

Comparisons of Trihalomethanes Formed under Different Analytical Conditions: White Paper

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March 30, 2010

Introduction

Trihalomethanes (THMs) are substances formed when chlorine is used to disinfect drinking water. THMs are just one category of disinfection byproducts (DBPs) formed in the treatment process. Analytical methods for THMs are generally grouped into two main categories (Koch et al. 1991, Reckhow and Edzwald 1991). First are the methods for estimating the total amount of THMs (also known as total Trihalomethane Formation Potentials or THMFP) that can be formed from all (or the majority) of the precursors present in a source water sample. These methods use a high chlorine dose to ensure maximum conversion of precursors to THMs. Second, are analytical methods that attempt to mimic the amount of THMs formed under drinking water treatment plant conditions. These methods use low chlorine doses recognizing that not all the precursors are likely to be converted to THMs during disinfection.

DWR's Bryte Lab has been conducting THMFPs since at least 1982 (DWR 1982). DWR's original method was adapted from USEPA 510.1 and was used from 1982 to 1992 (DWR 1994). In the original method, a sample was spiked with 120 mg/L of sodium hypochlorite and then incubated for 7 days. The sample was then quenched using sodium thiosulfate and analyzed for THMs using EPA Method 601. The original method was modified in July 1992. Modifications included diluting samples when organic carbon was 10 mg/L or more, buffering the sample to pH 8.3 using boric acid and sodium hydroxide, and then incubating for seven days at 25 °C. At the end of incubation, the solution is quenched with sodium thiosulfate and analyzed within seven days using a purge and trap collector and gas chromatography (EPA Method 524.2).. This modified method is referred to as 'DWR THMFP (Buffered)' and has been used by Bryte Lab as the primary method for analyzing THMs.

Total Trihalomethane Formation Potential (THMFP where the first T is customarily dropped) is a loosely defined term assumed to mean all (the maximum) amount of regulated trihalomethanes that can be formed from precursors in a sample of raw water. However, Standard Methods does not specify whether the sample should be filtered or not and different labs use either DOC or TOC (DWR Buffered uses DOC). In drinking water, THMs are regulated as the sum of four species (bromoform, bromodichloromethane, chloroform, dibromochloromethane). In most cases, one or more of the species is below the reporting limit (RL). There is no guidance in the regulations on how to deal with data below RL and different labs use zero, half the RL or RL when summing up the species. Past MWQI reports have used zero for data below RL.

THM formation is influenced by several factors including chlorine dose, contact time, pH, etc. The DWR Buffered has always been considered a high chlorine dose THMFP method with the recognition that it may convert more of the environmental precursors to THMs than are formed at a water treatment plant. A more refined method for measuring THMFP has been proposed using a chlorine dose based on the organic carbon and ammonia in a sample (Krasner et al. 1994) and is referred to as the Reactivity method. The chlorine dose is calculated as:

$$\text{Cl}_2 \text{ (mg/L)} = 3 \times \text{DOC} + 7.6 \times \text{NH}_3\text{-N}$$

Where Cl_2 is the chlorine dose applied and an incubation period of 7 days before quenching. All units are mg/L. Samples with DOC above 10 mg/L are diluted.

Between 1997 and 1998, MWQI collected duplicate samples which were analyzed by Bryte Lab using DWR Buffered and Reactivity-based THMFP methods.

Current Issues

Bryte Lab has indicated that it cannot continue to perform THMFP analysis without a dedicated chemist for this task. MWQI is the only program in DWR that requests these analyses, and so MWQI would have to provide the funding for a chemist dedicated to these analyses. An alternative option is to subcontract these analyses to an outside laboratory. However, contract labs perform THMFP analysis using either the Standard Methods or EPA protocols which are different than the DWR Buffered method. To be able to use historical DWR Buffered THMFP data, there is a need to develop correlations with future data generated by contract labs using Standard Methods protocols. Bryte has suggested that the Reactivity method may be comparable to Standard Method 5710B that the current contract lab (Weck Lab) utilizes for THMFP analysis. The goal of this report is to develop correlations between DWR Buffered and Reactivity THMFP data generated by Bryte Lab duplicate analyses between 1997-98.

