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SUBJECT: Distribution of Triazine Residues in Wells in Relation to Current and Proposed Maximum Contaminant Levels (MCLs)

Objective
The objective of this memo is to analyze the distribution of residues for detections of triazine parent and breakdown products and to compare their concentrations to current and proposed Maximum Contaminant Levels for triazines.

Background
The United States Environmental Protection Agency (USEPA) and the California Department of Health Services (DHS) establish human health-based drinking water standards including Maximum Contaminant Levels (MCL). For municipal wells, exceedance of an MCL may result in increased monitoring of and/or remediation of the drinking water source. Current MCLs for atrazine and simazine are 3 and 4 parts per billion (ppb), respectively (http://www.dhs.ca.gov/ps/ddwem/chemicals/MCL/mclindex.htm). DHS has recently proposed new regulations to lower the MCL for atrazine to 1 ppb (http://www.dhs.ca.gov/ps/ddwem/chemicals/PHGs/reviewstatus.htm#Atrazine).

The triazine herbicide, atrazine, is currently under special review by the USEPA (http://www.epa.gov/oppsrrd1/reregistration/atrazine/). In a previous estimation of dietary risks in 1994, the USEPA indicated that the total toxic residue of concern was the parent triazine compound plus dealkylated, chlorinated breakdown products (http://www.epa.gov/docs/fedrgstr/EPA-PEST/1994/November/Day-23/pr-54.html). For the recent revision of the revised atrazine human health risk assessment in support of the atrazine re-registration eligibility decision, the USEPA again considered aggregate exposures to atrazine and dealkylated degradates (http://www.epa.gov/oppsrrd1/reregistration/atrazine/hed_redchap_16apr02.PDF).

The aggregating of residues is confounded because atrazine and simaizne have common breakdown products, yet different MCLs. There are three chlorotriazine degradates of simazine and atrazine: deethyl atrazine (DEA), 2-amino-4-chloro-6-ethylamino-s-triazine (ACET also known as deisopropyl atrazine or deethyl simazine), and diamino chlorotriazine (DACT) (Figure 1). DEA is formed only as a result of atrazine degradation, whereas, both ACET and DACT may result from degradation of atrazine or simazine.

In 1992, DPR's Medical Toxicology Branch requested that the Environmental Monitoring Branch (EM) include the breakdown products in analysis for atrazine and simazine because of data that indicated similar toxicity of the metabolites (Meierhenry, 1992). The EM branch first reported detections of DEA and ACET triazine metabolites in well water in 1994 (Kim, 1994). At first only DEA and ACET were included but the Center for Analytical Chemistry, Environmental Monitoring Section of the California Department of Food and Agriculture eventually developed a multi-analyte screen that also included DACT. That method has been developed as CDPR method 168, which is available at: http://empm/em/chem.htm. Well samples taken since then have routinely been analyzed using the analytical screen. This memo contains an analysis of the distribution of triazine residue that have been detected in wells and a comparison of their concentrations with respect to exceeding current and proposed MCLs.

Discussion

Data for this analysis were obtained from DPR's Well Inventory Data Base as of November 7, 2002. To date, DPR is the only agency that has reported chemical analysis for atrazine, simazine and the three degradates in a sample, so this memo discusses only data from wells sampled by DPR. Well samples taken by DPR's Ground Water Program are primarily from domestic wells that typically serve single-family dwellings. These wells are more susceptible to contamination by pesticides than municipal wells because they draw water from shallower aquifers and they are situated near pesticide application sites (Troiano et al., 2001).

There were 559 sampling events reported in the Well Inventory Data Base where atrazine, simazine, DEA, ACET, and DACT were simultaneously measured. All of the data had a Minimum Detection Limit of 0.05 ppb or lower. Some of the data represented repeat sampling of wells so the data were actually obtained from 337 unique wells. One hundred thirty one wells had a detection of at least one of the five analytes, and this memo analyzes the distribution of the detected residues. In cases where there was more than one sampling event per well, results from only the most recent sampling event were retained in the data set.

