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Tracing dissolved organic carbon and trihalomethane formation potential between source water and finished drinking water at a lowland and an upland UK catchment

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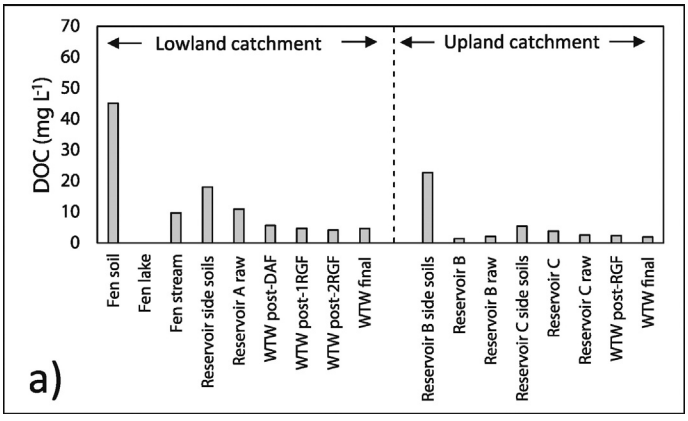
HIGHLIGHTS

- Origin and fate of trihalomethane precursors assessed in upland and lowland catchment.
- Reservoirs acted to dampen seasonal variations in water quality.
- The lowland fen acted as a significant source of dissolved organic carbon.
- Selectivity during drinking water treatment increased the proportion of brominated THM species.

GRAPHICAL ABSTRACT



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ABSTRACT

Rising dissolved organic carbon (DOC) concentrations in many upland UK catchments represents a challenge for drinking water companies, in particular due to the role of DOC as a precursor in the formation of trihalomethanes (THMs). Whereas traditionally, the response of drinking water companies has been focussed on treatment processes, increasingly, efforts have been made to better understanding the role of land use and catchment processes in affecting drinking water quality. In this study, water quality, including DOC and THM formation potential (THMFP) was assessed between the water source and finished drinking water at an upland and a lowland catchment. Surprisingly, the lowland catchment showed much higher reservoir DOC concentrations apparently due to the influence of a fen within the catchment from where a major reservoir inflow stream originated. Seasonal variations in water quality were observed, driving changes in THMFP. However, the reservoirs in both catchments appeared to dampen these temporal fluctuations. Treatment process applied in the 2 catchments were adapted to reservoir water quality with much higher DOC and THMFP removal rates observed at the lowland water treatment works where coagulation–flocculation was applied. However, selectivity during this DOC removal stage also appeared to increase the proportion of brominated THMs produced.

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1. Introduction

Natural organic matter (NOM) is a ubiquitous component of natural waters and comprises biogenic materials and substances at various stages of decomposition (Hope et al., 1994). NOM originates from plant, microbial and animal products both in the form of metabolised (excreted) or egested waste products and their decomposing remains (Wetzel, 2001). NOM may be leached into the hydrosphere from external (allochthonous) sources via runoff and percolation during rainfall events. Alternatively it may be produced in situ in the water body from aquatic plants, plankton and higher organisms (autochthonous NOM) (Hope et al., 1994; Kalbitz et al., 2000).

Trihalomethanes (THMs) are formed by the reaction between NOM and free chlorine during the disinfection stage of drinking water treatment (Rook, 1977; Hirose and Okitsu, 1982; Sánchez et al., 1993). Since conventional treatment is generally effective at removing particulate organic matter, dissolved organic matter (DOC) represents the problematic component. A minimum period of contact with free chlorine is necessary to ensure that drinking water meets microbiological safety standards. THM formation potential (THMFP) depends on DOC, pH, Cl_2 dosage and exposure times but Table 1 shows some examples of reported data from Maryland, US (Porter et al., 2005) and an upland catchment in the UK (Gough et al., 2014) showing final water THM values between 129 and 217 μg L^{-1}. However, population-based case control studies suggest a weak association between lifetime consumption of chlorinated drinking water and incidence of rectal, colon and bladder cancer (Cantor et al., 1998; Hildesheim et al., 1998). At high doses, individual THM species ($CHCl_3$, $CHCl_2Br$, $CHClBr_2$ and $CHBr_3$) were also found to be carcinogenic in rodent bioassays (National Cancer Institute, 1976; Dunnick et al., 1985; George et al., 2002). In the UK, current regulations stipulate a maximum THM concentration of 100 μg L^{-1} for water at the end of the distribution system (i.e. supplied to a customers' property) (DWI, 2010). If this level is exceeded then the water company responsible is liable to face a financial penalty. In this context, rising dissolved organic carbon (DOC) concentrations in waters draining upland catchments in the UK over the last few decades (Freeman et al., 2001; Worrall et al., 2003; Evans et al., 2012) are a major concern.

