Differentiation of Volatile Organic Compounds Content of Source, Bottled and Tap waters by Purge and Trap GC-MS: Are There Human Health Risks from Consumption of Drinking waters?

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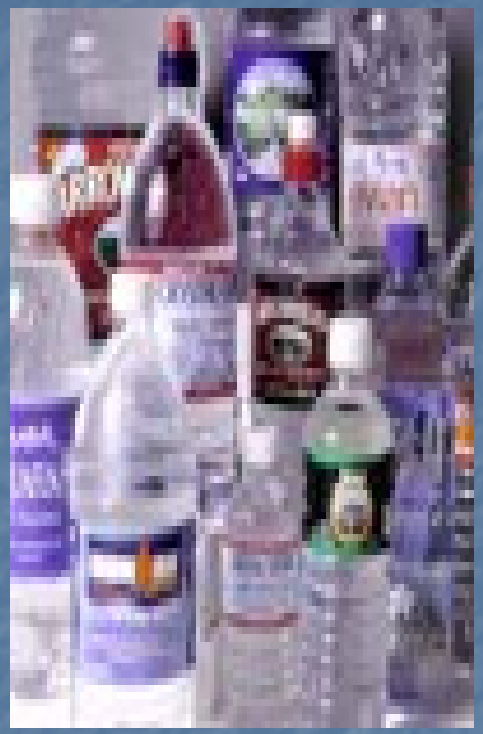
Drinking Water Types

- **Artesian Water** (originates from a confined aquifer).
- **Mineral Water** (> 250 ppm TDS).
- **Purified Water** (treatment: D, DI, RO).
- **Sparkling Water** (carbon dioxide).
- **Spring Water (**underground formation from which water flows naturally to the Earth's surface).
- **Distilled water** (No minerals or ions).
- **Tap water** (treated ground or surface water).



Bottled Water Consumption

- The average American drank 23.8 gallons of bottled water in 2004, up from 22.1 gallons in 2003, according to the International Bottled Water Association.
- Americans drink more bottled water than milk, beer or coffee.
- Notion: Bottled water comes from pristine springs and lakes.

Tap water Worries

- According to the National Water Quality Association, 56% of North Americans are worried about the quality of municipally treated tap water. This, along with the desire for better tasting drinking water, has fueled the tremendous growth of the bottled water industry.
- In many communities in United States, the water that comes out of the tap could be contaminated with scores of chemicals.
- Most common among the chemicals found were disinfection byproducts, nitrates, chloroform, barium, arsenic and copper.

TRIHALOMETHANES (THMs)

- Chloroform
- Bromodichloromethane
- Dibromochloromethane
- Bromoform

Objectives of Study

- (1) to evaluate the differences in concentrations of THMs in bottled, municipal (tap water) and source waters (Missouri river)
- (2) to evaluate possible human health risks from drinking waters containing organic precursors
- (3) investigate the efficiencies of three adsorbents to remove volatile organic compounds (VOCs) from drinking waters (On going expts).

Water Sampling/Collection

- Source: Missouri River by Jefferson city (N= 30)
- Tap: Jefferson City, Columbia (N=34)
- Bottled: Various brands from Supermarket chains
  - Spring (N=25)
  - Purified (N=58)
  - Distilled (N=12)
  - Flavored (N=34)

Table 1: Information for analyzed bottled water brands

Brand Code	Brand Name	Bottled water Type	Container	Capacity	N
1	Fiji	Spring	Plastic	500 ml	9
2	Dasani	Purified	Plastic	500 ml	7
3	Nestle	Purified	Plastic	0.5 L	7
4	Aquafina	Purified	Plastic	710 ml	10
5	Spring	Spring	Plastic	330 ml	8
6	Nursery	Purified	Plastic	280 ml	10
7	Kroger	Purified	Plastic	500 ml	7
8	Evian	Purified	Plastic	500 ml	8
9	Best Choice	Purified	Plastic	0.5 L	7
10	Ozarka	Spring	Plastic	0.5 L	8
11	Dillions	Distilled	Plastic	1 gal	6
12	Central	Distilled	Plastic	1 gal	4
13	Best Choice	Purified	Plastic	1 gal	2
14	Hinckley	Purified	Plastic	1 gal	2
15	Fruit$_2$O	Fruited/Sparkling	Plastic	473 ml	9[d]
16	Dasani	Fruited/Sparkling	Plastic	500 ml	7[e]
17	Dasani	Fruited/Sparkling	Plastic	500 ml	6[e]
18	Aquafina	Fruited/Sparkling	Plastic	500 ml	6[f]
19	Nestle	Purified	Plastic	0.5 L	6[g]

EXPERIMENTAL

Purge & Trap GC-MS system (US EPA Method 524.2: VOCs in Drinking Water and Wastewaters)