Observations on the co-occurrence of residues. Table 1 lists the number of detections for each residue in the data set. Some observations on the relative occurrence between residues:

1. Simazine was more frequently detected than atrazine. Of the 131 wells with detections, simazine residues were detected in 85 wells and atrazine in 19 wells. This is due to differences in their major use patterns. Historically, both herbicides had been registered for non-crop weed control, such as for rights-of-way: These uses have been recently discontinued. There is a dichotomy in their use on crops because atrazine is primarily

used on row crops such as corn, whereas simazine is used on grape, citrus, deciduous tree fruit and nut crops. Data for 70 of the 131 wells in this dataset were from a domestic well monitoring network located in Fresno and Tulare counties and they are located amongst the major crops on which simazine is used, e.g. grape, citrus, deciduous tree fruit and nut crops. Owing to California's cropping pattern, simazine's use is greater than atrazine. This data provides a contrast to use patterns in the Mid-western states where atrazine's use is greater than simazine because of the predominance of corn and soybean crops.

2. ACET and DACT breakdown products were detected more frequently than atrazine, simazine, and DEA. Of the 131 wells with any detection for the 5 triazine residues, the overall number of detections for ACET was 110 and for DACT was 105, whereas atrazine was 19, simazine was 85, and DEA was 19.

The data were further analyzed to determine the exact combinations of the five residues. Table 2 contains the number of counts for each specific combination, starting with detection of a single residue and none of the others and progressing through all of the possible combinations. For example, in the section in Table 2 entitled 'Single Residue Detected', 2 out of the 131 wells had detections of atrazine but none of the other residues were detected. Subsequent sections in Table 2 present counts of the higher order combinations culminating with the number of wells where all residues were detected. These are exact combinations so the total from the first order to the highest order combination adds up to 131 wells.

Some observations on the relative occurrence of residues are:

3. Simazine was a significant source for detections of ACET and DACT breakdown products. In light of the rather large number of potential combinations, a few combinations were dominant. The residue combination with the highest occurrence was the three-residue combination of simazine, ACET, and DACT with no detection of atrazine or DEA. This combination was measured in 63 of the 131 wells, which was approximately 50% of all potential combinations. In addition there were 7 wells where simazine and ACET residues were detected and 10 other wells where simazine and ACET were detected in the presence of atrazine and/DEA. In total there were 80 wells (61%) where ACET and simazine residues occurred together. These results are in contrast to the patterns observed in Midwestern United States where atrazine residues are frequently detected and DEA is detected more frequently than ACET (Thurman et al., 1992; Jayachandran et al., 1994). As previously indicated, the higher incidence of simazine detection and its breakdown products is due to the much higher use of simazine, as reflected in the major cropping patterns in the areas where the wells were located in California.

4. DEA detections were highly associated with atrazine detections. The frequency of atrazine detection was low at 19 of 131 wells but DEA co-occurred with atrazine in 15 of

the wells. Owing to the specificity of DEA as a breakdown product of atrazine, DEA is a good indication of atrazine. However, presence of DEA does not necessarily mean atrazine residues are present because DEA was detected in 4 additional wells where atrazine residues were not detected.

5. ACET association with atrazine was confounded by presence of simazine residues. A simple count of the occurrence of ACET with atrazine residues indicated co-occurrence in 14 of the 19 wells, which was potentially similar to the DEA association. But 8 of those wells also had detections of simazine. If simazine was the source for ACET, then ACET's association with atrazine would have been lowered to 6 of 19 wells or to approximately 30% of the combined detections. Furthermore, ACET was detected in 2 additional wells where DEA was not detected with one of those wells containing a detection for simazine.

6. Analysis of all residues and pesticide use information is required to adequately determine the potential source of breakdown products. The co-occurrence of ACET and DACT without any other residue was the second most frequent combination: ACET in combination with DACT was detected in 18 of the 131 wells. Both could have been derived from atrazine. However, owing to the lack of DEA detections and the higher use of simazine in relation to atrazine, the likely source was simazine. Thus, accurate interpretation of the pattern of detections for parent and residues requires additional information on pesticide use and on a complete analysis for all 5 residues.

Comparison of residue concentrations to current and proposed MCLs. Currently, atrazine and simazine MCLs are set at different levels, at 3 and 4 ppb, respectively. DHS is proposing to lower atrazine's MCL to 1 ppb. To determine the potential importance of including triazine breakdown products in a drinking water assessment, the distributions of individual and total chlorotriazine residues in the 131 wells were compared to current and proposed MCLs. A preliminary comparison of the means and moments for each separate residue indicated that mean concentrations were highest for the ACET and DACT breakdown products (Table 3). The maximum values in the data set for atrazine, simazine, and DEA were less than 1 ppb, whereas ACET and DACT maximum concentrations were greater than 1ppb. These data are in contrast to previous observations that DEA concentrations are more likely to be higher than ACET (Jayachandran et al., 1994; Mills and Thurman, 1994; Barbash et al., 1999). But these previous observations were derived from data collected in areas where atrazine use was predominant. Simazine was predominantly used around the majority of wells in this data set. DACT is the final breakdown product for either atrazine and simazine and it is potentially very stable (Figure 1). The high concentrations measured for DACT indicate that it indeed could be very stable in ground water and that it could be the greatest contributor to potential exceedance of an MCL.

