Department of Pesticide Regulation
Environmental Monitoring Branch
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July 26, 2011

STUDY 274: PROTOCOL FOR LONG-TERM GROUND WATER MONITORING FOR METHYL IODIDE, IODIDE, AND TOTAL IODINE

I. INTRODUCTION

Methyl iodide has been registered in California as a potential methyl bromide replacement for pre-plant soil fumigations. Concerns have been raised about methyl iodide and its breakdown products contaminating ground water. Empirical modeling by the Department of Pesticide Regulation (DPR) indicates that methyl iodide is unlikely to reach ground water, primarily due to short soil degradation and hydrolysis half-lives (Dias and Clayton 2008). DPR's modeling was conservative in that it explicitly did not include volatilization, which is the primary dissipation pathway of methyl iodide in soil (Kollman et al. 2009). Despite the fact that the restrictions included on the methyl iodide label adopt a health-conservative approach, DPR will conduct well monitoring for both methyl iodide and the iodide breakdown product as part of its obligation to continuously evaluate all registered pesticide products.

Iodide is a naturally occurring ground water constituent with unique soil chemistry. The U.S. Geological Survey, under contract with the State Water Resources Control Board, detected iodide in 549 of 962 wells sampled, with concentrations ranging from 0.002 to 12.8 mg/L, with a mean of 0.12 mg/L (SWRCB 2009; Figure 1). Information on the source and variation of naturally occurring concentrations is limited. Prior to conducting a monitoring study for iodide, local concentrations and potential variation over time must be adequately characterized before any trends can be assessed. As with the other halides, iodide was found to be conservative tracer, like bromide, but only in the laboratory, not in the field (Bowman 1984). The field data indicated a potential for rapid transformation of iodide to other oxidized forms, implying a low potential for the downward movement of the iodide anion. This may be due to complex iodide-organic matter interactions that inhibit iodide mobility in soils (Sheppard and Thibault 1992; Fuge and Johnson 1986; Hu 2007). Coarse, low-organic matter soils could facilitate downward movement of iodide to ground water, thus highlighting the need for further studies on iodide's movement and fate in soil.

Historically, DPR has determined the presence of pesticide residues in ground water by sampling water from domestic drinking water wells, preferably located in vulnerable soils. Domestic drinking water wells located in areas of high pesticide use have a high potential to contain agricultural chemical residues because they draw water from shallow aquifers that are primarily recharged by excess agricultural irrigation water. A study conducted by the Environmental Monitoring Branch's staff to age-date water in domestic wells has estimated that the most highly vulnerable areas, the median recharge time is six to seven years (Spurlock et. al. 2000). Depending on the variation observed in background sampling, it may take a decade of sampling to separate natural iodide concentration trends from residues resulting from agricultural pesticide applications. Thus, DPR proposes the initiation of ground water monitoring for methyl iodide and its major breakdown product, iodide to provide information on expected ambient concentrations and variation over time.

II. OBJECTIVE

The purpose of this study is to determine if methyl iodide use is impacting ground water resources in two to four regions in California.

III. PERSONNEL

Well sampling will be conducted by the Environmental Monitoring Branch. Project personnel include:

- Project Leader: Rick Bergin
- Field Coordinator: Craig Nordmark
- Quality Control: Vaneet Aggarwal
- Statistician: Terri Barry
- Senior Scientist: John Troiano
- Project Supervisor: Lisa Quagliaroli
- Chemists: California Department of Fish and Game

All questions concerning this protocol should be directed to Lisa Ross 916-324-4116, or e-mail: < lross@cdpr.ca.gov>.

IV. STUDY PLAN

a) Study Region Selection

Historical use of methyl bromide was used as a surrogate for future methyl iodide use; methyl iodide is expected to replace methyl bromide. Data obtained from DPR’s Pesticide Use Reports indicate that the top three methyl bromide uses make up 79% of the total use in 2009; ~4 million pounds of methyl bromide was used on strawberries, soil applications, and outdoor transplants (CDPR 2010; Table 1). Five areas have been identified as potential study regions due to high methyl bromide use and their prominence in strawberry production: Merced, Santa Barbara/San Luis Obispo, Santa Cruz/Monterey, Ventura, and Siskiyou (Table 2 and Figure 2). Up to four of these regions will be selected for well network establishment, based on well availability.

The following is a description of each region, listed in order of priority for well monitoring, as based on soil vulnerability and historical high-use of methyl bromide. Table 3 is a list of the prospective townships (ones that have high methyl bromide use) in which we will focus our sampling efforts.

1) Merced

Merced County is selected because of the historical use of methyl bromide on strawberry transplants (low-elevation nurseries) and the existence of coarse soils. Coarse soils with low organic matter contents, like Delhi loamy sand and Delhi sand, comprise the majority of soil types in northern Merced County. Many of the sections in this prospective area are designated as leaching Ground Water Protection Areas (GWPAs), as they also have shallow groundwater depths (Figure 3). GWPAs are sections of land that are sensitive to the downward movement of pesticides; if contamination were to occur anywhere, it would be more likely to occur here and sooner than in other soil types.

Methyl bromide use in this region is clustered into four townships, making this an ideal area for a well network, as opposed to other central valley locations (Fresno, Tulare, or Kern Counties) where the use is dispersed (Figure 3). The Merced region also benefits from an abundance of previously sampled wells.

2) Santa Cruz/Monterey

This region stretches from Watsonville in the north to Salinas in the south (Figure 4). The soil gets progressively coarser as one travels south; Clear Lake clay, Pacheco clay loam, and various silty clay loams dominate the north, while Chualar loam and various sandy and silty loams dominate the south. Shallow groundwater occurs on the west side of Salinas Valley; however, the few leaching GWPAs present are mainly outside of the projected use areas.