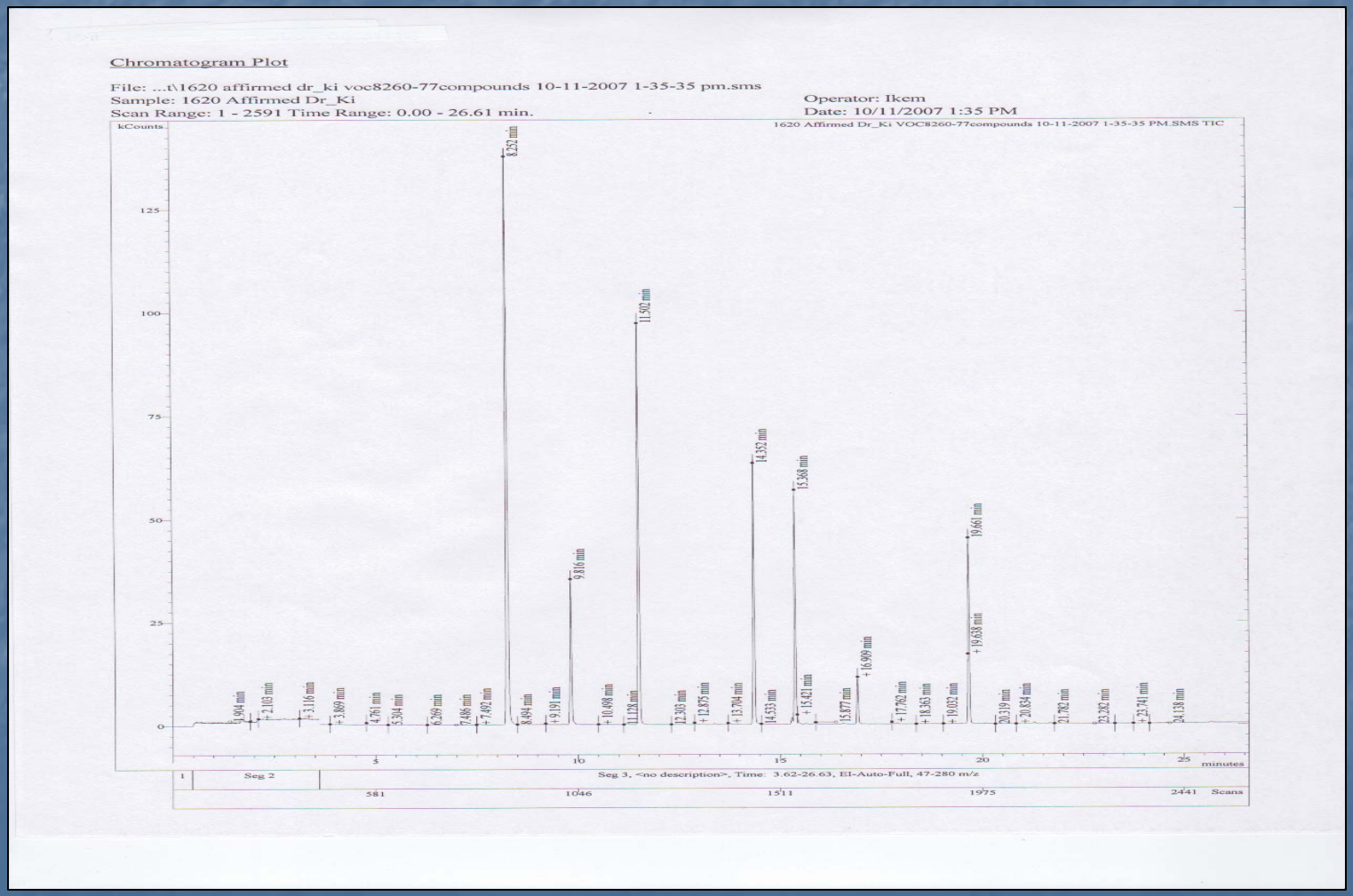
Capillary Column

VOCs Analysis (GC-MS Purge & Trap conditions)

- Internal/surrogate standard
  - Fluorobenzene (internal standard)
  - 4-Bromofluorobenzene (surrogate)
  - 1, 2-Dichlorobenzene-d4 (surrogate)
- Calibration VOC mixes (containing 63 analytes)
- Purge and Trap condition: 25 ml purge vessel (VOCARB 4000 Trap) and 40 ml/min helium purge flow. Line temperature: 120 oC, Turbo cool temperature: 30 oC, Valve temperature: 130 oC, mount temperature: 40 oC, MCS line temperature: 120 oC, purge ready temperature: 30 oC. Sample heater OFF, prepare time: 0.00 min, sample preheat time: 0.00 min, purge time: 11 min, dry purge time: 0.0 min, MCS desorb temperature: 40 oC, GC start option: start of desorb, GC cycle time 35 min, Cryo focuser: OFF, desorb preheat: 250 oC, desorb time: 4 min, desorb temperature: 250 oC, sample drain: ON, bake time: 7 min, bake temperature: 260 oC, bake gas bypass: OFF, MCS bake temperature: 250 oC and sample fill: 0.0 min.
- Detection limit varies: 0.02 – 1.6 ppb

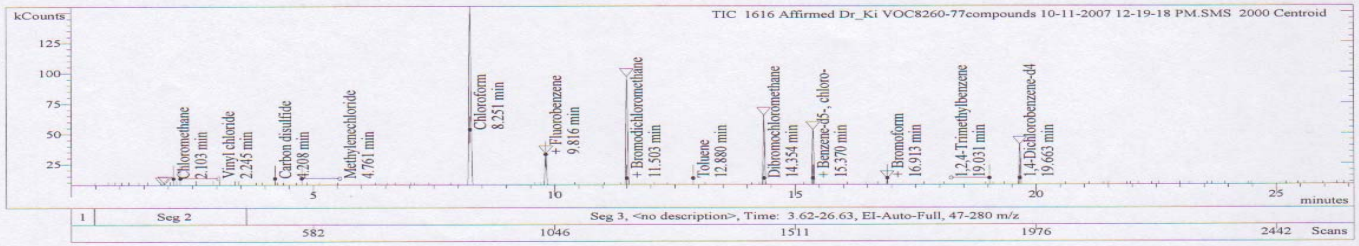
RESULT & IMPLICATIONS

Typical Chromatogram of VOCs in Drinking Waters Analyzed



Print Date: 30 Oct 2007 09:34:36

Sample ID:	1616 Affirmed Dr_Ki	Operator:	Ikem
Instrument ID:	Varian GC/MS #1	Last Calibration:	5/2/2006 12:52 PM
Acquisition Date:	10/11/2007 12:19 PM	Data File:	...2007 12-19-18 pm.sms
Calculation Date:	10/30/2007 9:33 AM	Method:	...8260-77compounds.mth
Inj. Sample Notes:	None		

