TRIHALOMETHANE FORMATION POTENTIAL: A TOOL FOR DETECTING NON-SPECIFIC ORGANIC GROUNDWATER CONTAMINATION

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Abstract

The trihalomethane formation potential (THMFP) was measured in groundwaters affected by infiltration of wastewater or landfill leachate from Mexico, Jordan and Thailand. THMFP was directly related to the concentration of dissolved organic carbon, except where leachate was produced from burnt waste or where bromide concentrations were unusually high indicating the proportion of brominated derivatives was dependent on the concentration of bromide. It is proposed that the THMFP provides a sensitive measure of low levels of organic contamination and can be used as a surrogate for dissolved organic carbon concentration where there are difficulties in measuring this parameter. A risk assessment model has been used and demonstrates indirect health effects due to the chlorination of leachate contaminated groundwater.

KEYWORDS: TRIHALOMETHANES, ORGANIC CARBON, GROUNDWATER CONTAMINATION, INDUSTRIALISING CITIES, WASTEWATER, LANDFILL LEACHATE

Introduction

There is some evidence that a persistent 'shadow' of above-background concentrations of dissolved organic carbon (DOC) exists beneath wastewater recharge sites (Foster et al., 1994) and beneath leaking landfills. The majority of this dissolved organic carbon is likely to be in the form of humic and fulvic acids. These are complex, natural organic compounds that are responsible for much of the brown colour in natural waters.

Landfill leachate has a high content of DOC, particularly in developing countries where the putrescible content of waste is high (Figure 1). This wastewater gives rise to a complex mixture of 'humic-like' organic acids, together with phenols, aromatic hydrocarbons, terpenes, proteins and lignins originating from decomposing plant material (Reinhard et al., 1984; Weis et al., 1989; Lyngekilde and Christensen, 1992). The high molecular weight acids are yellow-brown in colour and have acidic functionality of several ?mol mg^{-1} DOC (Weis et al, 1989). They differ from soil derived humic substances in generally having lower oxygen content, phenolic group content and molecular weight. Xenobiotics are also produced, for example phthalates, by the decomposition of PVC (Mersiowsky et al, 1999).

Wastewater may contain a wide and variable range of identifiable organic compounds (BGS et al, 1998). But these form only a small fraction of the total organic loading wastewater-affected groundwater (Peters et al, 1994). This organic loading can be difficult to quantify reliably where sites are remote from analytical facilities, especially taking into account the limited stability of the sample. A further problem is that the DOC measurement is frequently difficult to reproduce between laboratories. An analogue indicator of DOC would therefore be of benefit.

Trihalomethane formation

Dissolved organic material can react with chlorine during water disinfection for potable supply to form

trihalomethanes (THMs, haloforms). For effective disinfection an excess of chlorine over the sample consumption is needed and this free chlorine can react with organic compounds present in the water during storage or distribution of the treated water. The THM compounds most commonly formed are chloroform, bromodichloromethane, chlorodibromomethane, and bromoform (Hutton and Chung, 1994). Owing to its high reactivity, chlorine reacts very rapidly with many natural organic compounds present in raw water. There is concern that the reuse of renovated water with an enhanced organic load may lead to increased haloform production during chlorination. However, there is some evidence that polar high molecular weight natural organic material, such as humic acids, rather than anthropogenic organic compounds are the preferred precursors (Alawi et al, 1994). This agrees with the observed correlation of haloform production with fluorescence properties of water (Ibarluzea, 1994) and with its aromatic carbon content (Harrington et al, 1996).

The type and relative amounts of chlorination by-products vary with chlorine concentration, the concentration of organic precursor compounds, pH, temperature, and contact time (Alawi et al, 1994). Bromide, often present in raw water, from either natural or anthropogenic sources has an important effect on the speciation of any THMs produced. During chlorination, bromide is oxidized by chlorine to bromine and chlorination and bromination become competitive reactions. Bromine appears to be more effective as a halogen-substituting agent and, if bromine acts as an oxidant, it will be reduced to the bromide ion, which may then be re-oxidised by chlorine. This results in a high bromine incorporation into the THMs and may account for the mutagenic activity of chlorinated waters which cannot be solely ascribed to chloroform (Peters, 1994). However the presence of ammonia at concentrations as low as 1 mg l^{-1} inhibits haloform formation by competing for reaction sites on the organic molecules (Denne, 1984). Ammonia is generally present at low concentrations in unpolluted groundwater, but is high in domestic wastewater and can be high in landfill leachates (Robinson, 1996; Stuart & Klinck, 1998).

Miller et al (1993) considered the fate of THMs during the artificial recharge and recovery of treated water. THMs may be formed during the initial treatment process and then not completely attenuated during recharge and storage, or during chlorination of recovered water. For example Miller et al (1993) found that recharge of the Las Vegas aquifer with treated water from the Colorado river could be relied upon to absorb either the chloro-organic components or the THM precursor materials from the treated water.

Measurement of trihalomethane formation potential (THMFP) is a standard test, where water is buffered at pH 7, dosed with an excess of chlorine and held for 7 days at 25°C (APHA, 1992). THMFP is expressed in terms of chloroform equivalents using the equation:

$$THMFP = A + 0.728B + 0.574C + 0.472D$$

where A = chloroform concentration, B = dichlorobromomethane concentration, C = chlorodibromomethane concentration and D = bromoform concentration (APHA, 1992). THMFP has been shown to be proportional to the 24-hour test used to simulate THM concentrations in supplied water (Hutton and Chung, 1987).

For sources with a uniform type of DOC, THM formation should be directly related to the DOC concentration (Amy et al., 1987). This paper examines the potential of using THMFP as a surrogate test for organic loading of groundwater polluted by domestic wastes, landfill leachate or wastewater. This would allow DOC concentration in various types of polluted groundwater to be estimated from a knowledge of the THMFP.

Site descriptions

The proposed method was applied to groundwater from a number of sites from three industrialising countries where the groundwater was known to be contaminated by infiltrating wastewater or landfill leachate (Table 1). Sites were also selected on the basis of the availability of nearby piezometers or shallow dug wells suitable for taking groundwater samples. Samples were also taken from local potable supply boreholes, other abstraction points and from the raw wastewater but not generally from the raw leachate.

