Assessment of natural organic matter and ptaquiloside Irish drinking water

Summary

Welcome to the third edition of our project newsletter and many thanks for all the feedback on our first two issues dated 1st September 2014 and 1st of June 2015. The project aim is to assess natural organic matter (NOM) and ptaquiloside (Pta) in Irish drinking water. When present in drinking water NOM can give rise to disinfection by-products (DBPs).

Trihalomethanes (THMs) are the most eminent group of DBPs and in the period 2008—2010 the EPA found that 13% of public water supplies failed the 100 μg L^{-1} required parametric limit. Ireland had the highest reported non-compliance for THM exceedances across the 27 EU Member States during the period and at least two-fold greater than the next highest Member State, Estonia.

To date we have identified areas within Ireland which are at risk of receiving high NOM based on percentage peat, rainfall and slope in the catchment . We are currently using an exploratory analysis approach to identify land use factors responsible for causing higher THMs in Irish drinking water using national datasets.

We have collected approximately 16 months of data from our monthly sampling programme at our three sites, in counties Meath, Galway and Mayo.

Preliminary results are showing that GAC and ultra-filtration membranes are not fully effective for removing NOM at our study sites. High TON at our Boyne site has encouraged us to investigate nitrogenous DBP formation.

Our preliminary Pta data has shown spatial variation with less Pta on the western side of the country compared with the east. Preliminary results have also shown that Pta degrades very quickly in the natural environment. This data provides the first reported measurements of Pta in the Republic of Ireland.

Environmental Protection Agency
An Ghníomhaireacht um Chaomhnú Comhshaoil

Comhshaol, Pobal agus Rialtas Áitiúil
Environment, Community and Local Government

1st December 2015

Issue 3

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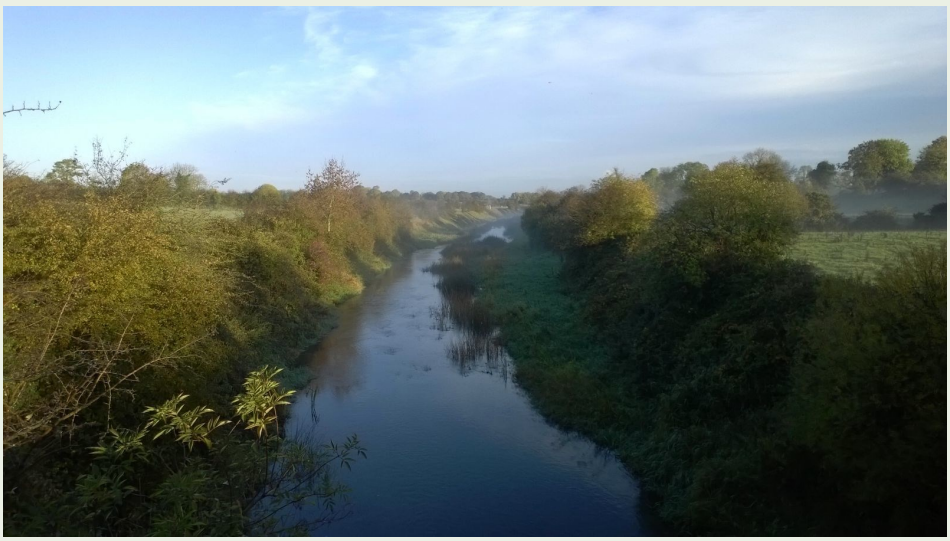
Special points of interest:

- Bracken study with CAFRE in North Ireland
- Preliminary NOM trends
- GAC Study - preliminary results
- Membrane study - preliminary results
- An account of NOM6 in Malmö



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NUI Galway
OÉ Gaillimh

GALWAY COUNTY COUNCIL
Comhairle Chontae na Gaillimhe

Trinity College Dublin
Coláiste na Tríonóide, Baile Átha Cliath
The University of Dublin

Comhairle Contae Lú
Louth County Council

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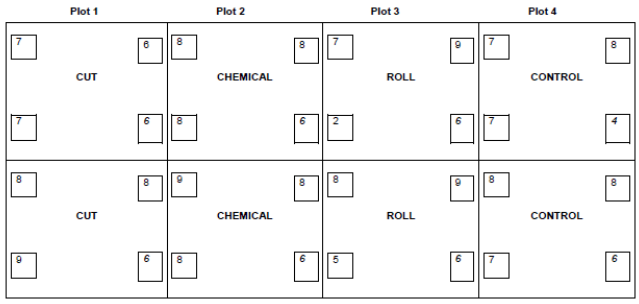
Bracken Management Study

In addition to the seasonal sampling of bracken vegetation and drinking water draining bracken stands it was proposed to measure the Pta content of bracken vegetation from six demonstration sites comparing the effectiveness, against an untreated area, of three different treatments fro bracken: cutting, rolling and spraying with Asulam. .

