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SUBJECT: ANNUAL AVERAGE CONCENTRATIONS OF 1,3-DICHLOROPROPENE BASED ON MONTHLY USE AND AIR MONITORING BY THE CALIFORNIA AIR RESOURCES BOARD: MONTEREY/SANTA CRUZ AND KERN COUNTIES, 2000 AND 2001

This memorandum gives estimated annual average concentrations of 1,3-dichloropropene (1,3-D) in air in Kern and Monterey counties in 2000 and 2001. The estimates are based on approximately two months of air monitoring and daily 1,3-D use in each county each year. Air monitoring was done by the California Air Resources Board in Kern County in Summer 2000 (ARB, 2000) and Summer 2001 (ARB, 2002a) and in Monterey/Santa Cruz County in Fall 2000 (ARB, 2001) and Fall 2001 (ARB, 2002b). 1,3-D use data for 2000 and 2001 were provided to the Department of Pesticide Regulation by Crop Data Management Systems, Inc., by agreement with Dow AgroSciences, Inc. Estimates of short-term and seasonal average concentrations, based on the monitoring data alone, have been given in previous memoranda (Powell, 2001, 2002a, 2002b and 2002c).

Method

In order to estimate annual average air concentrations using measured concentrations for only 7-9 weeks of each year, the assumption was made that ambient air concentration is a function of the amount of 1,3-D applied in the region. There is some support for this assumption in the work of Li *et al*. (2001) on methyl bromide. They investigated the correlation between ambient air concentrations in ARB monitoring and pounds of methyl bromide applied, for different concentration-averaging periods (1, 3-4 and 7-8 weeks) and use areas (1-, 3-, 5-, 7-, 9-, 11-, 13- and 15-mi squares around each monitoring site). The highest correlation ($R^2 = 0.95$) was obtained with the 7- to 8-week averaging period and the 7 x 7-mile use area. The estimated regression equation was: average ppb = 0.118 + 0.000141 x (lbs methyl bromide applied/week).

In the present case, average air concentration at each site over the 2-month monitoring period (actually 7 to 9 weeks) was regressed on pounds of 1,3-D used per day in a 2-township (6 mi x 12 mi) area around the site during that period. Twenty-four site-years were the data points for the regression analysis (six monitoring sites each year in each county). The best-fitting model was selected from models with ppb or ln(ppb) as the dependent variable, with lbs per day as an independent variable and with other independent variables (lbs/day-squared, a county term to

allow the counties to have different intercepts, and a county x lbs/day term to allow counties to have different slopes) added singly or in combination. The selected regression equation was then used to predict annual mean concentration for each site from daily use during the full year.

The monitoring-period average air concentration for each site was calculated by taking the arithmetic mean of the 24-hr samples for each calendar week (n = 1-5), then taking the arithmetic mean of the 7-9 weekly means at each site (Powell, 2001, 2002a, 2002b, 2002c). This average was used rather than the simple mean of all samples, because the numbers of sampled days varied across weeks, so the simple mean would undesirably give greater weight to weeks with more samples. For example, suppose that a site had five samples one week, all measuring 0.1 ppb, and one sample another week, measuring 1 ppb. Because there is serial correlation in air concentrations over time and space, the nonsampled days in each week were likely to have been similar to the sampled day(s) in the same week. The mean of the two weekly means, 0.55 ppb, is thus a better estimate of the two-week average than is the simple mean of 0.25 ppb.

Use of 1,3-D was determined from the records maintained by Crop Data Management Systems, Inc. (CDMS). Complete use data for 2001 were available from CDMS, but not from DPR's Pesticide Use Reporting system. For consistency, CDMS data were used for both years. Because CDMS does not report the section in which an application was made, it was not possible to determine the amount of use in a 7 x 7 mile square centered on each monitoring site. Instead, use was determined for the township where the site is located plus the adjacent township closest to the section containing the monitoring site (Table 1).

It was assumed that the applications affecting air concentrations during monitoring were any made 7 or fewer days before the first monitoring date (1,3-D continues to off-gas from soil for 7-14 days after application) and up to but not including the last day of monitoring (little 1,3-D is emitted from soil on the day of application). These dates are shown in Table 2.

