

Trihalomethane formation potential of drinking water sources in a rural location

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Abstract. Trihalomethanes, produced as a result of chlorination of drinking water, are considered a potential health hazard. The trihalomethane formation potential (THMFP) of a raw water source may indicate the maximum trihalomethanes (THMs) that are likely to be produced when chlorine reacts with natural organic matter (NOM) present in the water. A study was conducted to evaluate the THMFP in seven different drinking water sources in the vicinity of Kalpakkam, a rural township, on the east coast of India. Water from seven stations were analysed for THMFP. THMFP was compared with surrogate parameters such as dissolved organic carbon (DOC), ultraviolet absorbance (UV₂₅₄) and bromide. The data showed that THMFP was high in water from open wells as compared to closed bore wells, possibly due to more photosynthetic activity. Proximity to sea, and consequently the levels of bromide, was an important factor that influenced THM formation. THM surrogate parameters showed good correlation with THMFP.

Keywords: chlorination by-products; trihalomethane formation potential; dissolved organic carbon; ultraviolet absorbance; bromide

1. Introduction

Many developing countries suffer from lack of adequate clean drinking water and proper sewerage facilities for their citizens. As a result, waterborne diseases such as gastroenteritis and cholera cause widespread illness and death. Water-borne pathogens, especially, viruses, bacteria and protozoans are responsible for the outbreak of such diseases (Black and Veatch 2010). A good part of the disease causing microorganisms can be removed by means of water treatment techniques such as coagulation, flocculation and filtration. However, to further increase drinking water safety, disinfection must be applied as a final treatment step (Álvarez *et al.* 2010). There are several different disinfectants, such as chlorine, chlorine dioxide, ozone and UV which either deactivate or kill the pathogenic microorganisms (Richardson 2003). The mechanism of disinfection is mostly through cell wall disruption of microorganisms, changes in cell membrane permeability, damage to protoplasm or inhibition

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of enzyme activity (Jyoti and Pandit 2003). Among the commonly used disinfectants, chlorine is the one which is being extensively used in most of the countries (Boccelli *et al.* 2003).

Chlorine is relatively cheap, freely available and can be transported and stored relatively easily. Moreover, it has broad-spectrum activity against most of the water-borne pathogens (viruses, bacteria and protozoans). Therefore, chlorine is extensively used as a disinfectant for public drinking water system. At the same time, chlorination entails the risk of formation of chlorination by-products (CBP) such as trihalomethanes (THM), which are formed by the reaction of chlorine with organic compounds naturally present in water (Gallard and Gunten 2002). The formation of these CBPs mainly takes place due to reactions involving organic substances, such as humic acids and fulvic acids with the dosed chlorine (Chow 2006). These substances are the decomposition products of natural organic matter present in water. Studies on toxicity of the CBPs have focused on trihalomethanes (THMs), for which considerable data on carcinogenicity have been available (Richardson *et al.* 2007). Chloroform, bromodichloromethane, dibromo-chloromethane and bromoform are the principal trihalomethanes. The total trihalomethane (TTHM) is the sum of all THM concentrations. The U.S. Environmental Protection Agency (US EPA) has fixed a Maximum Contaminant Level of 0.080 mg/L (80 ppb) for TTHM in drinking water (Richardson 2003). The rate and degree of THM formation are a function of many parameters such as chlorine dose and residual, organic carbon and bromide concentration (Sketchell *et al.* 1995). One very useful parameter to assess the propensity for trihalomethanes formation is the THM formation potential (THMFP). A total or dissolved organic carbon (TOC or DOC) test is an associated test (Marhaba and Van 2000). The THMFP of a raw water source would indicate the maximum THMs that are likely to be produced following chlorination and hence is a very useful indicator as far as drinking water is concerned.

Rivers, reservoirs and wells (open or closed) are among the common sources of drinking water in rural areas of developing countries. In order to study the risk of THM formation in drinking water sources in a rural setting, natural freshwaters samples were collected from seven different locations in the vicinity of Kalpakkam (east coast of India) and the THMFP at each location was determined. The objective of the study was to find out how the THMFP was related to some of the commonly used surrogate parameters such as dissolved organic carbon (DOC) concentration, UV absorbance (UV₂₅₄), and bromide concentration in the water (due to ingress of saline water). It is shown that trihalomethane concentration increased with increasing dissolved organic carbon and ultraviolet absorbance for all the water samples, suggesting that these parameters work well as predictors of chlorination by-products formation potential in the tested waters.