Scope

This report compares historical DWR Buffered and Reactivity data at key MWQI stations. Comparisons are made under the following limitations:

- A. Data below RL are treated as zero (because that is how MWQI has treated such data in the past reports)
- B. Comparisons are performed on the sum of THMs (and not individual species)

The following assumptions are made:

- I. Reactivity can reliably predict Buffered

- II. Reactivity is equivalent to Standard Method 5710B which is used by contract labs. Thus SM 5710B will have a similar relationship to Buffered (as Reactivity)

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Methods

I downloaded MWQI data from the Water Data Library (WDL) and searched for sample numbers having results with Buffered and Reactivity methods. I used Minitab 15 for scatter plots and simple linear regression (Reactivity as a predictor of Buffered). Depending on the number of samples available at each station, I randomly selected one or more samples to be omitted from regression calculation (to be used later in verification of the regression model). At most stations, the total number of analyses were limited and so only one or two samples were used for verification of the regression model.

Results

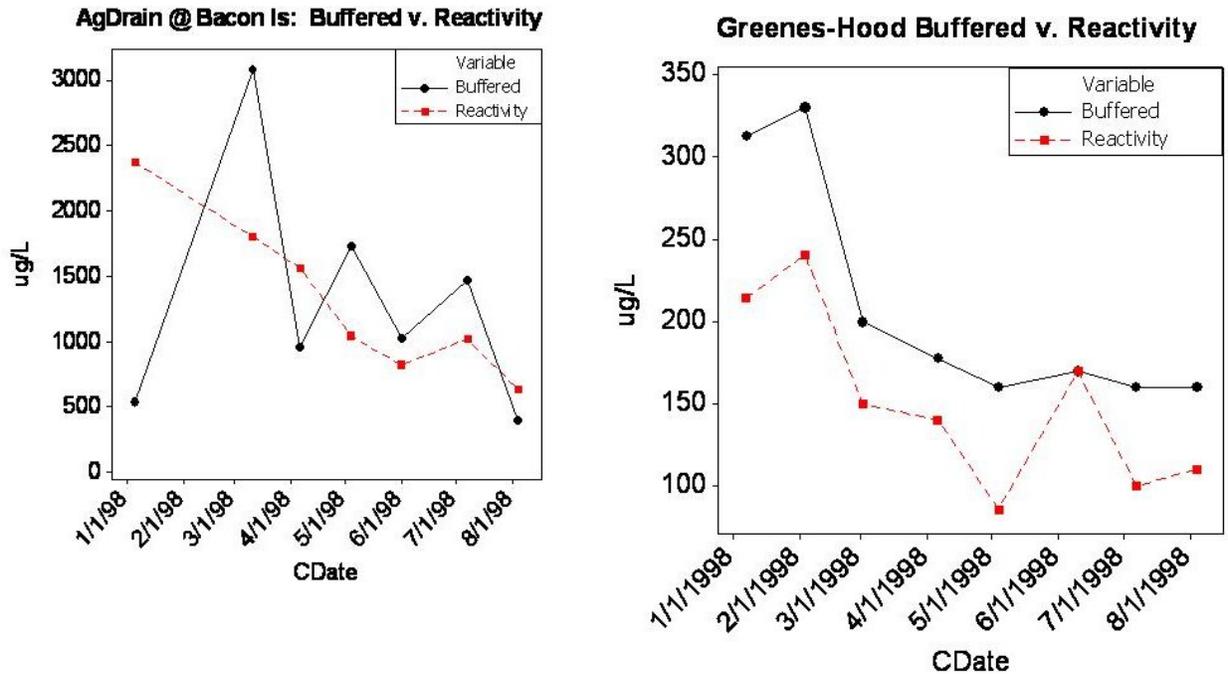
The number of stations with duplicate analyses of Buffered and Reactivity results is shown in Table 1. They include low DOC stations (American, SacWSInt, and Greenes/Hood); medium DOC stations (Banks, Old R at Bacon Is, Vernalis); high DOC Ag Drain (Twitchell). The number of duplicate analyses was variable at different stations. Table 1 also shows the number of samples randomly selected for developing simple linear regressions of Reactivity as a predictor of Buffered.