Table 1. Townships defining 1,3-dichloropropene use area for each Air Resources Board monitoring site.

		Monitoring site location [a]				
County	**Site**	**Township**	**Section**	**Nearest township(s)**		
Kern	ARB	29S27E	34	30S27E		
	ARV	31S29E	23	31S30E		
	CRS	27S25E	33	28S25E		
	MET [b]	11N20W	1	11N19W	12N20W	12N19W
	MVS	30S29E	30	30S30E		
	SHA	28S25E	10	27S25E		
	VSD	31S29E	19	31S28E		
Monterey	CHU	16S04E	3	15S04E		
	LJE	14S03E	10	13S03E		
	MES	11S02E	33	12S02E		
	OAS [b]	18S07E	31	18S06E	19S06E	19S07E
	PMS	12S02E	9	11S02E		
	SAL	14S03E	22	14S04E		
	SES	11S02E	22	11S03E		

[a] Corrected locations from Table 1 of Li *et al*. (2001)
[b] Where the monitoring site was in a section at a corner of the township, all 3 adjacent townships were included in the use area.

Table 2. Dates of 1,3-dichloropropene applications assumed to determine monitored air concentrations: Monterey/Santa Cruz and Kern Counties, 2000 and 2001.

	Application period	Monitoring period
Kern		
2000	July 12 – Aug 30	July 19 – Aug 31
2001	June 23 – Aug 29	June 30 – Aug 30
Monterey/Santa Cruz		
2000	Sept 4 – Nov 1	Sept 11 – Nov 2
2001	Sept 1 – Nov 6	Sept 8 – Nov 7

In addition to site-specific concentrations, regional average annual concentrations were estimated. Figures 1 and 2 show the townships with 1,3-D use and the locations of air monitoring sites in Kern and Monterey/Santa Cruz Counties, respectively. The use townships in Kern County formed two fairly distinct regions, designated Kern North and Kern South and indicated in Fig. 1 by the heavy diagonal line. One Kern North monitoring site (ARB, in

township 29S27E) was near the border between the use regions. Use in the Kern South township (30S28E) nearest the ARB site, however, was only in sections near the south and east sides of the township, i.e., the sides farthest from the site (based on the Pesticide Use Report database for 1999 and 2000; 2001 data were not yet available). 1,3-D use in two isolated townships (26S35E and 09N13W, not shown in Fig. 1) was not included in the regional totals. In Monterey/Santa Cruz, the townships with 1,3-D use formed a nearly continuous region within the Salinas Valley. This was treated as a single region, however, use in one somewhat separate township (18S01E) was not included in the regional total. The arithmetic mean of the site mean concentrations in each region-year was regressed on total daily pounds of 1,3-D used in the region.

Results

Individual sites

In the initial regression analysis of mean monitoring-period air concentration on mean daily monitoring-period 1,3-D use for 24 site-years, the best-fitting model had *ln*(ppb) as the dependent variable, and lbs/day, the county term and county x lbs/day interaction as the independent variables ($R^2 = 0.57$). Analysis of the residuals from that model suggested that the Kern County CRS site in 2000 was aberrant. Use associated with that site in 2000 (253 lbs/day) was near the median, while the air concentration of 2.83 ppb was almost 3 times greater than the second-highest concentration. The model refit without CRS 2000 was *ln*(ppb) = -4.031 + 0.00581 x lbs/day (+ 1.866 - 0.0038 x lbs/day for Kern County sites), and had $R^2 = 0.62$. This model was used to estimate annual average concentrations. Figure 3 plots measured air concentration by use during the monitoring periods for 23 site-years (CRS 2000 is not shown in Fig. 3). Figure 3 also shows the regression curve fitted to the data points excluding the Kern CRS 2000 site.

Pounds of 1,3-D used per day over the whole year, in the townships associated with each site, was put into the equation fit without CRS 2000 to predict *ln* annual average concentration for each site-year. Predicted *ln* concentration was then backtransformed by the unbiased method of Bradu and Mundlak as implemented in the SAS system by Powell (1991). The estimated annual average concentrations for the monitoring sites are shown in Table 3.

Table 3. Annual average 1,3-dichloropropene concentrations in air at ARB sites: Monterey/Santa Cruz and Kern Counties, 2000 and 2001.

