DIOXINS AND FURANS IN RILLITO, ARIZONA

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in consultation with the Arizona Department of Health Services

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Executive Summary

Concerns of Rillito citizens about emissions of dioxins and furans from the Arizona Portland Cement Plant (APCC) and stack testing at APCC led to an ambient air monitoring program conducted in 2004 - 2005. Ambient concentrations of dioxins and furans proved to be within health-based guidelines. These concentrations were somewhat higher than those measured at background sites but considerably lower than at urban sites. The distribution of the 17 toxic dioxins and furans in the ambient air of Rillito closely resembled the mobile source profile but was quite different from the APCC profile. The dioxin and furan concentrations measured during the one-year study suggested that mobile source emissions had a much greater impact at Rillito than the cement plant emissions.

Introduction to Dioxins and Furans

"Dioxins and furans" is a term used to describe a group of environmentally persistent chemicals that are metabolized slowly and therefore tend to bioaccumulate, especially in the fat and in the liver. These compounds are the unintended by-products of virtually all combustion. Although numbering 210 different compounds, the environmental community has focused on the 17 found to have adverse health effects in humans or animals. Several international organizations have classified one of the two most toxic of these compounds -- 2,3,7,8-tetrachlorodibenzo-para-dioxin (2,3,7,8-TCDD)—as a human carcinogen.

To assess the cumulative toxicity of a mixture of these compounds – also called "congeners" – the World Health Organization has assigned a Toxic Equivalency Factor (TEF) to each compound relative to the toxicity of 2,3,7,8-TCDD. These TEFs are the results of scientific judgment of a panel of experts using all of the available data and are selected to account for uncertainties in the available data and to avoid underestimating risk. Thus, they are "public health conservative" values. When this TEF is multiplied by its congener concentration, and all of these products are summed, the result is the Toxic Equivalency (TEQ) of the mixture. Table 1 gives the names, abbreviations, and toxicity factors for the 17 toxic dioxins and furans.

Typical units of measurement for ambient dioxins and furans are picograms per cubic meter (pg/m^3) or femtograms per cubic meter (fg/m^3). A picogram is one trillionth of a gram, or 0.000000000001 of a gram, or, in scientific notation,
1×10^{-12} gram. Femtograms are 1000 times smaller than picograms: one quadrillonth of a gram, or 0.000000000000001 of a gram, or 1×10^{-15} gram. Results of stack tests are reported in picograms per dry standard cubic meter (pg/dscm). Concentrations expressed in these units, both ambient and stack, can be reported directly or can be converted into the relative toxicity or TEQ. In this paper most results will be reported as their TEQ, the ambient in femtograms; the stack, in picograms.

Dioxins and furans belong to that class of compounds which are found in both the gaseous and particulate phase. Depending on the individual compound, temperature, and general particulate concentration, a particular congener can be either gaseous or particulate. The term "semi-volatile organic compounds" is used to describe these compounds that can partition between the two phases. In this paper concentrations of both the particulate phase and gaseous phase dioxins and furans will be presented.

Table 1. Dioxins and Furans

Name	Abbreviation	TEF*
2,3,7,8-tetrachlorodibenzo-p-dioxin	2,3,7,8-TCDD	1.0
1,2,3,7,8-pentachlorodibenzo-p-dioxin	1,2,3,7,8-PeCDD	1.0
1,2,3,4,7,8-hexachlorodibenzo-p-dioxin	1,2,3,4,7,8-HxCDD	0.1
1,2,3,6,7,8-hexachlorodibenzo-p-dioxin	1,2,3,6,7,8-HxCDD	0.1
1,2,3,7,8,9-hexachlorodibenzo-p-dioxin	1,2,3,7,8,9-HxCDD	0.1
1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin	1,2,3,4,6,7,8-HpCDD	0.01
1,2,3,4,6,7,8,9-octachlorodibenzo-p-dioxin	OCDD	0.0001
2,3,7,8-tetrachlorodibenzo-p-furan	2,3,7,8-TCDF	0.1
1,2,3,7,8-pentachlorodibenzo-p-furan	1,2,3,7,8-PeCDF	0.05
2,3,4,7,8-pentachlorodibenzo-p-furan	2,3,4,7,8-PeCDF	0.5
1,2,3,4,7,8-hexachlorodibenzo-p-furan	1,2,3,4,7,8-HxCDF	0.1
1,2,3,6,7,8-hexachlorodibenzo-p-furan	1,2,3,6,7,8-HxCDF	0.1
1,2,3,7,8,9-hexachlorodibenzo-p-furan	2,3,4,6,7,8-HxCDF	0.1
2,3,4,6,7,8-hexachlorodibenzo-p-furan	1,2,3,7,8,9-HxCDF	0.1
1,2,3,4,6,7,8-heptachlorodibenzo-p-furan	1,2,3,4,6,7,8-HpCDF	0.01
1,2,3,4,7,8,9-heptachlorodibenzo-p-furan	1,2,3,4,7,8,9-HpCDF	0.01
1,2,3,4,6,7,8,9-octachlorodibenzo-p-furan	OCDF	0.0001

*TEF: toxic equivalency factor: 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD are the two most toxic congeners and have a TEF set to 1.0. The toxicity of the other 15 is expressed as a decimal fraction of the most toxic two. Their toxicity ranges from 50% (0.5) to 0.01% (0.0001) of 2,3,7,8-TCDD.

Environmental scientists for the last two decades have determined that different types of combustion produce different patterns, or "profiles", of dioxins and furans congeners. Profiles from specific types of combustion can then be compared with those profiles in ambient air measurements. These comparisons shed light on which sources are most influential in the dioxin and furan composition of the ambient air.

Background of the Present Study

The kilns at APCC are subject to the dioxin and furan standard in the Portland Cement Maximum Achievable Control Technology Standard (40 CFR 63 Subpart LLL). The MACT Standard was promulgated on June 14, 1999. APCC was required to conduct a test to demonstrate compliance with the dioxin and furan emission limits by December 14, 2002. The permit (MP190310P1-00) requires that subsequent tests be conducted on an annual basis.

During tests conducted in December 2002, APCC failed to demonstrate compliance with the standard in four out of five operational configurations. APCC conducted follow-up tests in January 2003, and failed to demonstrate compliance in one out of five operational configurations. It was determined that the earlier exceedances were due to Alumina Cement Additive (ACA) in the feedstock and subsequently ACA was removed from the feedstock. An additional set of tests was conducted in late February 2003. The results from the February tests demonstrated that the emissions during the February tests were below the MACT standard. In June 2004, APCC conducted a dioxin furan test on Kilns 1, 2, and 3 to determine if they could operate at a higher baghouse inlet temperature and still meet the dioxin/furan (D/F) standard. APCC failed this performance test and was again required to show compliance at their normal operating temperature range. Subsequent tests for Kilns 1, 2, and 3 conducted in July 2004 and March 2005 showed that the standard was again being met.

Tests which demonstrated noncompliance with the dioxin and furan standard raised concerns in the community about potential exposure levels and the associated health impacts. In response to these concerns, ADEQ agreed to conduct an ambient air study to assess Dioxin and Furan ambient concentrations in the Rillito community. ADEQ staff enlisted the help of EPA Region 9 (San Francisco) and Region 7 (Kansas City) to obtain the necessary technical advice and laboratory assistance to carry out a dioxin and furan ambient air study. Conducted from February 2004 through January 2005 by ADEQ staff, this monitoring work at Rillito has provided the dioxin and furan concentrations necessary to assess human health risk. These concentrations will be discussed in the remainder of this paper, in the context of dioxin and furan congener profiles from APCC and from mobile sources.