Table 1. Stations with duplicate Buffered and Reactivity analyses

Long Station Name	Short Station Name	Total # of Samples Available	# of Samples randomly selected for regression	# of Samples for verification
American River at W.T.P	American	8	6	2
Delta P.P. Headworks at H.O. Banks PP	Banks	13	10	5
Sacramento R at Greene's Ldg/Hood.	Greenes-Hood	7	6	1
Old River at Bacon Island	OldR@Bacon	7	6	1
Sacramento R. at West Sacramento WTP	SacWSInt	8	6	2
Ag Drain on Twitchell Isl., PP. No. 1	Twitchell	6	5	1
San Joaquin R. nr. Vernalis	Vernalis	33	25	7

Scatter plots of these data indicated that generally, Reactivity was almost always lower than Buffered and the two methods tracked well. Exceptions were Bacon01 where it was obvious that data from the two methods had little relationship and Greenes/Hood where one data point was (in my opinion) a transcription error where both results were exactly the same, Fig 1. I removed the one 'outlier' at Greenes/Hood from regression analysis and did not use Bacon01 in regressions.

Fig 1. Bacon01 data indicate no relationship and Greenes/Hood has a Reactivity outlier

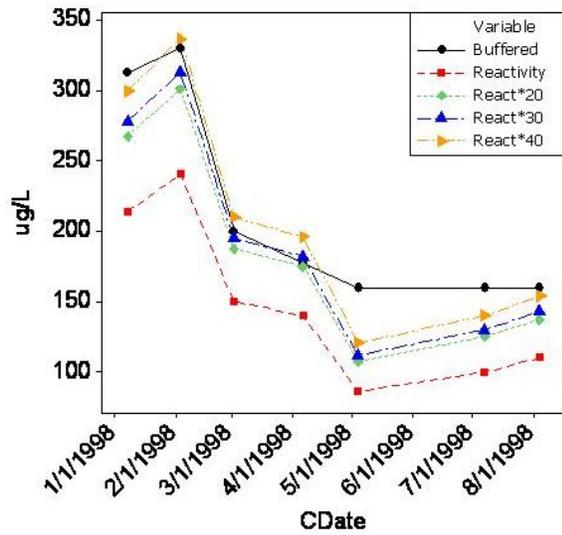


Note: CDate is collection (sampling) date

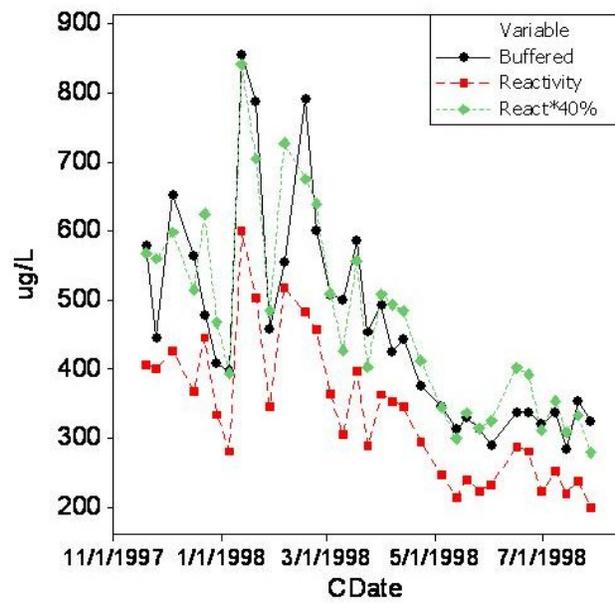
The remaining scatter plots are shown in Fig 2 and 3. These graphs show that Buffered and Reactivity follow what is theoretically to be expected. Buffered being a formation potential method is expected to convert more of the precursors to DBPs. The plots show actual data and also estimates of multiplying Reactivity to approximate Buffered. For example, Hood plots in Fig 2 are shown for Buffered, Reactivity, Reactivity raised by 20% (Reactivity multiplied by 1.2), 30% (Reactivity multiplied by 1.3), 40% (Reactivity multiplied by 1.4).