Site	Annual average daily 1,3-D use [a]	Estimated annual average concentration [b]	
	-- lbs day^{-1}--	--- ppbv---	---μg/m^3 ---
Kern 2000			
ARB Ambient Air Station (ARB)	0	0.15	0.69
Mettler Fire Station (MET)	194	0.24	1.07
Mountain View School (MVS)	0	0.15	0.69
Shafter Air Monitoring Station (SHA)	223	0.25	1.14
Vineland School District (VSD)	216	0.25	1.12
Kern 2001			
ARB Ambient Air Station (ARB)	0	0.15	0.69
Arvin High School (ARV)	262	0.27	1.24
Cotton Research Station (CRS)	197	0.24	1.08
Mettler Fire Station (MET)	258	0.27	1.23
Mountain View School (MVS)	40	0.17	0.76
Vineland School District (VSD)	297	0.29	1.33
Monterey/Santa Cruz 2000			
Chualar School (CHU)	87	0.04	0.19
La Joya Elem. School (LJE)	2	0.02	0.11
Oak Avenue School (OAS)	217	0.09	0.40
Pajaro Middle School (PMS)	61	0.04	0.16
MBUAPCD Ambient Air Station (SAL)	1	0.02	0.11
Salsepuedes Elem. School (SES)	41	0.03	0.14
Monterey/Santa Cruz 2001			
Chualar School (CHU)	45	0.03	0.14
La Joya Elem. School (LJE)	50	0.03	0.15
MacQuiddy Elem. School (MES)	133	0.05	0.25
Pajaro Middle School (PMS)	133	0.05	0.25
MBUAPCD Ambient Air Station (SAL)	66	0.04	0.16
Salsepuedes Elem. School (SES)	68	0.04	0.17

[a] From use records of Crop Data Management Systems, Inc., for the townships identified in Table 1.

[b] Calculated by backtransforming log concentrations predicted by the regression equation ln(ppb) = -4.031 + 0.00581 x lbs/day (+ 1.866 - 0.0038 x lbs/day if Kern). Equation estimated using mean air concentration and daily 1,3-D use during the 7- to 9-week monitoring periods, and applied to average daily use for the whole year in the townships associated with each site to predict annual average concentration.

Regions

For the regression analysis, mean air concentration for the Kern North region in 2000 was calculated without the apparently aberrant concentration at the CRS site (mean concentration with the CRS site was 1.05 ppb; without CRS it was 0.166 ppb). The best-fitting model was ppb = -0.3864 + 0.000343 x (lbs/day) (+ 0.2323 for the Kern regions), and had $R^2 = 0.99$. This model was used to estimate annual average concentrations. Figure 4 plots measured air concentration by use during the monitoring periods for 6 region-years. Figure 4 also shows the regression curve fitted to the data points.

Pounds of 1,3-D used in the region per day over the whole year was put into the fitted regression equation to predict annual average concentration for each region-year. Estimated annual average concentrations for the regions are shown in Table 4.

Table 4. Annual average 1,3-dichloropropene concentrations in air in six regions: Monterey/Santa Cruz and Kern Counties, 2000 and 2001.

Region	Annual average daily 1,3-D use [a]	Estimated annual average concentration [b]	
	--- lbs day^{-1} ---	--- ppbv---	---µg/m^3 ---
Kern North			
2000 [c]	871	0.14	0.64
2001	651	0.07	0.32
Kern South			
2000	850	0.14	0.64
2001	1162	0.24	1.09
Monterey/Santa Cruz			
2000	1235	0.04	0.18
2001	943	0	0

[a] From use records of Crop Data Management Systems, Inc., for the three counties.
[b] Calculated by applying the regression equation ppb = -0.3864 + 0.000343 x (lbs/day) (+ 0.2323 if Kern), estimated using mean air concentration and daily 1,3-D use during the 7- to 9-week monitoring periods, to daily use over the whole year in each region.
[c] Excluding the CRS site.

Limitations of the estimates

These annual concentration estimates were made by extrapolating far beyond the available data and thus confidence in them should be fairly low.