Sources

Dioxins and furans are produced by combustion, so only combustion emission sources figure directly into their airborne concentrations. For example, mobile source emissions in this comparison are limited to exhaust, and cement plant emissions are limited to combustion emissions from stacks. In this section the air pollution sources that affect Rillito are described. Where available, dioxin and furan emissions will be presented, as well as the conventional pollutants. The intention here is to provide the relative strengths of these sources. Considering only three sources – the APCC, Interstate 10, and the Union Pacific Railroad – the former has much greater emissions of all pollutants except volatile organic compounds (VOC) than the mobile sources (Table 2).

The total range of sources contributing to the dioxins and furans in this study needs to be explained. Dioxins and furans, like virtually all other air pollutants, are deposited on the ground and foliage surfaces through both wet and dry deposition. This deposition leads to appreciable concentrations of dioxins and furans on their surfaces. Windblown and vehicle-generated dusts that have been subject to dioxins and furans deposition can contribute to ambient concentrations at such sites as Rillito. Quantifying this source was beyond the scope of this study, so the focus remains on the combustion sources themselves.

Table 2. Annual Air Pollution Emissions for Three Major Sources in Rillito

	PM10	CO	NOx	SOx	VOC	DF
Units	Tons/yr	Tons/yr	Tons/yr	Tons/yr	Tons/yr	grams/yr TEQ
APCC[1]	439.0	3956.2	3460.2	11.6	5.7	0.5 [2]
Total Mobile	1.7	281.6	69.1	2.5	33.8	0.0006122
I-10	1	279	50	0.4	33	0.0006100
Railroad	0.7	2.8	19.5	2.1	1.0	0.0000022
Ratio	258.2	14	50.5	4.6	0.2	817

[1] Average of emission rates from 2001, 2002, and 2003 Emission Inventory Reports

[2] This emission estimate is based on the average of test results from February 2003 tests and July and April 2004 test results.

PM10	Particles 10 microns and smaller
CO	Carbon monoxide
NOx	Nitrogen oxides
SOx	Sulfur oxides
VOC	Volatile organic compounds
DF	Dioxins and furans, with the units of grams per year
I-10	Based on 52,000 vehicles per day on one mile of roadway, 10% diesel
Railroad	Based on one mile of line haul emissions, 20 trains per day
Ratio	APCC to total mobile

Description of Measurements

APCC Stack Testing

Five stack tests for Dioxins and Furans were conducted in December 2002. An additional five stack tests were conducted in January 2003. Four stack tests were also conducted on Kiln 4 in April 2004 and one stack test was conducted on Kilns 1-3 in June 2004. One stack test was also conducted in July 2004. The most recent five stack tests were conducted in March 2005. The required test method is EPA Method 23. Initial tests are required by the Portland Cement MACT Standard (40 CFR 63 Subpart LLL). Kiln 4 is required to be tested in two different configurations, raw mill on, and raw mill off. The subsequent tests only need be performed in the configuration that resulted in the highest emission rate. Tests were done on the following kilns and conditions (Table 3):

Table 3a - g. Stack Test Conditions and Results at APCC

Table 3a

December 9-14, 2002					
Kiln	Raw Mill Configuration	Average Baghouse Inlet Temperature (º F)	Results ng/dscm TEQ	Allowable ng/dscm TEQ	Pass/Fail
1-3	N/A	635	0.62	0.20	Fail
4	Off/Low Temp.	519	0.29	0.20	Fail
4	Off/High Temp.	694	4.7	0.20	Fail
4	On/Low Temp.	414	0.05	0.20	Pass
4	On/High Temp.	687	0.6	0.20	Fail

Table 3b

January 14-18, 2003					
Kiln	Raw Mill Configuration	Average Baghouse Inlet Temperature (º F)	Results ng/dscm TEQ	Allowable ng/dscm TEQ	Pass/Fail
1-3	N/A	607	0.02	0.20	Pass
4	Off/Low Temp.	484	0.03	0.20	Pass
4	Off/High Temp.	690	0.76	0.20	Fail
4	On/Low Temp.	459	0.03	0.20	Pass
4	On/High Temp.	678	0.06	0.20	Pass

Table 3c

February 24-28, 2003					
Kiln	Raw Mill Configuration	Average Baghouse Inlet Temperature (º F)	Results ng/dscm TEQ	Allowable ng/dscm TEQ	Pass/Fail
1-3	N/A	K1(718) K2(619) K3(646)	0.05	0.20	Pass
4	Off/Low Temp.	570	0.04	0.20	Pass
4	Off/High Temp.	600	0.10	0.20	Pass
4	On	700	0.04	0.20	Pass

Table 3d

April 13-29, 2004					
Kiln	Raw Mill Configuration	Average Baghouse Inlet Temperature (º F)	Results ng/dscm TEQ	Allowable ng/dscm TEQ	Pass/Fail
4	Off	625	0.06	0.20	Pass
4	Off	600	0.05	0.20	Pass
4	Off-Oil Temp.	600	0.06	0.20	Pass
4	On	692	0.04	0.20	Pass

Table 3e

June 2-3, 2004					
Kiln	Raw Mill Configuration	Average Baghouse Inlet Temperature (º F)	Results ng/dscm TEQ	Allowable ng/dscm TEQ	Pass/Fail
1-3	N/A	705(Kiln 1) 720 (Kiln 2) 706 (Kiln 3)	0.22	0.20	Fail

Table 3f

July 26-27, 2004					
Kiln	Raw Mill Configuration	Average Baghouse Inlet Temperature (º F)	Results ng/dscm TEQ	Allowable ng/dscm TEQ	Pass/Fail
1-3	N/A	653 (Kiln 1) 652 (Kiln 2) 671 (Kiln 3)	0.04	0.20	Pass

Table 3g

March 4-5, 8, 2005					
Kiln	Raw Mill Configuration	Average Baghouse Inlet Temperature (º F)	Results ng/dscm TEQ	Allowable ng/dscm TEQ	Pass/Fail
1-3	N/A	688 (Kiln 1) 687 (Kiln 2) 686 (Kiln 3)	0.13	0.20	Pass
1-3	N/A	649 (Kiln 1) 648 (Kiln 2) 670 (Kiln 3)	0.11	0.20	Pass
4	Off	693	0.13	0.20	Pass
4	Off	620	0.19	0.20	Pass
4	On	693	0.18	0.20	Pass

