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Ambient Air Monitoring Results of Polychlorinated Dibenzo-p-dioxins, Polychlorinated Dibenzofurans, Polychlorinated Biphenyls, and Polybrominated Diphenylethers at Urban Areas in California from 2002 to 2006

Extended Abstract 29

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INTRODUCTION

The Monitoring and Laboratory Division of the Air Resources Board (ARB) established a comprehensive ambient air quality monitoring program to collect data for polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs), and polybrominated diphenylethers (PBDEs). Because very little dioxin data were available for California urban areas, the California Ambient Dioxin Air Monitoring Program (CADAMP) was conducted primarily in urban regions of California consisting of 12 sites from 2002 through the middle of 2006.

CADAMP was modeled after the U.S. Environmental Protection Agency's National Dioxin Air Monitoring Network (NDAMN) and used similar sampling and analytical protocols. NDAMN focused in rural areas to study pathways by which dioxins enter the food chain and did not include the monitoring of PBDEs. In 2006, California banned the manufacture and distribution of several congeners of PBDEs because of growing concerns on their toxicity. The intent of CADAMP was to quantify the annual average ambient concentrations of PCDDs, PCDFs, PCBs, and PBDEs as well as the toxic equivalency quotients where applicable.

MONITORING

CADAMP air samples were collected at five urban sites (Livermore, Oakland, Richmond, San Francisco, and San Jose) in the San Francisco Bay Area Air Basin (BA), four urban sites (Boyle Heights, Reseda, Rubidoux, and Wilmington) in the South Coast Air Basin (SC), two urban sites (Fresno and Sacramento) in the Central Valley, and one rural site (Five Points) in the Central Valley. Urban CADAMP sites were chosen to represent areas with high population and/or a history of elevated criteria and toxic emissions and/or ambient concentrations. Data collected for each site ranged from one to four years in duration. The samples were analyzed by a contract laboratory, Axys Analytical Services Ltd., using high resolution GC/MS. A complete in-depth description of all monitoring aspects, including quality assurance, can be found at the CADAMP website: http://www.arb.ca.gov/aaqm/qmosopas/dioxins/dioxins.htm.[1]

DATA EVALUATION

An extensive analysis of CADAMP data was completed by Sonoma Technology, Inc. The report focused on spatial and temporal relationships, meteorological effects, and possible source contributions.[2] The purpose of this paper is to provide a unique summary that includes average concentrations, total toxicity equivalence, and appropriate references for further information.

The SC and BA are about 350 miles apart but are similar in that they represent major population centers within California. Although comparisons between each area was performed, the SC and BA comparison is shown here because most sites in these areas had at least three years of data. A summary of the average SC and BA ambient air measurements, combined, are presented in Table 1 for PCDDs (7 congeners), PCDFs (10 congeners), PCBs (14 congeners), and PBDEs (40 congeners). The data from four SC sites and five BA sites were used to calculate area averages for each congener. These area averages were then averaged with equal weight to produce the average congener concentrations shown in the Table 1.

As shown in the table, the percent difference for each congener between the two urban areas are on the same order of magnitude; PCDDs, in particular, are very close and do not differ by more than 20 percent. The data illustrate that the general profiles for PCDDs, PCDFs, and PCBs are similar among these two major urban areas. The mean difference among these congeners is only 12 percent with a range of –20 to 76 percent. This observation suggests that the mix of sources is generally similar. The percent differences for PBDEs do vary more than the congeners in the other three groups (range –70 to 140). There is also bias with respect to carbon number with BA having a positive bias for PBDEs with four, five, and six carbons, while SC has a positive bias for two, three, seven, and nine carbons. These differences suggest that not only the magnitude of certain emission sources of PBDEs are likely different between SC and BA, but each area may have PBDE emission source(s) unique to its region.

Because PCDDs, PCDFs, and PCBs represent a number of congeners with different levels of toxicity, results of CADAMP are often presented as toxicity equivalence (TEQ) to compare toxicities between individual congeners and between the groups themselves. See Figure 1. The TEQ's are based on the World Health Organization 1997 toxic equivalent factors (TEFs) and are reported in units of femtograms per cubic meter (fg/m^3). In Figure 1, the sum of the individual TEQs for each group of congeners for a site are added to produce a total TEQ for each site. As shown, the total average TEQs for SC (32 fg/m^3), BA (29 fg/m^3), SC and BA combined (31fg/m^3), and the average of all 11 urban sites (31 with a range of 26 to 32 fg/m^3) are nearly identical. The average TEQ of all 11 urban sites is 25 fg/m^3 when only using PCDDs and PCDFs. This value is similar to other values reported in other urban areas in the United States [e.g. Chicago (35 fg/m^3) and Oklahoma City (21 fg/m^3)].[3] The average urban site total TEQ for PCDDs, PCDFs, and PCB's are 15, 10, and 5.9 fg/m^3, respectively. Interestingly, the rural site (Five Points) total TEQ value is about half of the CADAMP urban sites, with most of the difference coming as a result of lower total TEQs of PCDFs and PCBs. A further look at the total TEQ for the average of all 11 urban sites (31 fg/m^3) reveals that only 3 of the 29 congeners (with toxicity equivalent factors) contribute one-half of the total value as shown in Figure 2. In addition, 14 (out of 29) congeners contribute nearly 98 percent of the total TEQ.

