VOLATILIZATION OF BROMODICHLOROMETHANE FROM CHLORINATED DRINKING WATER AS A CONTRIBUTOR TO RESIDENTIAL INDOOR AIR RISK

FOSTER, S. J., KURTZ, J.P. AND WOODLAND, A. K.

ABSTRACT

The US EPA has classified bromodichloromethane (BrDCM) as a B2 carcinogen but IRIS does not provide an inhalation Cancer Slope Factor. The OSWER Vapor Intrusion Guidance gives a provisional indoor air goal of 0.14 ug/m^3 (10^{-6} risk) derived from an Ingestion Slope Factor. This low goal has the potential to bring BrDCM under regulatory scrutiny. BrDCM and chloroform are common drinking water disinfection by-products. Therefore, background levels of BrDCM and chloroform are important when evaluating indoor air risks and distinguishing them from groundwater derived indoor air contamination. A Denver indoor air database of more than 1000 residential samples, collected over a five year time frame, was used to show that background indoor air BrDCM levels exceed the VI goal, with a median concentration of 0.32 ug/m^3 and a 95th percentile of 1.3 ug/m^3. Chloroform and BrDCM concentrations strongly correlate (r = 0.8) in indoor air. Drinking water and indoor air BrDCM to chloroform concentration ratios both show strong seasonal variability with the ratio varying by an order of magnitude between seasons. Volatile disinfection by-products are released into houses when tap water is used for showering, bathing, etc. The contributions of chloroform and BrDCM to indoor air from tap water were modeled using various EPA models. The results indicate that the ranges of chloroform and BrDCM in indoor air are consistent with tap water use.

INTRODUCTION

The US EPA's IRIS database (EPA, 2004) identifies bromodichloromethane (BrDCM) as a B2 carcinogen, but this database does not provide an inhalation cancer slope factor at this time. However, when the Office of Solid Waste and Emergency Response (OSWER) issued their Draft Vapor Intrusion Guidance (EPA, 2002) it listed a target indoor air concentration of 0.14 µg/m^3 at a risk level of one in one million (10^{-6}). This value was derived from a unit risk factor of 1.8 x 10-5 (µg/m^3)$^{-1}$ extrapolated from an oral slope factor. Investigations of indoor air at the CDOT MTL site in Denver have shown that BrDCM is present in indoor air at concentrations in excess of 0.14 µg/m^3 due to non-groundwater sources. Domestic tap water is a source of BrDCM and chloroform due to the disinfection process and this paper investigates the relationship between this source of BrDCM and chloroform and indoor air concentrations. Using modeling procedures from EPA it is possible to show that indoor air concentrations can be estimated with a reasonable decree of accuracy using tap water as the source of BRDCM and chloroform.

INDOOR AIR DATA

CDOT MTL Site residential indoor air data from October 1998 through December 2003 was evaluated for relationships between BrDCM and the other ten detected TO-15 SIM compounds. These indoor air sampling data were collected in SUMMA canisters and analyzed by either STL or ATL with low reporting limits for both BrDCM (0.075 µg/m^3) and chloroform (0.07 µg/m^3). Of the 1971 total residential indoor air samples, 1042 (53%) had detectable levels of BrDCM. These 1042 samples with detectable BrDCM were further evaluated as discussed below. A subset of these data has been used to evaluate background indoor air levels in the Denver area and will not be repeated here (EPA, 2001) (Foster, 2002).

RESULTS: CHLOROFORM-BROMODICHLOROMETHANE CORRELATION

Initially, correlations between the natural logs of the concentrations of the 11 SIM compounds were evaluated for the 1042 samples. All of the variables were composed of log-normal populations. The only significant correlation observed with BrDCM was one with chloroform (R=0.797) (Figure 1).

Groundwater and indoor air at the CDOT MTL site are currently undergoing remediation due to the presence of 1,1,1-TCA, TCE and 1,1-DCE. Prior to indoor air remediation these groundwater chemicals have correlated with the same chemicals in indoor air. Figures 2 and 3 respectively illustrate the lack of correlation between BrDCM and 1,1-DCE and between chloroform and 1,1-DCE, the chemical selected as a vapor intrusion indicator at the site. These data indicate that BrDCM and chloroform are not site related. Indoor air remediation systems at the site form an effective barrier between groundwater and indoor air, and indoor air is monitored for the presence of 1,1-DCE as confirmation of the effectiveness of the remediation system.