The validity of the estimates depends on the assumed relationship of ambient air concentration to amount of chemical applied. While a close relationship has been found between site-specific methyl bromide concentration and use within 7-mile-square areas, only 62 percent of the variance in site-specific 1,3-dichloropropene concentration could be accounted for by use in the 2-township areas considered here. At the level of regions consisting of 13 to 27 townships, there was good predictability (99 percent of the variance in concentration was accounted for by use), but this was based on only six datapoints and might not hold if more data were included. At both the site and regional levels, predictability was achieved by dropping the data from one of the sites (CRS site in Kern County in 2000). As a result, no estimate of annual concentration could be made for the site. The reasons for the apparent discrepancy between use and the high air concentrations at this site are unknown. Underreporting of use at that location is unlikely to be the explanation, because the total amount of use in the 2-township area required to account for the observed concentration would have been close to 1600 lbs/day, while the greatest amount used in any other 2-township area was 682 lbs/day. The high average air concentration at the CRS site is due entirely to extremely high measurements on the first two days of monitoring. These are unlikely to be in error, since on the day with the highest measured concentration, July 19, 2000, duplicate samples were taken that gave nearly identical results (26.7 and 29.8 ppb). There was an application of 4,443 lbs of 1,3-D on July 17 in the section to the northwest of the monitoring site (ARB, 2000). The high concentrations on July 19 and 20 may have resulted from this close application. This highlights the fact that the placement of monitoring sites in relation to applications is not systematic, which may be the source of much of the noise in the observed relationship of use to concentration.

The validity of the estimates also depends on the unknown representativeness of air concentrations at the monitored sites and days of the whole region and whole 2-month monitoring period. In addition, their validity depends on the correct identification of the area within which use affects concentrations at particular sites. The use area for each site or region was defined by geographic contiguity, without reference to meteorolgical or topographical information, and so may be in error.

It is not invalid to apply the concentration-to-use relationship observed in a 2-month averaging period to a 12-month averaging period. This is because the annual estimate is the same value that would be obtained by calculating six 2-month estimates and then averaging them. However, the assumption that the relationship of concentration to use is the same during the rest of the year as during the monitoring period is untested and seems likely to be untrue. The fact that Monterey and Kern Counties, which were monitored in different seasons and have very distinct climates, had different regression intercepts (and slopes, for the sites) suggests that the relationship is

different under different weather conditions. Lacking year-round monitoring data, however, this is the best estimate that can be derived currently, and it is probably more reasonable than assuming either that air concentrations are zero in the nonmonitored months, or that they remain at the monitored levels all year.