These stack test data above are summarized in Figure 1

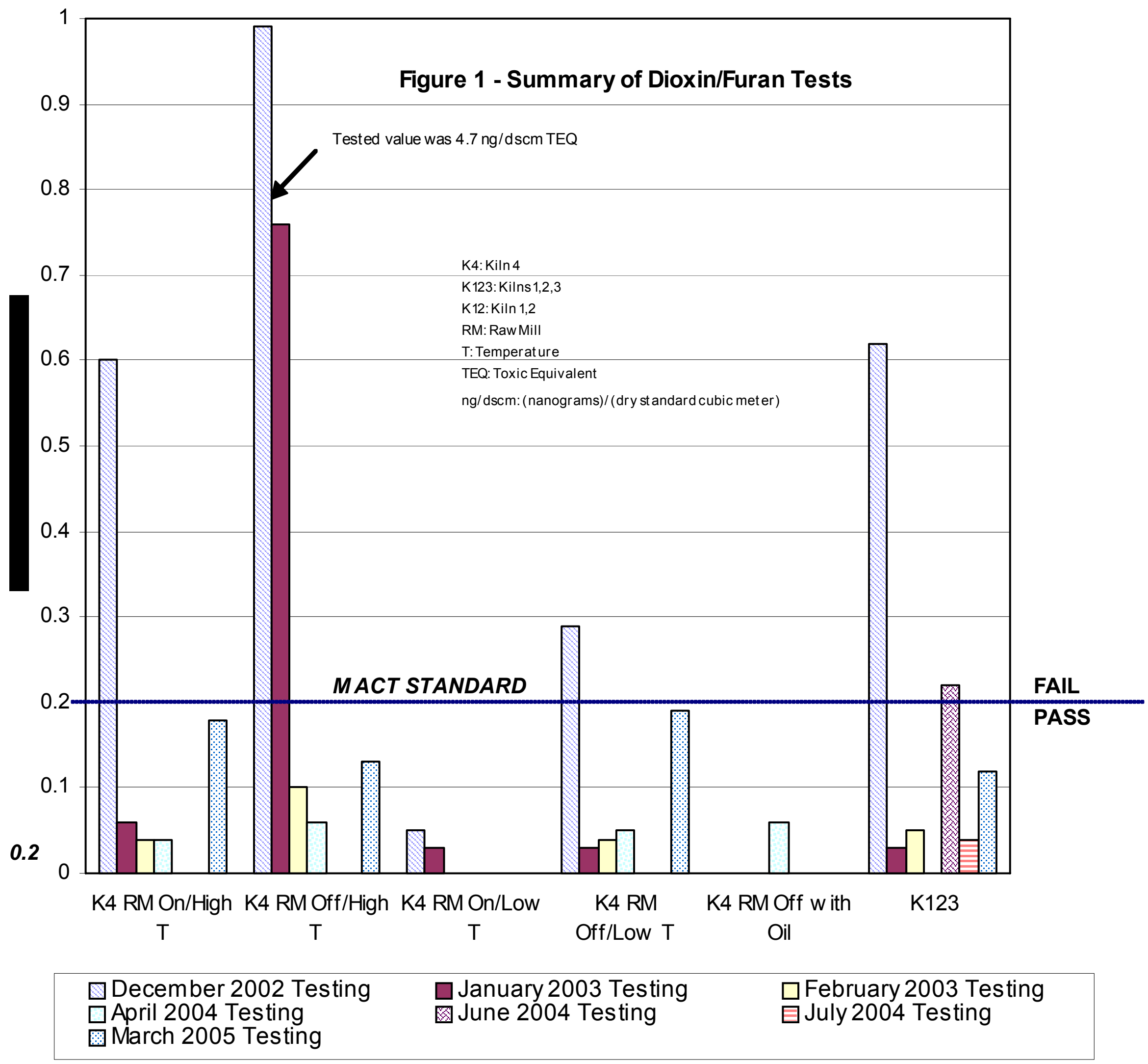


Figure 1 - Summary of Dioxin/Furan Tests
Tested value was 4.7 ng/dscm TEQ
K4: Kiln 4
K123: Kilns 1,2,3
K12: Kiln 1,2
RM: Raw Mill
T: Temperature
TEQ: Toxic Equivalent
ng/dscm: (nanograms)/(dry standard cubic meter)
[redacted]
0.2
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
MACT STANDARD
FAIL
PASS
K4 RM On/High T
K4 RM Off/High T
K4 RM On/Low T
K4 RM Off/Low T
K4 RM Off with Oil
K123
December 2002 Testing
January 2003 Testing
February 2003 Testing
April 2004 Testing
June 2004 Testing
July 2004 Testing
March 2005 Testing

To produce a congener profile, several of these tests have been averaged for their congener concentrations (Table 4)

Table 4. Rillito Dioxins and Furans: Stack Tests from APCC, with All Concentrations Expressed as Toxic Equivalents

Name	TEF	pg TEQ/dscm[1]
2,3,7,8-TCDD	1.0	6.533
1,2,3,7,8-PeCDD	1.0	7.576
1,2,3,4,7,8-HxCDD	0.1	0.292
1,2,3,6,7,8-HxCDD	0.1	0.351
1,2,3,7,8,9-HxCDD	0.1	0.257
1,2,3,4,6,7,8-HpCDD	0.01	0.078
OCDD	0.0001	0.001
2,3,7,8-TCDF	0.1	16.055
1,2,3,7,8-PeCDF	0.05	2.591
2,3,4,7,8-PeCDF	0.5	33.821
1,2,3,4,7,8-HxCDF	0.1	1.601
1,2,3,6,7,8-HxCDF	0.1	1.699
2,3,4,6,7,8-HxCDF	0.1	1.483
1,2,3,7,8,9-HxCDF	0.1	0.392
1,2,3,4,6,7,8-HpCDF	0.01	0.117
1,2,3,4,7,8,9-HpCDF	0.01	0.018
OCDF	0.0001	0.000
2,3,7,8-TCDD (TEQ)	---	72.864

[1] Average of stack tests conducted in April 2004 on Kiln 4 (RM On, RM Off with Oil, RM Off at 625 °F, RM Off at 600 °F), June 2004 test conducted for Kilns 1-3,and July 2004 test conducted for Kilns 1-3.

Ambient Air Measurements

Detailed descriptions of the sampling and analysis methods for dioxins and furans can be found in "Quality Assurance Plan: Monitoring for Polychlorinated Dibenzo-p-Dioxins and polychlorinated Dibenzofurans in Rillito, Arizona", Arizona Department of Environmental Quality, February 6, 2004 and "Determination of Polychlorinated, Polybrominated and Brominated/Chlorinated Dibenzo-p-dioxins and Dibenzofurans in Ambient Air", EPA, 1999. Dioxins and furans can be found in two phases: as particles, and as gases, or "semi-volatile organic compounds". This dual phase phenomenon requires that two sampling media be employed: a quartz fiber filter for airborne particulates; followed by a polyurethane foam cartridge for the gaseous and semi-volatile organic compounds. In the Rillito work, the long-term air pollution monitoring site at the Gremmler residence was used.

Conducted from February 2004 through January 2005, the sampling schedule followed that of the National Dioxin Air Monitoring Network (NDAMN). The sampling periods were selected to coincide with the quarterly NDAMN sampling. Each sampling period consisted of 26 (or 27) days, with 20 days actually being sampled. These 20 sampling days were divided into four-, and five-day periods, each period being separated by two days. This schedule allows the operator to change the filter and foam substrate in the daytime, rather than at midnight, the hour that the sampling begins. Because of a contract lapse in the national program, the month of May was not sampled at any NDAMN sites throughout the United States, nor was it sampled at Rillito. Dates of the sampling periods are given in Table 5. All sampling media were shipped to the EPA Region 7 laboratory in Kansas City for analysis.