When all residues are summed in a well water sample, the mean was 0.99 ppb, nearly 10 times the mean for atrazine or simazine alone (Table 3). The median value was 0.46 ppb, which was nearly half the mean value and indicates a skewed distribution caused by infrequent detections of higher values. The cumulative distribution for summed residues in the wells was plotted to compare the number of potential exceedances of current and proposed MCLs (Figure 2). For comparision, Figure 3 presents a plot for the summation of only ACET and DACT breakdown products. By visual comparison the curves for Figures 2 and 3 are similar, indicating that removal of atrazine, simazine, and DEA residues from the summation had only a small effect on the percentage of wells exceeding 1, 3, or 4 ppb values.

A curve was fit to each distribution to produce an estimate for the percentages and exact number of wells that exceeded 1, 3, and 4 ppb in concentration. First, the quantiles for a cumulative distribution was determined from a univariate analysis of each summed variate (SAS Inst, 1990). The best equation that fit the distribution based on the quantiles was determined with the TableCurve 2D[4] program (Aisn Software Inc®, licensed through Jandel Scientific, San Rafael, Ca, 94901).

Eq. 1. $$Y^{-1} = a + b/X$$

X was the value for the summed residues and Y was the cumulative quantile determined from the univariate analysis. The estimated quantile was then determined for current and proposed MCLs by solving for Y when X was assigned 1, 3, and 4 ppb.

Table 4 contains the estimates for the percentage of wells and the number of wells that exceed each level. None of the atrazine or simazine detections exceed current MCLs. But summation of all residues results in exceedances for both the atrazine or simazine MCLs. If the MCL for atrazine is reduced to 1 ppb and ACET and DACT breakdown residues are included in the assessment, the percentage of the 131 wells above the MCL would increase from approximately 9% at the 3 ppb MCL to approximately 30% of the wells at 1 ppb.

Conclusions

This analysis has shown the importance of measuring all triazine residues in well samples, especially if they are aggregated in future determinations of health risks. For the wells included in this analysis, none of the wells would have exceeded current or proposed MCLs for parent atrazine or simazine when only the concentration of the parents were considered. In contrast, ACET and DACT triazine breakdown products were detected frequently and at much higher concentrations than the parent residues. Their concentrations alone could cause a well to exceed the current MCL for atrazine or simazine.

It is important to note that this analysis is specific to this small subset of wells with detections and that the percentages do not reflect the statewide percentage of wells that would exceed the MCL. The analysis does indicate that, for domestic wells sampled by DPR, there will be exceedances of the MCL if the triazine breakdown products are included in a health risk assessment.

References

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Table 1. Number of wells with detection of specifed triazine residue.

Residue	Count[a]
Atrazine	19
DEA	19
ACET	110
DACT	105
Simazine	85

[a] Total number of wells with detection of a triazine residue was 131.

Table 2. Counts of occurrence of specific combinations of triazine residues. Cells marked with a 'P' indicate detection of the residue, whereas, cells marked with an '0' indicate no detection in the well sample.

	Atrazine	DEA	ACET	DACT	Simazine	Count[a]
Single Residue Detected						
	P	0	0	0	0	2
	0	P	0	0	0	1
	0	0	P	0	0	5
	0	0	0	P	0	10
	0	0	0	0	P	5
Two Residues Detected						
	P	P	0	0	0	2
	P	0	P	0	0	0
	P	0	0	P	0	0
	P	0	0	0	P	0
	0	P	P	0	0	0
	0	P	0	P	0	0
	0	P	0	0	P	0
	0	0	P	P	0	18
	0	0	P	0	P	7
	0	0	0	P	P	0
Three Residues Detected						
	P	P	P	0	0	3
	P	P	0	P	0	1
	P	P	0	0	P	0
	P	0	P	P	0	1
	P	0	P	0	P	0
	P	0	0	P	P	0
	0	P	P	P	0	1
	0	P	P	0	P	0
	0	P	0	P	P	0
	0	0	P	P	P	63
Four Residues Detected						
	P	P	P	P	0	2
	P	P	P	0	P	1
	P	P	0	P	P	0
	P	0	P	P	P	1
	0	P	P	P	P	2
Five Residues Detected						
	P	P	P	P	P	6

[a] Total number of wells with positive samples was 131.