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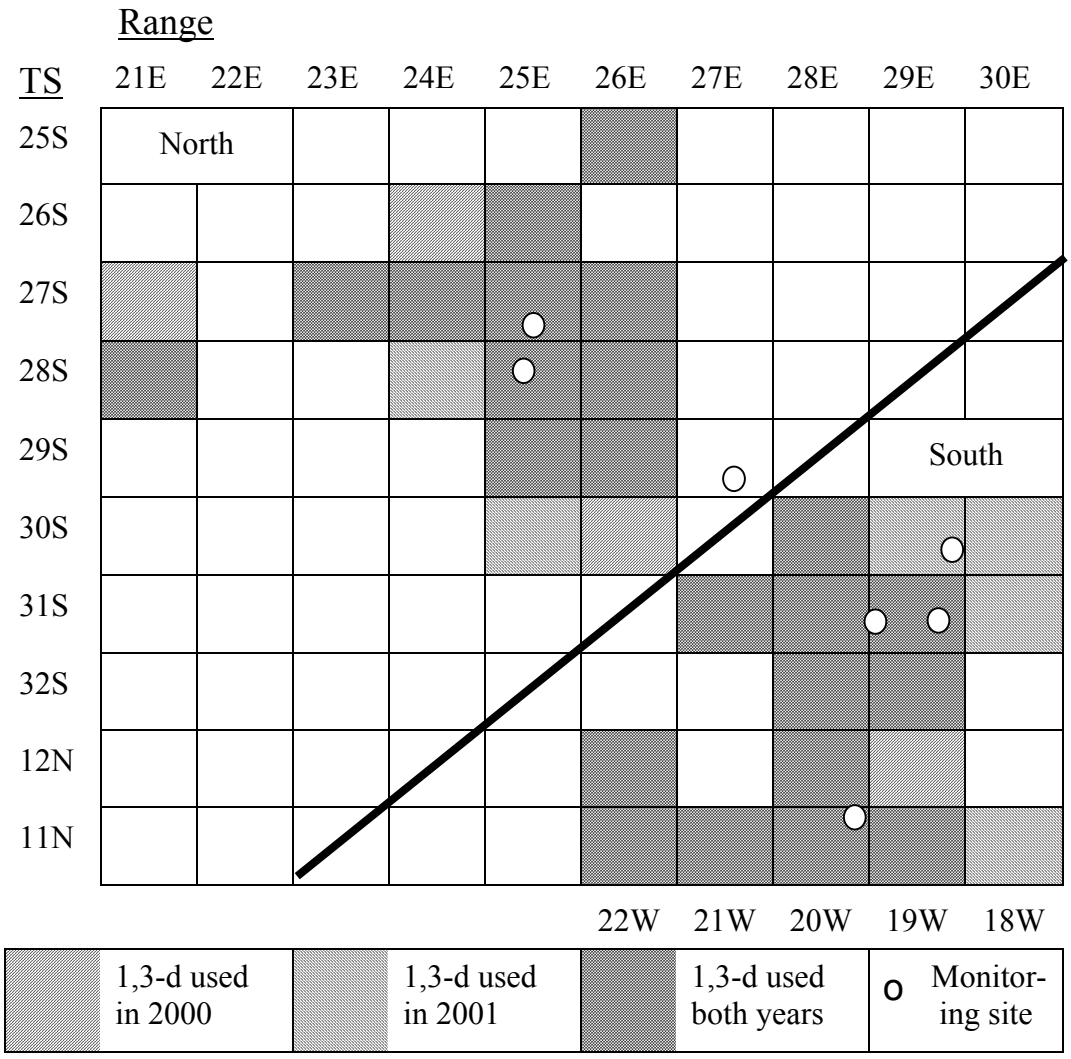
Fig. 1. 1,3-d use by township: Kern County [a]



[a] Two isolated townships, 26S35E with use in 2000 and 09N13W with use in 2001, are not shown in the figure nor included in the regional use totals.