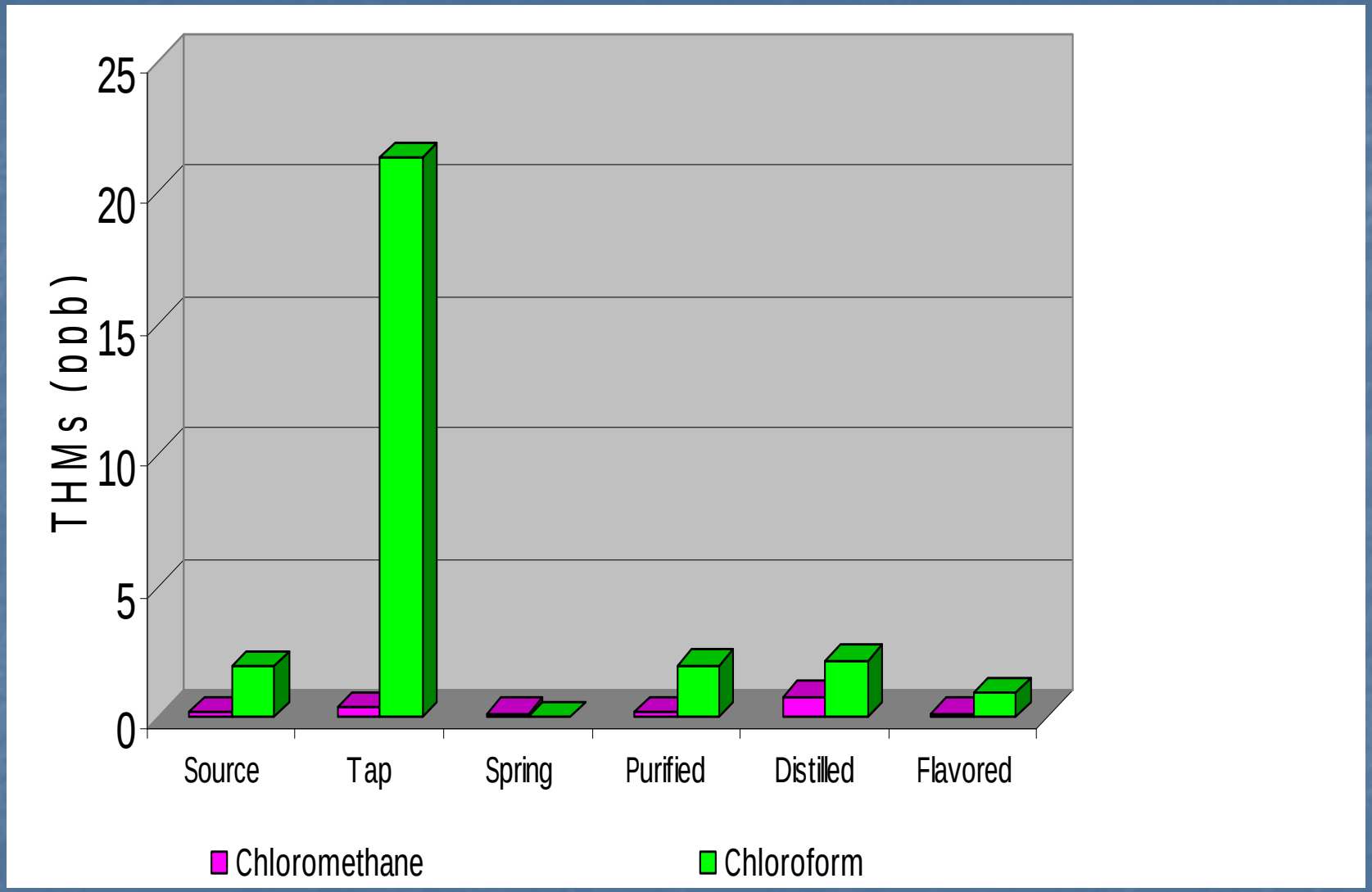


Target Compounds

#	RT	Peak Name	Res Type	Quan Ions	Area	Amount/RF
1	9.816	Fluorobenzene	Id.	96.0	41402	5.000 ppb
2	15.370	Benzene-d5-, chloro-	Id.	116.8	39648	5.000
3	1.904	Dichlorodifluoromethane	Miss.	85.0	0	0.000 ppb
4	2.103	Chloromethane	Id.	47.0+49.0+51.0	59	0.107 ppb
5	2.245	Vinyl chloride	Id.	62.0	67	0.029 ppb
6	2.638	Bromomethane	Miss.	94.0+96.0	0	0.000 ppb
7	2.786	Chloroethane	Miss.	47.0+49.0+51.0	0	0.000 ppb
8	3.116	Trichlorofluoromethane	Miss.	101.0	0	0.000 ppb
9	3.869	1,1-Dichloroethene	Miss.	61.0	0	0.000 ppb
10	4.093	Methane, iodo-	Miss.	141.7	0	0
11	4.208	Carbon disulfide	Id.	75.7	25	N/A
12	4.761	Methylenechloride	Id.	49.0	809	0.808 ppb
13	5.304	Ethene, 1,2-dichloro-, (E	Miss.	61.0	0	0.000 ppb
14	6.269	1,1-Dichloroethane	Miss.	63.0	0	0.000 ppb
15	7.492	Ethene, 1,2-dichloro-, (Z	Miss.	61.0	0	0.000 ppb
16	7.486	Propane, 2,2-dichloro-	Miss.	77.0	0	0.000 ppb
17	7.984	Bromochloromethane	Miss.	49.0	0	0.000 ppb
18	8.251	Chloroform	Id.	83.0	180882	73.065 ppb
19	8.494	1,1,1-Trichloroethane	Miss.	97.0	0	0.000 ppb
20	8.789	Carbon Tetrachloride	Miss.	117.0	0	0.000 ppb
21	8.824	1-Propene, 1,1-dichloro-	Miss.	75.0	0	0.000 ppb
22	9.195	Benzene	Id.	78.0	402	0.138 ppb
23	9.353	1,2-Dichloroethane	Miss.	62.0	0	0.000 ppb
24	10.498	Trichloroethylene	Miss.	130.0	0	0.000 ppb
25	10.983	1,2-Dichloropropane	Id.	63.0	56	0.055 ppb
26	11.128	Dibromomethane	Miss.	93.0	0	0.000 ppb
27	11.503	Bromodichloromethane	Id.	83.0	81376	48.762 ppb
28	12.303	1-Propene, 1,3-dichloro-,	Miss.	75.0	0	0.000 ppb
29	12.752	Toluene-d8	Miss.	97.9	0	0
30	12.880	Toluene	Id.	91.0	1178	0.209 ppb
31	13.363	1-Propene, 1,3-dichloro-,	Miss.	75.0	0	0.000 ppb
32	13.704	1,1,2-Trichloroethane	Miss.	97.0	0	0.000 ppb
33	13.782	Tetrachloroethylene	Miss.	166.0	0	0.000 ppb
