



Assessment of NOM and Pta in Irish drinking waters



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

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Issue 2

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Special points of interest:

- Upcoming NOM6 Conference in Sweden
- Irish Uplands Forum
- CAFRE Study
- Bracken Workshop

Summary

Welcome to the second edition of our project newsletter and many thanks for all the feedback on our first issue dated 1st September 2014. The aim of our project is to assess natural organic matter (NOM) and ptaquiloside (Pta) in drinking water. When present in drinking water NOM can give rise to disinfection by-products (DBPs). Trihalomethanes (THMs) are one such group of DBPs and in 2012, the EPA found that 13% of public water supplies failed the 100 µg L⁻¹ required parametric value.

It has been a busy winter and spring and we have begun to assemble an impressive amount of data. Sampling is per-

formed each month with all sites being sampled on the same day. We have observed TOC concentrations from raw water as high as 29,300 µg L⁻¹ at one site while others fluctuate seasonally between 4500 and 19,400 µg L⁻¹. CLS Ltd. tests THM concentrations from our treated water samples and these results are indicative of seasonal variation ranging between 91 and 248.6 µg L⁻¹.

In Autumn 2014 we received the Pta standard from the University of Copenhagen as the standard is not commercially available. Extensive work has been conducted on the development of a testing protocol and we are confident we have a robust/sensitive detection method. No Pta has been

detected in the raw water samples to date. Our next step is to sensitise the sample collection procedure following recommendations from colleagues in the University of Copenhagen.

In April 2015 we hosted a bracken workshop in Glendalough, Co. Wicklow in. National and international delegates with a knowledge and interest in bracken were in attendance.

In association with CAFRE (College of Agriculture, Food and Rural Enterprise), we are also availing of a unique opportunity to extend our investigations into the ptaquiloside concentration in bracken stands in response to different control measures.



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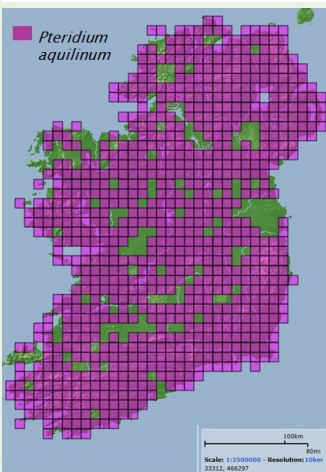
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Bracken risk mapping

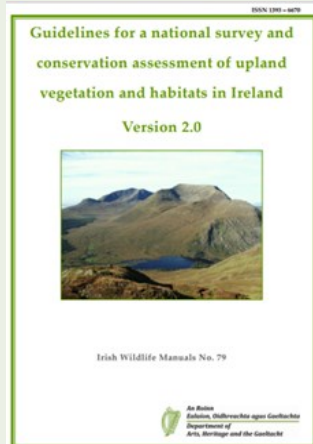
The intrusion of bracken is viewed as a concern as it can limit the amount and quality of land available for grazing. There are health and safety issues also, with bracken being poisonous to livestock as well as being a host for sheep ticks that can cause illness' such as Lyme's disease. More recently, concerns have been raised regarding the risk of naturally occurring toxins leaching into drinking water. There is currently no empirical data for Ireland on whether this should give



cause for concern. Ireland is at a disadvantage to the UK when it comes to assessing risk associated with bracken. The UK has the Landcover map (2000) which classes bracken as “stands of vegetation >0.25 ha in extent which are dominated by a continuous

canopy cover (>95%) of bracken at the height of the growing season”. In Ireland, we are limited to records of bracken presence, provided by the National Biodiversity Centre (see below left)

There are 6502 recordings, the earliest recording dated the 1st of January 1970. However, with bracken being “one of the five most abundant plants on Earth, being present in

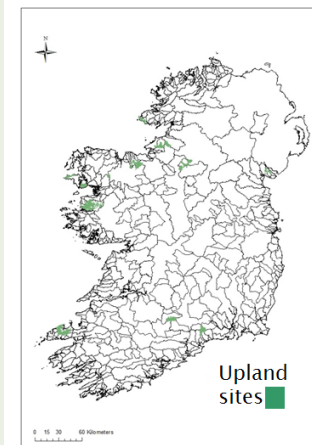


all continents except Antarctica.” this is unsurprising.

In 2008, the NPWS commissioned a scoping study and pilot survey of upland habitats. This was followed by the National Survey of Upland Habitats in 2010.