As a confirmation of the results for the above samples, that include pre and post remediation data, a second correlation between chloroform and BrDCM was computed for post remediation data only (R=0.82) (Figure 4). This correlation yields essentially identical results to that for all BrDCM detections.

There are a few anomalously high chloroform concentrations that fall far from the correlation line. These few results are likely due to an additional chloroform source in indoor air that is lacking in BrDCM. It has been noted (Sack, 1992) that several consumer products (household cleaners and fabric/leather treatment products) contain moderate levels of chloroform. Use of these in a residence on rare occasions could certainly produce the few anomalous results.

The indoor air data was evaluated for houses and apartments separately. The results are shown in Table 3 and it can be seen that houses have, on average, lower indoor air concentrations than apartments.

It is considered most likely that the BrDCM and chloroform in indoor air are derived from volatilization from tap water. In order to evaluate this more fully, the ratio of BrDCM to chloroform in indoor air was computed and plotted against the indoor air chloroform concentration (Figure 5). This plot shows the highly consistent ratio between these two VOCs. The high concentration end of this plot again shows the few anomalously chloroform-rich samples. Summary statistics for these are provided in Table 1. Further evidence for tap water as the source of indoor air BrDCM and chloroform is provided in Figure 6, which show the seasonality of the ratio of BrDCM top chloroform in tap water and the corresponding ratios for indoor air in Figure 7.

CHEMICAL SOURCES

The tap water supplied to the CDOT MTL site was supplied by the City of Glendale and the City of Denver. Glendale drinking water data for BrDCM and chloroform was supplied by the City of Denver. Median tap water BrDCM and chloroform concentrations used in this study were 9 and 23 µg/L, respectively. Chloroform levels were more variable than BrDCM levels.

ESTIMATION OF INDOOR AIR CONCENTRATIONS FROM TAP WATER

Approach to Parameter Estimation

As tap water is used in a household, volatile constituents are released into indoor air. The human activities that will release most volatile constituents are showering, bathing, dishwashing and washing clothing. These activities both consume large volumes of water and heat the water, leading to increased volatilization. Other activities will contribute volatile constituents, but to a lesser degree. It is possible to model the release of VOC from water, and a recent EPA publication (EPA, 2000a) provides the basis for the work contained in this poster. However, each of the human activities described (showering, bathing, etc.) releases VOC in the home over a relatively short period of time (10-30 minutes). When released, indoor air VOC concentrations will reach a maximum during the activity but will decrease as they are diluted by cleaner air entering the building. The number of clean air exchanges per 24-hour period will dictate how rapidly these VOC concentrations fall.

The mass of BrDCM and chloroform available to enter indoor air over a 24-hour period is given by the concentration of each constituent in tap water, the amount of water used and the efficiency with which the VOC leave the water into the atmosphere. The mass of VOC enters the air and can be modeled using indoor air-modeling procedures, as described in the EPA's J-E model (EPA, 2000b), that can be employed to determine the average 24-hour concentration. In this paper the average BrDCM and chloroform levels in tap water in the study area give the mass of VOC available. The four water-consuming activities (showering, bathing, dishwashing and clothes washing) were assumed to provide the majority of the VOC releases into indoor air. Other activities were assumed to be minor and contribute less to the error in the estimation that one or more of these activities. Rather than modeling each of these human activities to provide estimated concentrations into the room where the VOCs are released, the mass of VOC released was estimated for each activity. The mass released by each activity was modeled into the house over 24-hours. The estimated concentrations were derived by assuming that the VOC released into the building were evenly dispersed throughout the building.

VOC Releases from Household Appliances

VOC releases from household activities and appliances were estimated for selected VOC based on work by EPA (EPA, 2000a). This work provided release efficiencies for many VOC, but not BrDCM or chloroform. The release efficiencies described in EPA 2000b were used as the basis for BrDCM and chloroform from showering, bathing, dishwashing and clothes washing. Table 2 provides the release efficiencies used in this paper, and the basis for their selection. These efficiencies were either calculated using the algorithm provided, or estimated by extrapolation.