34	13.975	1,3-Dichloropropane	Miss.	76.0	0	0.000 ppb
35	14.354	Dibromochloromethane	Id.	129.0	47797	52.554 ppb
36	14.533	1,2-Dibromoethane	Miss.	107.0	0	0.000 ppb
37	15.425	Chlorobenzene	Id.	112.0	1131	0.312 ppb
38	15.615	1,1,1,2-Tetrachloroethane	Miss.	131.0	0	0.000 ppb
39	15.638	Ethylbenzene	Id.	91.0	189	0.028 ppb
40	15.872	m,p-Xylene	Id.	91.0	265	0.021 ppb
41	16.563	o-Xylene	Id.	91.0	259	0.040 ppb
42	16.604	Styrene	Id.	104.0	31	0.009 ppb
43	16.913	Bromoform	Id.	171.0+173.0+175.0	13967	20.657 ppb
44	17.248	Isopropylbenzene	Miss.	105.0	0	0.000 ppb
45	17.555	Bromofluorobenzene	Miss.	95.0	0	0.000 ppb

#	RT	Peak Name	Res Type	Quan Ions	Area	Amount/RF
46	17.762	Bromobenzene	Miss.	77.0	0	0.000 ppb
47	17.834	1,1,2 ,2-Tetrachloroethan	Miss.	83.0	0	0.000 ppb
48	17.915	1,2,3-Trichloropropane	Miss.	75.0	0	0.000 ppb
49	18.011	n-Propylbenzene	Miss.	91.0	0	0.000 ppb
50	18.130	2-Chlorotoluene	Miss.	126.0	0	0.000 ppb
51	18.367	1,3,5-Trimethylbenzene	Miss.	105.0	0	0.000 ppb
52	18.363	4-Chlorotoluene	Miss.	126.0	0	0.000 ppb
53	18.917	tert-Butylbenzene	Miss.	119.0	0	0.000 ppb
54	19.031	1,2,4-Trimethylbenzene	Id.	105.0	115	0.016 ppb
55	19.327	sec-Butylbenzene	Miss.	105.0	0	0.000 ppb
56	19.500	1,3-Dichlorobenzene	Miss.	146.0	0	0.000 ppb
57	19.638	4-Isopropyltoluene	Miss.	119.0	0	0.000 ppb
58	19.663	1,4-Dichlorobenzene-d4	Id.	152.0	12556	5.537 ppb
59	19.501	1,4-Dichlorobenzene	Miss.	146.0	0	0.000 ppb
60	20.319	1,2 -Dichlorobenzene	Miss.	146.0	0	0.000 ppb
61	20.380	n-Butylbenzene	Miss.	91.0	0	0.000 ppb
62	20.834	Ethane, hexachloro-	Miss.	200.6	0	0
63	21.782	1,2-Dibromo-3-chloropropa	Miss.	157.0	0	0.000 ppb
64	23.282	1,2,4-Trichlorobenzene	Miss.	182.0	0	0.000 ppb
65	23.575	1,3-Butadiene, 1,1,2,3,4,	Miss.	225.0	0	0.000 ppb
66	23.741	Naphthalene	Miss.	128.0	0	0.000 ppb
67	24.138	1,2,3 -Trichlorobenzene	Miss.	182.0	0	0.000 ppb