1 León, Mexico

Leon is one of the most important centres in Latin America for leather processing and shoe manufacturing. It is situated in a semi-arid intermontane valley about 300 km northwest of Mexico City. All wastewater from the city is collected into six open channels and carried untreated into the adjacent irrigation area by a complex canal system. Some water is used directly for irrigation of crops, whilst the remainder passes through one or more storage lagoons before being used.

This scheme has been operating for more than 40 years and infiltrating wastewater has formed a new shallow aquifer, with very poor water quality, beneath the irrigation area. A number of shallow irrigation wells draw water from this aquifer. The city is highly dependent on groundwater for potable supply and one of the main wellfields abstracts from a deeper aquifer within the complex volcanic and alluvial deposits below the irrigation area. This abstraction is causing poorer quality water to be drawn down and water supplied to the city is beginning to be affected. This site is described in more detail in Stuart and Milne (1997), Chilton et al (1998) and BGS (1998).

2 Mezquital, Mexico

The Mezquital Valley also has a semi-arid climate. It currently receives some 70% of the wastewater produced by Mexico City (about 40 $m^3 s^{-1}$). This water is transported for more than 30 km in tunnels and used directly to irrigate more than 45,000 ha of previously unproductive land. The distribution scheme has been developed for over 100 years and is now very complex with several major impoundments, and many interconnected main and lateral canals.

Widespread and prolonged wastewater irrigation has completely modified the groundwater system with water levels now being very close to the surface and substantial areas of land subject to waterlogging. In effect a new aquifer has been created within the valley which forms the main source of potable water for some 500,000 residents in the valley. However the wastewater origin of the groundwater means that many supplies do not meet the Mexican Drinking Water Limits. Water quality appears to be slowly deteriorating under the present irrigation regime. Further details are given in CNA et al (1998) and BGS et al (1998).

3 Wadi Dhuleil, Jordan

The Khirbet As Samra wastewater treatment plant serving Amman is situated in Wadi Dhuleil, some 42 km northeast of Amman. This plant consists of a series of ponds (oxidation and facultative) with a combined area of 181 ha. The treated water is discharged to Wadi Dhuleil and is of poor quality since the organic loading of the wastewater exceeds the plant design capacity.

The climate is semi-arid so there is little wadi baseflow.

Water is drawn off along the wadi down stream of the plant for small-scale irrigation and the wadi flow becomes progressively poorer and more saline due to irrigation returns. Groundwater in the underlying limestone aquifer has been affected by infiltration both from the treatment plant ponds and leakage from the wadi bed. The quality deterioration is exacerbated by over abstraction for irrigation with the consequent drawing down of shallow poor quality water into the aquifer. Further details are given in BGS et al (1998).

4 Hat Yai, Thailand

Hat Yai is the third largest city in Thailand and is situated at the southern end of the Thailand peninsula. The climate is tropical-humid with high but strongly seasonal rainfall. The city occupies a low-lying valley underlain by thick Quaternary and Recent sediments. This valley contains a sequence of aquifers separated by clay semi-confining layers and Hat Yai obtains about 55% of its urban water supply from groundwater.

Urban wastewater is disposed directly to a canal which passes through the city centre. Because of heavy abstraction of groundwater at depth in the city centre, a cone of depression has formed beneath the city. This has lead to relatively poor quality water thought to originate from the canal penetrating the aquifer system. Shallow water quality is now extremely poor with low redox and high concentrations of ammonium. Further details are given in Gooddy et al (1997) and BGS et al (1998).

5 Dzitya, Mexico

The village of Dzitya is situated to the northwest of the city of Mérida in the Yucatan peninsula, Mexico. In common with the city there is no mains drainage, and wastewater from the 1,100 inhabitants is disposed to the ground using septic tanks and cesspits. The Yucatan peninsula is formed from low-lying karst limestone with a shallow water table and groundwater is considered to be extremely vulnerable to pollution (Gonzáles Herrera, 1996).

Most properties in the village have a dug well for irrigation of smallholdings and water for limited numbers of stock. Some people also use this water for drinking after informal chlorination. Piped potable water is provided from a borehole also in the village.

6 Merida, Mexico

Up until 1998 the city of Mérida was served by a single large landfill site situated to the northwest between the city and the village of Dzitya. This accepted municipal, medical and industrial wastes, both solid and liquid. The site was not engineered and consists of a series of waste layers covered with fine material derived from the waste. The climate is tropical-humid and therefore large amounts of leachate are generated from the waste. It was calculated that 13,000 m^3 could have been produced annually (Klinck & Stuart, 1999). There is no provision for leachate containment or treatment and all leachate infiltrates to the ground. A plume of contaminated groundwater can be detected under the site and a few hundred metres to the northwest. Further information can be found in Gonzáles Herrera (1996, Klinck et al (1997) and Klinck & Stuart (1999).

7 Tha Muang, Thailand

Solid wastes (some 3.5 tonnes per day) from the small town of Tha Muang, Kanchanaburi province, central Thailand, are disposed to a walled compound about 100 m square. The site has been in use for about 30 years. There is evidence that the wastes, which have a very high putrescible content, are burnt on a regular basis to reduce waste volume. Pleistocene gravels, sands and silts in the basin of the Mae Klong river underlie the site.

The site is surrounded by houses and irrigated fields. Local groundwater from shallow dug wells is used for crop irrigation, fish farming and for informal potable supply. Further details can be found in Klinck et al (1999) and Klinck & Stuart (1999).

8 Mae Hia, Thailand

The Mae Hia waste disposal site served the major city of Chiang Mai in northern Thailand from 1958 to 1989. The site was closed after complaints from local residents about groundwater pollution and vermin. A mixture of filling, with soil cover, and open dumping disposed waste. The site is now soil covered although a leachate lagoon remains within the original dump area. The site is situated on a sequence of Quaternary colluvial deposits consisting of sand and gravel layers interbedded with clayey units.

Approximately 100 houses exist in the vicinity of the site. Originally water supply was from dug wells into the colluvial aquifer. The water level is shallow (between 0.5 and 10 metres). Many of these wells are only used for irrigation, cleaning and cooking because of poor water quality. Karnchanawong et al (1996) identified a persistent plume of contaminated groundwater moving eastwards from the site. Further details can be found in Karnchanawong et al (1996), Karnchanawong et al (1999), Klinck et al (1999) and Klinck & Stuart (1999).