2. Materials and methods

2.1 Study area

Kalpakkam is situated about 75 km south of Chennai (erstwhile Madras) on the Bay of Bengal coast of India. The Kalpakkam Township, housing about 30,000 persons, is supplied with drinking water drawn from the Palar river basin, situated about 10 km south of the township and brought through a pipeline. The Pudupattinam Kuppam, Meyyur Kuppam and Kokilimedu are fishing villages situated within 800 m from the sea, where as Vengampakkam and Anupuram are villages located further away, about 5 km and 7 km, respectively, from the coast (Fig. 1). The source of drinking water to these two villages is ground water, obtained from open well pumped through a pipeline. Pudupattinam Kuppam,

Meyyur Kuppam and Kokilimedu villages are supplied with water drawn from bore wells sunk within 800 m from the seashore. MAPS Open Reservoir, one of the sampling stations, is a temporary storage pond that receives water from the Palar River and stores the water to be used as cooling water and service water supply for an electrical power plant. It is also used as source of drinking water for the plant personnel.

2.2 Water sample collection and storage

Water samples for the study were collected in triplicate from the seven sampling stations mentioned above. The samples were collected in glass bottles with PTFE-lined screw caps and kept on ice until analysed. Upon reaching the laboratory, the samples were filtered immediately using 0.45 $\mu\text{g/L}$ membrane filters and stored at 4°C until use. All THM and THM-surrogate analysis were performed on aliquots of these filtrates.

2.3 Dissolved organic carbon

Dissolved organic carbon (DOC) analysis was performed by oxidative catalytic combustion method (APHA 2005) using a Shimadzu TOC Analyzer (TOC-VCPH/CPN) with zero air as the carrier gas at a flow rate of 150 ml/min. The filtered samples were acidified with HCl and sparged with zero air to remove carbonates. The samples were injected into a heated reaction chamber (680°C) packed with platinum catalyst. The water gets vaporized and the organic carbon is oxidized to carbon dioxide and water by catalytic combustion. The CO₂ formed is transported to the detector using the carrier gas and measured directly by a non-dispersive IR detector. The amount of CO₂ is directly proportional to the concentration of carbonaceous material in the sample. All samples were analyzed in triplicate. Standards ranging from 0 to 16 mg/L were prepared with de-ionised, ultra-filtered (DIUF) water.

2.4 UV₂₅₄

UV₂₅₄ is a measure of the unsaturated organic bonds in a sample, indicating the potential for chlorine reaction sites (APHA 2005). It is often used to measure colour, a secondary (aesthetic) regulated variable. UV₂₅₄ samples, after filtration, were analysed within 48 h of collection using a Shimadzu UV-1601 UV-VIS spectrophotometer. DIUF water was used as blank. UV₂₅₄ absorbance in this study, measured using a 1 cm quartz cell, is reported as absorbance per cm multiplied by 1000.

2.5 Bromide analysis

Bromide was measured by suppressed conductivity detection on a Dionex Ion Chromatograph (Dionex 2010i system) model with an AS4A-SC analytical column according to U.S. Environmental Protection Agency Method 300.1 (US EPA 1999). The detection limit associated with this method is 10 $\mu\text{g/L}$. Each sample was analyzed in duplicate.

2.6 Chlorination

Predetermined chlorine dose (8 mg/L) (providing a free chlorine residual of \approx 5 mg Cl₂/L at the end of a 7-d reaction (incubation) period) was added to the sample. The incubation pH was controlled at

7.0 ± 0.2 with phosphate buffer; temperature was controlled at 25 ± 0.2°C and light exposure was limited by using amber glass bottles. All bottles had Teflon-lined septa caps and care was taken to eliminate all head space at the start of the incubation. After 7 day reaction in the dark, all chlorine dosed water samples were analyzed for THM (APHA 2005).

2.7 Trihalomethane

All solvents used were of analytical grade. Standards of chloroform (CHCl₃), bromodichloromethane (CHBrCl₂), dibromochloromethane (CHBr₂Cl) and bromoform (CHBr₃) were obtained from Sigma-Aldrich (USA). The solvents used (n-hexane and methanol) were from Ranbaxy (India). A standard stock solution of each compound containing 0.1 mg/10 mL was prepared in methanol. Intermediate standard solutions were obtained by dilution of the standard stock solution using methanol. Blank chromatograms were obtained by injecting pure solvents.