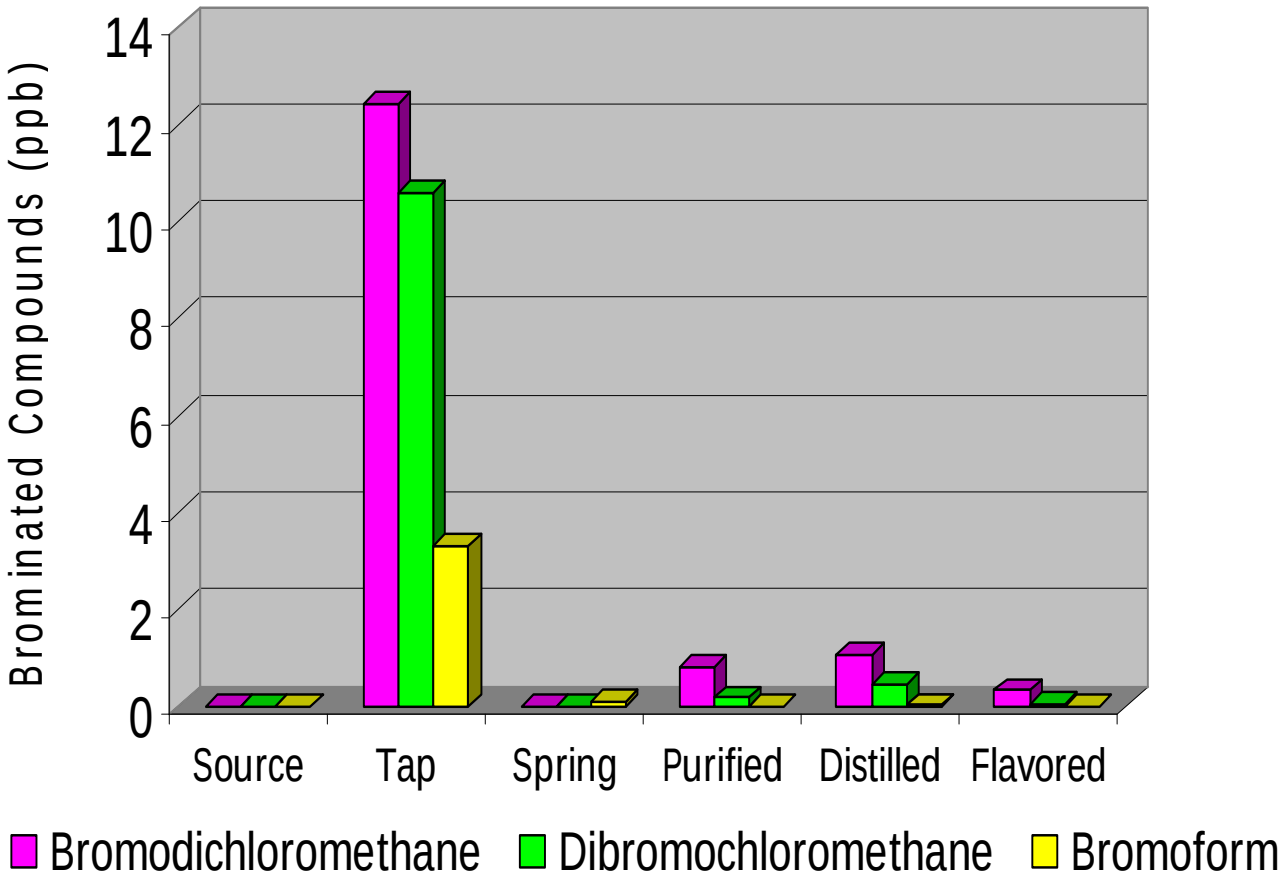
Summary of THMs (ppb) in Source & Drinking waters