Table 1. Average PCDD, PCDF, PCB, and PBDE Concentrations for SC and BA Combined (fg/m^3)

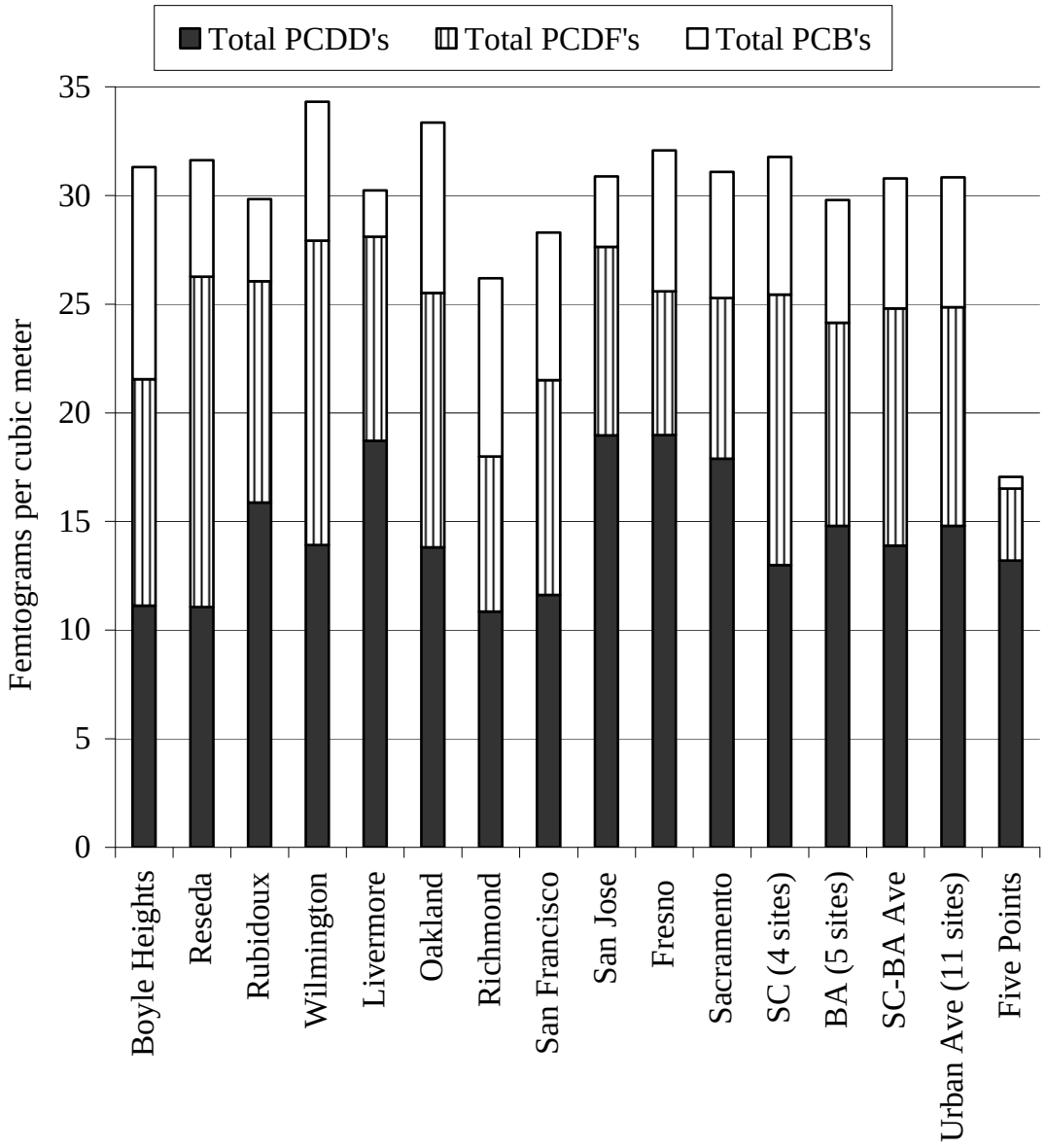
PCDDs	Ave	PD*
2,3,7,8-TCDD	1.7	-20
1,2,3,7,8-PeCDD	6.5	-10
1,2,3,4,7,8-HxCDD	6.4	-10
1,2,3,6,7,8-HxCDD	15	6
1,2,3,7,8,9-HxCDD	19	-9
1,2,3,4,6,7,8-HpCDD	170	-20
OCDD	600	-10
PCDFs		
2,3,7,8-TCDF	6.5	20
1,2,3,7,8-PeCDF	5.9	27
2,3,4,7,8-PeCDF	11	28
1,2,3,4,7,8-HxCDF	12	50
1,2,3,6,7,8-HxCDF	12	43
1,2,3,7,8,9-HxCDF	0.8	37
2,3,4,6,7,8-HxCDF	14	50
1,2,3,4,6,7,8-HpCDF	67	61
1,2,3,4,7,8,9-HpCDF	6.8	54
OCDF	48	76
PCB's		
3,3',4,4'-TeCB	630	-2
3,4,4',5-TeCB	32	-10
2,3,3',4,4'-PeCB	2900	-20
2,3,4,4',5-PeCB	210	-30
2,3',4,4',5-PeCB	8200	-20
2',3,4,4',5-PeCB	180	-20
3,3',4,4',5-PeCB	44	25
2,3',4,4',5,5'-HxCB	200	-3
2,2',3,3',4,4',5-HpCB	600	3.1
2,2',3,4,4',5,5'-HpCB	1900	5.4
2,3,3',4,4',5,5'-HpCB	20	18
2,3,3',4,4',5-HxCB	380	-1
2,3,3',4,4',5'-HxCB	85	2.1
3,3',4,4',5,5'-HxCB	2.4	51