Table 5. Dioxin and Furan Sampling Dates in Rillito

Start Date	End Date	Number of Days	Actual Sampling Days
2/12/2004	3/9/2004	26	20
3/11/2004	4/6/2004	26	20
4/8/2004	5/4/2004	26	20
5/27/2004	6/22/2004	26	20
6/24/2004	7/20/2004	26	20
8/5/2004	8/31/2004	26	20
9/2/2004	9/28/2004	26	20
9/30/2004	10/26/2004	26	20
11/3/2004	11/30/2004	27	20
12/2/2004	12/28/2004	26	20
1/6/2005	2/1/2005	26	20
2/12/2004	2/1/2005	287	220

The results of the ambient air sampling program are summarized in this section. These concentrations should be interpreted with the following insights:

1. Each value is expressed as the toxic equivalent (TEQ) of the concentration in femtograms per cubic meter (fg/m^3).

2. The annual average is calculated in the following way. First, the average of the 11 semi-volatile organic compound concentrations is determined. Second, the average of the 11 particulate concentrations is determined. Third, the two averages are added. Fourth, this annual average concentration is converted to the TEQ.

3. In laboratory analyses zero concentrations are never reported. The laboratory can determine two lower limits. The lower of these two is called the minimum detection limit. The higher of the two is called the minimum reporting limit. In this study the concentrations at the lower end of laboratory sensitivity will be based on the more conservative values (i.e. minimum reporting limits).

4. Values below the minimum reporting limit have been treated in two ways. In the first method, they have been assigned a concentration of one half of the reporting limit. In a separate analysis, they have been set equal to zero.

5. When most of the laboratory analyses are below the reporting limit, as Table 6 shows, the treatment of sub-reporting-limit values has important consequences in calculating the annual averages.

Table 6. Dioxins and Furans in Rillito: Frequency of Values below the Reporting Limit

Statistic	Particulates	Semi-volatiles	Total
Number of analyses	187	187	374
Number of Non-reported	75	175	250
Percentage of Non-reported	40%	94%	67%

6. This importance can be seen in Table 7, in which the TEQs have been calculated first with the sub reporting limit values as zero and second with the sub reporting limit values as one half of the reporting limit. The latter method produces a TEQ 3.74 times greater than the former.

7. Various statistical methods can be applied to such data sets to reduce the influence of the nondetectable values (see, for example, "Guidance for Data Quality Assessment", EPA QA/G-9, EPA/600/R-96/084, January 1998). Cohen's method and the method of proportions are two such methods. Their application is restricted to those compounds whose nondetectable frequency is within the method's limits. For Cohen's method, only three compounds are suitable and they comprise only 14% of the TEQ. The method of proportions could be applied to five compounds (15% of the TEQ), but this method does not yield a specific numerical value for the average. Of the total TEQ, 74% of the toxicity resides in compounds that were either not detected at all or only one to three times out of the eleven. No statistical method can be applied to these compounds. In summary, the available statistical treatments for these dioxins and furans data either don't apply or don't change the answer appreciably.

Table 7. Annual Average Dioxin and Furan Concentrations in Rillito with Two Methods of Treating Sub Reporting Limit Values (TEQ fg/m^3)

Congener	Non-reported Values Treated As	
	Zero	½ Reporting Limit
2,3,7,8-TCDD	0.000	1.000
1,2,3,7,8-PeCDD	0.000	7.000
1,2,3,4,7,8-HxCDD	0.155	0.791
1,2,3,6,7,8-HxCDD	0.618	1.127
1,2,3,7,8,9-HxCDD	0.800	1.309
1,2,3,4,6,7,8-HpCDD	1.245	1.280
OCDD	0.046	0.046
2,3,7,8-TCDF	0.527	0.559
1,2,3,7,8-PeCDF	0.000	0.350
2,3,4,7,8-PeCDF	0.409	3.750
1,2,3,4,7,8-HxCDF	0.491	1.095
1,2,3,6,7,8-HxCDF	0.255	0.859
2,3,4,6,7,8-HxCDF	0.073	0.741
1,2,3,7,8,9-HxCDF	0.682	1.223
1,2,3,4,6,7,8-HpCDF	0.425	0.457
1,2,3,4,7,8,9-HpCDF	0.074	0.134
OCDF	0.003	0.004
TEQ	5.802	21.726

Given the insights just discussed, the ambient concentrations are now presented as annual averages, with the particulate and semi-volatile phases shown separately, in Tables 8 and 9. In Table 8 the averages have been calculated with those values below the reporting limit set to zero. In Table 9 the averages are based on setting those values below the reporting limit to one half the value of that limit. The logical interpretation of these tables is to view their respective averages as a range. The low end of the range is 5.8 fg/m^3 and the upper end is 21.7 fg/m^3. Dioxins and furans in Rillito, averaged for the year, lie somewhere in this range, not below and not above it. Because of the generally low levels of dioxins and furans that led to multiple nondetectable values, and because of the uncertainty of those concentrations below the minimum reporting limit (they can be anywhere from zero up to the limit itself), it is impossible to pinpoint an exact concentration. All that can be said for certain is that the annual average of dioxins and furans in Rillito, expressed as the toxic equivalent in femtograms per cubic meter, is 5.8 – 21.7.

Table 8. Rillito Dioxins and Furans: Annual averages, with all concentrations expressed as Toxic Equivalents in fg/m^3, and with values below the Reporting Limit set to zero

Congener	TEF	Particulate	Semi-volatiles	Ambient
2,3,7,8-TCDD	1.0	0.000	0.000	0.000
1,2,3,7,8-PeCDD	1.0	0.000	0.000	0.000
1,2,3,4,7,8-HxCDD	0.1	0.155	0.000	0.155
1,2,3,6,7,8-HxCDD	0.1	0.618	0.000	0.618
1,2,3,7,8,9-HxCDD	0.1	0.800	0.000	0.800
1,2,3,4,6,7,8-HpCDD	0.01	1.245	0.000	1.245
OCDD	0.0001	0.046	0.000	0.046
2,3,7,8-TCDF	0.1	0.100	0.427	0.527
1,2,3,7,8-PeCDF	0.05	0.000	0.000	0.000
2,3,4,7,8-PeCDF	0.5	0.409	0.000	0.409
1,2,3,4,7,8-HxCDF	0.1	0.491	0.000	0.491
1,2,3,6,7,8-HxCDF	0.1	0.255	0.000	0.255
2,3,4,6,7,8-HxCDF	0.1	0.073	0.000	0.073
1,2,3,7,8,9-HxCDF	0.1	0.682	0.000	0.682
1,2,3,4,6,7,8-HpCDF	0.01	0.415	0.011	0.425
1,2,3,4,7,8,9-HpCDF	0.01	0.074	0.000	0.074
OCDF	0.0001	0.003	0.000	0.003
TEQ		5.364	0.438	5.802

Notes:

All particulate and semi-volatile concentrations reported below the reporting limit were assigned a value of zero.

"Ambient" concentrations are the sum of the particulate and semi-volatiles concentrations.