Fig 2. Scatter plots Buffered, Reactivity and Reactivity times a multiplier

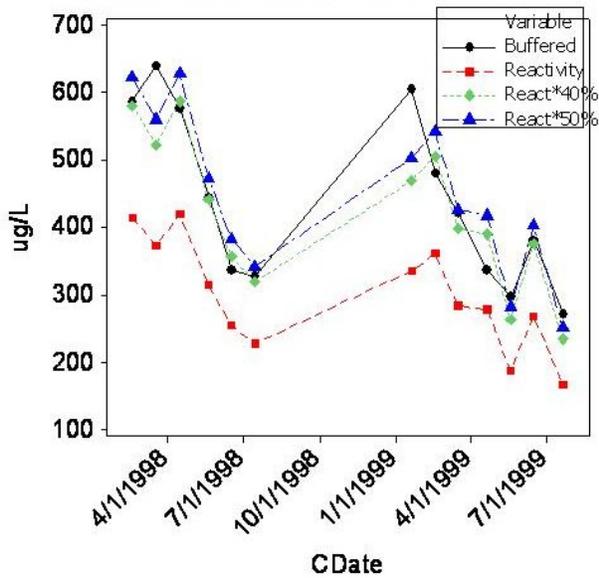
Hood Buffered, Reactivity, React*20, React*30, React*40



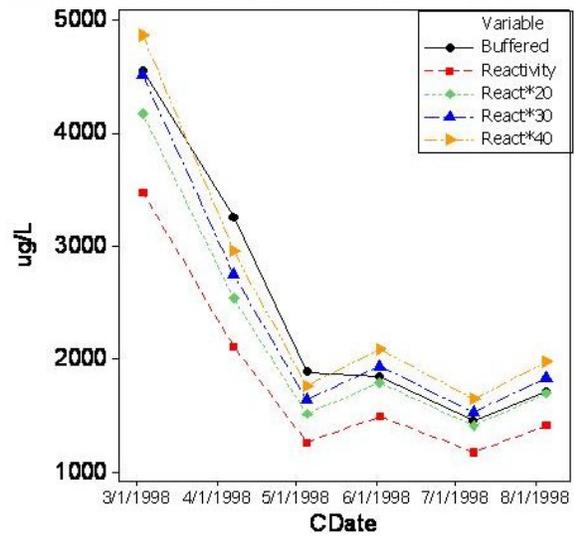
Vernalis Buffered, Reactivity, React +40%



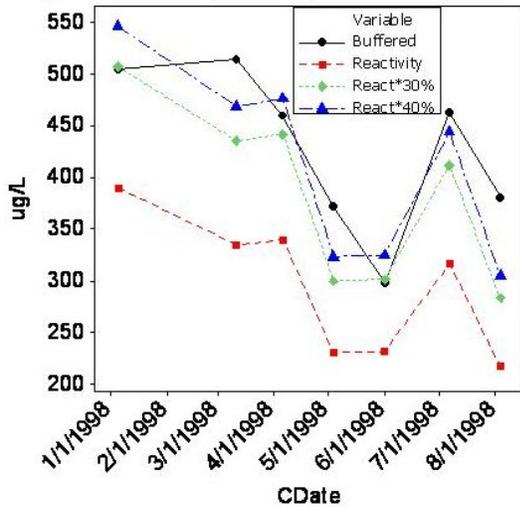
Banks Buffered, Reactivity, React +40%, React +50%