PBDE's	Ave	PD*
2,4-DiBDE	150	17
2,4'-DiBDE	390	27
2,6-DiBDE	0.2	41
3,4-DiBDE	260	15
4,4'-DiBDE	790	60
2,2',4-TriBDE	1600	32
2,4,4'-TriBDE	3200	40
2,4,6-TriBDE	0	0
2,4',6-TriBDE	25	140
3,3',4-TriBDE	0	0
3,4,4'-TriBDE	170	52
2,2',4,4'-TetraBDE	62000	-50
2,2',4,5'-TetraBDE	2500	-20
2,2',4,6'-TetraBDE	300	N/C
2,3',4,4'-TetraBDE	2100	-40
2,3',4',6-TetraBDE	370	-10
2,4,4',6-TetraBDE	180	-20
3,3',4,4'-TetraBDE	37	67
3,3',4,5'-TetraBDE	110	N/C
2,2',3,4,4'-PentaBDE	2100	-70
2,2',4,4',5-PentaBDE	55000	-70
2,2',4,4',6-PentaBDE	11000	-60
2,3,3',4,4'-PentaBDE	4.2	710
2,3,4,5,6-PentaBDE	2.9	11
2,3',4,4',6-PentaBDE	200	-60
3,3',4,4',5-PentaBDE	14	-40
2,2',3,3',4,4'-HexaBDE	9.8	N/C
2,2',3,4,4',5'-HexaBDE	310	-40
2,2',3,4,4',6'-HexaBDE	140	-40
2,2',4,4',5,5'-HexaBDE	3400	-50
2,2',4,4',5,6'-HexaBDE	3500	-70
2,2',4,4',6,6'-HexaBDE	340	-70
2,2',3,4,4',5,6-HeptaBDE	19	100
2,2',3,4,4',5',6-HeptaBDE	1100	120
2,3,3',4,4',5,6-HeptaBDE	94	96
2,2',3,4,4',5,5',6-OctaBDE	410	N/C
2,2',3,3',4,4',5,5',6-NonaBDE	920	120
2,2',3,3',4,4',5,6,6'-NonaBDE	1100	120
2,2',3,3',4,5,5',6,6'-NonaBDE	710	140
2,2',3,3',4,4',5,5',6,6'-DecaBDE	21000	110

* PD (Percent difference) = 100 x [SC Average (4 sites) – BA Average (5 sites)] / [Average of SC and BA].

N/C- not calculated; only two sites in 2005 had available data.

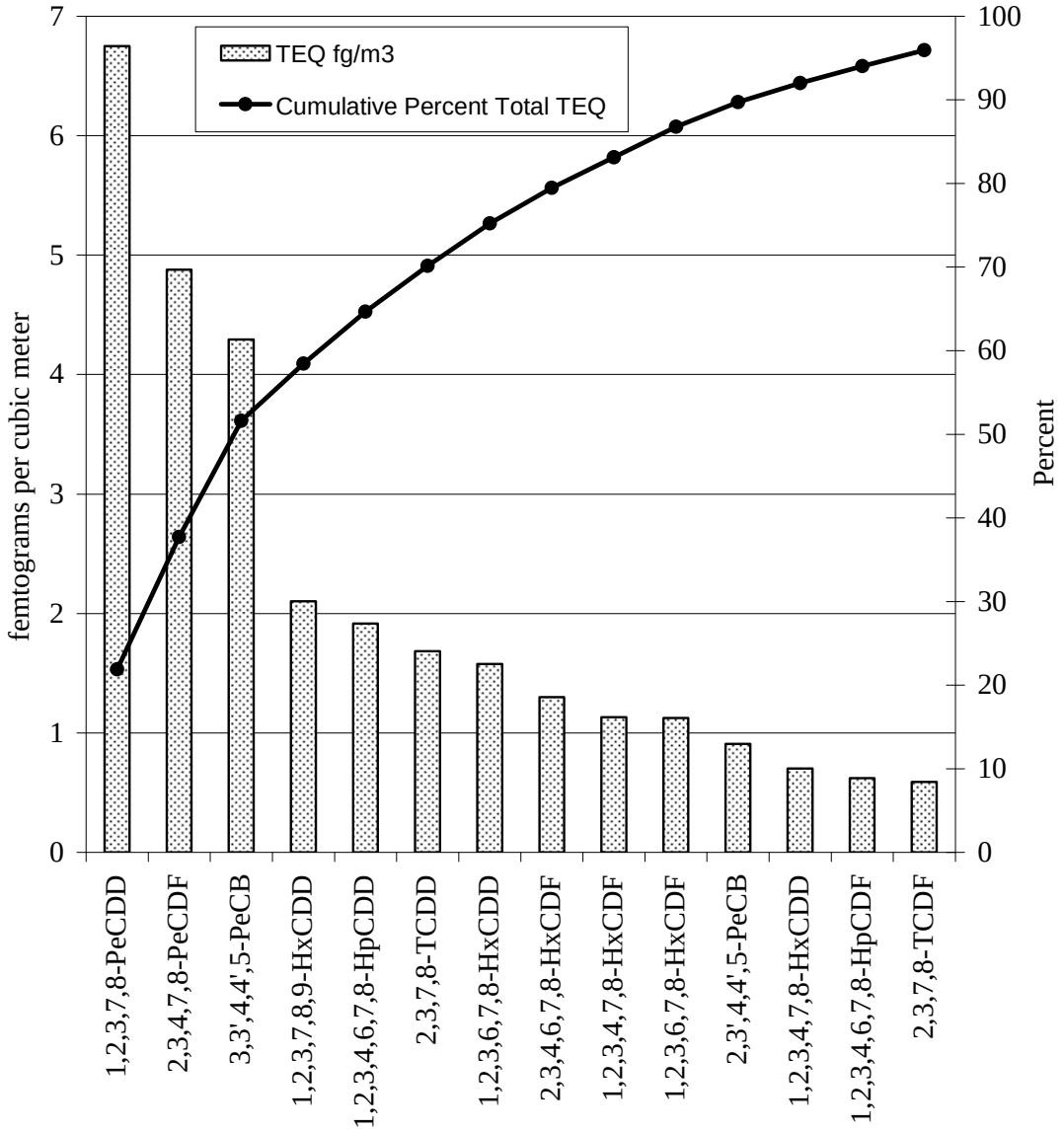
Figure 1. Total Toxicity Equivalence (TEQ)