Note: No available standard yet for chloromethane

WHO Std for Chloroform: 200 ppb

Summary of THMs in Source & Drinking waters Cont'd



WHO Standards (1) Bromodichloromethane = 100 ppb

(2) Dibromochloromethane = 80 ppb

(3) Bromoform = 80 ppb

Averages of Total VOCs (ppb) in Source & Drinking waters

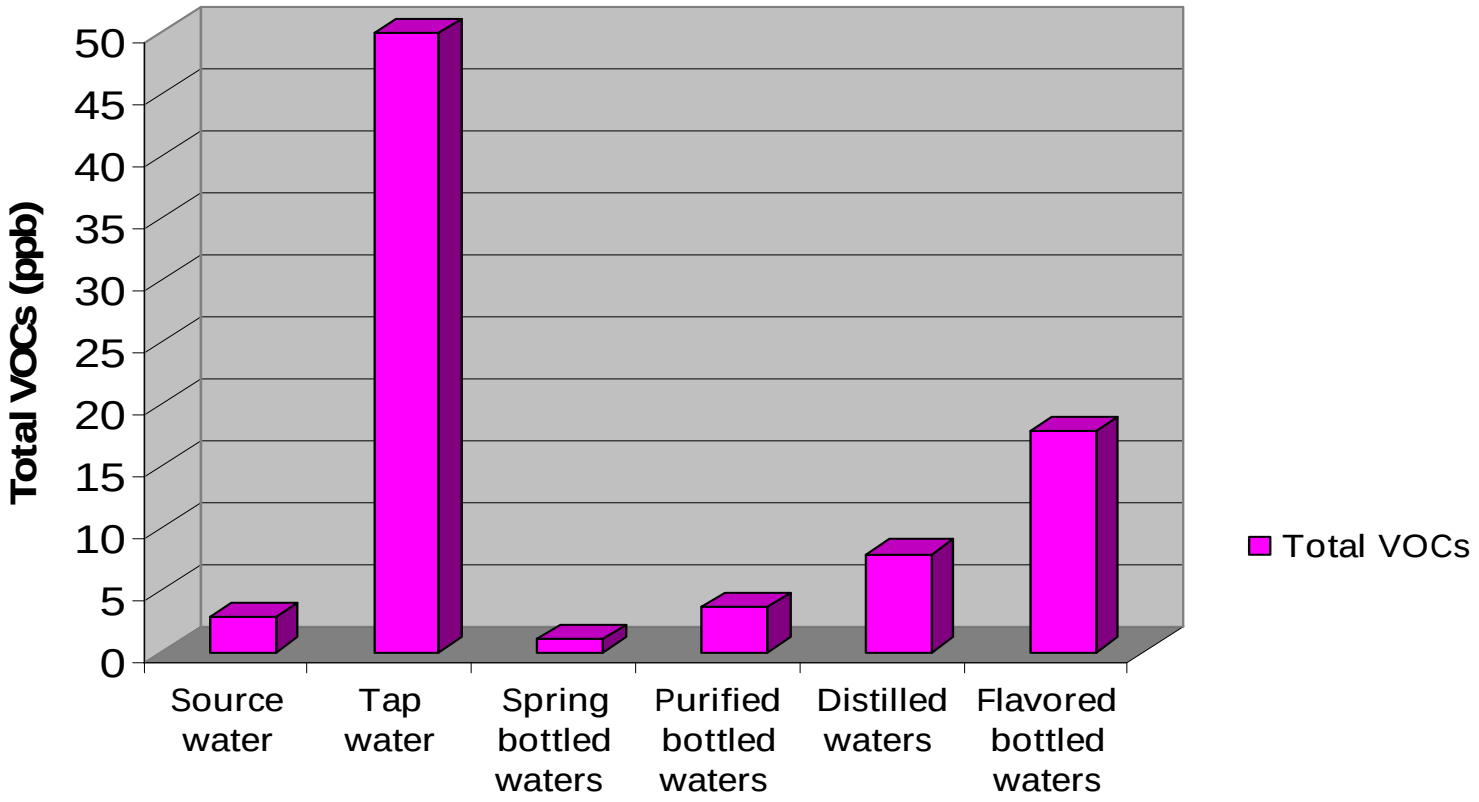


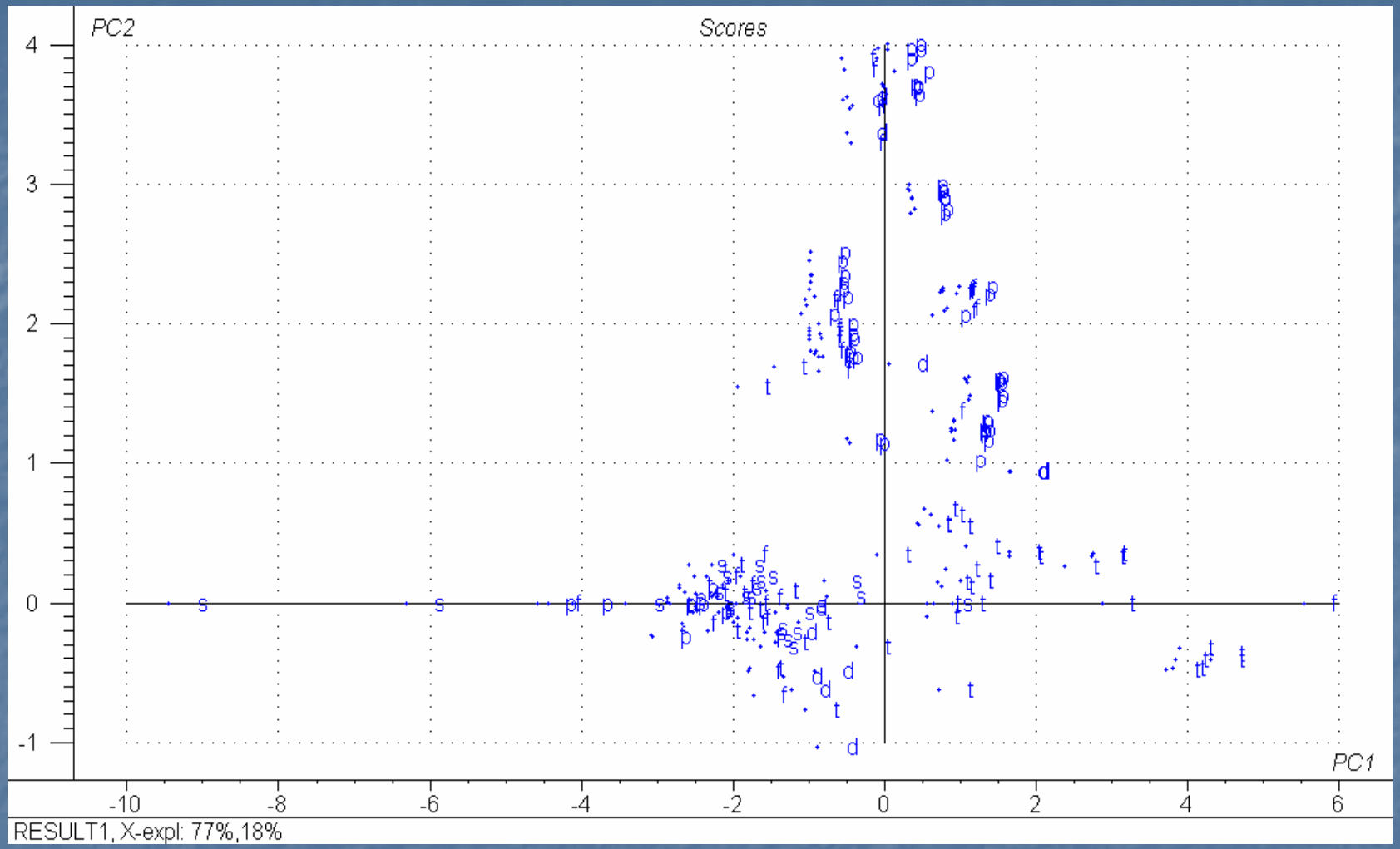
Table 3: Major THMs and total VOCs (ppb) in source, tap and bottled waters from Mid Missouri