Even though the soils in this region aren't as coarse as other areas, 40% (~2 million pounds) of all the methyl bromide applied in California in 2009 occurred in these two counties (CDPR 2010; Table 2). Such high use makes this area a preferred study region.

3) Santa Barbara/San Luis Obispo

This region lies in northern Santa Barbara County, situated around the city of Santa Maria and parts of lower San Luis Obispo County (Figure 5). It has the coarsest soil of all the strawberry fruit production regions; a variety of well-drained loamy sands, sandy loams (Sorrento, Pleasanton, Betteravia, and Garey) and sands (Oceano and Marina) compose the majority of soils in this area. Groundwater elevation contour maps indicate that water levels range from 230 feet to 60 feet; the groundwater becomes progressively shallower as one move towards the ocean (SBCWA 2009).

4) Ventura

This region is located south of Ventura and east of Oxnard (Figure 5). Poorly drained, medium-texture soils exist in this region; Camarillo loam, Pacheco silty clay loam, and Hueneme sandy loam are the major soil classifications. These medium-textured soils, coupled with uneven shallow groundwater distribution, are represented by only a few, scattered GWPAs. The lack of coarse soils and low historical well availability make this region less desirable for a network. This region should only be considered if adequate well networks cannot be established in the Monterey and Santa Barbara regions.

5) Siskiyou

This region was selected due to the many high-elevation strawberry nurseries clustered in northern Siskiyou County; 3,200 acres were used for strawberry transplants in 2010 (Herman 2010). The depth to groundwater in this region is generally less than 70 feet in the agricultural areas around Macdoel and Dorris (Figure 3). Fordney loamy fine sand and Leavers sandy loam make up two-thirds of the soil around Macdoel. However, this region also contains a duripan, a hardpan formed by cemented silica and associated with volcanic activity, at a depth of 20 to 40 inches (NRCS 2010). This duripan may restrict water movement to groundwater and thus the movement of chemicals to ground water as well. In addition, a network in Merced County could substitute for Siskiyou County because of its coarse soils and prominence in strawberry nursery production. A smaller well network will be considered in this region depending on the well networks established in other areas and the availability of departmental resources.

b) Well Selection

We will attempt to locate about 20-30 wells in each region, depending on the region's size. Wells will be sampled in sections of historically high methyl bromide use, as a surrogate for future methyl iodide applications. Only one well may be sampled in a selected section in order to ensure adequate coverage in each region; nine wells within a township, evenly dispersed, is the desired density. Sections with vulnerable soils and shallow ground water will be given precedence. Vulnerable sections generally have coarse soils, indicating a potential for residue leaching, and a shallow ground water table. Domestic wells will be given priority and will be selected according to procedures in SOP FSWA006.01 (Nordmark 2008b). Where domestic wells are unavailable, other types of wells, such as irrigation, municipal, stock, community, and small water system wells, will be sampled.

Wells may be excluded or included into the networks as the study progresses, depending on emerging methyl iodide use patterns and well availability.

c) Sampling Frequency

The sampling scheme for this study is divided into two phases to account for the characterization of background iodide concentrations in selected wells and the potential transit time to ground water.

1) Phase I

The Phase I objective is to characterize intrawell variation of resident iodide concentrations to determine if a sampling frequency of once per year is sufficient to measure potential temporal increases in chemical concentration (see Appendix A). Since iodide could be a naturally occurring constituent in ground water, knowledge of potential temporal variation in concentration is needed to determine an appropriate sampling frequency. For the first year, wells will be sampled quarterly and analyzed for iodide. A subset of all the wells (25%) will also be sampled for total iodine on a quarterly basis in order to verify that iodide is the dominant iodine species in ground water. Methyl iodide is not a naturally occurring constituent in ground water so well water samples will only be analyzed once per year. At the end of four sampling events, the data will be reviewed to determine if a switch to Phase II is warranted. Otherwise, Phase I will continue until background iodide concentrations are adequately quantified.

2) **Phase II**

During Phase II, each well will be sampled for methyl iodide and iodide annually. The same subset of wells selected for total iodine analysis in Phase I will also be sampled for that constituent on an annual basis. Phase II is expected to last a decade, unless periodic reviews of the data indicate otherwise.

V. SAMPLING AND ANALYTICAL METHODS

Samples will be collected using the methods described in SOP FSWA001.01 (Nordmark 2008a) and they will be analyzed for methyl iodide, iodide, and total iodine according to published U.S. Environmental Protection Agency (U.S. EPA) methods (U.S. EPA 2006; U.S. EPA 1998; U.S. EPA 2007). Quality control includes samples that contain known amounts of analyte (blind spikes) and deionized water (field blanks) that are prepared and analyzed according to standard operating procedure (SOP) QAQC001.00 (Segawa 1995). Reporting limits for methyl iodide, iodide, and total iodine for previously conducted analyses indicated levels at 0.05 ppb, 6.0 ppb, and 6.0 ppb respectively, and these will be requested of the participating laboratory. However, the reporting limits may vary depending on the contract laboratory capabilities. The reporting limit is the smallest amount that can be reliably detected and is set by the testing laboratory for each compound.