SUMMARY

CDAMP provides a unique dataset (71 compounds) that has been used to generate robust averages for PCDDs, PCDFs, PCBs, and PBDEs at urban sites in California. The total average TEQ for PCDDs, PCDFs, and PCBs measured at urban sites is 31 fg/m^3, which is approximately twice the total TEQ found at the rural site. In addition, the variation of congener averages is generally small when comparing SC to the BA. Finally, about half of the measured 29 congeners with TEFs contribute to nearly all of the total TEQ.

Figure 2. Top Contributors of TEQ: Average of All 11 Urban Sites



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1. Gill, K.; Monger, K. "Air Monitoring for Dioxins, Furans, Polychlorinated Biphenyls, and Polybrominated Diphenyl Ethers in Urban Locations of California," AWMA annual conference, San Francisco, 2005.

2. Charrier, J.G.; Hafner, H.R.; Wade, K.S; Brown, S.G.; MacDonald C.P., California Ambient Dioxin Air Monitoring Program 2002 to 2006 Data Analysis of Dioxins, Furans, Biphenyls, and Diphenylethers, STI-907024.45-3292-FR2, Sonoma Technology Inc., Petaluma, CA, March 31, 2010.

3. Venier, V; Ferrario, J; Hites, R. Polychlorinated Dibenzo-p-dioxins and Dibenzofurans in the Atmosphere Around the Great Lakes, Environ. Sci. Tehnol. 2009, 43 p. 1036-1041.

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Monitoring and Laboratory Division

Nomenclature

- Polychlorinated Dibenzo-p-dioxins (PCDDs) dioxins
- Polychlorinated Dibenzofurans (PCDFs) furans,
- Polychlorinated Biphenyls (PCBs), and
- Polybrominated Diphenylethers (PBDE's)

Background

- Previously, the U.S. EPA established a National Dioxin Air Monitoring Network (NDAMN) to estimate rural ambient air concentrations of dioxins, furans and PCBs throughout the U.S. (1998 through 2002 with up to 30 sites).
- ARB started monitoring for dioxins, furans, PCBs, and PBDEs (flame retardants) in 2002 at Urban sites.
- Sampling conducted by BAAQMD, SCAQMD, and ARB.
- ARB design similar to NDAMN (1/28 days vs. 1/3 months)

Data Analysis

- Data analysis contract was performed by Sonoma Technology Inc.
  - Focus was on spatial and temporal relationships, meteorological effects, and possible source contributions.
- Today's presentation is focused on core questions concerning the four groups of congeners:
  - Are urban areas on average the same?
  - What is the average total toxicity value?
  - Which congeners contribute the most to the total toxicity?

Primary Sampling Sites 2002-2004 with the most robust dataset

South Coast Air Basin

- Boyle Heights
- Reseda
- Rubidoux
- Wilmington

San Francisco Bay Area Air Basin

- Livermore
- Oakland
- Richmond
- San Francisco
- San Jose

Central Valley sites include: Sacramento, Fresno, Five Points

Sampling Head
Chart Recorder
Magnehelic Gauge
Timer and Flow Controller
Based on U.S. EPA Method TO-9A