Sample collection and analytical procedures

Samples were collected directly in pre-cleaned amber glass bottles with PTFE-lined screw caps for THMFP and HDPE bottles for bromide and ammonium, and filtered through 0.45 (m silver membranes into chromic acid washed glass vials for DOC determination.

For THMFP determination the method uses three principal reagents: a dosing solution (50 ml sodium hypochlorite solution having 4-20% available chlorine made up to 250 ml); a pH 7 phosphate buffer (6.81 g potassium dihydrogen phosphate and 1.17 g sodium hydroxide dissolved in 100 ml); and a quenching solution (10% sodium sulphite). All reagents were made up with 'Milli Q' grade water. 30 ml of the solution to be chlorinated was placed in a 40-ml vial with a PTFE septum and a screw cap. 1 ml of dosing solution and 1 ml of phosphate buffer were added and the sample stored at 25^{o}C for 7 days. 1 ml of sodium sulphite was added to prevent further reaction and the vials refrigerated until analysis.

Analyses for THMs were carried out using a gas chromatograph fitted with an OV-101 packed column and an electron capture detector. The flow rate was adjusted to 25 ml/min of nitrogen to elute all compounds of interest within 10 minutes. 3 ml of sample were extracted with 2 ml pentane and a 3 (l aliquot injected onto the column. Standards were prepared in the range 0-80 (g l^{-1} for

each component using the EPA 601 trihalomethanes mix (200 (g/ml in methanol). Procedural and method blanks were also run at regular intervals.

DOC was analysed using a TOCSIN II aqueous organic carbon analyser. Briefly, the inorganic carbon is first purged with nitric acid, before pyrolysis of the remaining organic carbon in a furnace at 900°C. The carbon dioxide produced is hydrogenated over a catalyst and converted to methane which is then passed into a flame ionisation detector. Calibration solutions are prepared using a potassium hydrogen phthalate (KHP) stock solution and made using a range of standards from 0-15 mg l^{-1} and cross checked with a 10 mg l^{-1} standard made from a glucose stock solution. All samples were diluted so as to fall in the calibration range, some samples needed to be diluted by up to 20 times.

Results

1 Dissolved *Organic Carbon*

The results for DOC in wastewater-affected areas clearly reflect the differences in organic content of the infiltrating wastewaters and the local climate (Table 2). In León, where the wastewater is discharged directly to the cultivated area adjacent to the city boundaries, the carbon content of the water is extremely high (42 - 265 mg/l). This is probably due both to the semi-arid climate and to discharge of tannery wastes with a high organic content as well as domestic wastewater (Stuart and Milne, 1997). The mean concentration is reduced slightly by the lower concentration of DOC in water leaving the first storage lagoon.

The organic carbon contents of wastewater reaching Wadi Dhuleil and Mezquital are similar. These wastewaters both come from cities in relatively arid areas, which produce mainly domestic wastes. In both cases, wastewater is transported over a considerable distance before reaching the discharge area. In Hat Yai, Thailand where the climate is much wetter, the effluent in the canal water is much more dilute. Since wastewater is discharged directly to the canals in the study area (Gooddy et al, 1997), this low concentration must be due to dilution by storm water.

Once water has entered the subsurface, the differences in the carbon content of the infiltrating water appear to be less important. The results of this study indicate that the DOC content of groundwater affected by infiltrating wastewater is surprisingly uniform and is generally in the range 3 - 9 mg l^{-1}. This contrasts with 'natural' concentrations of <2 mg l^{-1}.

The DOC does show some correlation with other components of the wastewater. For example, Figure 2 shows the relationship with chloride for both wastewaters and groundwaters from wastewater infiltration sites. The León wastewaters have both the highest carbon and the highest chloride content. Wastewaters from Amman and the Rio Salado, Mezquital have a similar ratio to León. León wastewater contains high concentrations of chloride derived from importation of salt-dressed hides for tanning (Stuart & Milne, 1997). The Rio Salado in Mezquital has always contained relatively saline water. Amman wastewater may be saline due to the arid climate and the relatively high chloride concentration in the city water supply. Wastewater from the Emisor Central in Mezquital has much lower chloride and may be more typical of domestic effluent (CNA et al, 1998).

As these wastes infiltrate to groundwater, the combined impact of organic degradation and evaporation

change the relationship completely. Many of the groundwaters contain higher chloride contents than the original wastewater. This is most extreme for Amman, where the groundwater chloride concentrations are up to 5 times greater than the concentrations in the wastewater.

For leachate-impacted groundwaters the chloride concentrations detected in the groundwater are higher and range from 6 to 24 mg l^{-1}. The highest concentrations were detected in Mérida, Mexico, where the large waste disposal site is situated on karstic limestone with a shallow water table. Very high DOC concentrations were found in groundwater samples from within the landfill boundary. Lower concentrations were found in Mae Hia, Thailand, where the disposal site had been closed and covered with soil for some eight years prior to this study.

2 THM formation

The rate of formation of THMs was measured in two samples taken from the plume of contaminated groundwater close to the site at Mae Hia over a period of 10 days. The results for one of these are shown in Figure 3. THMs were formed rapidly under the chlorine-saturated conditions used. After 1 day concentrations reached 60% and after 2 days reached 75% of the full THMFP measurement (7 days). This is more rapid than observed by Hutton & Chung (1994) who found the 1 day THM concentration to be only 30% of the THMFP, although the 1 day test was performed under slightly different conditions.

The THMFP test is therefore likely to be reasonably representative of the informal chlorination procedures used by individual water users at these types of sites. In these cases, drinking water is saturated with chlorine before use, either in jerrycans or from a container of chlorine tablets suspended in the well. The results found here are therefore considered to be acceptable for use in a health risk assessment for drinking groundwater from these sites.

The dominant trihalomethane formed was chloroform, comprising the largest proportion of the total THMs in 85% of samples. Chloroform was found to be present in all of the samples as was bromodichloromethane. Bromoform was the least commonly detected THM (none was found in any of the sites in Hat Yai) and found in only 28 % of samples. However, bromoform was detected in most of the groundwaters tested around Amman, reflecting the high concentrations of bromide present.