VI. DATA ANALYSIS

Data from Phase I will be used to generate a study memorandum quantifying the intrawell variation of methyl iodide, iodide, and total iodine concentrations. The analysis of Phase I is focused on quantifying the baseline background levels of iodide in the candidate wells. Examination of intrawell summary statistics will be conducted to assess whether intrawell variability during the initial year indicates that an acceptable assessment of background levels has been achieved. This analysis will include, at a minimum, calculation of mean, median, standard deviation, and coefficient of variation (CV) within each well. Evidence of potential seasonal variation will be assessed by examining the temporal pattern of concentration results within each well. This assessment will be by simple graphical analysis in the first year of Phase I, but may include other statistical methods suitable for correlated data if Phase I continues for two or more years. These intrawell summary statistics may also be aggregated for further analysis, as appropriate, according to the spatial distributions of wells included in the study.

Comparison of Phase I results to the California Department of Public Health ground water data may also be performed to aid in assessing background levels of iodide. For example, a comparison of the median CV of the Phase I iodide concentration to the median CV of the California Department of Public Health wells iodide concentration. Interwell geographic patterns of analyte concentrations may be evaluated using Geographic Information System methods or, if appropriate, spatial statistical methods such as kriging, and/or comparison of interwell variances both within and between sampling areas. It should be emphasized that this study is regional in nature and that study objectives require collection of data and analysis that will be applicable statewide to potential methyl iodide use areas. A recommendation will be made to move to Phase II based on Phase I results indicating that a sufficient characterization of background iodide levels in candidate wells has been achieved. Phase I could be extended for a second year or beyond.

Subsequent progress reports, including intra and interwell trend analysis (where feasible), will be published periodically. Analytical results will be provided to participating property owners for their respective wells after the first year of sampling (Phase I). Results for all subsequent analyses will be provided within 16 weeks of sampling.

VII. TIMETABLE

Phase I

- July 2011-October 2011: Establish well networks; commence 1st round of sampling.
- January 2012: Commence 2nd round of sampling.
- April 2012: Commence 3rd round of sampling.
- July 2012: Commence 4th round of sampling.
- September-October 2012: Mail results to well owners.
- October 2012: Write 1st year study memorandum; decide if Phase II begins.

Phase II (conducted annually)

- October-November: Conduct annual sampling
- December-January: Obtain analysis results from laboratory.
- February-March: Mail annual results to property owners.
- March-April: Write yearly progress memorandum.

VIII. BUDGET

Phase I (*assuming Phase I only lasts 4 quarters)

Budget Component	Units	Expense per Unit	Total Component Expense
Method Validation	1	$5,000	$5,000
Methyl Iodide Analysis	120	$200	$24,000
Iodide Analysis	480	$100	$48,000
Total Iodine Analysis	120	$150	$18,000
Travel	1	$25,000	$25,000
PY	2	$100,000	$200,000
Total			$320,000

Phase II (annual budget)

Budget Component	Units	Expense per Unit	Total Component Expense
Methyl Iodide Analysis	120	$200	$24,000
Iodide Analysis	120	$100	$12,000
Total Iodine Analysis	30	$150	$4,500
Travel	1	$25,000	$25,000
PY	1.5	$100,000	$150,000
Total			$215,500

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X. TABLES AND FIGURES

Table 1: 2009 Methyl Bromide Use Listed by Application Site

Application Site	Lbs MeBr
STRAWBERRY (ALL OR UNSPEC)	2,514,078
SOIL APPLICATION, PREPLANT-OUTDOOR	1,199,670
N-OUTDR GRWN TRNSPLNT/PRPGTV MTRL	370,354
RASPBERRY (ALL OR UNSPEC)	295,804
WALNUT (ENGLISH WALNUT, PERSIAN WALNUT)	176,547
N-OUTDR CONTAINER/FLD GRWN PLANTS	161,344
GRAPES	71,686
ORNAMENTAL TURF (ALL OR UNSPEC)	60,861
LETTUCE, HEAD (ALL OR UNSPEC)	56,865
TOMATO	49,114
N-OUTDR GRWN CUT FLWRS OR GREENS	36,933
UNCULTIVATED NON-AG AREAS (ALL OR UNSPEC)	24,500
GRAIN CROPS (ALL OR UNSPEC)	24,215
ALMOND	20,450
N-GRNHS GRWN CUT FLWRS OR GREENS	16,500
PEACH	15,920
BLACKBERRY	14,716
UNCULTIVATED AGRICULTURAL AREAS	12,355
PECAN	12,074
RYE (ALL OR UNSPEC)	9,234
LANDSCAPE MAINTENANCE	7,095
SWEET POTATO	4,228
WHEAT, GENERAL	4,194
GRASSES GROWN FOR SEED (ALL OR UNSPEC)	3,528
PRUNE	2,961
ASPARAGUS (SPEARS, FERNS, ETC.)	2,181
BLUEBERRY	1,995
CHERRY	1,941
EGGPLANT (ORIENTAL EGGPLANT)	1,464
SPINACH	1,260
RESEARCH COMMODITY	704
N-GRNHS GRWN TRNSPLNT/PRPGTV MTRL	644
CELERY, GENERAL	380
LEMON	353
PLUM	269
PEPPERS (FRUITING VEGETABLE)	171
KIWI FRUIT	107
COTTON, GENERAL	95
CHESTNUT	14
APRICOT	11
RICE (ALL OR UNSPEC)	6
FRUITS (DRIED OR DEHYDRATED)	2
TOTAL	5,176,824