TEF: toxic equivalency factor

TEQ: toxic equivalency

Table 9. Rillito Dioxins and Furans: Annual averages, with all concentrations expressed as Toxic Equivalents in fg/m^3, and with values below the Reporting Limit set to one half the reporting limit

Congener	TEF	Particulate	Semi-volatiles	Ambient
2,3,7,8-TCDD	1.0	0.500	0.500	1.000
1,2,3,7,8-PeCDD	1.0	3.500	3.500	7.000
1,2,3,4,7,8-HxCDD	0.1	0.441	0.350	0.791
1,2,3,6,7,8-HxCDD	0.1	0.777	0.350	1.127
1,2,3,7,8,9-HxCDD	0.1	0.959	0.350	1.309
1,2,3,4,6,7,8-HpCDD	0.01	1.245	0.035	1.280
OCDD	0.0001	0.046	0.001	0.046
2,3,7,8-TCDF	0.1	0.127	0.432	0.559
1,2,3,7,8-PeCDF	0.05	0.175	0.175	0.350
2,3,4,7,8-PeCDF	0.5	2.000	1.750	3.750
1,2,3,4,7,8-HxCDF	0.1	0.745	0.350	1.095
1,2,3,6,7,8-HxCDF	0.1	0.509	0.350	0.859
2,3,4,6,7,8-HxCDF	0.1	0.391	0.350	0.741
1,2,3,7,8,9-HxCDF	0.1	0.873	0.350	1.223
1,2,3,4,6,7,8-HpCDF	0.01	0.415	0.043	0.457
1,2,3,4,7,8,9-HpCDF	0.01	0.099	0.035	0.134
OCDF	0.0001	0.003	0.001	0.004
TEQ		12.805	8.921	21.726

Notes:

All particulate and semi-volatile concentrations reported below the reporting limit were assigned a value one half the limit.

"Ambient" concentrations are the sum of the particulate and semi-volatiles concentrations.

TEF: toxic equivalency factor

TEQ: toxic equivalency

Discussion of Ambient Measurements

Comparison with AAAQG

The Arizona Ambient Air Quality Guidelines (AAAQG) have recommended concentrations not to be exceeded for about 300 toxic compounds, including 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), one of the two most toxic of the 17 dioxins and furans. With the 1999 value of 23 fg/m^3 as a guideline, the dioxin and furan concentrations, which average 5.8 – 21.7 fg/m^3, are within this guideline.

The ambient concentration determined in Rillito is the sum of the 17 congeners, expressed as the toxic equivalency of the mixture relative to the single congener 2,3,7,8-TCDD. Since the TEQ range of the mixture is less than the guideline value of the congener, the overall toxicity of the Rillito dioxins and furans is within the health-based guideline.

Comparison with Urban and Background Sites

Ambient sampling programs for dioxins and furans, conducted by the U. S. EPA, the California Air Resources Board, and other investigators around the world, have accumulated a wealth of data in a wide variety of settings. In the EPA program in 2001, the annual average dioxin and furan concentrations at 22 rural sites ranged from 2 to 28 fg/m^3 TEQ. At eight remote sites the range was 0.3 to 2.8 fg/m^3 TEQ. Included in these remote sites are two Arizona sites: the Grand Canyon (1.4 fg/m^3 TEQ) and Chiricahua National Monument (0.4 fg/m^3 TEQ). The California program has sampled at five sites in the San Francisco area and at five in the Los Angeles area: concentrations have ranged from 20 to 40 fg/m^3 TEQ. Figures 2 and 3, which display these and other published data, place the Rillito concentration of 5.8 – 21.7 fg/m^3 TEQ (average of 13.7) above the remote sites, within the range of the rural sites, and somewhat lower than most of the urban sites. Of considerable interest are the highest annual average concentrations reported: from 160 to 480 fg/m^3 TEQ.

Figure 2. Annual Average Dioxin and Furan Concentrations from Sites with Lower Concentrations

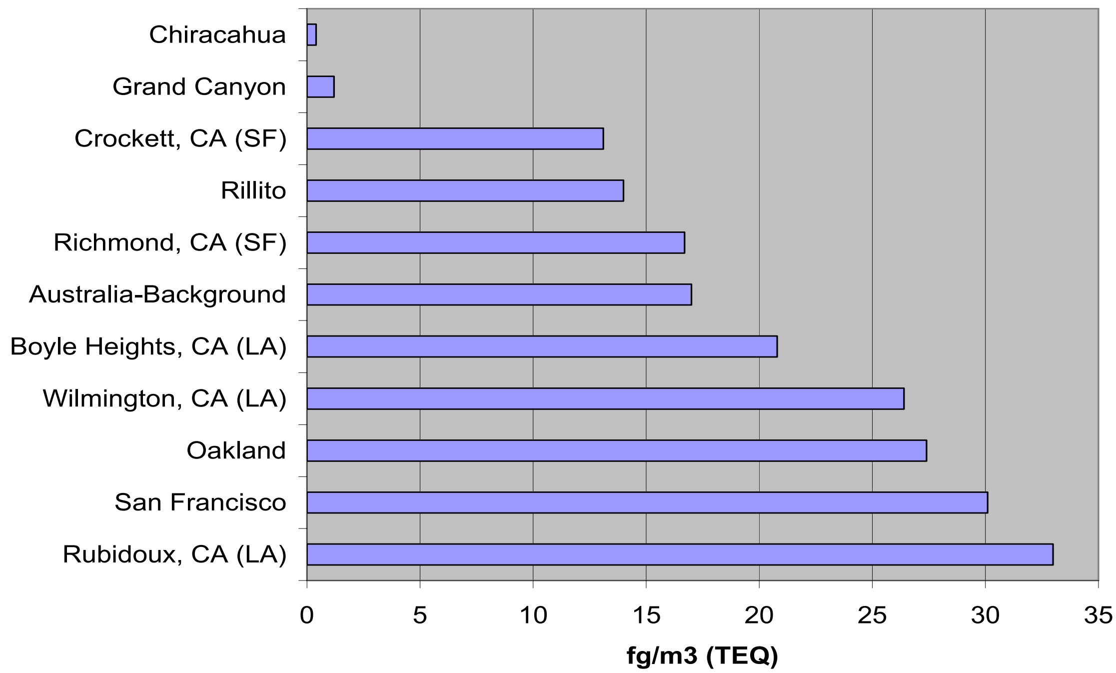
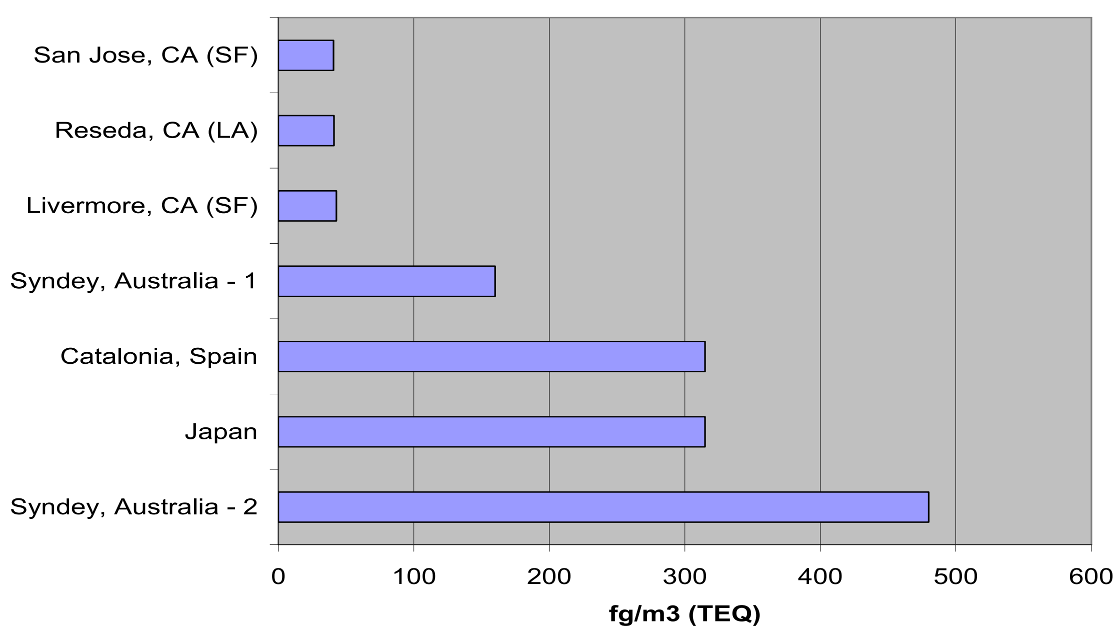


