingerprint has characteristics of both Aroclor® 1254 and 1260. In contrast though, EM-4 has higher percentages of low chlorinated congeners (PCB 8 through PCB 87). This suggests a contribution from Aroclor® 1242, and possibly 1026. This fingerprint is present in highest proportions in southern San Pablo Bay (Fig. 4).

End-Member 4. This fingerprint is interpreted as a moderately degraded source of multiple Aroclors®. The pattern bears little resemblance to any Aroclor® pattern. The presence of a PCB 153 peak suggests a possible Aroclor® 1260 contribution. The presence of PCB 95, 101 and 110 suggests possible 1254 and/or 1260 contributions. The presence of lower chlorinated congeners (PCBs 28, 31, 44 and 70) suggests a possible contribution from Aroclors® 1026

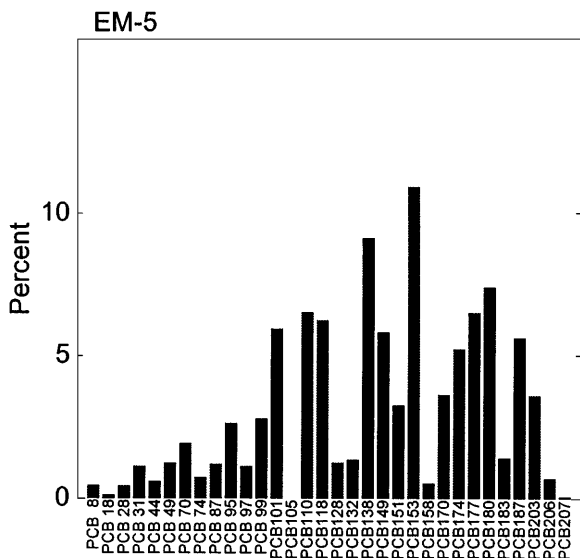
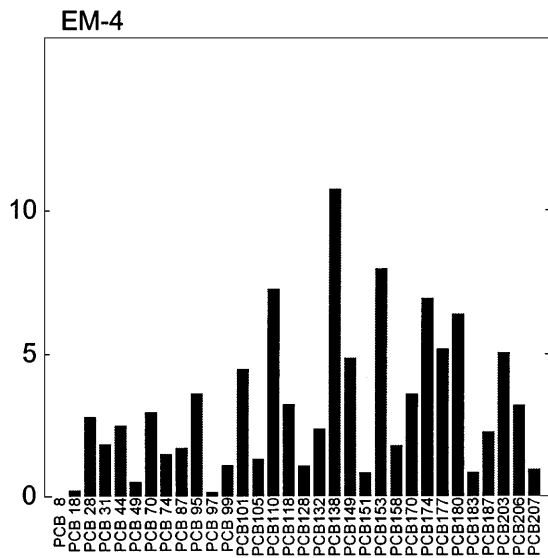
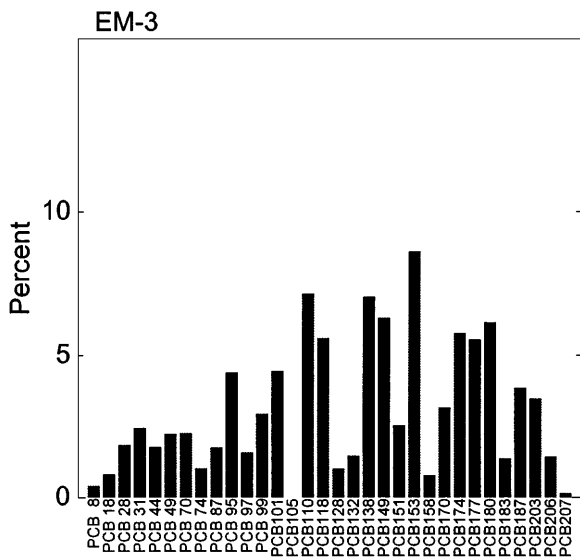
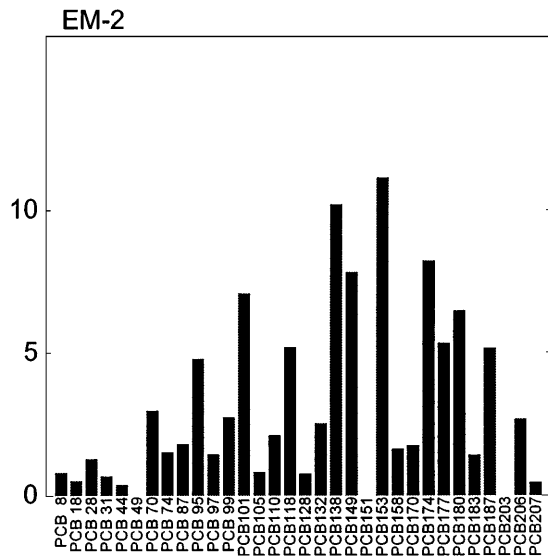
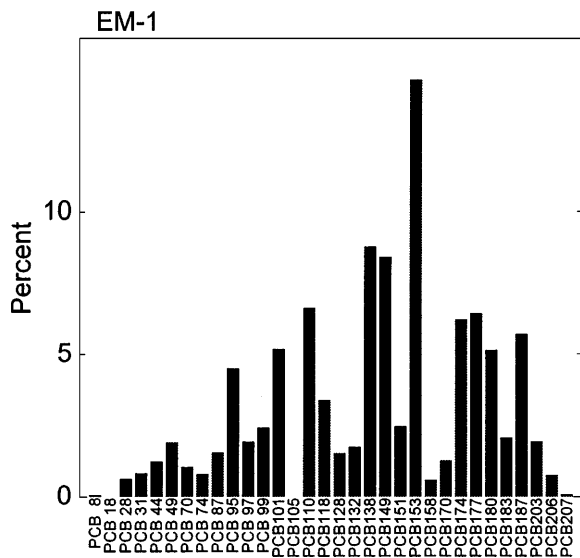
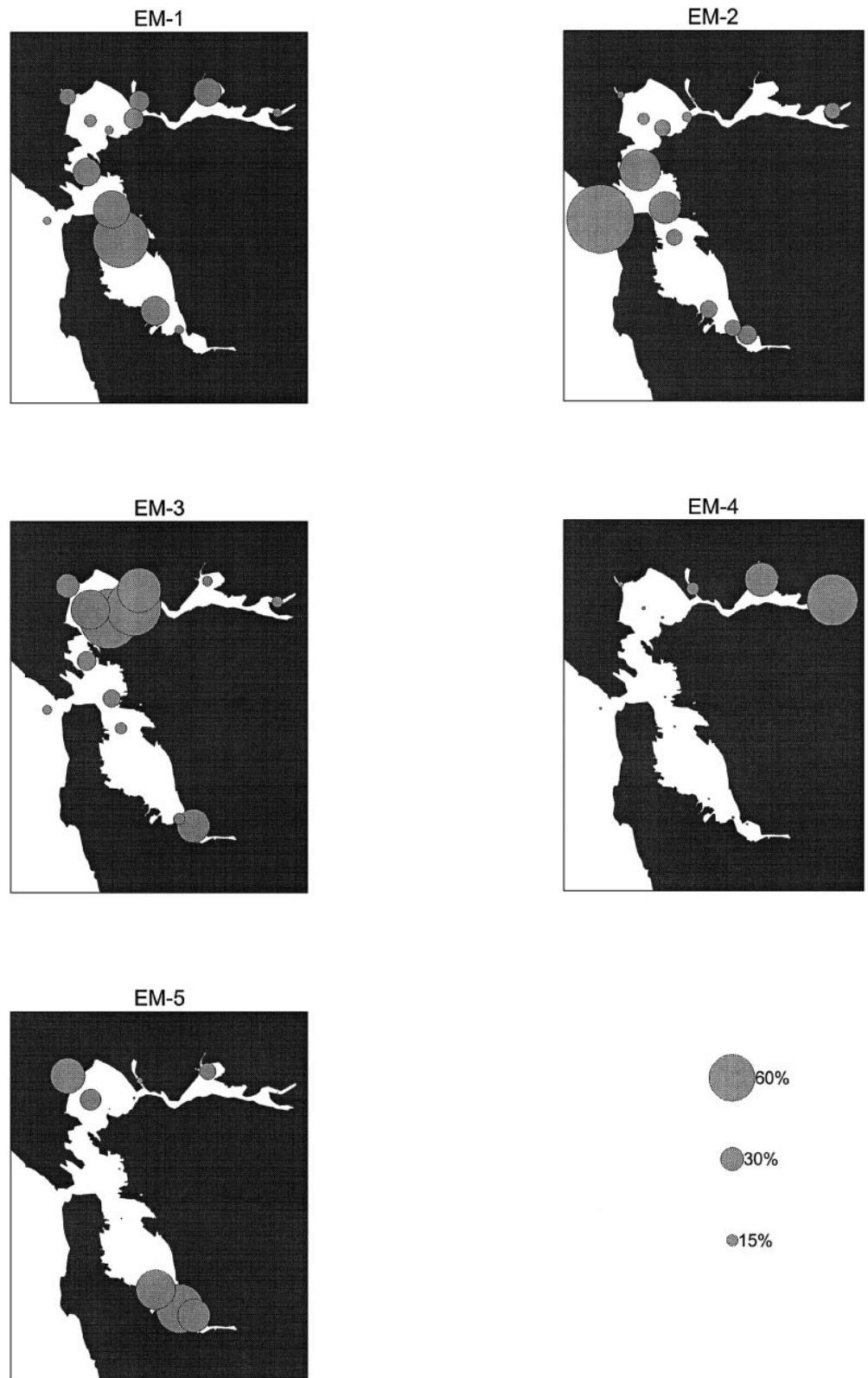


Fig.3 End-member composition histograms of 14 samples, 32 congener data set of PCBs, April 1995 particulate water analyses from San Francisco Bay

Fig. 4 Sample mixing proportions of seven PCB end-member fingerprint patterns resolved through PVA of 14 samples; 32 congener data set of PCBs; April 1995 particulate water analyses from San Francisco Bay



and/or 1242. EM-4 is present in highest proportions in sample BG20 (San Joaquin River: 59%), and has successively lower contributions in samples to the west (BF20: 38%; BD50: 14%) (Fig. 4).

End-Member 5. End-member 5 is interpreted as a slightly degraded Aroclor® 1254/1260 mixture. This fingerprint has characteristic peaks for PCB 95, PCB 99, PCB 101, PCB 110 and PCB 118; typical of Aroclor® 1254. The pat-

tern also exhibits characteristics of Aroclor® 1260, as discussed for EM-1 above. Again, as for EM-1, this pattern exhibits a higher proportion of PCB 138 than is present in either Aroclor® 1254 or 1260, suggesting a slightly degraded mixture of Aroclor® 1254 and 1260. This fingerprint is present in high proportions in two of the areas studied: northern San Pablo Bay and South Bay (Fig. 4).

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