Table 2: 2009 Methyl Bromide Use Listed by California County	
County	**Lbs MeBr**
Monterey	1,462,544
Siskiyou	656,353
Santa Cruz	563,854
Ventura	529,654
Santa Barbara	507,081
Merced	184,686
San Luis Obispo	162,378
Fresno	157,982
Tehama	133,855
San Joaquin	112,709
Tulare	110,054
Sutter	94,386
Kern	68,198
Glenn	65,706
Shasta	63,672
Stanislaus	62,439
Orange	51,525
Riverside	33,753
Lassen	33,448
Madera	32,100
San Diego	25,719
Placer	21,678
Butte	16,738
Yuba	9,606
Santa Clara	5,143
Imperial	3,559
Napa	3,366
Los Angeles	1,527
Solano	1,230
Colusa	1,052
San Benito	380
Kings	201
Alameda	146
Yolo	98
Contra Costa	5
TOTAL	5,176,824

Table 3: Identification of Townships with Historically High Methyl Bromide Use in Each of the Potential Study Regions				
REGION NAME				
Merced	Santa Cruz / Monterey	Santa Barbara/ San Luis Obispo	Ventura	Siskiyou
24M05S13E	27M15S04E	40S11N34W	56S02N20W	47M48N01W
24M05S12E	27M15S03E	40S11N35W	56S02N21W	47M47N01W
24M05S11E	27M15S02E	42S10N35W	56S02N22W	47M46N01W
24M05S10E	27M14S02E	42S10N34W	56S02N23W	47M46N02W
24M06S10E	27M14S03E	42S10N33W	56S01N23W	47M45N02W
24M06S11E	27M14S04E	42S11N34W	56S01N22W	47M48N01E
24M06S12E	27M13S04E	42S09N33W	56S01N21W	47M47N01E
24M06S13E	27M13S03E	42S09N34W	56S01N20W	47M46N01E
24M07S13E	27M13S02E	42S09N32W	56S03N21W	
24M07S12E	27M12S01E	42S08N34W	56S03N22W	
24M07S11E	27M12S02E	42S08N33W		
24M07S10E	27M12S03E			
	44M12S01E			
	44M12S02E			
	44M12S03E			
	44M11S03E			
	44M11S02E			
	44M11S01E			

Figure 1: Detections by the U.S. Geological Survey of iodide in ground water (2004-2008).