Polyurethane foam
XAD
Polyurethane foam

Analysis

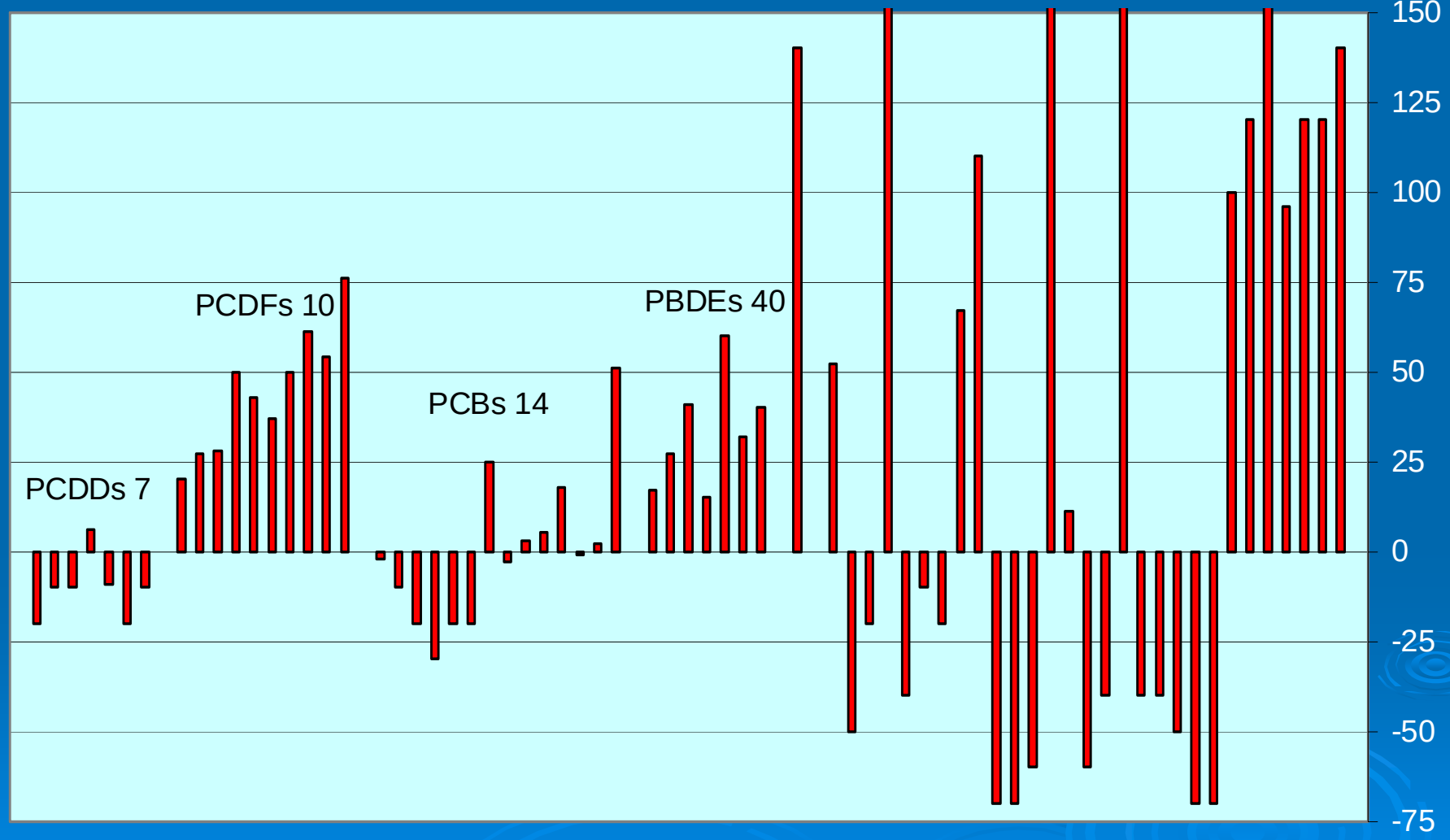
- Laboratory analysis was performed by Axys Analytical Services using high resolution GC/MS and established procedures from U.S. EPA
  - Method TO-9A/1613A for 17 Dioxins & Furans
  - Method 1668A for 14 PCBs
  - Draft Method 1614 for 40 PBDEs
  - Single sample was split 3 ways for analysis and archived

Average dioxin Concentrations for SC and BA Combined (femtograms/m3)

PCDDs	Average	PD*
2,3,7,8-TCDD	1.7	-20
1,2,3,7,8-PeCDD	6.5	-10
1,2,3,4,7,8-HxCDD	6.4	-10
1,2,3,6,7,8-HxCDD	15	6
1,2,3,7,8,9-HxCDD	19	-9
1,2,3,4,6,7,8-HpCDD	170	-20
OCDD	600	-10

*PD (Percent difference) = 100 X [SC Ave (4 sites) – BA Ave (5 sites)] / [Average of SC and BA].