Traditionally, efforts to minimise THM formation have been focussed on water treatment processes. For example, considerable amounts of research have concentrated on adjusting the coagulation–flocculation process to improved THM precursor removal (so-called enhanced õcoagulation; Matilainen et al., 2010; Gough et al., 2014). In addition, alternative chemical disinfectants including ozonation, chloramination, and dosing with chlorine dioxide (Craun, 1993; Langlais et al., 1991; Kristiana et al., 2009), and non-chemical disinfection such as UV (Templeton et al., 2005), have been explored. However, increasingly, water companies are adopting a more holistic approach with increased emphasis on "at source", as opposed to "end of pipe" solutions (Grayson et al., 2012). A key focus in this new approach is on the role of catchment processes and management in affecting drinking water quality.

In this study, DOC and THM formation potential (THMFP) were measured at intervals between the water source and final drinking water in 2 contrasting catchments (a lowland fen- and an upland peat-dominated catchment) in north Wales in order to investigate the origin and fate of THM precursors and the efficacy of existing treatment processes.

2. Methods

2.1. Site description and sampling regime

Sampling was undertaken at a lowland and an upland drinking water catchment in north Wales. The lowland catchment is dominated by pastoral agricultural land and also features a large alkaline fen from which one of the main reservoir inflow streams originates. The drinking water reservoir (herein referred to as Reservoir A) is a 0.86 km^2 man-made, shallow (max. 4 m depth), lowland reservoir with high DOC concentration. The inflow stream originating in the fen area is known to contain high DOC levels with reports of 6.0–12.7 mg DOC L^{-1} in the reservoir being *ca.* 2 to 4 times the levels reported in nearby reservoirs (Hughes et al., 2013). Since the creation of the reservoir, a marshy wetland has formed around its perimeter, especially where trees were also felled. The high reservoir DOC concentrations have led to issues relating to THM compliance (i.e. <100 μg total THM L^{-1}; DWI, 2010) at the water treatment works (WTW) which is located next to the reservoir.

The upland catchment is comprised, almost exclusively of acidic, ombrotrophic, carbon-rich *Sphagnum*-dominated bog soils and also supports some low-intensity sheep grazing. This catchment features 2 deep, oligotrophic drinking water reservoirs (herein referred to as Reservoirs B and C). These reservoirs supply a WTW located a number of kilometres away via overland streams. At the WTW the water from the 2 sources is blended before treatment. Although DOC concentrations are relatively low, this site was chosen since it typifies the type of environment prone to increased DOC exports in response to climate change (Freeman et al., 2001; Worrall and Burt, 2005).

Where possible, samples were collected on 2 occasions (November 2004 and May 2005) in order to investigate potential seasonal variations in the production and transport of THM precursors. At the lowland site, sampling of the fen area was included since this is known to be an important source of DOC. Water samples were collected from a small lake located within the fen, from the stream connecting the fen to the

Table 1
Selected THMFP and STHMFP data from previous studies. All data shown as μg L^{-1}. Errors shown in parentheses.

Maryland, US						Reference
	Region 1	Region 2	Region 3	Region 4	Total	
$THMFP_{max}$	134	207	129	169	207	Porter et al. (2005)
$THMFP_{min}$	14	24	17	18	14	
Mean THMs						
Total	41.0	70.2	45.6	53.7	52.7	
$CHCl_3$	25.0	48.1	28.9	34.4	34.1	
$CHBrCl_2$	11.7	16.1	12.8	13.2	13.4	
$CHBr_2Cl$	4.0	5.0	4.3	4.1	4.4	
$CHBr_3$	0.3	0.3	0.3	0.3	0.3	
Upland catchment, UK						
	Raw water	Post-DAF	Post-1RGF	Post-2RGF	Final	
$STHMFP_{7d}$	121 (10)	72 (7)	72 (8)	75 (7)	81 (9)	Gough et al. (2014)
$THMFP_{7d}$	1384 (87)	216 (16)	190 (14)	216 (19)	217 (17)	
Br-THMs	66.4 (19.4)	25.5 (7.3)	19.0 (5.5)	18.1 (5.1)	21.3 (6.1)	