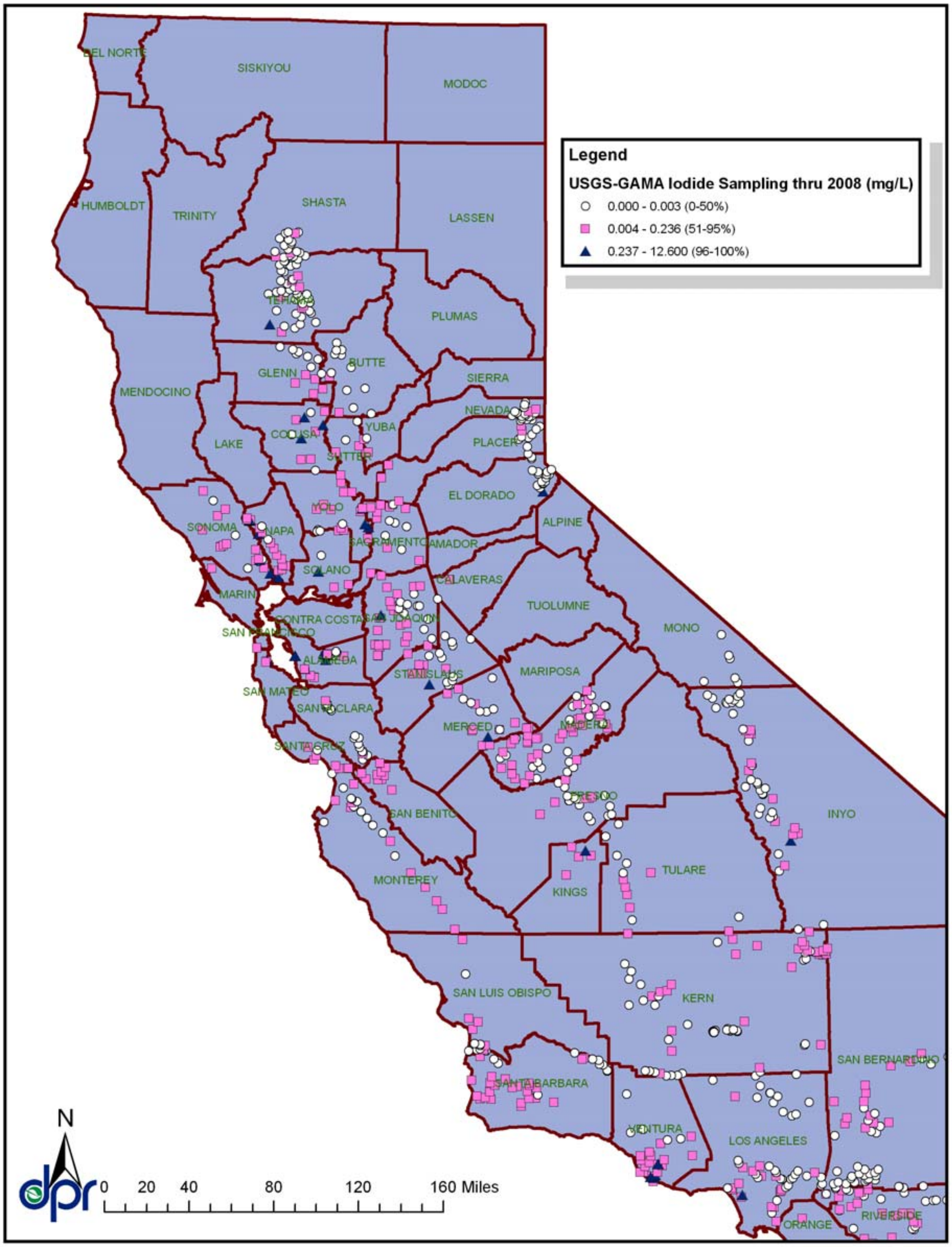


Figure 2: 2000-2010 Methyl Bromide Use in California

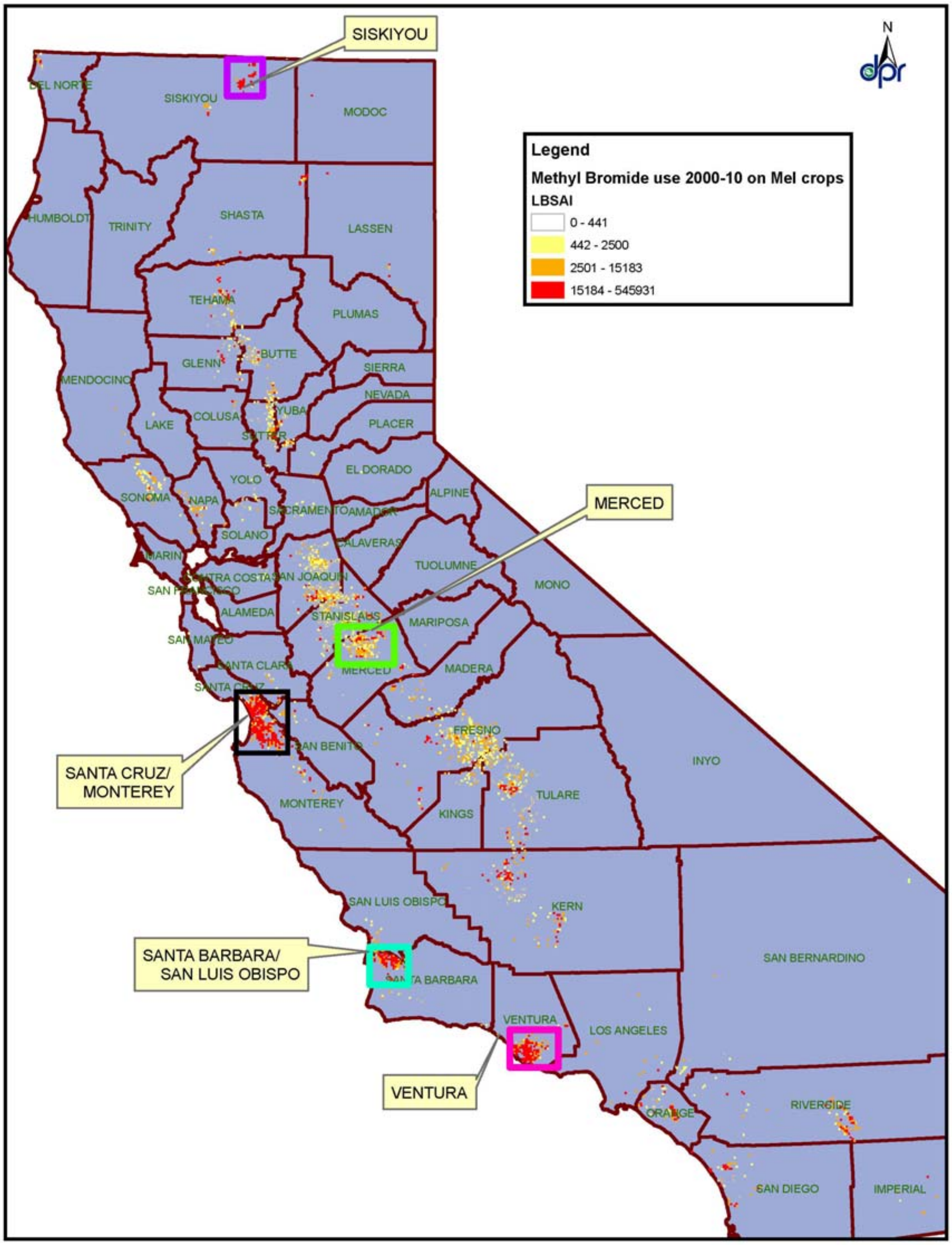


Figure 3: 2000-2010 Methyl Bromide Use in Merced and Siskiyou Counties

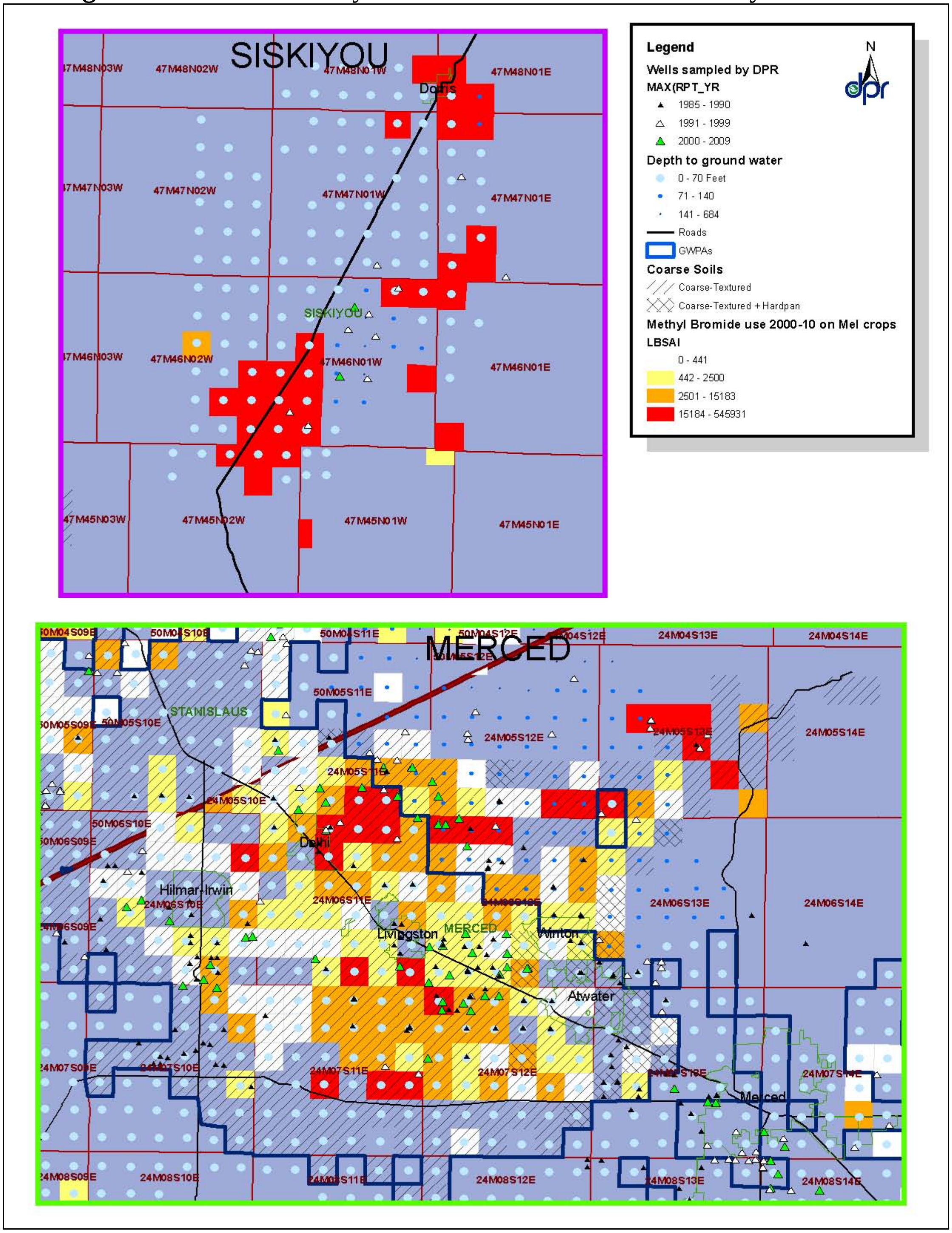


Figure 4: 2000-2010 Methyl Bromide Use in Santa Cruz and Monterey Counties

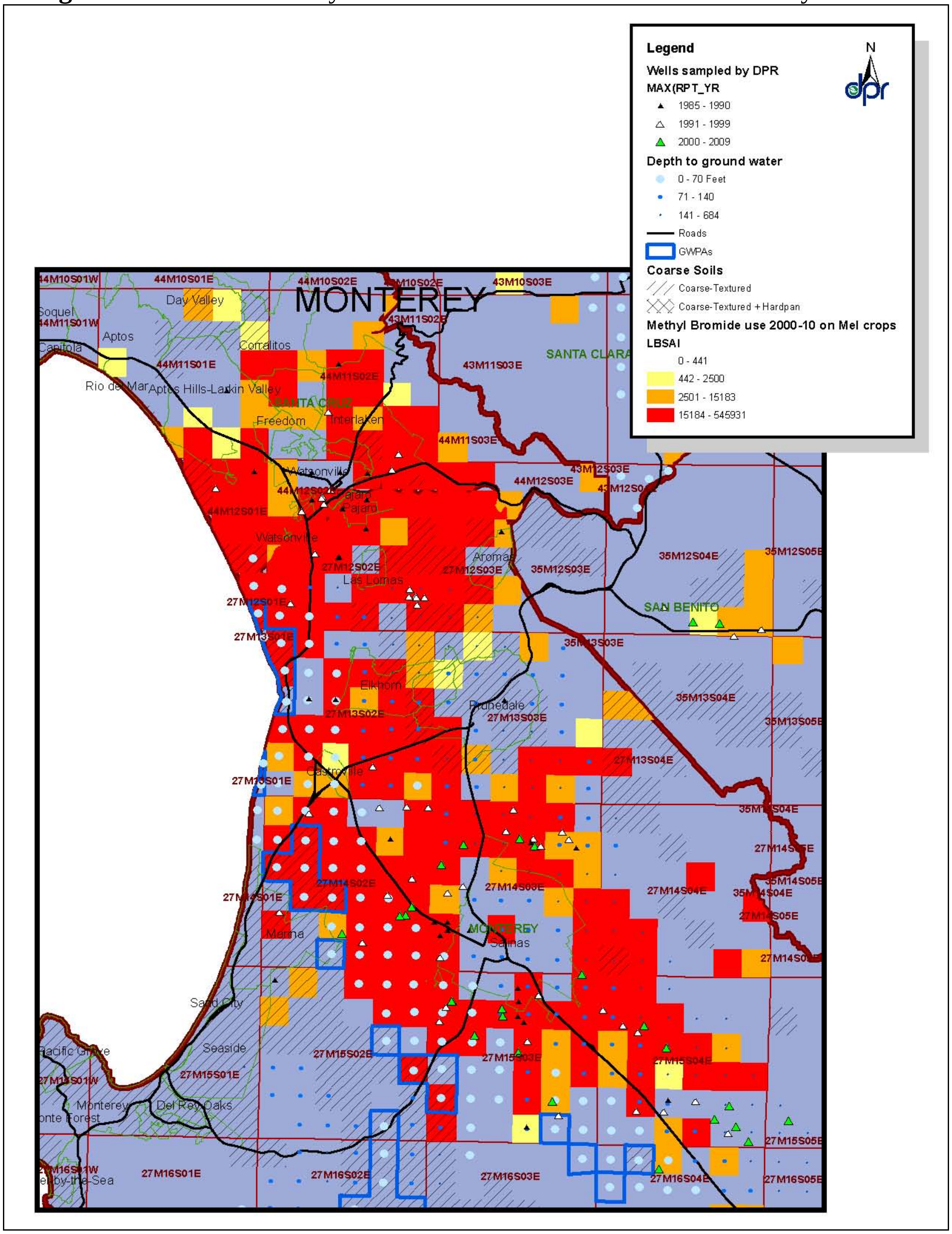
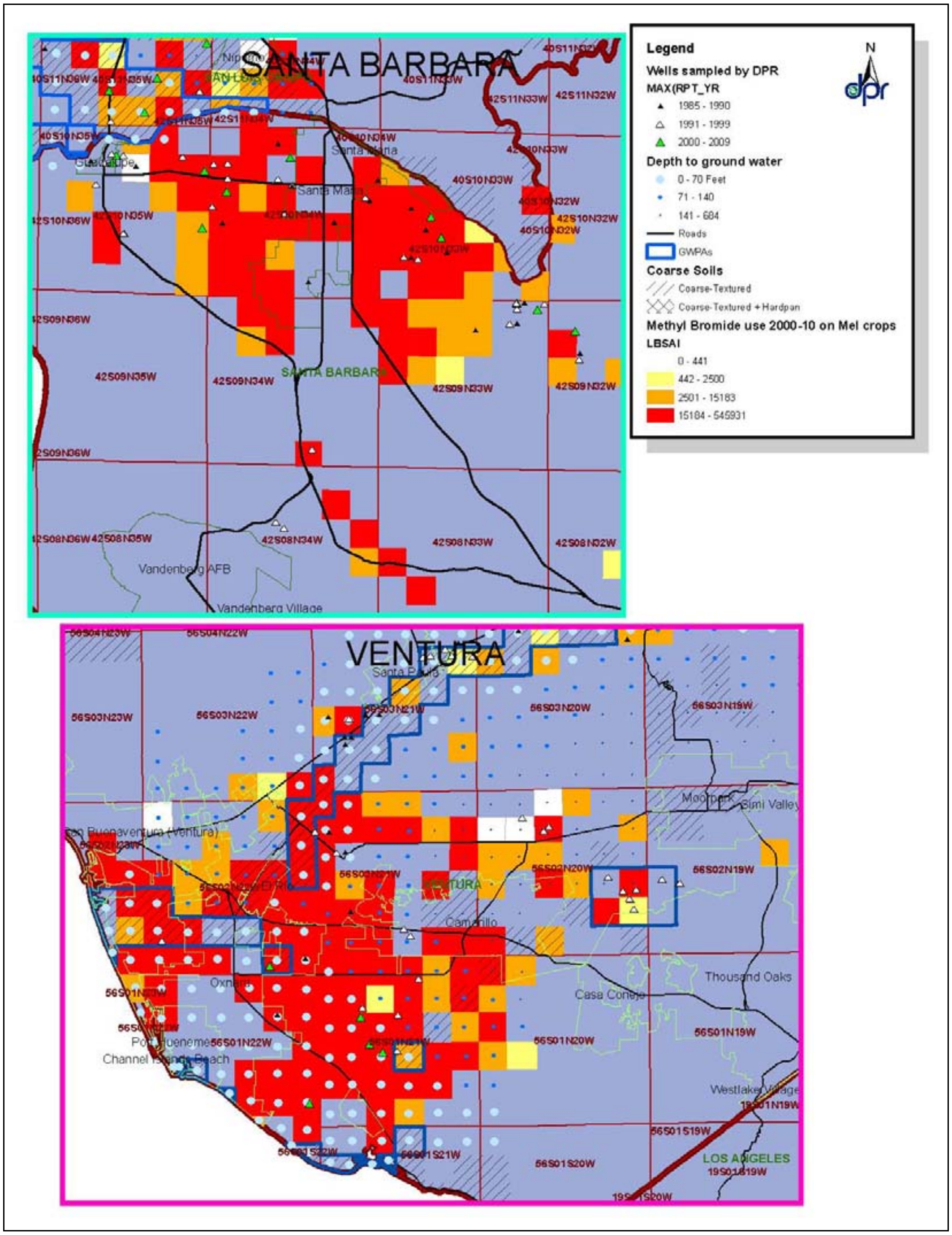


Figure 5: 2000-2010 Methyl Bromide Use in Santa Barbara, San Luis Obispo, and Ventura Counties



XI. APPENDICES

Appendix A: Sample Size Determination of Background Iodide Concentrations

Department of Pesticide Regulation

Mary-Ann Warmerdam
Director

MEMORANDUM

Arnold Schwarzenegger
Governor

TO: Randy Segawa
Environmental Program Manager I
Environmental Monitoring Branch

FROM: Terrell Barry, Ph.D.
Research Scientist III
Environmental Monitoring Branch
916-324-4140

Original signed by

DATE: December 21, 2010

SUBJECT: ESTIMATION OF SAMPLE SIZE REQUIRED TO CHARACTERIZE BACKGROUND IODIDE CONCENTRATIONS IN METHYL IODIDE WELL NETWORK WELLS

Introduction

The Department of Pesticide Regulation (DPR) is planning a combination of soil sampling and well monitoring studies to provide ongoing performance evaluation of mitigation measures required for the use of the newly registered fumigant, methyl iodide. The well monitoring portion of the studies will measure both methyl iodide and its breakdown product, iodide. Iodide is a naturally occurring compound so background levels must be quantified before use of methyl iodide begins. This memorandum presents the rational for selecting the number of samples per well required to characterize the background concentration of iodide.