South Coast vs Bay Area Percent Difference



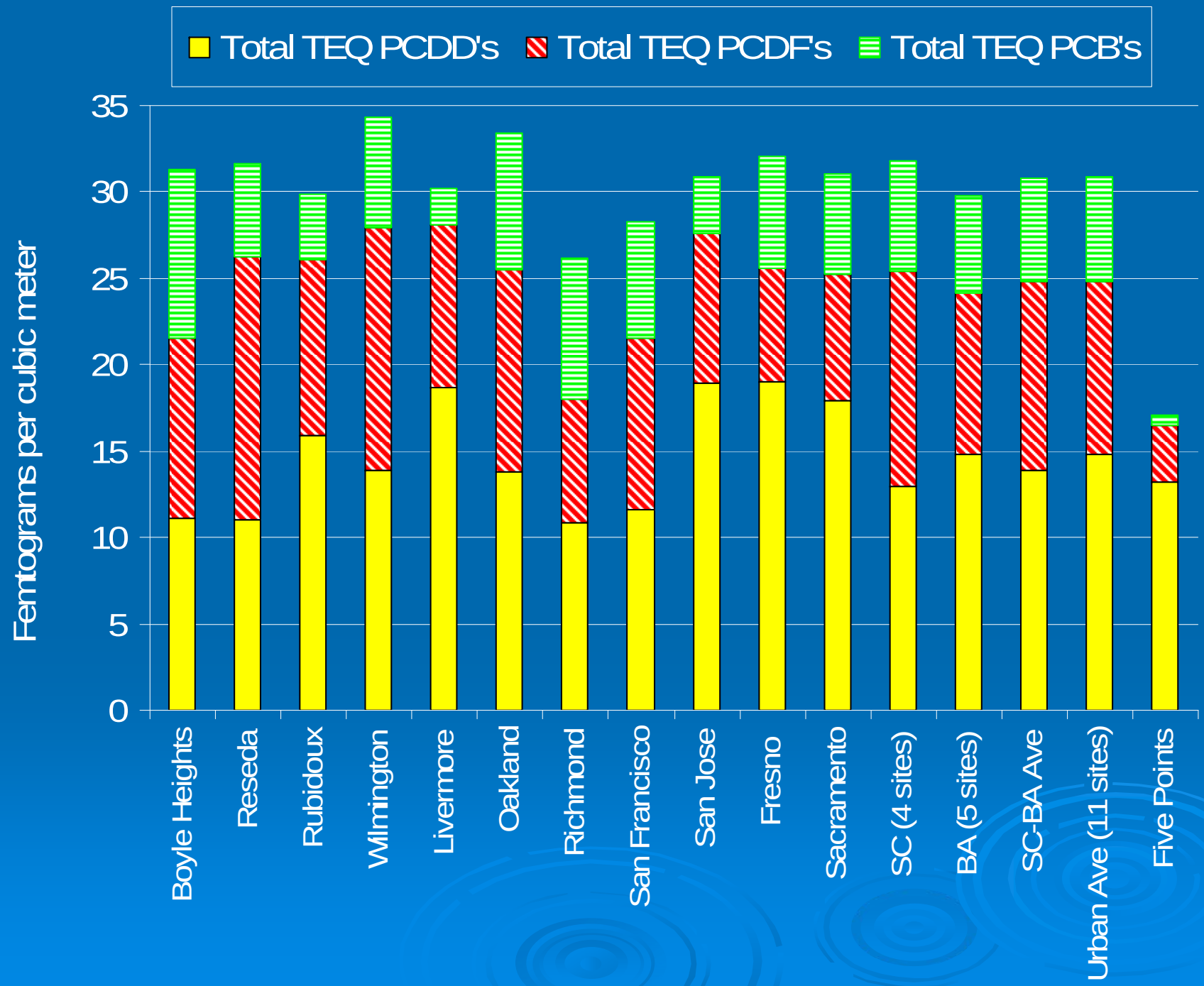
Comparison of South Coast and Bay Area

- Dioxins, furans, and PCBs have similar ambient concentrations with most congeners being within +/- 50 percent.
- PBDEs have greater differences but most congeners are within +/- 100 percent.
- Data suggest common sources.

Toxicity Equivalence

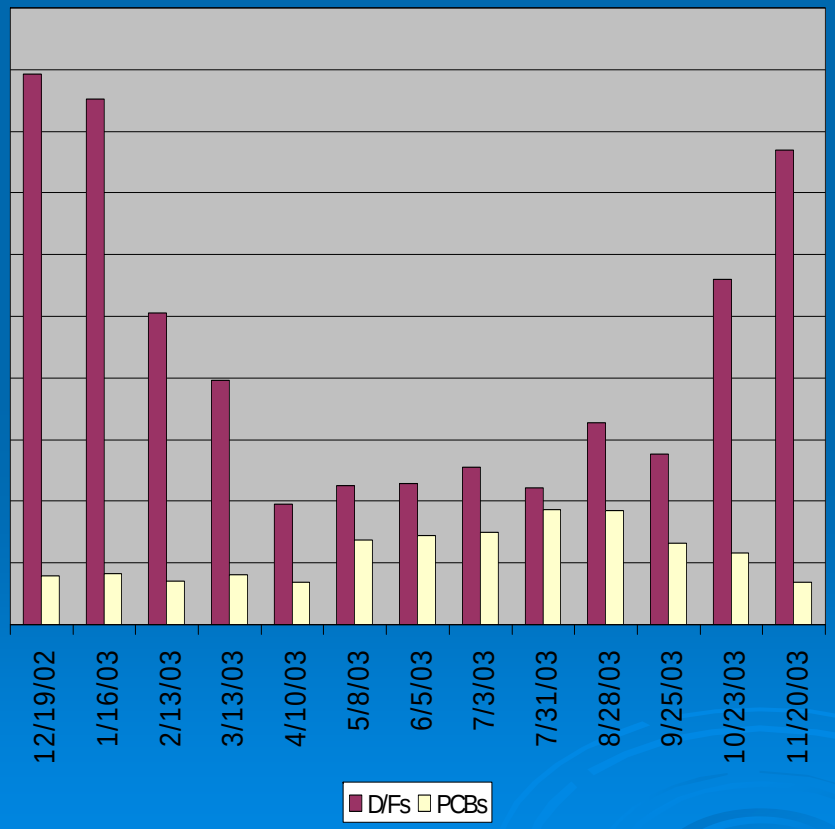
- Each congener has an assigned Toxicity Equivalence Factor (TEF) that was define by the World Health Organization (WHO).
- ARB currently uses WHO 1997-8 TEFs.
- Toxicity for PCDDs, PCDFs, and PCBs are expressed as toxicity equivalent (TEQ) to 2,3,7,8-TCDD.
- TEF of 2,3,7,8-TCDD is 1.
- TEQ_x = $Concentration_x$ times (TEF_x).