The results for the THMFP are summarised in Table 3. The THMFP is very low in uncontaminated water (<25 µg l^{-1}), but is clearly increased in contaminated groundwater with most sites having mean concentrations of between 100 and 300 µg l^{-1}. The exceptions are the landfill sites of Mérida, where the THMFP is very high, and Tha Muang where the THMFP is scarcely above background. These exceptions are discussed in section x.

3 Relationship with DOC

There is a clear positive relationship between THMFP and DOC concentration for each site. As an example, data from Mae Hia is shown in Figure 4. The ‘reactivity’ of the DOC can be estimated from the slope of the relationship between THMFP and DOC. Table 4 gives the differing reactivity of the DOC at the different sites.

There are definite differences between the groundwaters and wastewaters. The THMFP determination was not generally carried out for the leachates. Groundwater DOC tends to have a reactivity of between 20 and 31 ?g mg^{-1}. Exceptions to this are Mezquital (38 ?g mg^{-1}), Wadi Dhuleil

(45 ?g mg^{-1}) and Tha Muang (about 2 ?g mg^{-1}).

DOC reactivity for the wastewaters was much more variable. Wastewater from León has a very low reactivity averaging just 2.8 ?g mg^{-1} and Wadi Dhuleil wastewaters are also low (around 10 ?g mg^{-1}). The single leachate measured was also very low (1.2 ?g mg^{-1}). Wastewater from Mezquital has a very similar reactivity to the groundwater (27 ?g mg^{-1}), whereas the wastewater in Hat Yai is much more reactive than the groundwater with an average of 42 ?g mg^{-1}. Some explanation can be found from the other components in the wastewaters or leachates.

Jiang et al (1998) showed that the formation of the individual THMs in groundwater used for potable supply in Cincinnati could be modelled as first order reactions depending only on TOC concentration except for bromoform formation which was not well represented by this approach. Both bromide and ammonium are known to affect the rate of THM formation from organic matter, in addition to the degree of humification. Additionally ageing of the wastewater arrears to result in increased 'DOC reactivity'.

Bromide

Hutton and Chung (1994) showed that bromine incorporation is rapid early on with the initial rate related to the bromide concentration. The rate is limited at high bromine concentrations by the number of available halogenation sites on the organic molecule. Eventually a saturation level is reached with three bromine atoms being incorporated into each THM. This means that bromide can have a catalytic effect on the overall THMFP, as well as producing enhanced concentrations of brominated products (Peters et al, 1994).

Formation of brominated THMs was related to the concentration of bromine in the groundwater at all of the sites studied (Figure 5). The largest bromide concentrations were found in the groundwaters of Wadi Dhuleil and Mezquital. This is reflected in the high percentage of brominated products (Table 4).

Ammonium

In, contrast, ammonium inhibits the reaction by competing for reaction sites on the organic material (Denne et al, 1984). It may also react directly with chlorine, reducing the concentrations available to react with the organic matter. Both the León and Wadi Dhuleil wastewaters contain high concentrations of ammonium (>70 mg l^{-1}), as does the Merida leachate (511 mg l^{-1}). These high concentrations may contribute to the apparent lack of carbon reactivity. Concentrations are of ammonia are lower in the canals of Hat Yai and Mezquital since they are well aerated and DOC reactivities are in the same range as for groundwater DOC.

Ageing of DOC

The wastewaters in Mezquital and Wadi Dhuleil had been transported for 20-30 km before discharge and the ageing of the DOC during the period of transfer may have contributed to an increased 'reactivity' as compared to León where discharge is directly from the city.

Other factors

The very low reactivity of the DOC at Tha Muang is thought to be due to an entirely different reason, that is the burning of the waste, which is carried out at this site. The residual DOC derived from the wastes appears to be lacking in the functional groups which react with chlorine or bromine.

None of these factors described above account for the high rate of THM formation in Hat Yai wastewaters. The limited buffering capacity of the sediments and the low pH of the groundwater (Gooddy et al, 1997) may be a factor, giving the effect of accelerated ageing.

4 Correlations between parameters

Selected interparameter correlations are shown in Table 5. Tha Muang has been considered separately from the other landfill sites due to its different behaviour and has been omitted from the calculations for landfills. These show the correlation between THMFP and DOC to be only moderate overall, but greater at landfill sites (0.87) than at wastewater sites (0.82). This correlation is much improved for wastewater sites when Dzitya is excluded.

The landfills also show a correlation between SEC - DOC and also SEC - THMFP but the wastewater sites do not. For the wastewater sites where the linear regression of bromine-related parameters is dominated by the high bromide concentrations in Wadi Dhuleil, which are correlated with SEC.

None of the sites shows the expected correlation between THMFP and bromide and indeed only at Tha Muang is there is a positive relation between THMFP and percentage brominated products, although this is not a strong linear relationship.

Health risks from chlorination of polluted water

The THMs have been shown to have both genotoxic and carcinogenic effects particularly in the liver and kidney. Because the four compounds usually occur together, it has been the practice to consider these as a group and a number of countries have set potable quality guidelines on this basis. However, the WHO guideline values for water disinfection products are now set separately at 200 (g l^{-1} for chloroform, 100 (g l^{-1} for bromoform and chlorodibromomethane, and 60 (g l^{-1} for bromodichloromethane (WHO, 1993).

The WHO estimate an overall GV by combining the individual components as follows:

where C = concentration and GV = guideline value. Applying this to the highest of the result from Mae Hia, shown in Figure 2, with a high bromine concentration gives the additive toxicity as 1.7, almost twice the guideline value.

A risk assessment has also been calculated for groundwater consumption by the local population at Mae Hia using the USEPA approved Risk*Assistant model. This estimates both the toxic and carcinogenic risks. The toxic risk (expressed as the hazard quotient, HQ) is based on the

comparison of actual exposure to a substance to a reference dose, as follows:

$$HQ = \frac{\text{total amount ingested}}{\text{body weight} \times \text{exposure period} \times \text{reference dose}}$$

The reference dose, the dose which can occur over a prolonged period without ill effect, is extrapolated from toxicological studies of exposure that demonstrate a critical effect. Reference doses are tabulated in the IRIS and HEAST databases maintained by the USEPA. It is general practice to assume that a toxic chemical has an effect below which toxic effects do not occur.