Iodide Well Concentrations Database and Sample Size Estimation

DPR obtains from the California Department of Public Health (CDPH) testing results for a large number of constituents, including pesticides, industrial chemicals, and basic water parameters for all public water system water supplies. The iodide monitoring data is part of these results and comprised a total of 3390 records. Most samples were collected prior to 1995, but the most recent results are from 2010. Craig Nordmark, DPR Environmental Monitoring Branch, processes this data to match CDPH well numbers to DPR well numbers using a CDPH provided translation table. Seventy five of the records could not be matched to any well number or other code in the translation table. Twenty appear to be records for actual wells (12 unique wells), the rest from treatment plants and other non-well sources based on descriptive site names. Non-well numbers matched 360 of the remaining records, only two of those appear to be for samples taken from points other than wells. All records that could not be matched to a true well number were removed. A total of 435 records were eliminated in this process leaving 2955 records for 845 wells.

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As discussed above, the database processed to match DPR well numbers initially contained 2955 records for 845 wells. Each well had between 1 and 14 iodide sample results. CDPH sends the records with the value of 0 or above. The reporting limits are unknown. Several steps to remove outliers and suspect results were taken. The first set of records removed were those values with iodide results over 10000ppb. These four records were very large, from four different wells, and were likely either expressed in incorrect measurement units or had the decimal place misplaced. The second set of records removed were those records with values greater than three standard deviations over the grand mean value of the remaining records. The screening value was 192ppb. A total of 30 records meeting the criteria were removed. The third step to remove outliers was to examine the records that Craig Nordmark flagged as "Questionable." Some of these records were an order of magnitude larger than other replicates for the same well so it could be argued to be the result of a misplaced decimal. If this was the case the record was removed rather than corrected. A total of five records meeting this criteria were removed. A total of 2918 records for 845 wells remained.

I used the Pivot Table function in EXCEL to obtain the number of measurements (reps), the mean, and standard deviation (SD) of iodide concentrations for each well. The Coefficient of Variation was calculated as CV = (Mean/SD)*100. Since the SD can not be calculated unless at least two reps are present, all wells that had only one rep were then removed. In addition, any well for which the CV could not be calculated was removed. As stated above, each well had between 1 and 14 iodide sample results. CDPH sends the records with the value of 0 or above. The CV could not be calculated if the mean was 0 (nondetect). A total of 148 wells were removed in this step. A total of 691 wells remained in the data set.

The summary statistics for the remaining wells, shown below, were calculated using MINITAB. The variables are as follows: r = reps, mean = mean, std dev = SD, cv = CV.

Descriptive Statistics: r, mean, std dev, cv

Variable	N	N*	Mean	SE Mean	StDev	Minimum	Q1	Median	Q3
r	691	0	3.9103	0.0610	1.6027	2.0000	3.0000	4.0000	5.0000
mean	691	0	19.892	0.827	21.743	0.167	8.200	12.857	26.000
std dev	691	0	6.923	0.353	9.289	0.000	2.217	3.674	6.850
cv	691	0	55.01	2.26	59.30	0.00	15.71	30.00	70.26

Variable	Maximum
r	14.0000
mean	159.000
std dev	65.233
cv	300.00

MINITAB terms:
N = number of wells
N* = number of wells excluded from analysis
Mean = arithmetic mean
SE Mean = standard error of the mean
StDev = standard deviation
Minimum = minimum value
Q1 = lower quartile value
Median = median value
Q 3 = upper quartile value
Maximum = maximum value

Variables analyzed:
r = number of records per well
mean = mean iodide concentration in each well
std dev = standard deviation of iodide concentration in each well
cv = Coefficient of Variation of iodide concentration in each well.

One method of estimating sample size is to use the CV and specify an acceptable percent difference between the true mean and sample mean:

$$r \approx \frac{4(CV)^2}{(\%\mu)^2}$$

This equation provides with 95% confidence how many samples are necessary to achieve an estimate of the true mean within the specified percentage (% u). I used this for the estimation of background iodide concentration from candidate wells in the network because the CV's for each of the 691 wells can be used as a general indication of the variation expected within each well. Both the mean and the CV are skewed (Figure 1) so I chose to use the median CV for sample size estimation. The calculations are shown below for the sample size needed for each network well to estimate a true well mean iodide concentration within a 30% difference down to within a 15% difference with a 95% confidence:

$$r = 4(30)^2 /(30)^2 = 4$$

$$r = 4(30)^2 /(25)^2 = 6$$

$$r = 4\ (30)^2 /(20)^2 = 9$$

$$r = 4(30)^2 /(15)^2 = 16$$

It is clear that the required sample size will increase rapidly if a smaller difference from the true mean is desired. One option for setting sample size is to begin with the four samples taken once per quarter at each background well and evaluate the results at the end of the first year. The CV may be smaller for the wells in the methyl iodide well network, this will likely become apparent by the end of the first year.

Figure 1. Distribution of well iodide means (ppb) and coefficient of variation (CV) (%). Total number of wells is 691.