Two main methods available for the concentration of THMs in water are purge-and-trap technique and liquid-liquid extraction technique. In the present study, the liquid-liquid extraction procedure (Allonier 2000) US EPA method 551.1 (US EPA 1995) was used. After 7-d reaction period, the analysis was carried out by extracting 500 mL of dechlorinated (using 0.1 mL of 0.1 M sodium thiosulphate) raw water sample with 5 mL of n-hexane in a one litre separating funnel. After 15 min, the organic phase was decanted into a 5 mL volumetric flask. An aliquot of 3 µL extract was injected in to a gas chromatograph (Chemito 8510, India), equipped with a ⁶³Ni Electron Capture Detector. The column used was a glass column, 6 mm ID × 2.5 m long, packed with 1.85% OV-17 + 1.95% on Chromosorb W (HP) (80/100 mesh) and operated at 50°C. The injector temperature was set at 150°C, while the detector was set at 250°C. Nitrogen was used as the carrier gas at a flow rate of 40 mL/min. Calibration was performed by means of 10 standard solutions (100 to 1000 µg/L) prepared by diluting the standard solution. Calibration curves were made for all the four THM standards. The minimum detection limits for the compounds were: chloroform - 1.1 ppb, bromodichloromethane - 1.0 ppb, dibromochloromethane - 0.8 ppb, and bromoform - 0.8 ppb. The analytical method had an accuracy of 87% and precision (in terms of coefficient of variation) of 1.3% (determined using 50 ppb bromoform, n = 6)

2.8 Trihalomethane formation potential (THMFP)

THMFP is useful for the evaluation of a treatment system or for the prediction of THM levels from a particular source of water. In this study, THMFP was estimated to know about the amount and reactivity of THM precursors in the source water. Total concentration of trihalomethane, TTHM, is the sum of the concentrations of all the four regulated THM species: chloroform, bromodichloromethane, dibromochloromethane and bromoform. THMFP is the difference between the final and initial THM concentrations (sum of the differences THM_f^j - THM_i^j). The initial concentrations of THM in raw water are close to zero and considered negligible and THMFP is equated to the final THM concentration of the sample (APHA 2005).

3. Conclusions

The concentrations of THMs obtained in all stations and the TTHM values are presented in Table 1. The trihalomethane formation potential, DOC, UV₂₅₄ and bromide measured from all seven stations

are given in Table 2. Among the four species of THM, only bromoform was detected in the samples collected from Pudupattinam Kuppam, Meyyur Kuppam and Kokilimedu (358, 296 and 306 $\mu\text{g/L}$, respectively). This may be attributed to the higher concentrations of bromide (11.26, 10.47, 13.30 mg/L), as these areas are within 800 m from the sea and therefore concentrations of bromide are expected to be more due to seawater intrusion. When water containing significant amounts of bromide ions is chlorinated, chlorine oxidizes the bromide ion to hypobromous acid, which leads to the formation of organobromo derivatives (Rajamohan *et al.* 2007, Khalanski and Jenner 2012). Speciation of THM in bromide-containing waters is important as brominated species are more toxic than their chlorinated counterparts. But in the samples collected from the Kalpakkam Township, MAPS Open Reservoir, Vengampakkam and Anupuram areas, bromoform was absent and only chloroform (98, 88, 87 and 170 $\mu\text{g/L}$, respectively), bromodichloromethane (185, 166, 587 and 298 $\mu\text{g/L}$, respectively) and dibromochloromethane (201, 120, 193 and 233 $\mu\text{g/L}$, respectively) were present. As can be seen from Fig. 1, these sampling points are relatively farther from the sea coast and the bromide concentrations are low (0.19, 0.27, 1.77 and 1.29 mg/L , respectively).