Table 3. Mean, median, standard deviation (SD), minimum, and maximum values concentration of triazine residues in wells.

Residue	Number of Wells	Mean	Median	SD	Minimum	Maximum
	#	ppb				
Atrazine	19	0.11	0.09	0.09	0.02	0.37
Simazine	85	0.11	0.10	0.05	0.04	0.25
DEA	19	0.14	0.07	0.16	0.05	0.57
ACET	110	0.39	0.24	0.40	0.02	1.78
DACT	105	0.70	0.36	1.03	0.05	5.34
Summation of all residues	131	0.99	0.50	1.33	0.04	7.19

[a] Total number of wells with positive samples was 131.

Table 4. Effect of summation of different combinations of triazine residues on the percentage and number of wells that exceed current and proposed MCL levels for atrazine and simazine.

Residue	Number of Wells	Percentage of wells exceeding:			Number of wells exceeding:		
		4 ppb[a]	3 ppb[b]	1 ppb[c]	4 ppb[a]	3 ppb[b]	1 ppb[c]
	#	%			#		
Atrazine	19	0	0	0	0	0	0
Simazine	85	0	0	0	0	0	0
DEA	19	0	0	0	0	0	0
ACET	110	0	0	11	0	0	12
DACT	105	2	5	22	2	5	23
ACET+DACT	121	4	8	29	5	10	35
Simazine+ACET+DACT	126	5	9	31	6	11	39
Atrazine+DEA+ACET+DACT	126	4	8	30	5	10	38
All Residues	131	5	9	31	6	11	41

[a] Current MCL level for simazine.
b Current MCL level for atrazine.
[c] Proposed MCL level for atrazine.

Figure 1. Relationship between the chemical structures of atrazine and simazine and their breakdown products.