Carcinogenic compounds differ from toxic compounds in that there is no lower limit for the existence of risk. Carcinogenic risks are statements of probability; for example one in a million (1:1,000,000) increased risk of cancer. The risk is calculated by calculating the lifetime average daily dose (LADD) multiplied by a slope factor. The LADD is calculated as:

$$LADD = \frac{\text{total amount ingested}}{\text{body weight} \times \text{lifetime}}$$

The slope factor is the gradient of the line of the dose – response curve derived from laboratory toxicological studies. Slope factors are available in the USEPA databases.

The difficulty with such risk assessments lies in the calculation of the exposure factors used to estimate the dose. For a typical Thai population the exposure factors shown in Table 6 were used. Using these factors suggests that the disinfection of groundwater contaminated by leachate at Mae Hia does pose a health risk. Taking the same result from Mae Hia as an example, the Hazard Quotient was 2.77, i.e. a toxic risk due to chloroform exists, and the carcinogenic risk was 3:10,000. The USEPA range of concern is for an increased carcinogenic risk of 1:1,000,000.

We stress that great care needs to be taken in the interpretation of these results. The model is very sensitive to uncertainty in the parameterisation of the exposure factors, especially exposure duration and ingestion rates and conservative estimates were used here. However, what the modelling does demonstrate that there are indirect health effects due to the chlorination of leachate contaminated groundwater. Additional risks may be associated with the consumption of locally grown fruit and vegetables.

Conclusions

The trihalomethane formation potential is a valuable tool for quantifying non-specific organic contamination of groundwater by urban wastes, landfill leachate and domestic wastewater. It has advantages over measurement of dissolved organic carbon since specialised sample preservation, a very rapid turnaround time or sophisticated analytical equipment are not required. It is also closely related to one of the principal risk factors associated with enhanced DOC concentrations in drinking water

The reactivity of the dissolved organic carbon in groundwater was consistently in the range 20-38 (g trihalomethanes formed per mg carbon for the sites studied. The exceptions were at Tha Muang, Thailand, where waste was burnt during disposal and in Wadi Dhuleil where groundwater bromide concentrations were very high.

The trihalomethane formation potential can be used to estimate the health risk to local groundwater users from the by-products of water chlorination. This has shown that this risk may make groundwater unsafe for drinking and therefore it is recommended that a regular monitoring programme of THM formation potential in chlorinated water is instigated in areas where groundwater has been affected by wastewater.

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Table 1 Summary of study sites

Site	Scheme type	Samples	
		Type	Number
León, Mexico	Irrigation close to the city with domestic and tannery wastewater	Wastewater	4
		Shallow piezometers	4
		Irrigation wells	2
		Potable supply boreholes	5
Mezquital, Mexico	Irrigation with wastewater transported by tunnel from Mexico City	Wastewater	3
		Shallow piezometers	5
		Irrigation wells	2
		Potable supply boreholes	5
Dzitya, Mérida, Mexico	Unsewered sanitation from small village to the NW of Mérida	Dugwells	8
		Potable supply borehole	1
Mérida, Mexico	Large landfill serving city of Mérida	Leachate	3
		Shallow piezometers	8
		Dugwells (irrigation and domestic supply)	8
Wadi Dhuleil, Jordan	Wadi Dhuleil receives effluent from wastewater treatment lagoons serving Amman	Wastewaters	2
		Observation boreholes	2
		Irrigation boreholes	7
		Industrial boreholes	2
Hat Yai, Thailand	Urban wastewater is disposed to canals	Wastewaters	4
		Shallow piezometers	6
Tha Muang, Kanchanaburi, Thailand	Small landfill serving rural community	Dugwells (irrigation)	7
Mai Hia, Thailand	Old landfill previously serving city of Chiang Mai	Dugwells	12

Table 2 Dissolved organic carbon concentrations in wastewater and groundwater in study areas

Site	Date	DOC concentration (mg l-1)					
		Wastewater or leachate		Contaminated groundwater		Uncontaminated groundwater	
		Mean	Range	Mean	Range	Mean	Range
Wastewater sites							
León	2/97	198	42 - 265	3.4	1.0 - 8.4	0.88	0.3 - 1.5
Mezquital	2/97	33	9.8 - 51	3.6	2.3 - 4.9	1.2	0.8 - 1.7
Wadi Dhuleil	5/97	35	34 – 36	3.1	0.6 - 9.9	-	-
Hat Yai	2/97	9.3	5.7 - 13	3.3	1.6 - 6.3	-	-
Dzitya	4/97	-	-	9.4	4.2 -37	-	-
	11/97	-	-	6.4	4.3 - 7.0	-	-
Landfill sites							
Mérida	4/97	1,920	535-3,298	23.5	3.1-131	-	-
	11/97	-	-	12.4	3.1 - 84	-	-
Tha Muang	5/97	-	-	5.9	3.8 - 7.8	-	-
	11/97	-	-	15.6	3.6 – 54	-	-
Mai Hia	5/97	-	-	6.4	1.1 – 24	-	-
	11/97	-	-	7.0	2.4 - 15	-	-

Table 3 THM formation potentials of wastewater and groundwater in study areas

Site	Date	THMFP (µg l-1)					
		Wastewater or leachate		Contaminated groundwater		Uncontaminated groundwater	
		Mean	Range	Mean	Range	Mean	Range
Wastewater sites							
León	2/97	553	362 - 673	105	120 - 397	9	7 – 11
Mezquital	2/97	901	719 - 1107	108	61 - 218	21	19 – 22
Wadi Dhuleil	5/97	345	320 - 370	108	25 - 620	-	-
Hat Yai	2/97	396	238 - 786	94	66 - 155	-	-
Dzitya	4/97	-	-	231	170 - 514	-	-
	11/97	-	-	146	0 - 286	-	-
Landfill sites							
Mérida	4/97	2372	193 – 4,551	682	93 – 2,892	-	-
	11/97	-	-	287	53 – 2,554	-	-
Tha Muang	5/97	-	-	21	18 – 24	-	-
	11/97	-	-	20	13 – 39	-	-
Mai Hia	5/97	-	-	137	9 – 428	-	-
	11/97	-	-	150	70 - 281	-	-