Among all the freshwater samples collected, the samples from Vengampakkam showed the highest values of THMFP (mean 869 $\mu\text{g/L}$), DOC (6.1 mg/L) and UV_{254} (234). Similarly, the samples from

Table 1 Concentration of trihalomethane species in drinking water samples

Sampling stations	CHCl_3 $\mu\text{g/L}$ (mean \pm SD)	CHBrCl_2 $\mu\text{g/L}$ (mean \pm SD)	CHBr_2Cl $\mu\text{g/L}$ (mean \pm SD)	CHBr_3 $\mu\text{g/L}$ (mean \pm SD)	TTHM = THMFP ($\mu\text{g/L}$)
Kalpakkam Township	98 \pm 0.51	185 \pm 0.37	201 \pm 0.21	BDL	485 \pm 0.66
MAPS Open Reservoir	88 \pm 0.17	166 \pm 0.86	120 \pm 0.23	BDL	375 \pm 0.90
Pudupattinam Kuppam	BDL	BDL	193 \pm 0.57	358 \pm 0.59	552 \pm 0.83
Meyyur Kuppam	BDL	BDL	205 \pm 0.47	296 \pm 0.56	501 \pm 0.73
Kokilimedu	BDL	BDL	279 \pm 0.23	306 \pm 0.28	586 \pm 0.36
Vengampakkam	87 \pm 0.35	587 \pm 0.46	193 \pm 0.56	BDL	869 \pm 0.80
Anupuram	170 \pm 0.63	298 \pm 0.22	233 \pm 0.47	BDL	702 \pm 0.81

Table 2 Trihalomethane formation potential (THMFP), Dissolved organic carbon, UV_{254} and bromide in the drinking water from different sources

Sampling station	THMFP ($\mu\text{g/L}$) (mean \pm SD)	DOC (mg/L)	UV_{254} abs $\times 1000$	Bromide (mg/L)	Source	Distance from sea
Kalpakkam Township	485 \pm 0.66	3.70	154	0.19	Palar water	--
MAPS Open Reservoir	375 \pm 0.90	3.01	125	0.27	Palar water	--
Pudupattinam Kuppam	552 \pm 0.83	4.47	174	11.26	Borewell water	800 m
Meyyur Kuppam	502 \pm 0.73	4.22	162	10.47	Borewell water	800 m
Kokilimedu	586 \pm 0.36	5.03	193	13.30	Borewell water	800 m
Vengampakkam	869 \pm 0.80	6.10	234	1.77	Open well	5 Kms
Anupuram	702 \pm 0.81	5.90	226	1.29	Open well	7 Kms



Fig. 1 Map of the study area showing sampling stations (image credit: Google Maps)

Anupuram also showed relatively higher values of THMFP ($702 \mu\text{g/L}$), DOC (5.9 mg/L) and UV_{254} (226). Such high levels of THMFP, DOC and UV_{254} are attributed to the presence of higher dissolved organic matter resulting from the growth and decay of vegetation as well as higher photosynthetic activity, as the samples were collected from open wells (Gallard and Gunten 2002). Although humic and fulvic acids have been the focus of many THMFP studies, algae can also potentially contribute to THMFP (Huang *et al.* 2009). The values for the water samples from Pudupattinam Kuppam (THMFP $552 \mu\text{g/L}$, DOC 4.47 mg/L , UV_{254} 174), Meyyur Kuppam (THMFP $502 \mu\text{g/L}$, DOC 4.22 mg/L , UV_{254} 162) and Kokilimedu (THMFP $586 \mu\text{g/L}$, DOC 5.03 mg/L , UV_{254} 193) are comparatively less. This is attributed to the fact that the wells are closed bore wells, resulting in low production of natural organic matter (little algal growth or photosynthesis). The analysed parameters in the samples collected from Kalpakkam Township (THMFP $485 \mu\text{g/L}$, DOC 3.70 mg/L , UV_{254} 154) and MAPS Open Reservoir (THMFP $375 \mu\text{g/L}$, DOC 3.01 mg/L , UV_{254} 125) were still less, as the source of water for these sampling points is the Palar River basin. The river is characterised by subsurface flow and the production of natural organic matter is low due to low algal growth. Transport of organic matter from the sediments to bulk water may also be minimal under the existing low flow conditions (Volk *et al.* 2002).

Chlorophyll is generally considered a good indicator of CBP formation because algal biomass can contribute a large fraction of DOC to the precursor pool (Volk *et al.* 2002). However, in the present work, chlorophyll levels in the water samples could not be analysed. The DOC in water depends on watershed characteristics and photosynthetic productivity, which vary annually and seasonally within reservoirs (Gergel *et al.* 1999) as well as globally and regionally (Pace and Cole 2002). Identifying the relative influence of carbon inputs and the spatial variation in THM formation potential was the objective of this study. Analysis of the data showed that the relationships between DOC and THMFP ($R^2 = 0.9012$) (Fig. 2) and between THMFP and UV_{254} ($R^2 = 0.8946$) (Fig. 3) were quite strong, suggesting that these surrogate measures work well as predictors of THM formation potential in