Sample Type	Target compounds	Mean	SD	Min	Max	N	Guideline (µg/l)
Source water: Missouri River	(a) Chloromethane (CH_3Cl)	0.17	0.08	0.06	0.35	30	NP
	(b) Chloroform ($CHCl_3$)	1.95	0.42	0.06	3.09	30	200
	(c) Bromodichloromethane ($CHBrCl_2$)	0.00	0.00	0	0	30	100
	(d) Dibromochloromethane ($CHBr_2Cl$)	0.00	0.00	0	0	30	80
	(e) Bromoform ($CHBr_3$)	0.00	0.00	0	0	30	80
	∑ b + c + d + e = Four major THMs	1.95	0.42	0.06	3.09	30	100
	∑ 67 volatile organic compounds	2.79	0.30	2.37	4.09	30	NP
	∑ Ratios of 1, 2, 3 & 4 to guidelines	0.01	0.00	0.00	0.02	30	< 1
Tap water (after chlorination)	(a) Chloromethane (CH_3Cl)	0.4	0.2	0	1.1	34	NP
	(b) Chloroform ($CHCl_3$)	21.3	40.4	0	142.2	34	200
	(c) Bromodichloromethane ($CHBrCl_2$)	12.4	24.2	0	90.0	34	100
	(d) Dibromochloromethane ($CHBr_2Cl$)	10.6	21.0	0	72.8	34	80
	(e) Bromoform ($CHBr_3$)	3.3	6.5	0	20.4	34	80
	∑ b + c + d + e = Four major THMs	47.6	89.9	0	322.4	34	100
	∑ 67 volatile organic compounds	49.9	90.0	1.4	325.1	34	NP
	∑ Ratios of 1, 2, 3 & 4 to guidelines	0.4	0.8	0	2.7	34	< 1
Spring bottled waters (3 brands)	(a) Chloromethane (CH_3Cl)	0.14	0.11	0.1	0.6	25	NP
	(b) Chloroform ($CHCl_3$)	0.02	0.03	0.0	0.1	25	200
	(c) Bromodichloromethane ($CHBrCl_2$)	0.00	0.00	0.0	0.0	25	100
	(d) Dibromochloromethane ($CHBr_2Cl$)	0.00	0.00	0.0	0.0	25	80
	(e) Bromoform ($CHBr_3$)	0.10	0.10	0.0	0.3	25	80
	∑ b + c + d + e = Four major THMs	0.12	0.11	0.0	0.3	25	100
	∑ 67 volatile organic compounds	0.99	0.90	0.2	3.3	25	NP
	∑ Ratios of 1, 2, 3 & 4 to guidelines	0.00	0.001	0.0	0.0	25	< 1

Table 3 Cont'd: Major THMs and total VOCs (ppb) in source, tap and bottled waters from Mid Missouri

Sample Type	Target compounds	Mean	SD	Min	Max	N	Guideline (µg/l)
Purified bottled waters (8 brands)	(a) Chloromethane (CH_3Cl)	0.21	0.20	0.1	1.0	58	NP
	(b) Chloroform ($CHCl_3$)	1.99	1.67	0.0	4.8	58	200
	(c) Bromodichloromethane ($CHBrCl_2$)	0.81	0.86	0.0	2.5	58	100
	(d) Dibromochloromethane ($CHBr_2Cl$)	0.19	0.26	0.0	0.7	58	80
	(e) Bromoform ($CHBr_3$)	0.00	0.01	0.0	0.1	58	80
	∑ b + c + d + e = Four major THMs	2.99	2.62	0.0	7.6	58	100
	∑ 67 volatile organic compounds	3.60	3.01	0.2	9.7	58	NP
	∑ Ratios of 1, 2, 3 & 4 to guidelines	0.02	0.02	0.0	0.1	58	< 1
Distilled waters (3 brands)	(a) Chloromethane (CH_3Cl)	0.79	0.70	0.1	2.1	12	NP
	(b) Chloroform ($CHCl_3$)	2.18	3.39	0.1	9.4	12	200
	(c) Bromodichloromethane ($CHBrCl_2$)	1.07	2.42	0.0	6.3	12	100
	(d) Dibromochloromethane ($CHBr_2Cl$)	0.45	0.86	0.0	2.3	12	80
	(e) Bromoform ($CHBr_3$)	0.03	0.07	0.0	0.2	12	80
	∑ b + c + d + e = Four major THMs	3.73	6.67	0.1	18.1	12	100
	∑ 67 volatile organic compounds	7.89	7.29	0.9	20.4	12	NP
	∑ Ratios of 1, 2, 3 & 4 to guidelines	0.03	0.05	0.0	0.1	12	< 1
Flavored bottled waters (5 brands)	(a) Chloromethane (CH_3Cl)	0.16	0.12	0.0	0.5	34	NP
	(b) Chloroform ($CHCl_3$)	0.91	1.36	0.0	3.8	34	200
	(c) Bromodichloromethane ($CHBrCl_2$)	0.34	0.59	0.0	1.7	34	100
	(d) Dibromochloromethane ($CHBr_2Cl$)	0.06	0.11	0.0	0.3	34	80
	(e) Bromoform ($CHBr_3$)	0.00	0.00	0.0	0.0	34	80
	∑ b + c + d + e = Four major THMs	1.32	2.04	0.0	5.7	34	100
	∑ 67 volatile organic compounds	17.88	24.17	1.3	68.5	34	NP
	∑ Ratios of 1, 2, 3 & 4 to guidelines	0.01	0.01	0.0	0.0	34	< 1

Principal Component Analysis



Score loading plot of log transformed data on PC1 and PC2 (PC: principal components, s: spring bottled water, p: purified bottled water, t: tap water, d: distilled drinking water, f: fruited drinking water).