Indoor air concentrations were estimated for each activity using the following equation.

$$C_{building}\ (\mu g/m^3) = E / Q_{building}$$

Where:

$C_{building}$ = Indoor air concentration ($\mu g/m^3$)
E = Emissions rate into the building ($\mu g/s$)
= $C_w * V_w * PR$
C_w = Concentration in tap water ($\mu g/L$)
V_w = Volume of water used (L)
PR = Percent released
$Q_{building}$ = Building ventilation rate (m^3/s)

	=	$(L_b * W_b * H_b * ER) / 3{,}600$ s/h
L_b	=	Building length (m)
W_b	=	Building height (m)
H_b	=	Building height (m)
ER	=	Air exchange rate (1/h)

MODELING RESULTS

Estimated versus Measured VOC Concentrations

The results of the estimated indoor air concentrations compared to measured indoor air concentrations for apartments and houses are shown in Table 3. It can be seen from this table that there is fairly good agreement between the estimated concentration and the measured concentration for both houses and apartments. They are generally within a factor of three, with the estimated concentration being higher then the measured concentration. Both the estimated and measured are based on average 24-hour VOC concentrations.

The overestimate in indoor air concentrations could be due to:

- The assumptions in the source estimates are too high and the volume of water used in the house/apartment is actually lower than that assumed.
- The percentage of VOC actually released from tap water is lower than that used in the calculation.
- The assumption that VOC sources are evenly distributed throughout the house when in reality they are limited to small rooms, such as the bathroom or kitchen, in upper areas of the house while the indoor air samples were typically collected in the basement. Dispersion from these smaller rooms might occur slowly and the VOC may not actually reach the sampling equipment in the amounts expected from the assumption in the model.

The estimated and measured VOC concentrations in apartments were higher than houses. This is probably due to the smaller dimensions of the apartment and use of the same air exchange rates as in houses. Even though there is probably less human activity in an apartment, apartments probably have lower air exchange rates for a number of reasons. They may be in the center of a larger building protected from direct ventilation to the outdoors by a common entry way or other apartments and they are less likely to used forced air or furnace type central heating. However, the magnitude of difference between measured and estimated indoor air BrDCM and chloroform concentration is close.

It can also be seen from Table 3 that the ratio of BrDCM to chloroform was consistent for both measured and estimated indoor data. In the model used to estimate VOC concentrations this ratio is dependent on the release efficiency of BrDCM and chloroform from tap water. The release efficiency of chloroform was either calculated, as for the showering scenario, from the chemical's Henry's Law constant, or extrapolated from the data proved by EPA 2000a. Chloroform's Henry's Law constant was similar to that of ethyl benzene, which was evaluated in EPA 2000a. However, the Henry's Law constant for BrDCM was not close to any of the VOC evaluated in EPA 2000a and the extrapolation used could lead to an inaccurate release efficiency from water. It was found that by assuming different loss efficiency for BrDCM the ratio of BrDCM to CCl_4 ranged from 0.09 (assuming an efficiency similar to acetone) to 0.3 (assuming an efficiency similar to chloroform). The actual values used were between these two chemicals.

CONCLUSION

It has been shown from data collected at the CDOT MTL site, from both pre- and post-remediated dwellings, that chloroform and bromodichloromethane in tap water correlates with indoor air chloroform and bromodichloromethane concentrations. It has also been shown that modeled indoor air concentrations, based on starting levels of chloroform and bromodichloromethane in tap water, lead to concentrations that are within a factor of three of actual measured concentrations. The modeled levels are higher than those found in indoor air. The ratio of bromodichloromethane to chloroform in modeled indoor air is also consistent with the ratio of bromodichloromethane to chloroform measure in indoor air. This information should be strongly considered when establishing indoor air remediation goals for site with vapor intrusion of chloroform and/or bromodichloromethane from soil or groundwater.

TABLES

Table 1. Descriptive Statistics for BrDCM and Chloroform in Residential Indoor Air

Chemical	Sample Number	Minimum	Maximum	Mean	Std.Dev.	95%
Chloroform	1042	0.15	50.0	2.24	3.54	2.45
BrDCM	1042	0.04	10.0	0.48	0.59	0.51
BrDCM/Chloroform	1042	0.01	13.9	0.29	0.44	0.32

Table 2
Release Rates From Tap Water VOC

		Chemical Release Efficiencies		
Activity	Water Volume (Liters)	Chloroform	BrDCM	Source and Basis
Showering	220	53%	46.5 %	7.95ln(H) + 68.2
Bathing	220	32%	25%	Ethyl benzene and extrapolation
Dishwashing	55	98%	75%	Ethyl benzene and extrapolation
Clothes washing	110	35%	15%	Ethyl benzene and extrapolation