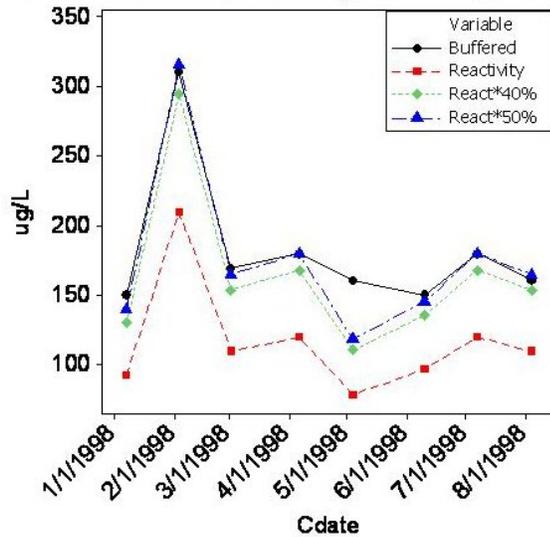
Twitchell Buffered, Reactivity, Reactivity +20%, +30%, +40%



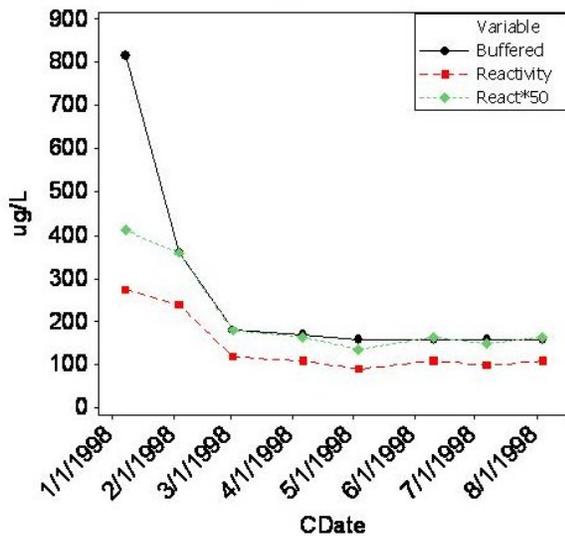
OldR@Bacon Buffered, Reactivity, React +30%, React +40%



American Buffered, Reactivity, React*40%, React*50%



Sac @ WSInt Buffered, Reactivity, React +50%



Regressions

Results of simple linear regressions of Reactivity as a predictor of Buffered are shown in Table 2-4. Stations with fewest samples are grouped together in Table 2. The tables show Buffered estimated by a regression equation of Reactivity (predictor) as well as by a simple multiplication Reactivity factor to estimate Buffered. Absolute deviations are the differences between measured Buffered and predicted Buffered. The same is repeated between measured Buffered and Buffered estimated by simple multiplication.