Figure 3. Annual Average Dioxin and Furan Concentrations from Urban Sites with Higher Concentrations



Seasonal Variation

Concentrations of nearly all air pollutants (the photochemically produced ozone is an exception) tend to be higher in winter than summer, with spring and fall midway between the two. This seasonal pattern is a result of the surface nocturnal temperature inversions lasting three to four hours longer in the winter. This pattern also reflects the generally higher daytime wind speeds in the summer. Because winter conditions have less horizontal and vertical dispersion, air pollutant concentrations tend to be higher. Dioxin and furan concentrations in Rillito are no exception, as Figures 4 and 5 illustrate.

Figure 4. Monthly Variation of Dioxin and Furan Concentrations

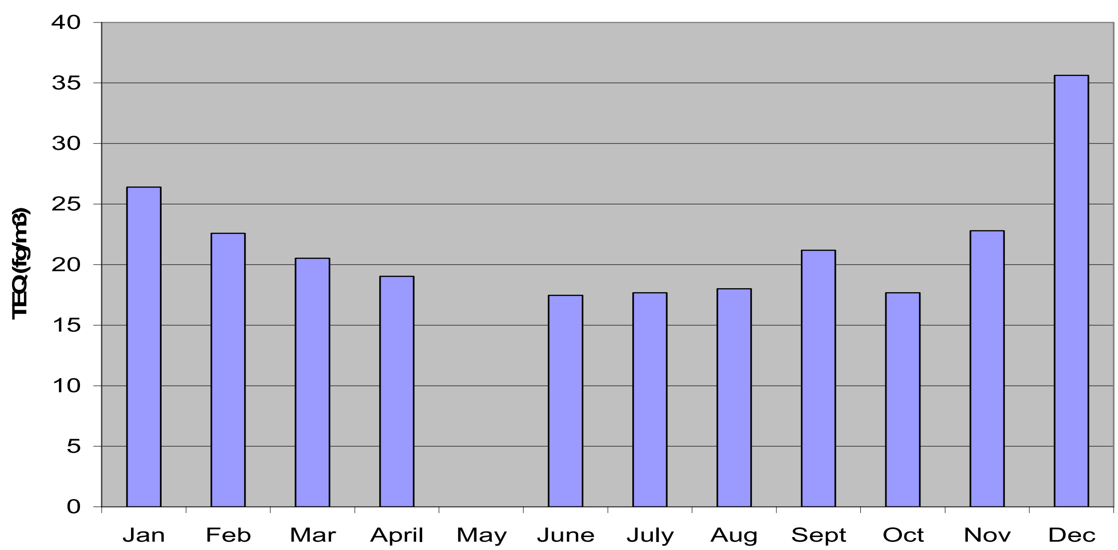
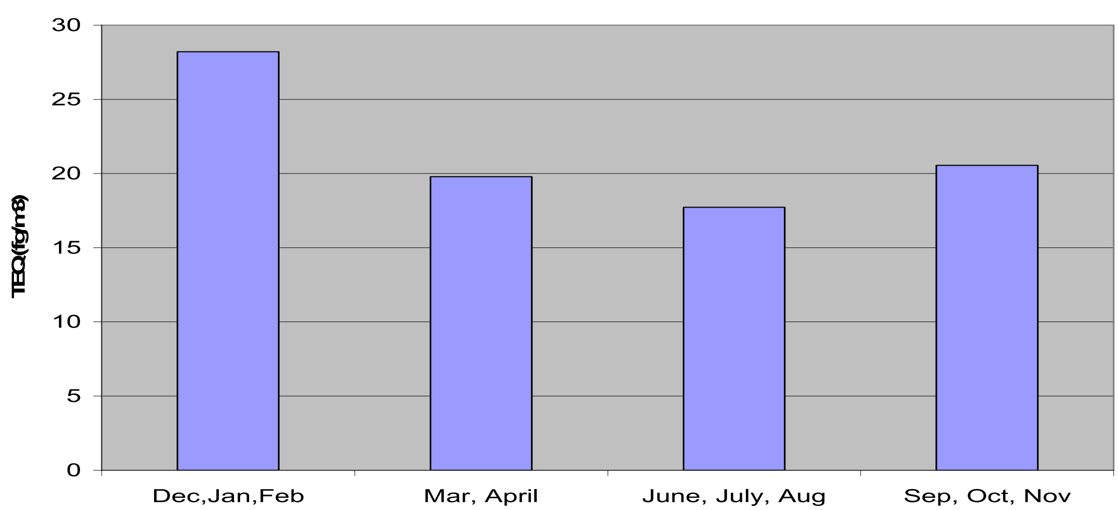


Figure 5. Seasonal Variation of Dioxin and Furan Concentrations



Comparison of Congener Profiles

In this section three profiles of the 17 dioxins and furans are examined:

1. the profile determined in the ambient monitoring at Rillito;

2. the profile of the APCC kiln emissions determined by the stack testing; and

3. the profile for mobile sources, virtually the same for diesel and gasoline fuels, taken from the literature (D. Cleverly et al, "The Congener Profiles of Anthropogenic Sources of Chlorinated Dibenzo-p-Dioxins and Chlorinated Dibenzaofurans in the United States", Organohalogen Compounds, Vol 32: 430-435, 1997).

Each profile is simply a bar chart that shows the percentage contribution of each of the 17 congeners to their total concentration, unweighted by the toxic equivalency. For the ambient profile, the percentages come from the annual averages calculated by setting the nondetectable values to one half the reporting limit. When the profile of an emissions source is similar to an ambient profile, then the measured ambient concentrations can be viewed as resulting from these emissions. Conversely, when the source profile is substantially different from the ambient profile, its emissions are not a major contributor to the ambient concentrations. The following Figures 6-7 depict these three profiles.

In the figures and following discussion, the 17 congeners are assigned a letter name, as shown in Table 10.