The six demonstration sites across Northern Ireland were chosen by Mr. Graeme Campbell, Department of Agriculture and Rural Development (DARD), Northern Ireland, where bracken has been identified as a problem. These sites were Whitepark Bay and Glenarm, Co. Antrim, Garvagh,

Co. Tyrone, Drumsurn and Bann Estuary, Co. Derry, Murlough, Co. Down.



Four treatments were established at each site in July 2014. Plots were approximately 20 x 40 m wide . The treatment design was as follows:

The height of the plants in each quadrat were noted. Cutting and rolling were repeated in July 2015.

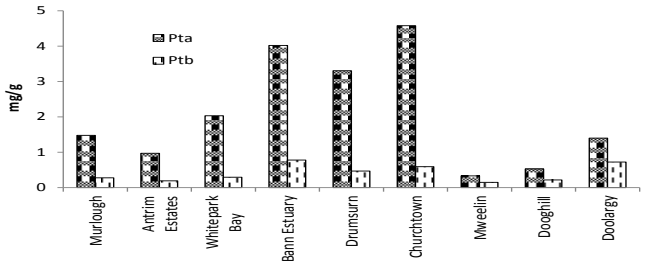
We sampled on the 23rd of July after the second treatment had been applied. 10 fronds were selected randomly from each treatment (4) at each site (6) on the same day and placed in black plastic bags.

The following day pinnae were stripped from the rachis. Six grams of wet frond material was set aside from each

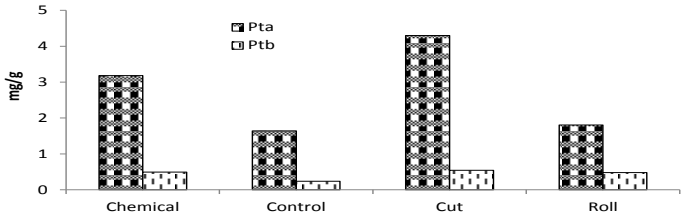
sample and the remainder was placed in a brown envelope. The wet weight was recorded and the samples were placed in the oven at 60°C for 48 H to determine moisture content.

On the third day the 6 g of wet frond material was blended up in 200 ml of 90 °C MQ (ultrapure) water and filtered through cheesecloth. The mull was blended again in 200 ml of 90 °C MQ water and filtered through cheesecloth. The extract was diluted to the 500 ml mark with MQ water. An aliquot of this was centrifuged at 3000 rpm for 5 minutes. 10 ml of the supernatant was put through an SPE cartridge to concentrate the Pta.

The following results were obtained from the Liquid Chromatography Mass Spectrophotometer:



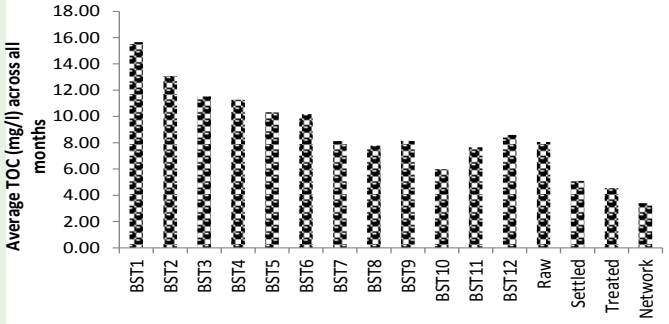
The values reported here are similar to those reported for Scotland (~ 2mg/g). There was variation between sites. More Pta was observed in the plots which had



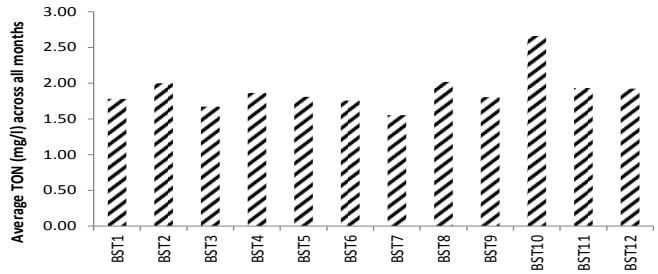
been cut and had Asulam applied to them. There was variation across sites also in the range of 4 mg/g between Garvagh, Co. Derry and Glenarm, Co. Antrim.