Fig. 2. 1,3-d use by township: Monterey/Santa Cruz County

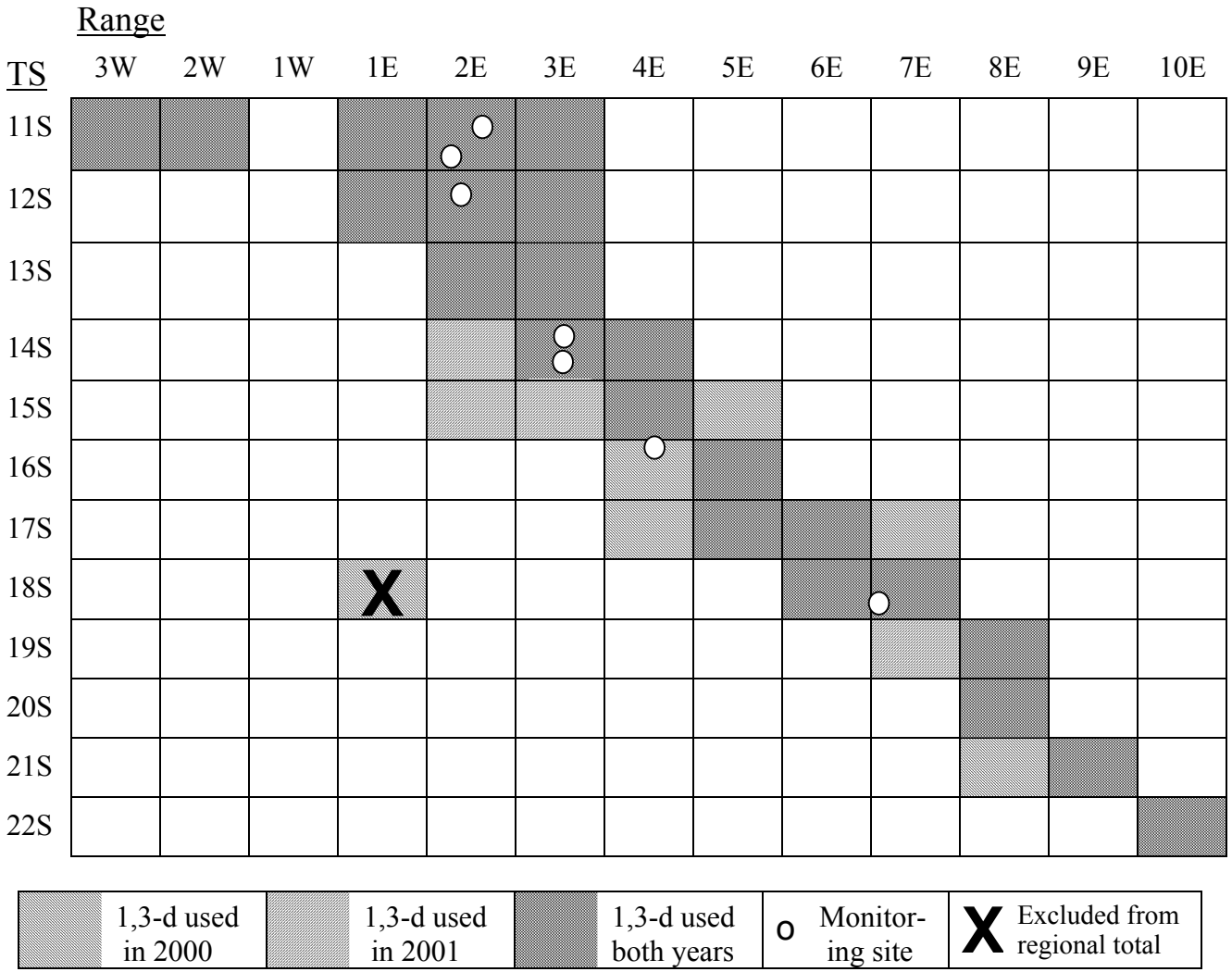


Fig. 3. Site mean air concentration vs. use of 1,3-D in townships adjacent to site during the 2000 and 2001 ARB monitoring periods (Kern CRS site in 2000 not shown).

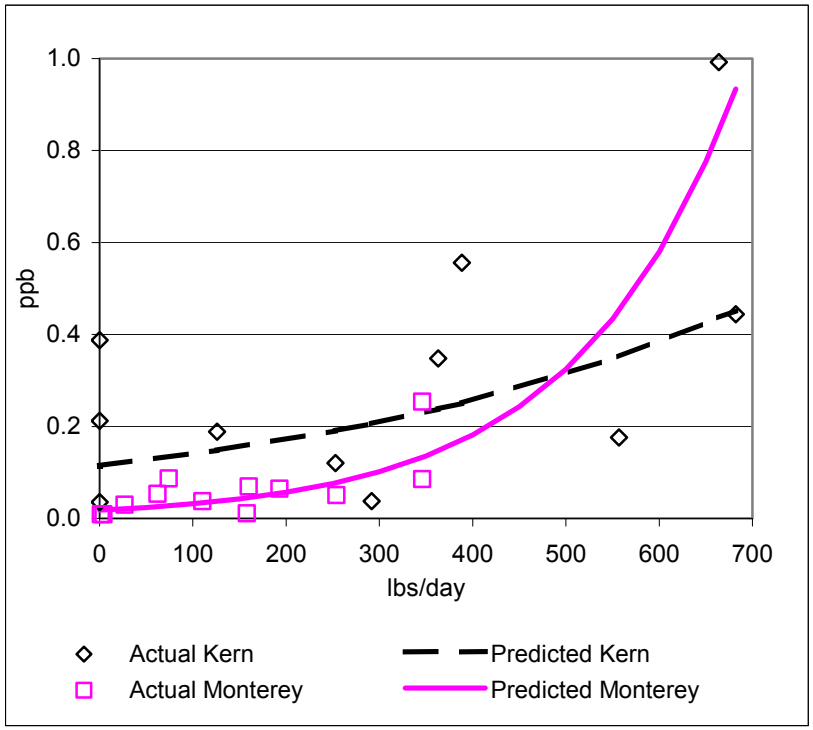


Fig. 4. Regional mean air concentration vs. regional useof 1,3-D during the 2000 and 2001 ARB monitoring periods.