Perrin et al., 2014. Guidelines for a national survey and conservation assessment of upland vegetation and

habitats in Ireland. Version 2.0. Irish Wildlife Manuals, No. 79. NPWS, DAHG, Dublin, Ireland.



The objectives of this survey were to map upland habitats and vegetation and to assess conservation status of upland habitats listed in Annex 1 of the EU Habitats Directive. Nineteen percent of Ireland is considered to support upland habitats. This study surveyed a sample set of 14 upland sites. Bracken was listed as one of the classifications in this survey and so the percentage coverage of bracken is available for these 14 sites (see above). Alternatively, remote sensing



could and has been used to quantify bracken percentage coverage to varying degrees of success in the UK. Remote sensing is the science of studying an object without actually coming into contact with it and offers the only practical method of effectively quantifying bracken distributions over large areas. Green vegetation appears as red/ deep purple because of the photosynthetic activities of plants. Holland & Alpin, (2013) used a combination of 30 m Landsat sensory imagery and 4 m IKONOS imagery. The higher resolution imagery can be very costly and doesn't have the multi-temporal aspect provided by the freely available Landsat.

The marked spectral contrast between dead bracken and other vegetation can be exploited in the classification process where there is sufficient access to winter and summer data.

ISPRS Journal of Photogrammetry and Remote Sensing 75 (2013) 48–63



Super-resolution image analysis as a means of monitoring bracken (*Pteridium aquilinum*) distributions

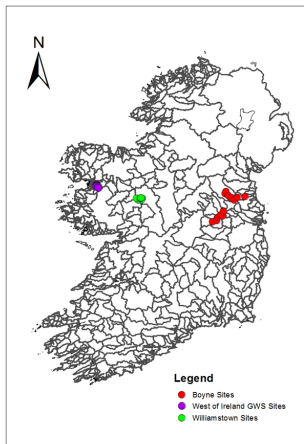
Jennie Holland, Paul Aplin*

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NOM Monitoring

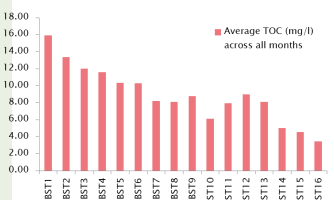
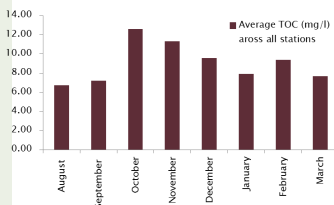
We have begun to assemble a comprehensive dataset with 9 monthly sets of data collected.

Parameters measured



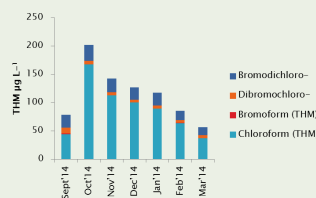
include dissolved TOC, SRP, NH₄ and TON UV254 and Florescence –EEMs. Total THMs are tested by CLS Ltd.

Sites (13) along the Boyne are monitored up to the raw water intake in Donore. Settled and filtered water along with a location on the network are also monitored to give an indication of THM development in the network. The following bar charts illustrate the seasonal and spatial



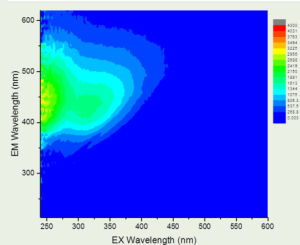
variation that exists in a sampling program.

In Williamstown the study foci are the catchment and network. The graph below illustrates the seasonal pattern of total THMs at one location in the network. On the same day 5 samples are taken for TOC concentrations at locations in the Williamstown catchment to give an indication of TOC sources.



At our private GWS in Mayo, the study focus is on characterising the types of NOM present.

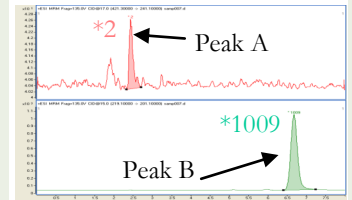
Florescence – EEMs (see image below) will be used to disentangle this following training provided by delegates from the Chalmers University of Technology and Danish Technical University during a week long conference on natural organic matter (NOM6) in Malmö in September 2015.