Congener	WHO-97 TEF	Congener	WHO-97 TEF
2,3,7,8-TCDD	**1**	3,3’,4,4’-TeCB	0.0001
1,2,3,7,8-PeCDD	**1**	3,4,4’,5-TeCB	0.0001
1,2,3,4,7,8-HxCDD	0.1	2,3,3’,4,4’-PeCB	0.0001
1,2,3,6,7,8-HxCDD	0.1	2,3,4,4’,5-PeCB	0.0005
1,2,3,7,8,9-HxCDD	0.1	2,3’,4,4’,5-PeCB	0.0001
1,2,3,4,6,7,8-HpCDD	0.01	2’,3,4,4’,5-PeCB	0.0001
OCDD	0.0001	**3,3’,4,4’,5-PeCB**	**0.1**
2,3,7,8-TCDF	0.1	2,3,3’,4,4’,5-HxCB	0.0005
1,2,3,7,8-PeCDF	0.05	2,3,3’,4,4’,5’-HxCB	0.0005
2,3,4,7,8-PeCDF	**0.5**	2,3’,4,4’,5,5’-HxCB	0.00001
1,2,3,4,7,8-HxCDF	0.1	3,3’,4,4’,5,5’-HxCB	0.01
1,2,3,6,7,8-HxCDF	0.1	2,2’,3,3’,4,4’,5-HpCB	0
1,2,3,7,8,9-HxCDF	0.1	2,2’,3,4,4’,5,5’-HpCB	0
2,3,4,6,7,8-HxCDF	0.1	2,3,3’,4,4’,5,5’-HpCB	0.0001
1,2,3,4,6,7,8-HpCDF	0.01		
1,2,3,4,7,8,9-HpCDF	0.01		
OCDF	0.0001		

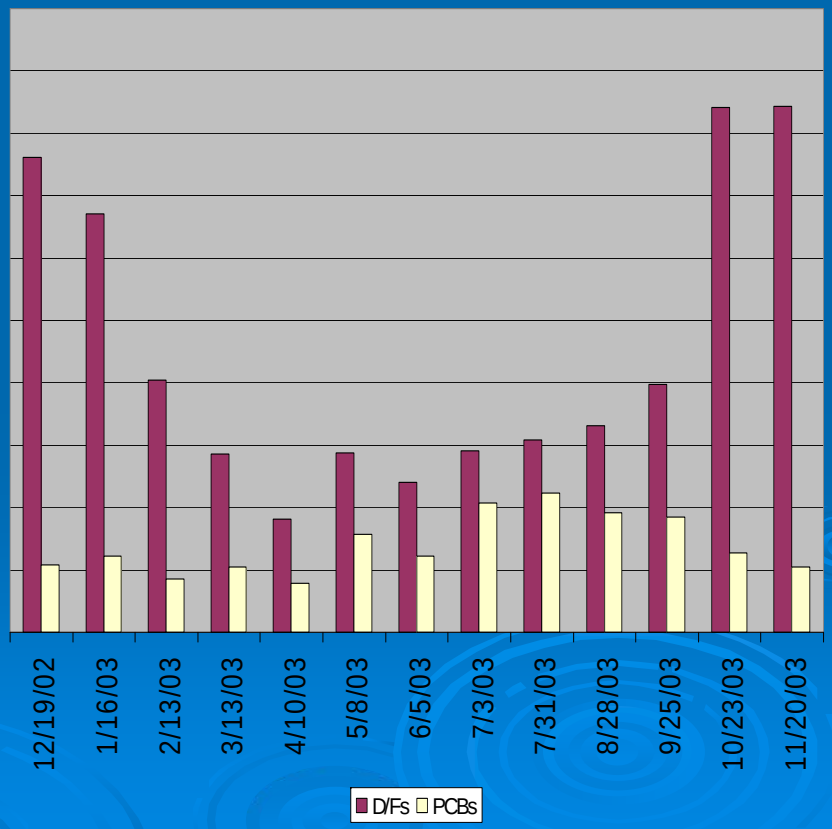

Total TEQ PCDD's
Total TEQ PCDF's
Total TEQ PCB's
Femtograms per cubic meter
35
30
25
20
15
10
5
0
Boyle Heights
Reseda
Rubidoux
Wilmington
Livermore
Oakland
Richmond
San Francisco
San Jose
Fresno
Sacramento
SC (4 sites)
BA (5 sites)
SC-BA Ave
Urban Ave (11 sites)
Five Points