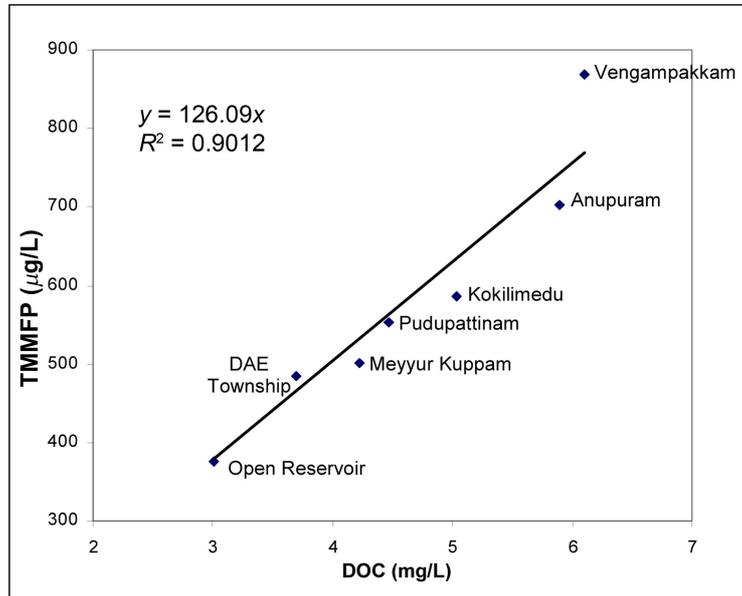


Fig. 2 Dependence of THMF on DOC

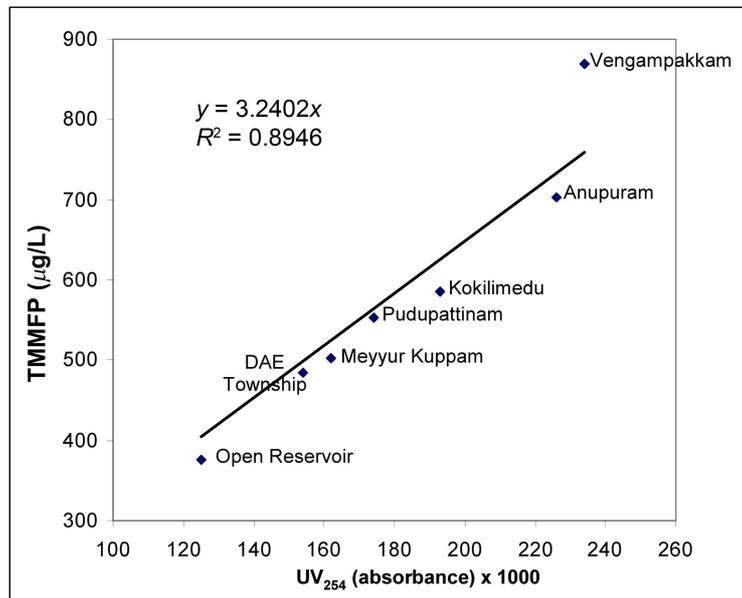


Fig. 3 Dependence of THMF on unsaturated organics (UV₂₅₄)

the water samples analysed. The actual values of THMs observed in drinking water samples collected at the consumer end at three stations (Kalpakkam Township, Anupuram and MAPS Open Reservoir) are given in Table 3. The values are in accordance with THMF of the stations, as indicated in Fig. 2.

Table 3 Concentration of trihalomethane species in drinking water samples

Sampling station	TRO mg/L	CHCl ₃ µg/L	CHBrCl ₂ µg/L	CHBr ₂ Cl µg/L	CHBr ₃ µg/L	Total THM (µg/L)
Kalpakkam Township	0.44	0.647	0.584	2.88	5.98	10.091
Anupuram	0.46	0.544	0.390	4.80	17.74	23.474
MAPS Open Reservoir	0.37	0.693	0.235	0.354	1.546	2.828

In conclusion, analysis of water samples from the seven drinking water sources at Kalpakkam showed that samples containing more dissolved organic carbon also returned higher THMFP values. The values of THMFP were more in water from open wells as compared to closed bore wells, possibly due to more photosynthetic activity. Proximity to sea, and consequently the levels of bromide, was an important factor that influenced THM formation. In short, in all the water samples analysed, THM surrogate parameters showed good correlation with THMFP.