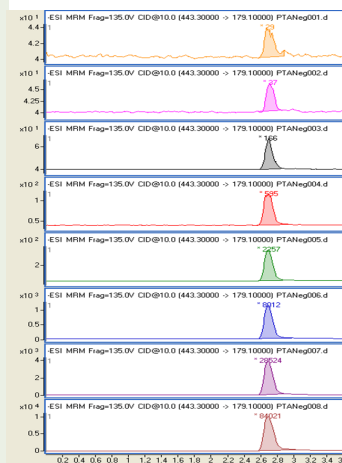
Ptaquiloside Monitoring

Nine monthly water and vegetation samples were collected and stored in the freezer at -20°C. We began work on the testing protocol in October 2014 following the arrival in late Autumn of the ptaquiloside (Pta) standard from the University of Copenhagen. Different columns and Liquid Chromatography-Mass Spectrophotometer settings were trialled with both Pta and its degradation compound pterosin B (Ptb) to establish the behaviour with the MS. We are very happy with our detection sensitivity. The graph below demonstrates the performance of the Pta limit of detection using 1 µl injections serial dilution 1 in 4 from low to high concentrations.

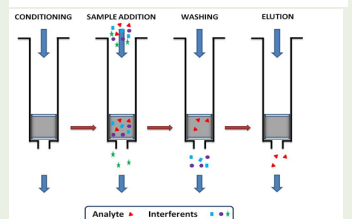
Peaks A and B below illustrate the Pta and Ptb, respectively, that remained after the conversion had been performed.



The first 6 sets of samples have been tested and preliminary results suggest that no Pta was present in the samples. These findings are in agreement with other studies carried out internationally however, further work is needed on the sampling protocol. Pre-concentration of Pta in the sample was performed using solid phase extraction (SPE). An Oasis Max SPE column from Waters was conditioned with 2 ml of methanol followed by 2 ml of MQ water; 20 ml of sample was added; and rinsed with 2 mL of MQ water followed by 2 mL of 15% methanol. Elution was performed using 2 x 0.25 mL of 80% methanol. Before analysis the eluate was diluted with 1:1 MQ of water.



Pta is converted or hydrolysed to Ptb using NaOH before stopping the reaction with H₂SO₄.



Bracken Technical Workshop, Glendalough, Co. Wicklow

On the 17th of April 2015, we hosted a bracken technical workshop in Glendalough, Co. Wicklow. Delegates in attendance were from a broad spectrum of public and private sector employments. Cara Heraty from the Wicklow Uplands Council gave a local welcome and an overview of the group's interest and concerns about bracken. Niall Dunne from the EPA spoke on EPA research initiatives and drinking water policies. Distinguished Professor Hans Christian Bruun Hansen from the University of Copenhagen summarised his group's work on the fate of ptaquiloside in soils, highlighting the facts and challenges. Prof. Bruun Hansen's



PhD student Frederik Clauson-Kaas shared his work on ptaquiloside in natural waters. Frederik discussed the successes and challenges of his work from isolating reference compounds from bracken, to quantification by UPLC-MS/MS and finishing with surface water sampling in Yorkshire, UK. Dr. Carmel Ramwell, experienced researcher with FERA, described in depth her original bracken study 'Ptaquiloside in drinking water: A preliminary risk assessment'. Dr. Ramwell posed the question "Is bracken a realistic risk?" and considered proximity of drinking water abstraction points, bracken coverage, soil type, rainfall and slope in their risk assessment. Dr. Mary Tubridy, consultant to WUC, described her study identifying best management of Upland Habitats in Co. Wicklow. Dr. Tubridy is secretary of the Irish Upland Forum www.irishuplandsforum.org that promotes sustainable upland management. Graeme Campbell of CAFRE demonstrated the work of their ongoing bracken control project which is using field plots to compare the effectiveness of different control

methods such as spraying, cutting, rolling and bruising. We will link up with Graeme to attempt to measure the phytochemical response of these techniques. A site visit was led by Wesley Atkinson (NPWS) and an open discussion on the concerns of the farming community was led by Pat Dunne (IFA). The Department's position on Asulam was clarified by Tom Medlycott (DAFM-Pesticide). Land managers must apply for a derogation each year. Comdt. Derek Hanley (Defence forces) stressed his concerns in the Glen of Imal with the dangers around bracken coverage to the army.

We received remote interest and input from international bracken experts, in Australia—Dr. Mary Fletcher, the Azores—Dr. Carlos Pinto and Dr. Paulo Aranh, Venezuela—Professor Alonso Amelot and the UK—Professor Rob Marrs.

For more information or clarification on anything in this newsletter please do not hesitate to contact me using any of the options below.

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