Seasonal Variations
Sample TEQ Averages

South Coast 2003



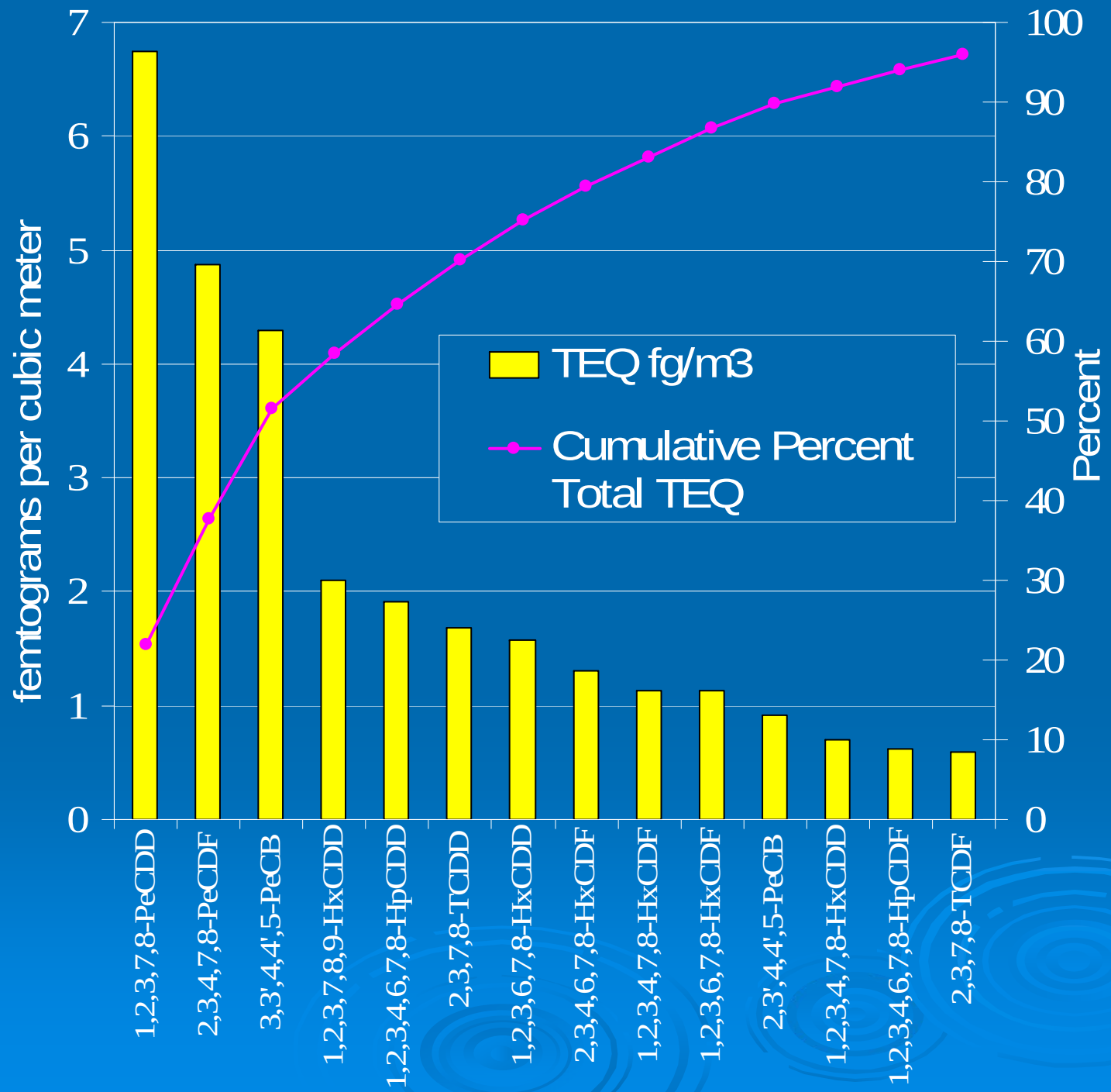
Bay Area 2003



Observed Seasonal Variation

- South Coast and Bay Area have similar seasonal patterns. All monitoring years were also similar.
- Average sample TEQ for Dioxins and furans are highest during cooler months (winter).
- Average sample TEQ for PCBs are highest during warmer months (summer).
- Partial-year studies need to consider seasonal variation when comparing data.

Congener	WHO-97 TEF	Congener	WHO-97 TEF
2,3,7,8-TCDD	**1**	3,3’,4,4’-TeCB	0.0001
1,2,3,7,8-PeCDD	**1**	3,4,4’,5-TeCB	0.0001
1,2,3,4,7,8-HxCDD	0.1	2,3,3’,4,4’-PeCB	0.0001
1,2,3,6,7,8-HxCDD	0.1	2,3,4,4’,5-PeCB	0.0005
1,2,3,7,8,9-HxCDD	0.1	2,3’,4,4’,5-PeCB	0.0001
1,2,3,4,6,7,8-HpCDD	0.01	2’,3,4,4’,5-PeCB	0.0001
OCDD	0.0001	**3,3’,4,4’,5-PeCB**	**0.1**
2,3,7,8-TCDF	0.1	2,3,3’,4,4’,5-HxCB	0.0005
1,2,3,7,8-PeCDF	0.05	2,3,3’,4,4’,5’-HxCB	0.0005
2,3,4,7,8-PeCDF	**0.5**	2,3’,4,4’,5,5’-HxCB	0.00001
1,2,3,4,7,8-HxCDF	0.1	3,3’,4,4’,5,5’-HxCB	0.01
1,2,3,6,7,8-HxCDF	0.1	2,2’,3,3’,4,4’,5-HpCB	0
1,2,3,7,8,9-HxCDF	0.1	2,2’,3,4,4’,5,5’-HpCB	0
2,3,4,6,7,8-HxCDF	0.1	2,3,3’,4,4’,5,5’-HpCB	0.0001
1,2,3,4,6,7,8-HpCDF	0.01		
1,2,3,4,7,8,9-HpCDF	0.01		
OCDF	0.0001		


femtograms per cubic meter
Percent
TEQ fg/m3
Cumulative Percent Total TEQ
0
1
2
3
4
5
6
7
0
10
20
30
40
50
60
70
80
90
100
1,2,3,7,8-PeCDD
2,3,4,7,8-PeCDF
3,3',4,4',5-PeCB
1,2,3,7,8,9-HxCDD
1,2,3,4,6,7,8-HpCDD
2,3,7,8-TCDD
1,2,3,6,7,8-HxCDD
2,3,4,6,7,8-HxCDF
1,2,3,4,7,8-HxCDF
1,2,3,6,7,8-HxCDF
2,3',4,4',5-PeCB
1,2,3,4,7,8-HxCDD
1,2,3,4,6,7,8-HpCDF
2,3,7,8-TCDF

Conclusions

- California's average urban TEQ is 31 fg/m3.
- Urban sites within California have similar average annual concentrations.
- Only 5 congeners contribute two-thirds of the overall TEQ.
- More information can be found on the web at: arb.ca.gov /aaqm/qmosopas/dioxins/dioxins.htm