Table 4 DOC reactivity and factors influencing THM formation

Site	Mean for wastewater/leachate				Mean for contaminated groundwater			
	DOC reactivity (?g mg-1)	NH4 (mg l-1)	Br (mg l-1)	% Br products	DOC reactivity (?g mg-1)	NH4 (mg l-1)	Br (mg l-1)	% Br products
Wastewater sites								
León	2.8	72	0.71	18	31	0.04	0.35	18
Mezquital	27	10	0.73	12	39	0.04	0.84	34
Wadi Dhuleil	9.8	91	0.95	36	45	1.3	3.41	56
Hat Yai	42	9.0	0.25	6	27	6.2	0.16	9
Dzitya Apr	-	-	-	-	25	0.31	0.24	12
Dzitya Nov	-	-	-	-	23	0.1	0.51	12
Landfill sites								
Mérida Apr	1.2	511	12.6	15	24	3.6	0.62	15
Mérida Nov	-	-	-	-	31	0.14	0.77	14
Tha Muang May	-	-	-	-	3.2	0.05	0.79	22
Tha Muang Nov	-	-	-	-	0.77	0.05	0.57	18
Mai Hia May	-	-	-	-	20	4.0	0.51	18
Mai Hia Nov	-	-	-	-	21	0.33	0.42	14

Table 5 Correlation **matrices for groundwater at different types of site**

Site type	Parameter	Br	DOC	NH4	THMFP	Br products
Wastewater (n = 61)	Br	1				
	DOC	-0.08	1			
	NH4	-0.05	0.06	1		
	THMFP	-0.06	0.70	0.25	1	
	Br products	0.82	-0.14	-0.07	-0.03	1
	SEC	0.93	-0.09	0.08	-0.03	0.84
Landfills except Tha Muang (n = 56)	Br	1				
	DOC	0.67	1			
	NH4	0.23	0.56	1		
	THMFP	0.66	0.87	0.44	1	
	Br products	0.44	0.19	0.34	0.12	1
	SEC	0.66	0.73	0.47	0.60	0.37
Tha Muang (n = 14)	Br	1				
	DOC	0.34	1			
	NH4	-0.25	-0.18	1		
	THMFP	0.40	0.75	-0.33	1	
	Br products	0.67	0.38	-0.59	0.70	1
	SEC	0.57	0.82	-0.35	0.91	0.69

Coefficients > 0.7 in bold

Table 6 Exposure factors used in risk assessments at Mae Hia

Factor	Estimate
Exposure duration	Difference in time from inception of landfill to present time (40 years). Assumes population has remained static
Body weight	Data obtained from Provincial Public Health Office in Chiang Mai. Men – 58 kg, women 50 kg.
Life expectancy	Data obtained from Provincial Public Health Office in Chiang Mai. Men and women – 60 years until recently. Now AIDS has reduced life expectancy for men to 50.2 years
Water ingestion rate	Based on bottled water consumption of 3 l d-1. Seems low for hot climate and 6 – 10 l d-1may be more appropriate

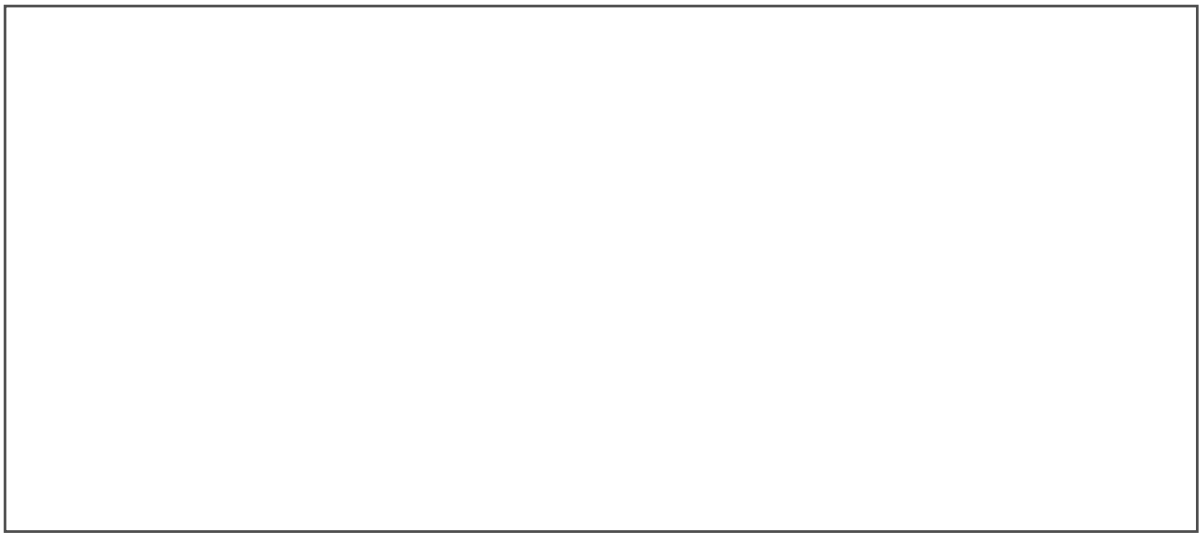

Figure 1. Waste composition for Chiang Mai city, Thailand (from Stuart and Klinck, 1998)