Table 10. Dioxins and Furans: Letter Names

2,3,7,8-TCDD	A
1,2,3,7,8-PeCDD	B
1,2,3,4,7,8-HxCDD	C
1,2,3,6,7,8-HxCDD	D
1,2,3,7,8,9-HxCDD	E
1,2,3,4,6,7,8-HpCDD	F
OCDD	G
2,3,7,8-TCDF	H
1,2,3,7,8-PeCDF	I
2,3,4,7,8-PeCDF	J
1,2,3,4,7,8-HxCDF	K
1,2,3,6,7,8-HxCDF	L
2,3,4,6,7,8-HxCDF	M
1,2,3,7,8,9-HxCDF	N
1,2,3,4,6,7,8-HpCDF	O
1,2,3,4,7,8,9-HpCDF	P
OCDF	Q

Figure 6. **Dioxin and Furan Congener Profiles, Expressed as Percentages of their Total Concentrations, Unweighted by Toxic Equivalency, for (a) Rillito Ambient Air, (b) Cement Kiln Emissions, and (c) Mobile Sources**

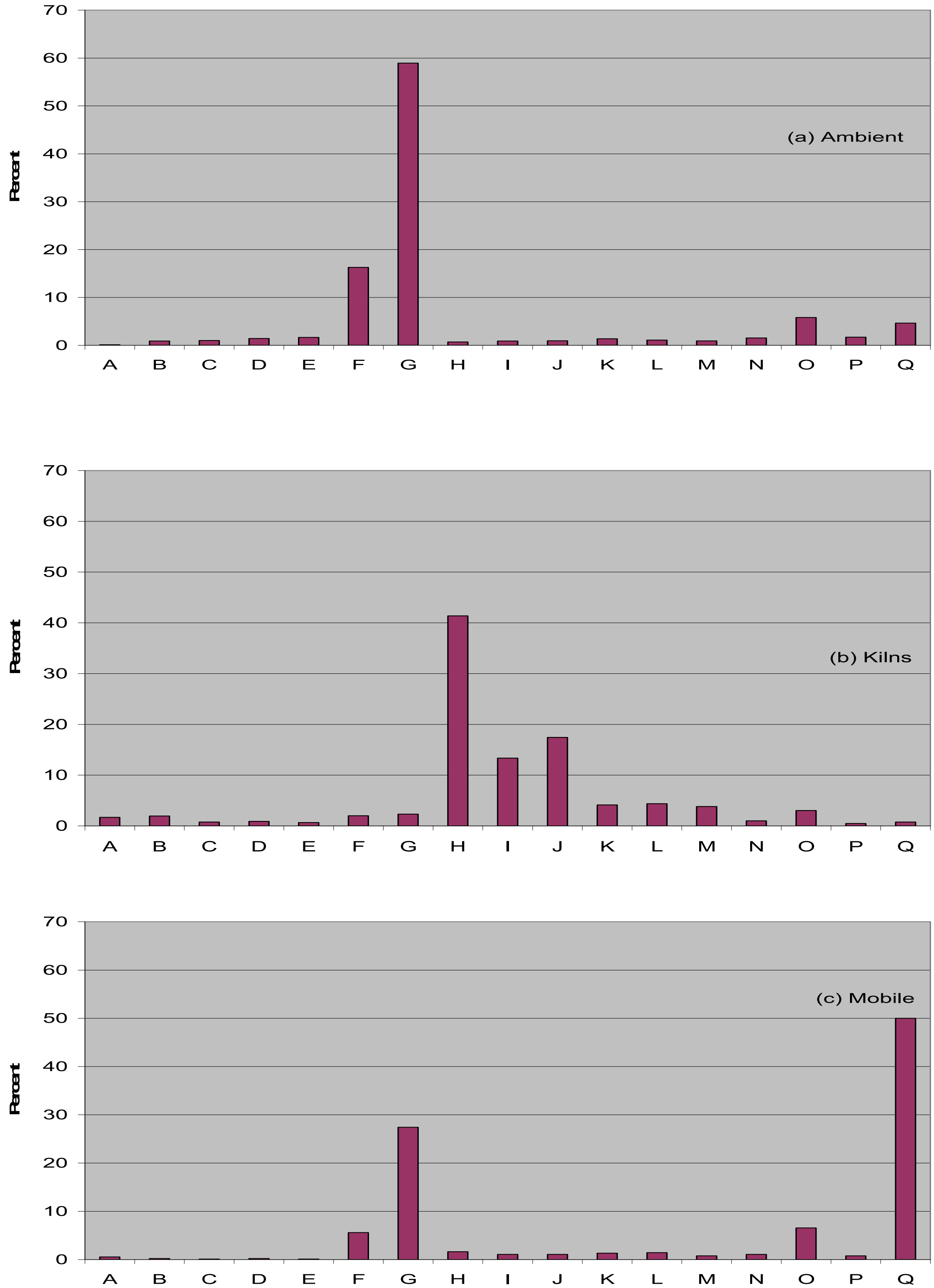
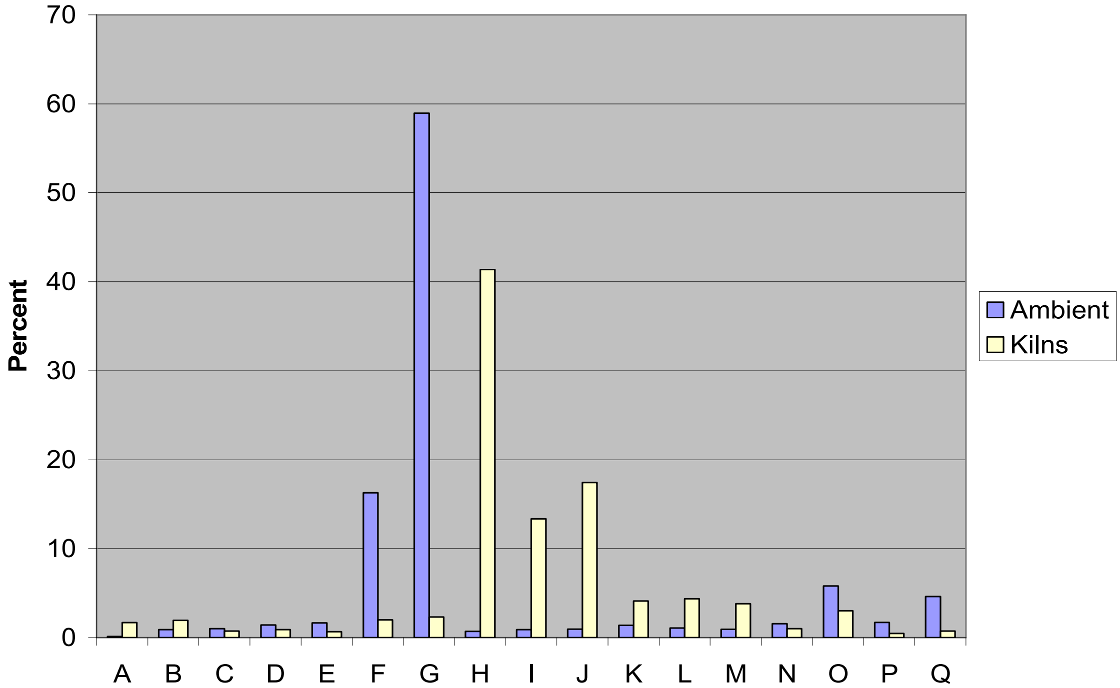
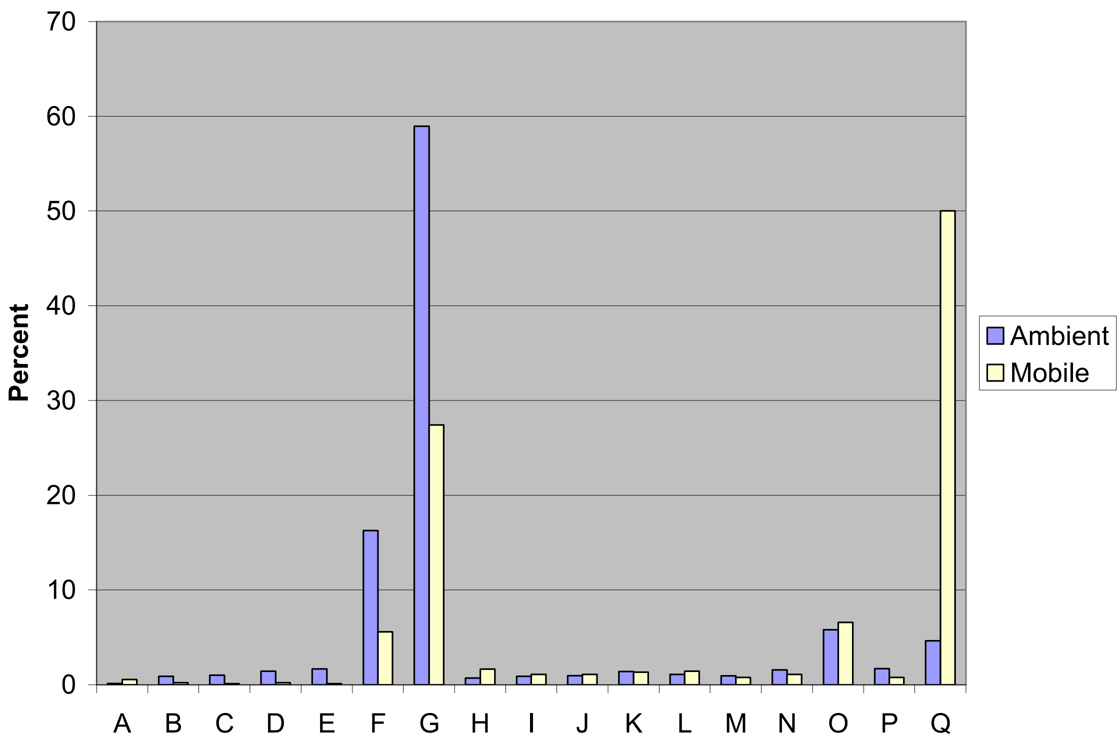