Fig 3. Scatter plots of measured and predicted Buffered at Banks and Vernalis

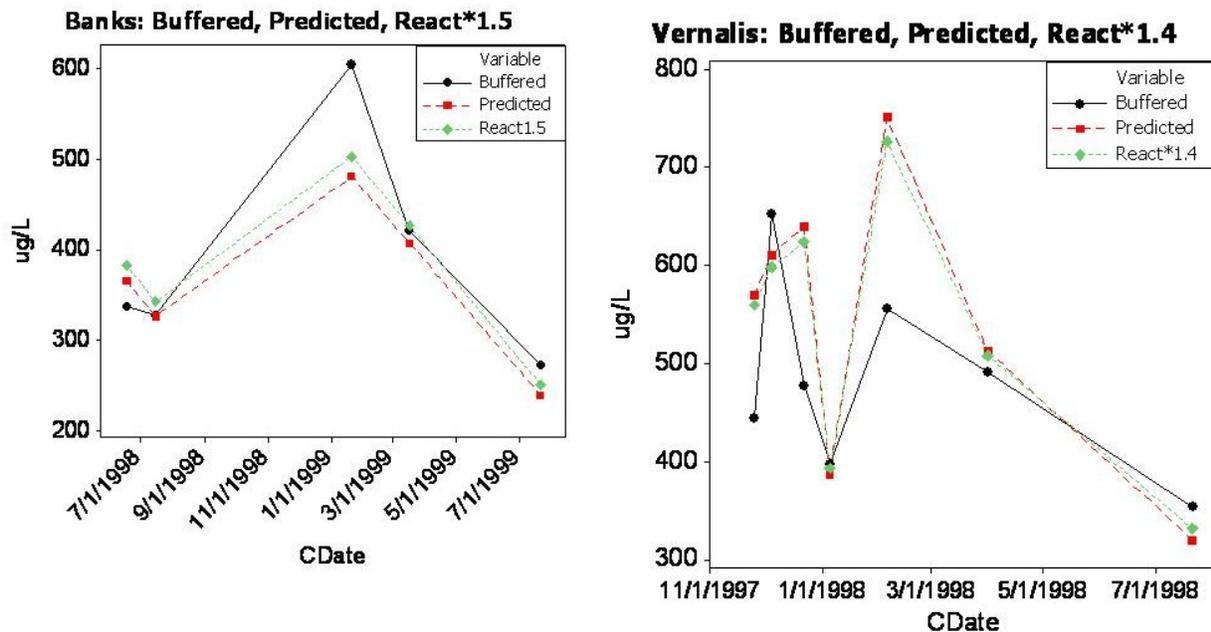


Table 2. Buffered estimated by regression and simple multiplier

Station	CDate	Observed Result ¹		Estimated Buffered		Absolute Deviations	
		Buffered	Reactivity	By Regression ²	Reactivity x multiplier	From Regression ³	From Multiplier ⁴
American	1/7/98	150	93	159	140 (150%)	6	10
American	2/3/98	310	210	224	315 (150%)	-28	5
Greenes/Hood	4/6/98	178	140	207	196 (140%)	16	9
OldR at Bacon	6/1/98	298	232	388	325 (140%)	30	2
SacWSInt	1/7/98	816	275	662	413 (150%)	-19	-7
SacWSInt	5/4/98	160	91	90	137 (150%)	-44	-49
Twitchell	7/8/98	1457	1173	1627	1525 (130%)	12	-15

¹Note: These results were not used in developing the regression equations (below)

²Regression equations

²Greenes/Hood: Buffered = 36.5 + (1.22*Reactivity); p = 0.000, R² = 95.8%

²Twitchell: Buffered = 79 + (1.32*Reactivity); p = 0.004, R² = 94%

²OldR at Bacon: Buffered = 192 + (0.843*Reactivity); p = 0.07, R² = 83.2%

²American: Buffered = 107 + (0.559*Reactivity); p = 0.103, R² = 40.8%

²SacR @ W. Sac Intake: Buffered = -193 + (3.11*Reactivity); p = 0.013, R² = 77.3%

³Absolute Deviation = ((Predicted - Observed Buffered)/Observed Buffered)*100. Predicted calculated by regression

⁴Absolute Deviation = ((Predicted - Observed Buffered)/Observed Buffered)*100). Predicted calculated by multiplier i.e. Column G in table above

Table 3. Buffered estimated by regression and simple multiplier at Banks

Station	CDate	Observed Result ¹		Estimated Buffered		Absolute Deviations	
		Buffered	Reactivity	By Regression ²	By multiplier: Buffered = (Reactivity*1.5)	From Regression ³	From Multiplier ⁴
Banks	6/17/1998	337	255	365	383	8	14
Banks	7/15/1998	328	228	326	342	0	4
Banks	1/20/1999	604	335	481	503	-20	-17
Banks	3/17/1999	421	284	407	426	-3	1
Banks	7/21/1999	272	167	239	251	-12	-8

¹Note: These samples were not used to develop the regression equation (below)

²Regression equation

Buffered = - 1.9 + (1.44*Reactivity); p = 0.001, R² = 81.0%

³Absolute Deviation = ((Predicted - Observed Buffered)/Observed Buffered)*100). Predicted calculated by regression

⁴Absolute Deviation = ((Predicted - Observed Buffered)/Observed Buffered)*100). Predicted calculated by multiplier i.e. Column F in table above

Table 4. Vernalis Buffered THMFPs estimated by regression and by simple multiplier