Table 3
Modeled and Measured Indoor Air VOC Concentrations

Volatile Chemical	Estimate House Conc. (µg/m^3)	Measured House Conc. (µg/m^3)	Estimate Apartment Conc. (µg/m^3)	Measured Apartment Conc. (µg/m^3)
Chloroform	2.31	0.98	2.76	1.6
BrDCM	0.67	0.22	0.75	0.33
Ratio BrDCM/CCl_4	0.29	0.22	0.27	0.21

FIGURE 1. INDOOR AIR CORRELATION OF BRDCM WITH CHLOROFORM

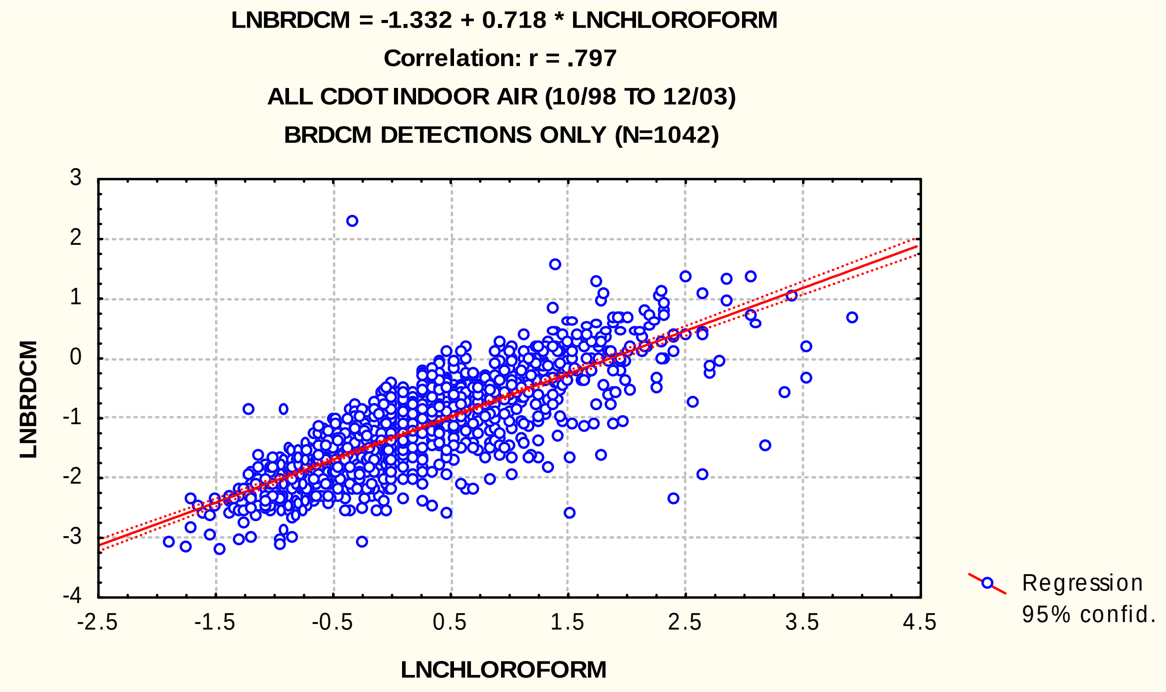