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References

- Allonier, A.S., Khalanski, M., Bermond, A. and Camel, V. (2000), "Determinations of trihalomethanes in chlorinated seawater samples using a purge-and-trap system coupled to gas chromatography", *Talanta*, **51**(3), 467-477.
- Álvarez-Urriarte, J.I., Iriarte-Velasco, U., Chimeno-Alanís, N. and González-Velasco, J.R. (2010), "The effect of mixed oxidants and powdered activated carbon on the removal of natural organic matter", *J. Hazard. Mater.*, **181**(1-3), 426-431.
- American Public Health Association, Washington, D.C Health, (2005), *Standard Methods for the Examination of Water and Wastewater*, 21st Edition.
- Black and Veatch (2010), *White's Handbook of Chlorination and Alternative Disinfections*, 5th Edition, A John Wiley and Sons INC., Publications.
- Boccelli, D.L., Tryby, M.E., Uber, J.G. and Summers, R.S. (2003), "A reactive species model for chlorine decay and THM formation under rechlorination conditions", *Water Res.*, **37**(11), 2654-2666.
- Chow, A.T. (2006), "Disinfection byproduct reactivity of aquatic humic substances derived from soils", *Water Res.*, **40**(7), 1426-1430.
- Gallard, H. and Gunten, U.V. (2002), "Chlorination of natural organic matter: kinetics of chlorination and of THM formation", *Water Res.*, **36**, 65-74.
- Gergel, S.E., Turner, M.G. and Kratz, T.K. (1999), "Dissolved organic carbon as an indicator of the scale of watershed influence on lakes and rivers", *Ecol. Appl.*, **9**(4), 1377-1390.
- Huang, J., Grahama, N., Templeton, M.R., Zhang, Y., Collins, C. and Nieuwenhuijsen, A. (2009), "Comparison of the role of two blue-green algae in THM and HAA formation", *Water Res.*, **43**(12), 3009-3018.
- Jyoti, K.K. and Pandit A.B. (2003), "Hybrid cavitation methods for water disinfection: simultaneous use of chemicals with cavitation", *Ultrason. Sonochem.*, **10**(4-5), 255-264.
- Khalanski, M. and Jenner H.A. (2012), "Chlorination chemistry and ecotoxicology of the marine cooling water systems". In: S. Rajagopal, H.A. Jenner and V.P. Venugopalan (eds.), *Operational and environmental consequences of large industrial cooling water systems*, DOI 10.1007/978-1-4614-1698-2_9, ©Springer Science+Business Media,

- LLC 2012.
- Marhaba, T.F. and Van, D. (2000), "The variation of mass and disinfection by-product formation potential of dissolved organic matter fractions along a conventional surface water treatment plant", *J. Hazard. Mater.*, **74**(3), 133-147.
- Pace, M.L. and Cole, J.J. (2002), "Synchronous variation of dissolved organic carbon and color in lakes", *Limno. Oceanogr.*, **47**(2), 333-342.
- Rajamohan, R., Vinnitha, E., Venugopalan, V.P. and Narasimhan, S.V. (2007), "Chlorination by-products and their discharge from the cooling water system of a coastal electric plant", *Curr. Sci. India*, **93**(11), 1608-1612.
- Richardson, S.D., Plewa, M.J., Wagner, E.D., Schoeny, R. and DeMarini, D.M. (2007), "Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: A review and roadmap for research", *Mutat. Res.*, **636**(1-3), 178-242.
- Richardson, S.D. (2003), "Disinfection by-products and other emerging contaminants in drinking water", *Trends Anal. Chem.*, **22**(10), 666-684.
- Sketchell, J., Peteraon, H.G. and Christofi, N. (1995), "Disinfection by-product formation after biologically assisted GAC treatment of water supplies with different bromide and DOC content", *Water Res.*, **29**, 2635-2642.
- US EPA (1995), Determination of chlorination disinfection by-products, chlorinated solvents halogenated pesticides/herbicides in drinking water by liquid-liquid extraction and gas chromatography with electron capture detection. Standard 551.1.
- US EPA (1999), Determination of inorganic anions in drinking water by Ion chromatography. Method 300.1.
- Volk, C., Wood, L., Johnson, B., Robinson, J., Zhu, H.W. and Kaplan, L. (2002), "Monitoring dissolved organic carbon in surface waters", *J. Environ. Monitor*, **4**(1), 43-47.