Station	CDate	Observed Result ¹		Estimated Buffered		Absolute Deviations (%)	
		Buffered	Reactivity	By Regression ²	By multiplier: Buffered = (Reactivity*1.4)	From Regression ³	From Multiplier ⁴
Vernalis	11/25/1997	445	400	569	560	28	26
Vernalis	12/4/1997	652	427	611	598	-6	-8
Vernalis	12/22/1997	478	446	640	624	34	31
Vernalis	1/5/1998	398	281	387	393	-3	-1
Vernalis	2/5/1998	556	519	751	727	35	31
Vernalis	4/1/1998	492	363	513	508	4	3
Vernalis	7/21/1998	354	237	320	332	-10	-6

¹Note: These samples were not used to develop the regression equation (below)

²Regression equation

Buffered = - 42.7 + (1.53*Reactivity); p = 0.000, R² = 91.8%

³Absolute Deviation = ((Predicted - Observed Buffered)/Observed Buffered)*100). Predicted calculated by regression

⁴Absolute Deviation = ((Predicted - Observed Buffered)/Observed Buffered)*100). Predicted calculated by multiplier i.e. Column F in table above

Discussion

The scatter plots show that in general, Reactivity was always lower than Buffered at all the stations (disregarding AgDrain at Bacon Is). Reactivity and Buffered correlated fairly well based on the scatter plots. Regressions of Reactivity as a predictor of Buffered were significant at all the stations except American. Disregarding American, R^2 ranged from 82% to 96% indicating Reactivity could predict Buffered, Table 2-4. A confounding observation at American was using all the data (without omitting 2 for verification) improved the regression significantly (Buffered = $31.7 + 1.29$ Reactivity; $p = 0.000$, $R^2 = 93.6\%$). Scatter plots of validation samples at Banks and Vernalis (where there were enough samples to provide meaningful graphs) indicated that at these stations, a simple multiplier may work just as good as a regression equation (Fig 3). The overall observation was that neither regression nor using a multiplier provides a perfect prediction.

In the past, attempts have been made to relate high dose formation potentials to THMs at a water treatment plant (Hutton and Chung 1994, Reckhow and Edzwald 1991). Hutton and Chung used absolute deviations between DWR Buffered and simulated distribution system (SDS) data and observed that for total THMs, the majority of the deviations fell in the 0-10% and few in the 11-20% ranges. In this study, the deviations are a lot higher than that. In Table 2, about half of the deviations were in the 11-20% range and the rest were above that. In Table 3 (Banks), the deviations were better with all of them below 20%. At Vernalis (Table 4), slightly more than half of the deviations were between 10-20% and the others were above 20%. These observations indicate that there is more variation between Buffered and Reactivity than between Buffered and SDS.

However, these deviations are not all that bad when compared to the relative (not absolute) deviations that Bryte uses for other types of analyses. For example, the acceptable RPDs for duplicate DOC/TOC is 30%. (There is a small difference in relative and absolute differences). Thus using the 30% RPD limit, only one (SacWSInt) out of seven comparisons would have been an exceedance in Table 2. All the comparisons at Banks would have been within limits. Two out of seven comparisons at Vernalis would have exceeded the limit.

Conclusions

There are occasions when it is necessary to compare data generated by one analytical method to those of another related method for several reasons. One method may be a lot cheaper, or faster or easier than the other. For example in DWR Buffered, organic carbon is estimated using UVA to determine if dilution is necessary – UVA is faster and cheaper than conducting a full DOC analysis. Analytical methods become superseded by new ones in long term monitoring. In long term trend analysis, it is inevitable that newer often more precise methods will be used alongside data generated by older methods. Obviously, data by new and older methods are most likely to prove statistically significantly different (although this problem may also occur for concurrently used up-to-date methods, a problem we have discussed using equivalence). Conversion factors are not without limitations because of the inherent variability found in chemical analysis. Taking that caveat into consideration, it appears from this project as well as others (Hutton and Chung 1994) that it will be possible to convert future THMFP data analyzed using SM 5710B to historical DWR Buffered method.

Literature Cited

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Krasner SW, Sclimenti MJ, Means EG. 1994. Quality degradation: Implications for DBP formation. *Journal of the American Water Works Foundation* 86: 34-47.

Reckhow DA, Edzwald JK. 1991. Bromoform and iodoform formation potential tests as surrogates for THM formation potential. *Journal of American Water Works Association*: 67-73.