FIGURE 2. RELATIONSHIP BETWEEN INDOOR AIR 1,1-DCE AND BRDCM

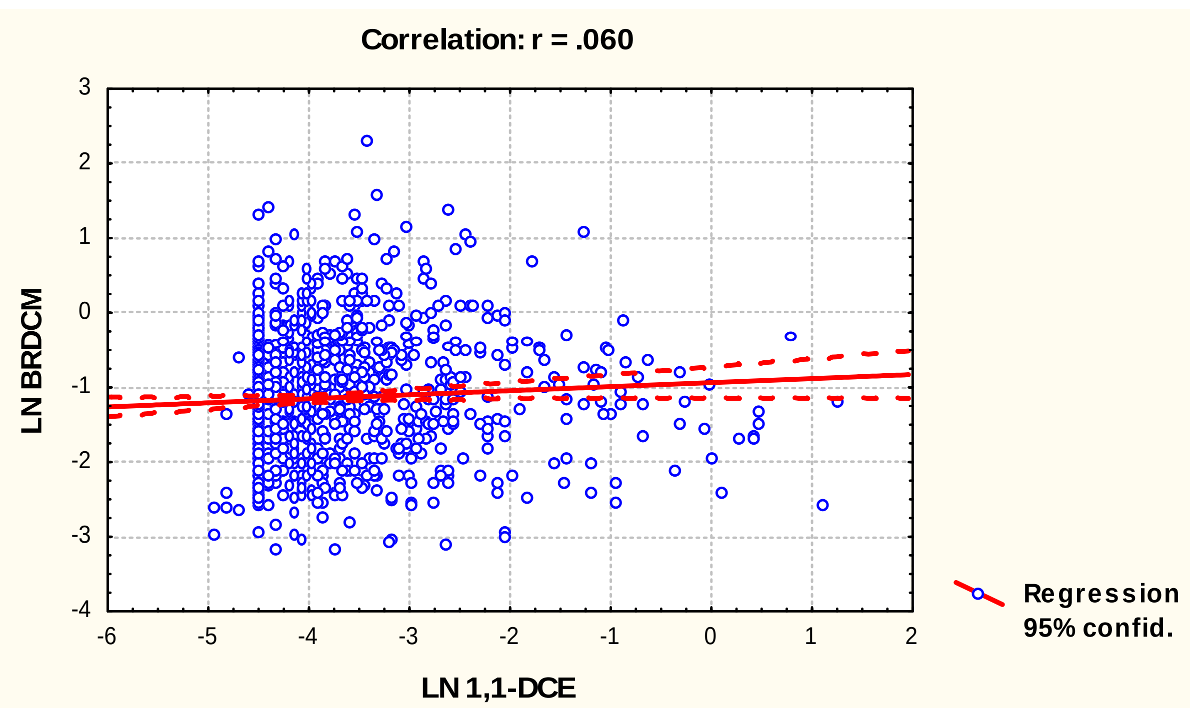


FIGURE 3. RELATIONSHIP BETWEEN INDOOR AIR CHLOROFORM AND 1,1-DCE

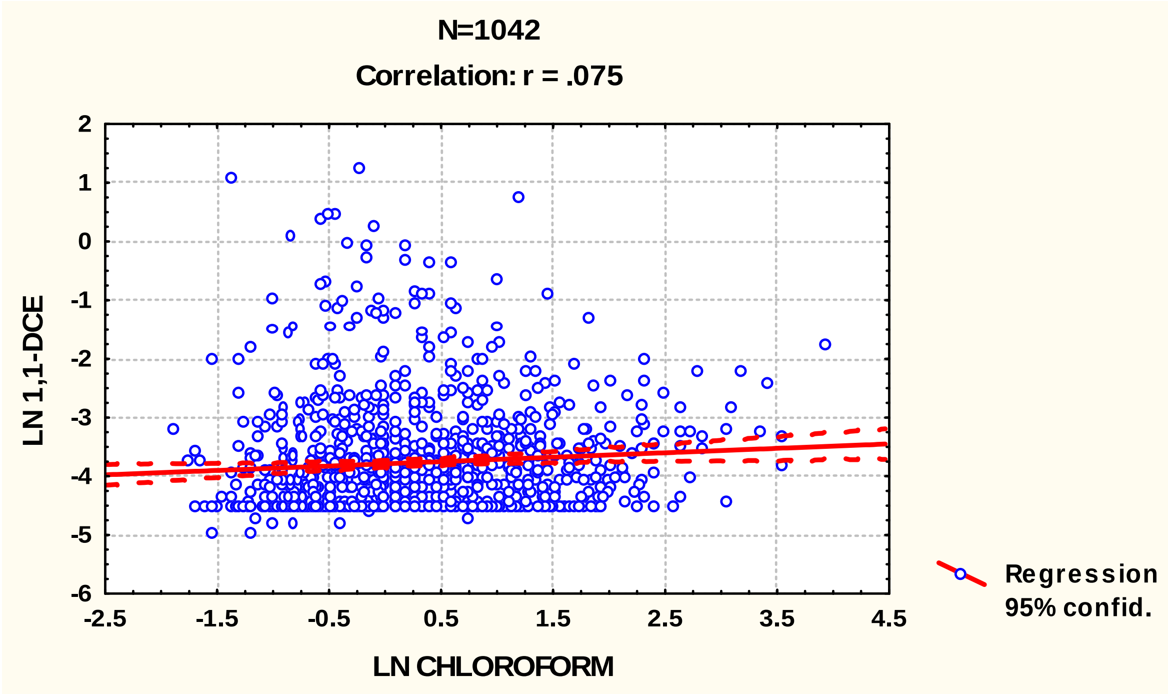


FIGURE 4. CORRELATION OF POST-REMEDIATION DATA FOR BRDCM AND CHLOROFORM

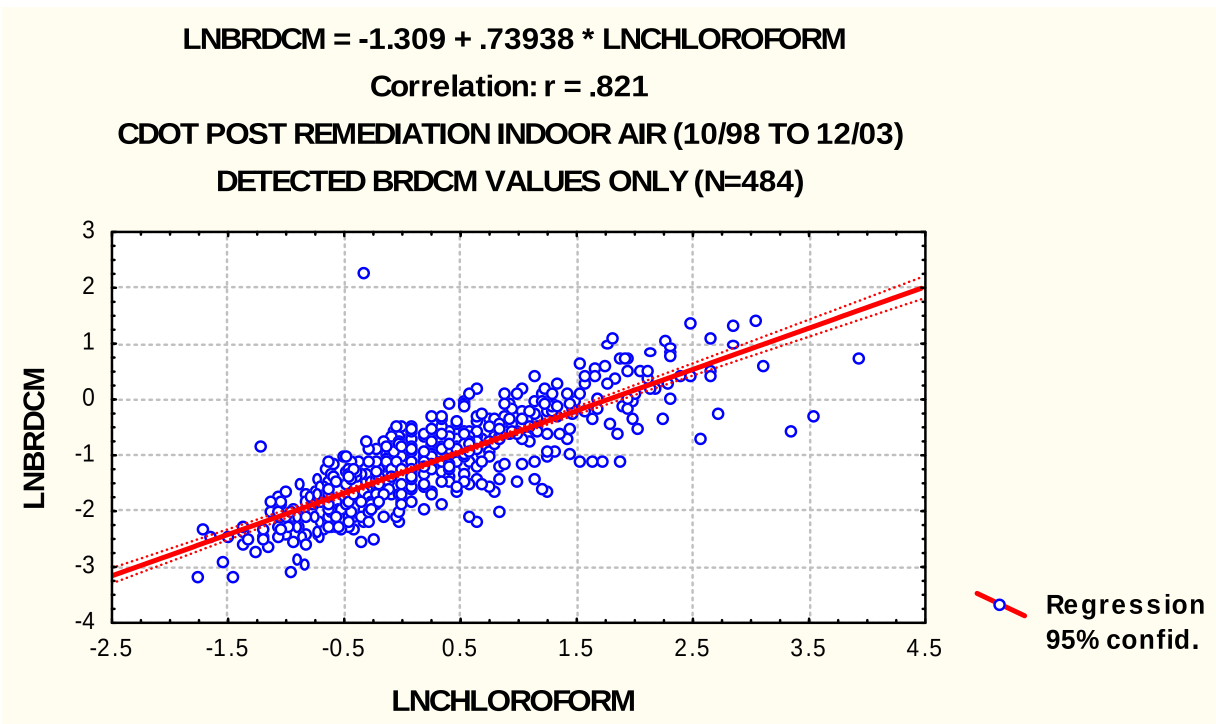


FIGURE 5. CORRELATION OF CHLOROFORM WITH BRDCM/CHLOROFORM

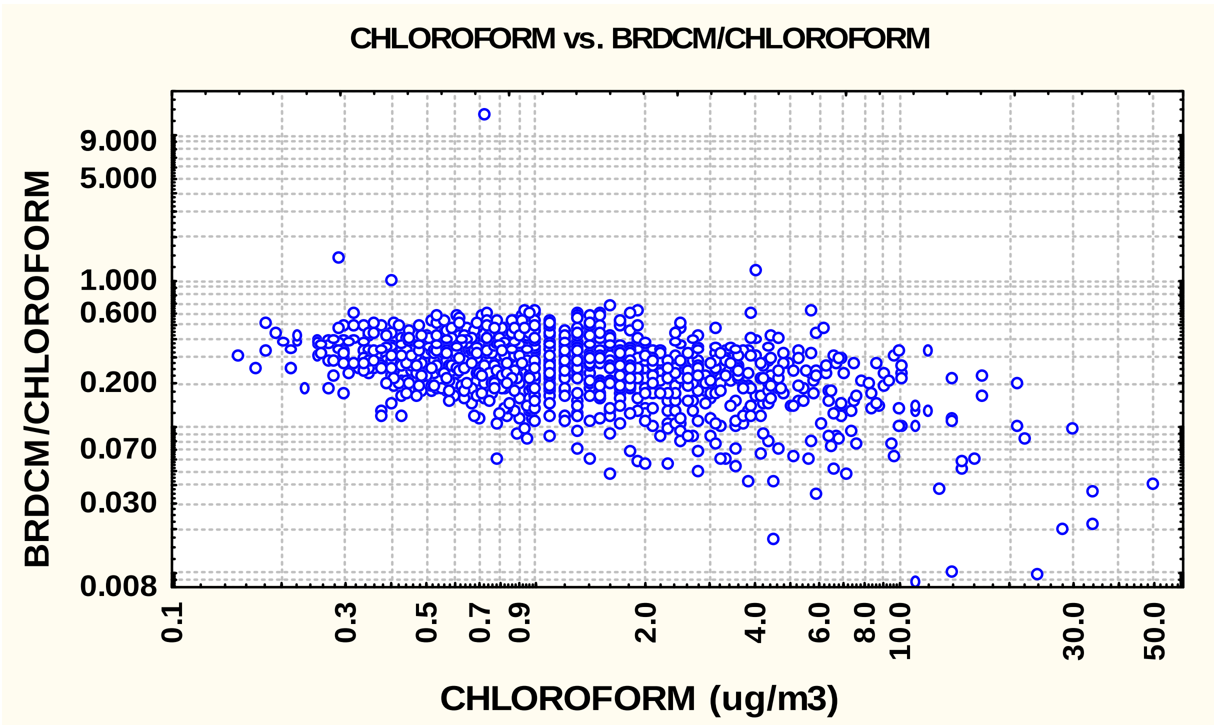