NOM Assessment

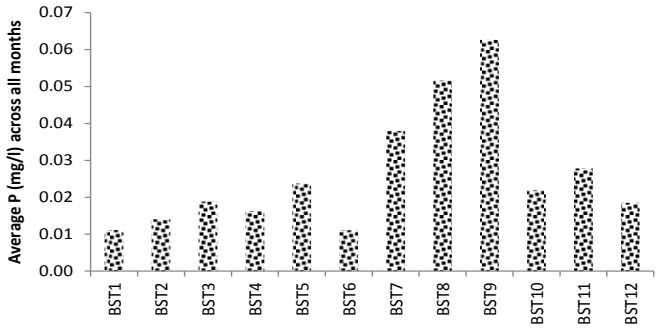
The data collected to date details TOC, SRP, NH_4, TON, UV254, THMs and Florescence –Excitation Emission Matrices at three sites across Ireland. In Staleen, THMs were consistently below 100 µg L^{-1}, and the increase in development of THMs along the network was also consistent. There was a decrease in NOM downstream.



High nitrogen values were reported for some sites in the Boyne,

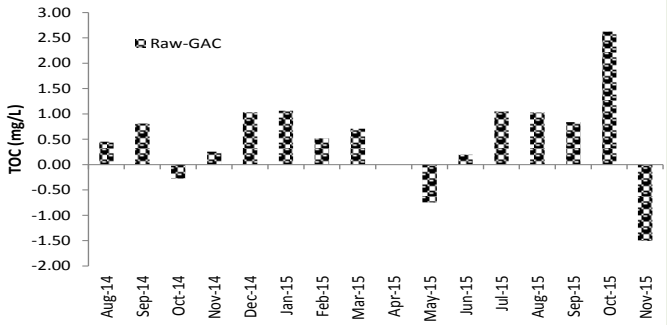


and it appeared that some sites were susceptible to algal blooms on a couple of occasions.



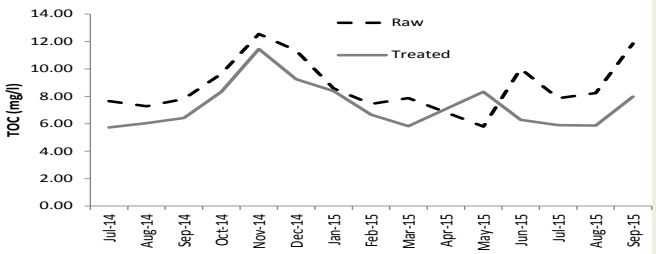
Site BST7 is located on the Kells Blackwater downstream of municipal and industrial effluent and has been classed as hypertrophic. BST8 is located on the Moynalty river downstream of intensive agriculture, pig rearing and a wastewater treatment plant. We will be sending treated water samples away for analysis of haloacetic acids, nitrogenous disinfectant by-products and total organic halides. In addition, it is hoped we will be able to identify the faecal contamination origin in the raw water (distinguish human, porcine and bovine origin using faecal stanols and evaluate the % of each source in the raw water samples.

In Williamstown, raw water is treated using ozone and a GAC filter. THMs are being produced occasionally at the water treatment plant and more frequently at locations on the distribution network. The GAC filter is inefficient at removing adequate



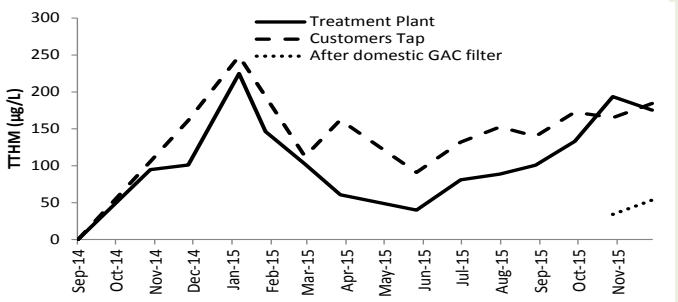
amounts of NOM at times and has released NOM into the treated water on occasion (see above negative TOC values for TOC rerelease, Oct-14; May-15; Nov'-15).