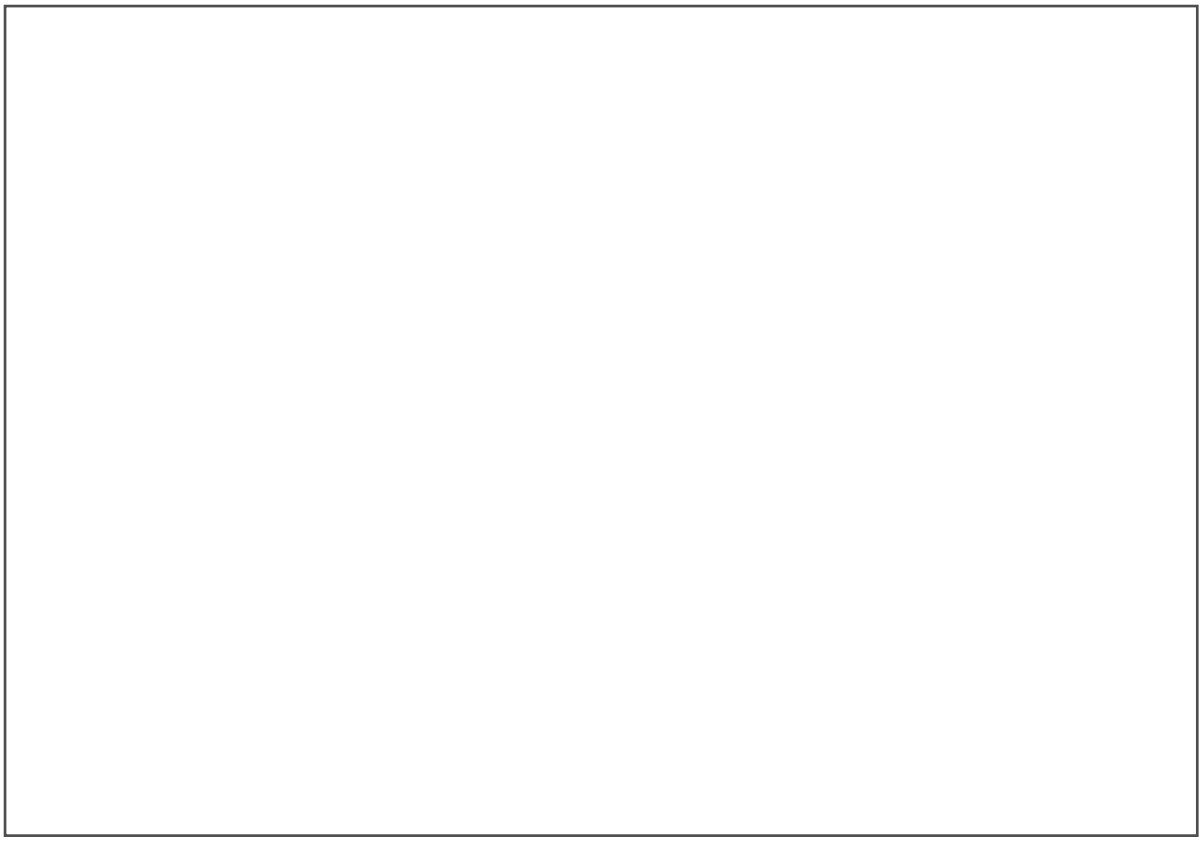

Figure 2 DOC and chloride in the wastewaters and groundwaters from the wastewater infiltration sites

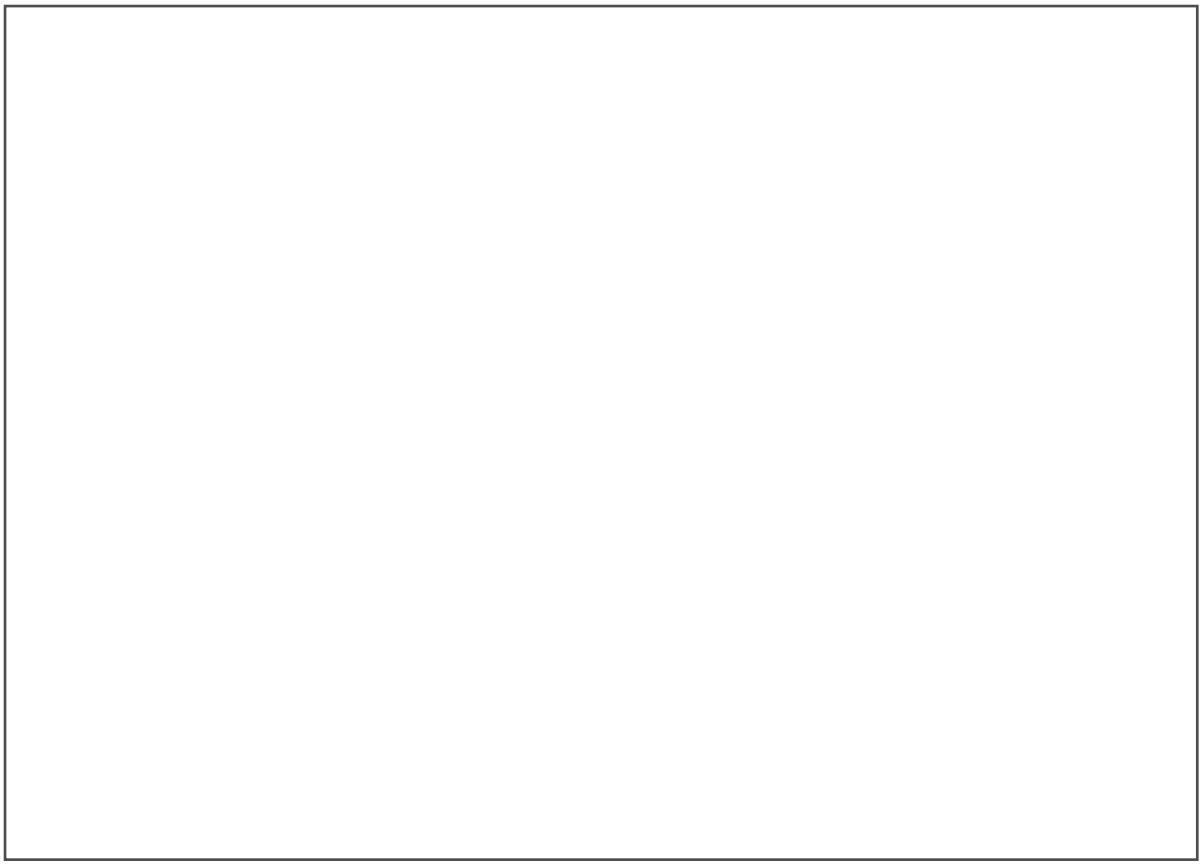

Figure 3 **Rate of trihalomethane formation in leachate affected groundwater from Mae Hia, Thailand**