FIGURE 6. BRDCM/CHLOROFORM RATIO IN TAP WATER WITH TIME

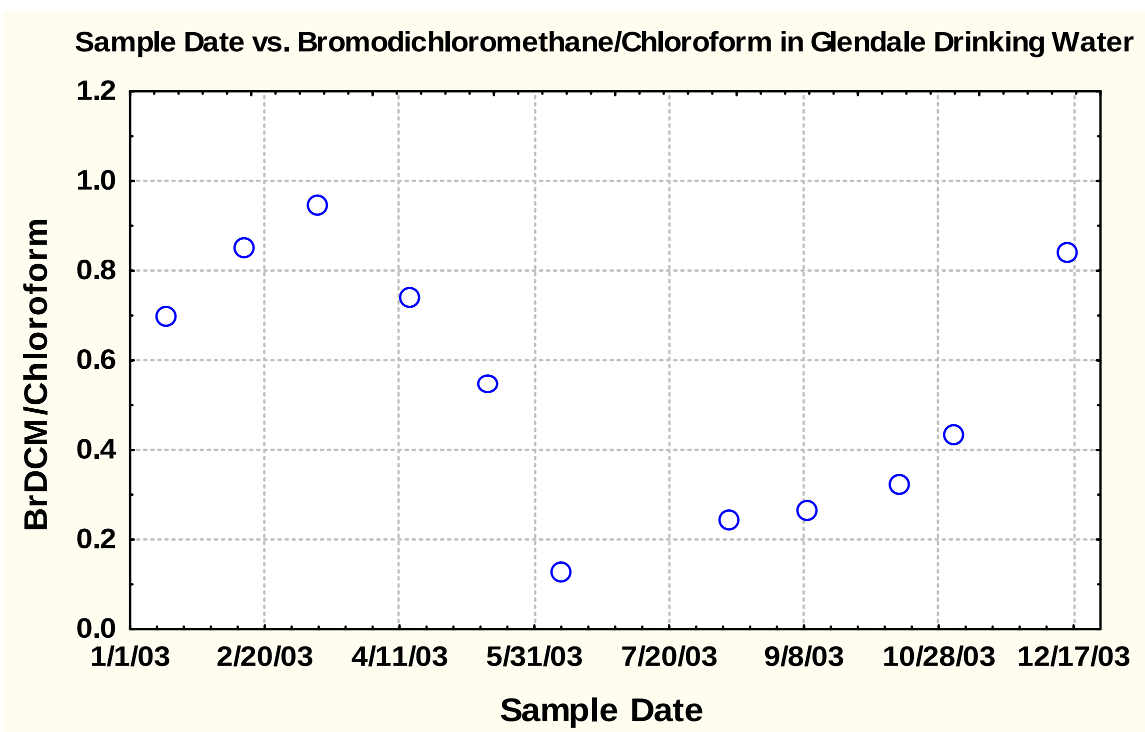
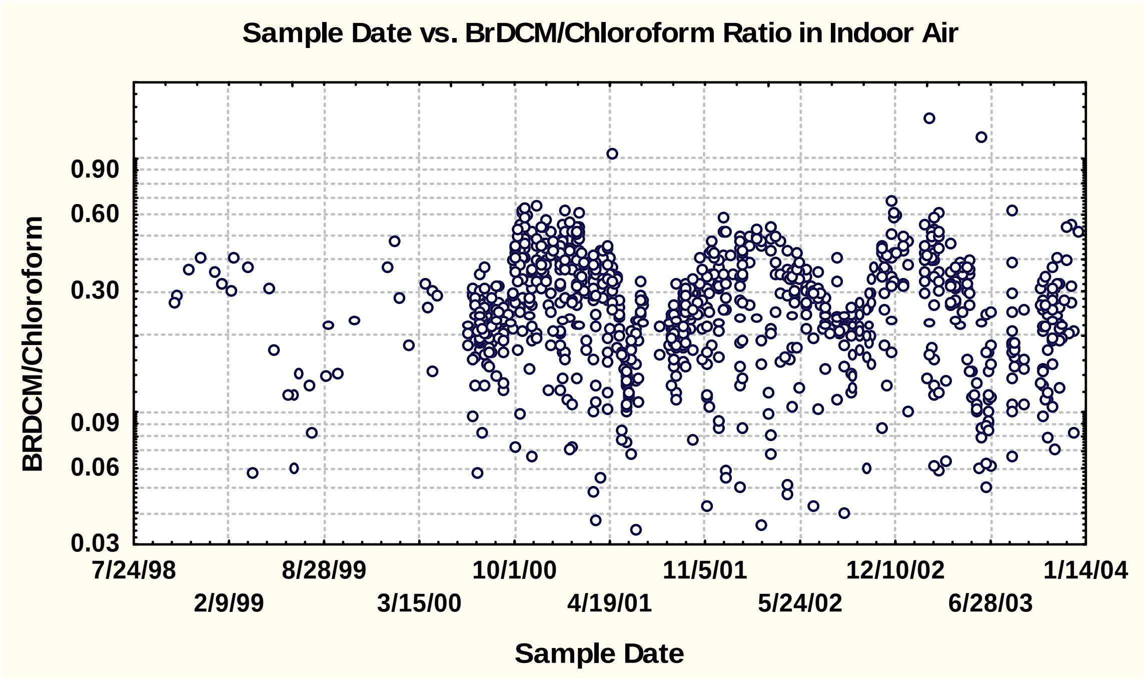


FIGURE 7. BRDCM/CHLOROFORM RATIO IN INDOOR AIR WITH TIME



REFERENCES

EPA. (2000a). Volatilization Rates from Water to Indoor Air, Phase II. In National Center for Environmental Assessment (Ed.):Office of Research and Development.

EPA. (2000b). User's Guide for the Johnson and Ettinger (1991) Model for Subsurface Vapor Intrusion into Buildings. In OERR (Ed.):OERR.

EPA. (2001). Draft Guidance for Evaluating Vapor Intrusion to Indoor Air Pathways from Groundwater and Soils (Subsurface Vapor Intrusion Guidance). In OSWER (Ed.):US EPA, OSWER.

EPA. (2002). Draft Guidance for Evaluating Vapor Intrusion to Indoor Air Pathways from Groundwater and Soils (Subsurface Vapor Intrusion Guidance). In OSWER (Ed.):US EPA, OSWER.

EPA. (2004). Integrated Risk Information System.

Foster, S. J., Kurtz, J.P. & Woodland, A.K. (2002, June 30, 2002). *Background Indoor air risks at selected residences in Denver Colorado.* Paper presented at the Indoor Air 2002, Monterey, California.

Sack, T. M., Steele, D.H., Hammerstrom, K and Remmers, J. (1992). A Survey of Household Products for Volatile Organic Compounds. *Atmospheric Environment, 26A*(No. 6), 1063-1070.