Similarly, at the Private GWS site where ultrafiltration membranes are being used to treat raw water



inadequate amounts of NOM are being removed.

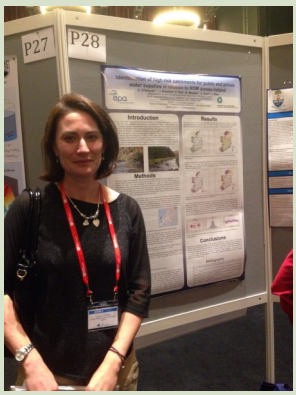
THMs are consistently produced with additional development down the distribution network.



NOM6 Malmö Sweden

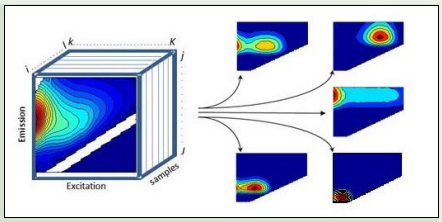
Dr Connie O'Driscoll attended the NOM6 the 6th international natural organic matter conference held on 7th of September in Malmö, Sweden. This visit included a technical tour of one of Sydvatten's water treatment plants, Vombverket, and the Kävlinge River where water is abstracted from. The image above is from one of the infiltration ponds.

The welcome ceremony was held that evening in Malmö city hall, built in the mid 1500s and later remodelled in the 1800s. The welcome ceremony was followed by a buffet reception and an array of exquisite Swedish dishes. The conference was held in the Malmö Live Hotel. The Tuesday morning session opened with a keynote speech from Professor Jean-Philippe Croue, Curtin University, Western Australia, and was entitled "The four main challenges in NOM research". These challenges were defined as how to 1) isolate NOM, 2) analyse NOM, 3) investigate the reactivity of NOM in the natural environment, and 3) how to treat NOM. There was a choice of talks from three sessions with researchers represented from every continent. The second keynote speech was delivered by Dr. Ina Kristiana, Curtin University, Western Australia, and was entitled "The wonderful world of NOM analytical methods".



That afternoon Dr. O'Driscoll presented her poster "Identification of high risk catchments for public and private water supplies in relation to NOM across Ireland". This research detailed the preliminary exploratory analysis of the national datasets and linked higher THMs to percentage peat in the catchment and treatment type.

During the evenings Dr. O'Driscoll attended a PARAFAC course held by gurus Kate Murphy and Colin Stedmon. A Matlab toolbox was provided http://www.models.life.ku.dk/drEEM. The **drEEM** toolbox was developed to support and extend the application of PARAFAC to fluorescence Excitation Emission Matrix (EEM) datasets. The toolbox contains numerous MATLAB functions for importing, assembling and exporting datasets, applying spectral corrections, visualising EEMs, detecting sample outliers, and developing and validating PARAFAC models.



The Wednesday morning session opened with Dr. Catherine Paul, Lund University, Sweden, discussing "NOM in drinking water distribution systems" with a focus on the role of molecular tools to investigate the role of bacteria in the purification of drinking water. Mid-morning, Prof. Chris Evans, CEH, UK, spoke about the "Dynamics of NOM in natural waters" and the controls of DOC movement to water, from sulphur emissions to climate change and disturbance to peat systems for land use purposes.

On Thursday morning Professor Bill Cooper, University of California and Professor Michael Gonsior delivered a talk entitled "A retrospective of NOM for water applications" in tandem. Professor Cooper began by discussing 1970s research such as the discovery of trihalomethanes and Professor Gonisor continued with state of the art technologies and methodologies including ultra-high resolution mass spectrophotometry.

Doctoral researcher Maebh Grace, NUIG, gave a presentation on "A novel filtration configuration for targeted humic acid removal from drinking water".

Professor Wolfgang Uhl, NIWR, Norway, gave the final keynote speech "Traditional and emerging technologies for NOM reduction in water treatment plants" and stressed that a holistic approach is needed, a change of thinking towards catchment area management rather than focusing on treatment alone.

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