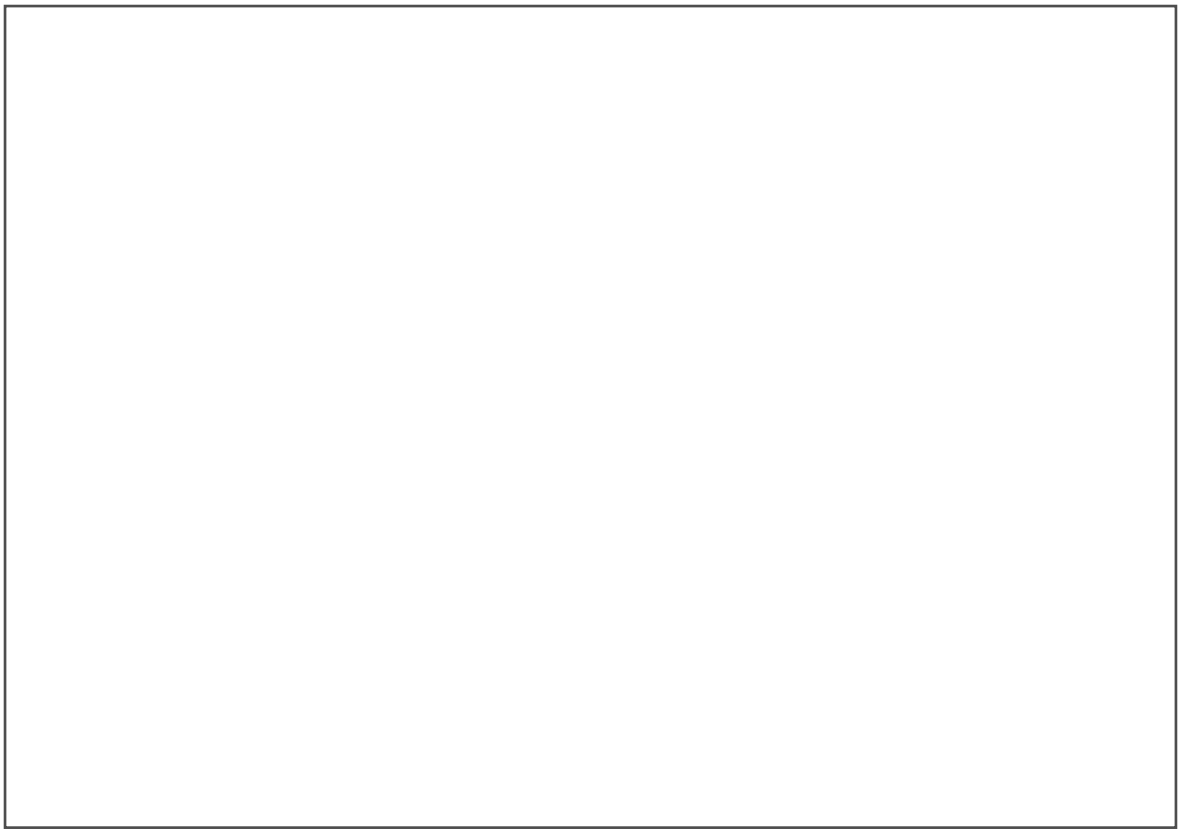

Figure 4 DOC concentration and THMFP for Mae Hia

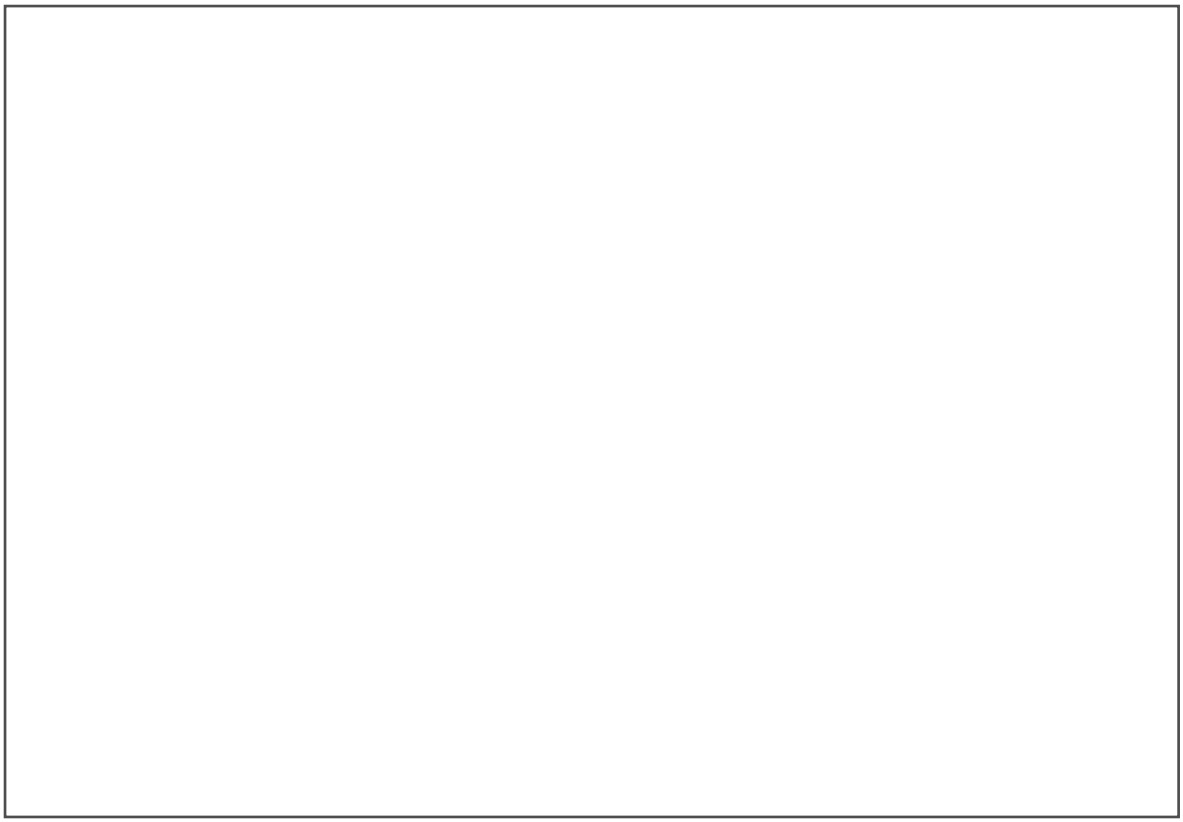

Figure 5 Percentage brominated THM formation against bromide concentration for groundwaters at wastewater infiltration sites

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