Eigenvalues / Eigenvectors Based on Correlation Matrix

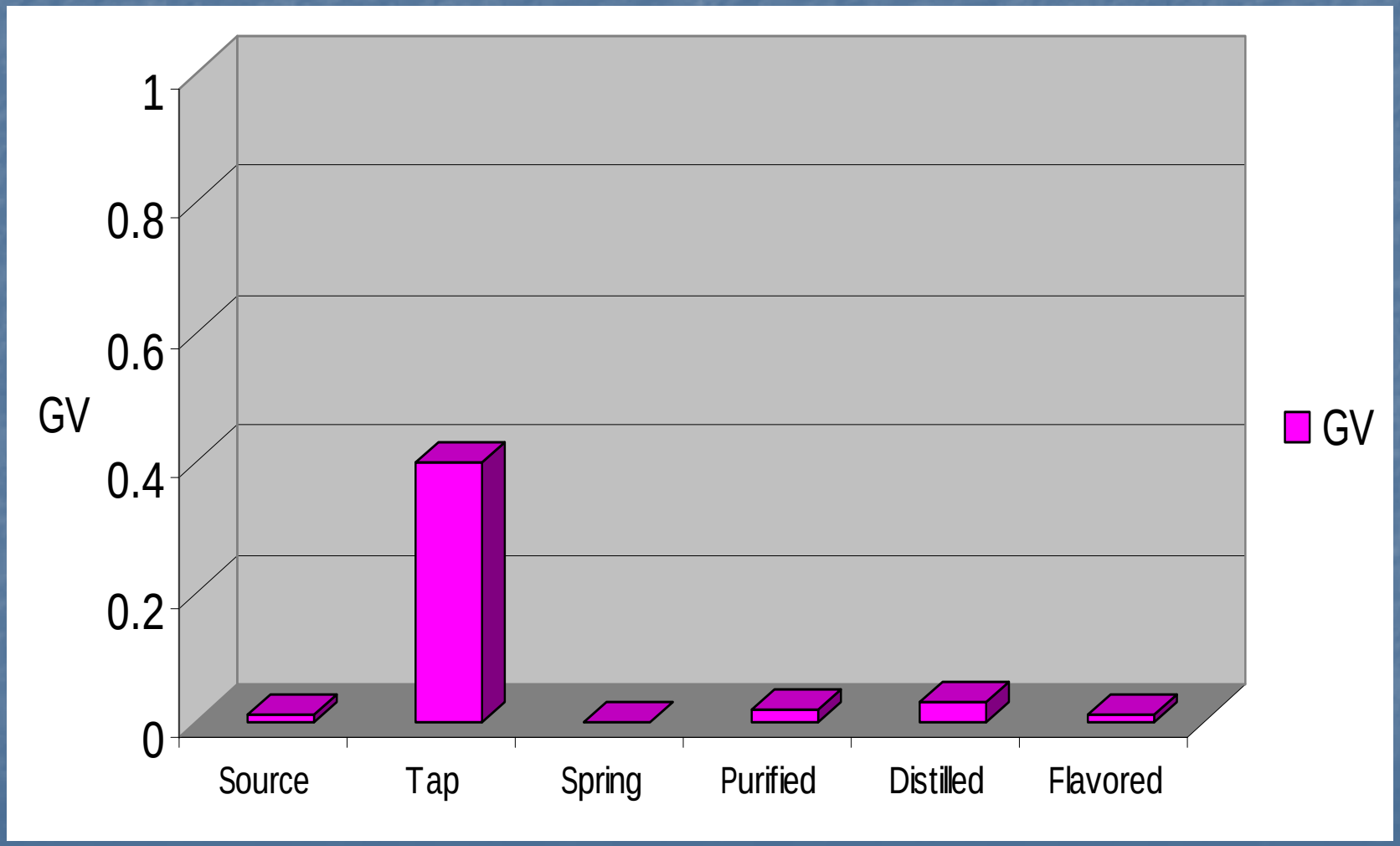
Factor	PC 1	PC 2	PC 3	PC 4	PC 5	Communality
Bromodichloromethane	-0.5300	-0.0255	0.0702	0.2348	0.8114	1.0000
Bromoform	-0.4632	0.2994	0.6214	-0.5207	-0.1962	1.0000
Chloroform	-0.5109	0.0006	0.0176	0.6759	-0.5308	0.9999
Chloromethane	-0.1109	-0.9529	0.2256	-0.1504	-0.0784	1.0000
Dibromochloromethane	-0.4808	-0.0412	-0.7468	-0.4407	-0.1232	1.0000
Eigen values	3.4889	1.0337	0.2780	0.1878	0.0116	∑5.0000
% variance	69.8	20.7	5.6	3.8	0.2	
Cumulative % variance	69.8	90.5	96.0	99.8	100.0	

PC: Principal component

Human Health Perspectives

- Cancer risks
- GV = C1/GV1 + C2/GV2 + C3/GV3 + C4/GV4
  - GV1 of Chloroform: 200 ppb
  - GV2 of Bromodichloromethane: 100 ppb
  - GV3 of Dibromochloromethane: 80 ppb
  - GV4 of Bromoform: 80 ppb
- Guideline value (GV) should be < 1 for good water!

Human Health Criteria



CONCLUSIONS

- VOCs (including industrial chemicals) were detected in samples analyzed
- 4 major THMs were also detected & all were below the stipulated WHO standards
- No cancer risks from drinking waters analyzed
- Aeration/adsorbents further reduces VOCs in finished waters

QUESTIONS?