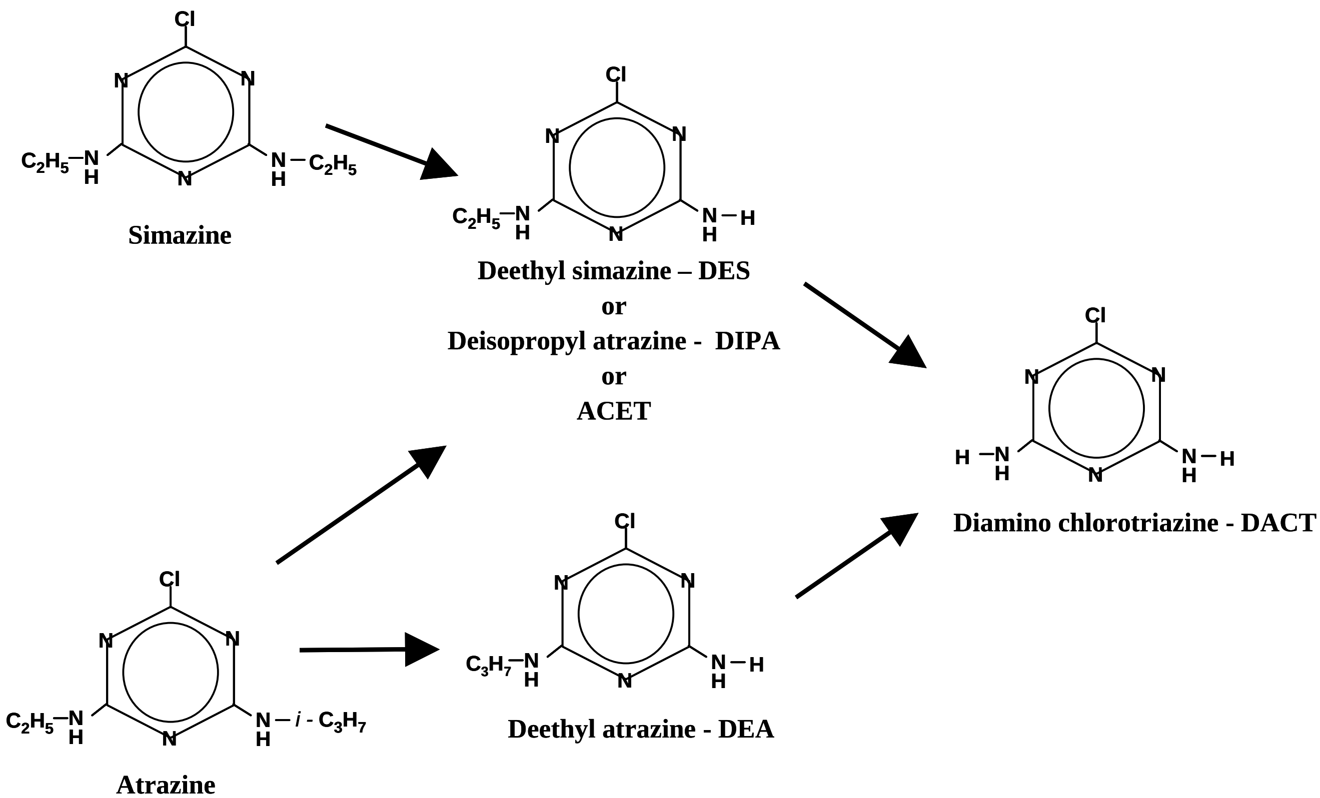

Figure 2. Comparison of the cumulative distribution for the summation of the concentration of all triazine residues in a well, i.e. atrazine, simazine, DEA, ACET, and DACT, to current and proposed MCL levels.

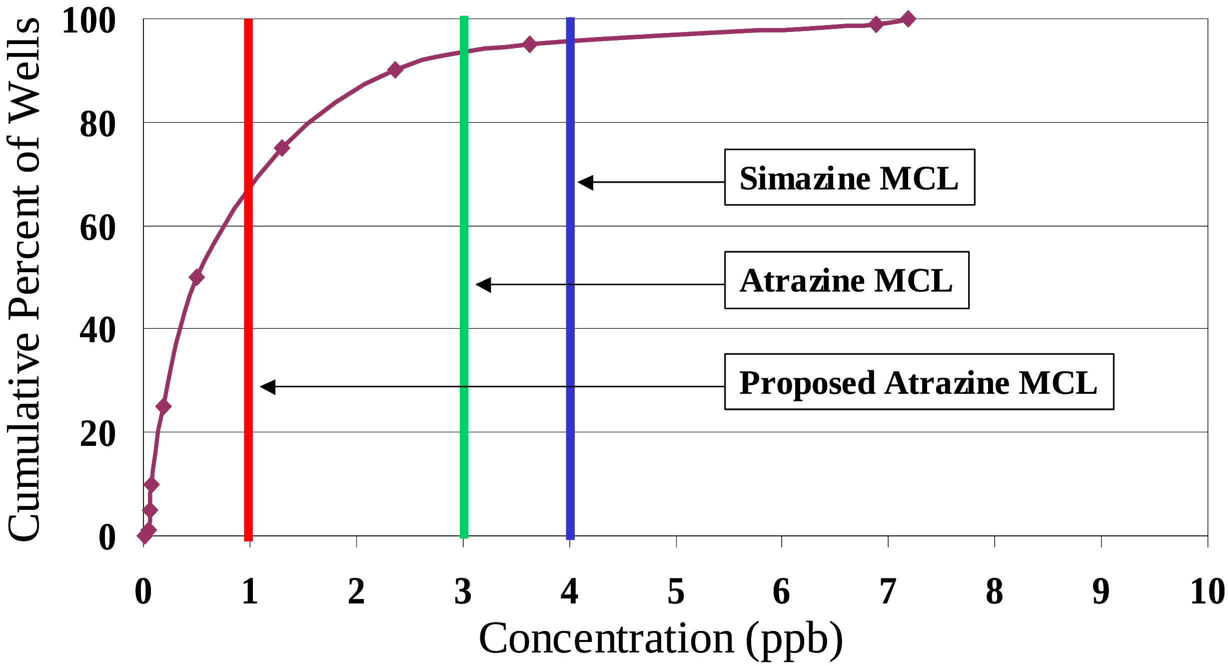

Figure 3. Comparison of the cumulative distribution for summation of only ACET and DACT residues in wells to current and proposed MCLs for atrazine and simazine.