Figure 7. **Dioxin and Furan Congener Profiles, Expressed as Percentages of their Total Concentrations, Unweighted by Toxic Equivalency, for (a) Ambient Air and Cement Kiln Emissions, and (b) Ambient Air and Mobile Emissions**





These bar graphs clearly show that both sources, the cement plant and the mobile, contribute to the ambient concentrations, although the mobile source profile resembles the ambient profile considerably more than does the cement plant's. From Figure 7a the three most prominent congeners in the kiln profile – H, I, and J – are nearly absent from the ambient profile. In contrast, Figure 7b reveals that the four most prominent congeners of the mobile profile – F, G, O, and Q – coincide with the four most prominent congeners of the ambient profile. Taken together, these profiles strongly suggest that dioxins and furans from the interstate and railroad have a much greater effect on the ambient concentrations in Rillito than do the emissions from the cement plant. The better match of the mobile profile with the ambient can also be seen in the percentages given in Table 11.

Table 11. Dioxin and Furan Profiles, the Percentage Contribution to the Total Concentration, Unweighted by Toxic Equivalency (TEQ), for Rillito Ambient Air, APCC Kiln Emissions, and Mobile Sources

Congener	Letter	Rillito Ambient	APCC Kilns	Mobile Sources
2,3,7,8-TCDD	A	0.13	1.68	0.55
1,2,3,7,8-PeCDD	B	0.89	1.95	0.22
1,2,3,4,7,8-HxCDD	C	1.00	0.75	0.11
1,2,3,6,7,8-HxCDD	D	1.43	0.90	0.22
1,2,3,7,8,9-HxCDD	E	1.66	0.66	0.11
1,2,3,4,6,7,8-HpCDD	F	16.27	2.00	5.59
OCDD	G	58.95	2.33	27.41
2,3,7,8-TCDF	H	0.71	41.37	1.64
1,2,3,7,8-PeCDF	I	0.89	13.35	1.10
2,3,4,7,8-PeCDF	J	0.95	17.43	1.10
1,2,3,4,7,8-HxCDF	K	1.39	4.12	1.32
1,2,3,6,7,8-HxCDF	L	1.09	4.38	1.43
2,3,4,6,7,8-HxCDF	M	0.94	3.82	0.77
,2,3,7,8,9-HxCDF	N	1.55	1.01	1.10
1,2,3,4,6,7,8-HpCDF	O	5.81	3.03	6.58
1,2,3,4,7,8,9-HpCDF	P	1.70	0.46	0.77
OCDF	Q	4.62	0.74	50.00
(blue)	Ambient & mobile similarities			
(orange)	Kiln and ambient dissimilarities			
(purple)	Kiln and ambient similarity			

To summarize the congener profile analysis, the data are highly suggestive that the ambient dioxins and furans, while influenced to a small degree by the cement plant, are much more closely related to the mobile source emissions. What the data also suggest is that other sources are contributing, as well. For example, congeners F and G of the ambient profile far outweigh the same congeners of the mobile profile, while the mobile congener Q is ten times greater than its ambient counterpart. These ambiguities may stem from deposition of dioxins and furans onto soil, followed by chemical alteration, with their subsequent resuspension, or from other combustion sources in the vicinity.

Health Significance of Ambient Concentrations

Dioxins and furans are produced as trace byproducts of many combustion processes including burning of trash and landfills, forest fires, industrial combustion processes (such as Portland cement kilns), and combustion of gasoline and diesel in vehicles. They accumulate in the food chain, and, as a result, people are exposed to small amounts in the food supply and have low concentrations of dioxins and furans in their fat tissue.

In this report, evaluation of human health risks associated with exposure to emissions of dioxins and furans is based on an assessment of long-term exposure levels and potential health outcomes. In the case of exposures to dioxins and furans, the health outcome of concern is increased cancer risk. The annual AAAQG for 2,3,7,8-TCDD was set at a level that corresponds to a lifetime cancer risk of one-in-one million (0.000001). That is, the concentration of 2,3,7,8-TCDD in air that would result in a theoretical increase in cancer risk for an individual of one-in-one million after a lifetime of exposure at that level.

As discussed above, people are exposed daily to dioxins and furans through their diet. The USEPA has estimated that more than 90 percent of dioxin and furan exposure in the United States occurs though food, and current typical daily intake of dioxins and furans in food are in the range of 0.000001 microgram TEQ per kilogram body weight per day. The daily dose of dioxins and furans received through inhalation of air at concentrations equal to the annual AAAQG is small compared to current daily dietary intake, comprising less than 0.5% of the dose received daily from food.

Conclusions

1. Dioxin and furan concentrations in Rillito are lower than the Arizona Ambient Air Quality Guidelines.

2. Emissions from the cement plant contribute marginally to the ambient dioxins and furans at Rillito, with mobile source emissions being the dominant source. Because the ambient and mobile profiles do not match perfectly, however, other sources such as resuspended soil dusts onto which dioxins and furans have been deposited may be a factor.