Assessment of natural organic matter and ptaquiloside in Irish drinking waters

Environmental Protection Agency
An Ghníomhaireacht um Chaomhnú Comhshaoil

Comhshaol, Pobal agus Rialtas Áitiúil
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Introduction

There is an urgent need to understand the composition and quantity of natural organic matter (NOM) in raw drinking water. Presence of NOM causes many problems for drinking water treatment processes. Natural organic matter (NOM) refers to a wide spectrum of carbon-based compounds that form as a result of natural processes in the environment. In addition to problems of aesthetics such as colour, taste and odour, it contributes to the fouling of membranes, serves as precursor for the formation of disinfection by-products (DBP) such as carcinogenic trihalomethanes (THMs) and increases the exhaustion and usage rate of coagulant and disinfectant dosages. Natural organic matter (NOM) is one of the primary sources of environmental pollution to drinking water supplies in Ireland. In 2012, the EPA found that 13% of public water supplies, 39.7% of public group water schemes, and 6.2% of private group water schemes failed to meet the THMs parametric value of 100 µg L^{-1}.

There is increased awareness and concern surrounding naturally occurring toxins such as ptaquiloside (Pta) from bracken in Irish drinking waters. However, there is inadequate empirical evidence available to water managers upon which to form decisions surrounding the management of bracken. Furthermore there is concern over the recent ban on Asulam® the most effective herbicide used to treat bracken.

Natural organic matter and bracken distribution are expected to increase in drinking waters and so there is wide interest in this project from the perspective of water managers. The aims of this project are to:

- Identify high risk catchments for public and private water supplies in relation to NOM and Pta across Ireland
- Survey and monitor a small number of high risk catchments
- Estimate likely NOM and ptaquiloside concentrations in raw surface and groundwater sources in the selected catchments using predictive modelling
- Assess the risks of THMs and Pta to humans based on knowledge of toxicity
- Develop recommendations to reduce risk of NOM in Irish waters

Key partners in this project include TCD, NUIG, NFGWS and DEFRA, UK. The EPA, Irish Water and DWI, UK will form the project steering group.

Project term: 1-Mar-2014 to the 1-Sept-2016

Funder: EPA, Ireland

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NUI Galway OÉ Gaillimh

GALWAY COUNTY COUNCIL
Comhairle Chontae na Gaillimhe

The Food & Environment Research Agency

UISCE ÉIREANN : IRISH WATER

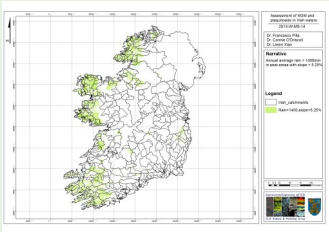
TRINITY COLLEGE DUBLIN
COLÁISTE NA TRÍONÓIDE, BAILE ÁTHA CLIATH
THE UNIVERSITY OF DUBLIN

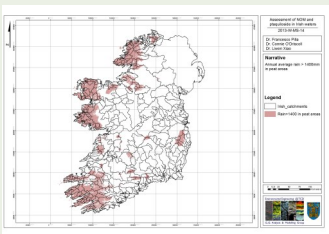
Comhairle Contae Lú
Louth County Council

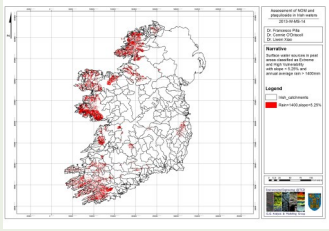
NOM risk mapping

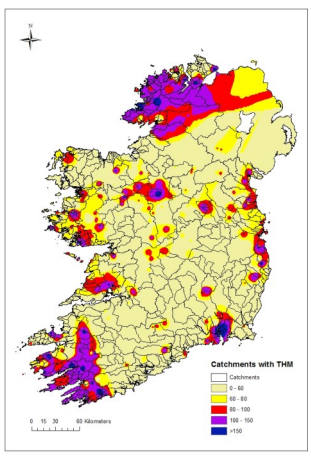
In order for contamination to occur there must be a pollutant source, an initial mobilisation of the pollutant and a means via which it is transported. The risk of contamination is likely to be greatest where each of these three aspects is optimised. We considered that soil organic content was the main source of NOM, and run-off/shallow subsurface flows were the main pollutant transport pathways. Groundwater vulnerability maps were also collected for groundwater risk assessment.We collected National Soil Dataset maps from the EPA Envision website, the most recent rainfall Long-Term Average map from Met Éireann with a 1 km² spatial resolution, slope data from the DEM (2002) and a groundwater vulnerability map, combining 2 GIS layers of subsoil thickness and permeability. Historical results for THM sampling events (2006-2012) were obtained from the EPA.

Catchments with peat coverage and rainfall greater than 1400 mm were deemed high risk (Fig. 1); catchments with peat, rainfall >1400 mm and slope <5.25 were considered high risk; and catchments with peat, >1400 mm rainfall and Extreme and High groundwater vulnerability (Fig. 3). An inverse distance weighted analysis was carried out on the THM samples from 2012 to highlight catchments that have exceedances of THMS (Fig. 4).









Ptaquiloside Monitoring

As it stands no national bracken percentage cover map of Ireland exists. The proposed approach this project will adopt is to: Identify areas of definite bracken using vegetation survey maps from the National Survey of Upland Habitats, NPWS project and use this information to train Landsat images to identify areas of likely dense bracken through supervised pixel recognition. Sites were chosen using the NSUH survey data, the proximity to drinking water abstraction points and the proximity of the abstraction point to the householders tap.

Doughill, Co. Mayo is a mountain stream supplying two houses. There is no treatment for this supply. The conductivity and pH readings were low.

Mweelin Well, Co. Galway is a spring source. The spring is located in an area of extreme vulnerability. The conductivity on one sampling occasion was high and the pH was circumneutral.

Doolargy, Co. Louth is spring source supplying one household and a farm. On one sampling occasion the conductivity was low and the pH was high. There is no treatment on this supply.

Water samples will be taken in 120 ml amber glass bottles, stored in the dark on ice in cold boxes prior to analysis. In addition, vegetation will be collected from each site and stored in the freezer. Analyses will be carried out in the NCBES at NUIG with the help of Brendan Harhen. The NCBES houses an Agilent 6460 Triple Quad LC-MS.

NOM Monitoring

Staleen PWS experiences THM exceedances. Water is abstracted from the R. Boyne at Roughgrange, Co. Meath. The Boyne catchment encompasses 66% of Co. Meath with small areas of Co.'s Cavan, Louth, Westmeath, Offaly and Kildare. The catchment area is ~2,693 km² with a main channel length of 113 km. A characteristic of the catchment is the limited average gradient of 1.24 m/km, from the headwaters of the main channel to the sea at Drogheda. Upstream catchment sites highlighting a suite of land management uses such as peat harvesting, forestry, intensive agriculture, pig-rearing, municipal and industrial effluent were chosen for monitoring sites. In addition samples are being taken at the treatment plant, before coagulation after coagulation and after rapid gravity filter and chlorine gas disinfection.

A **West of Ireland GWS** has been chosen as it represents a collection of schemes with identical treatment technologies experiencing THM exceedances. Water is abstracted from a lowland lake source to a membrane filtration treatment plant. A preliminary source protection report carried out by DkIT on the source water highlighted land management uses include intensive agriculture, municipal waste, coniferous forestry and peat harvesting. Suitable sites for catchment monitoring were selected based on land management uses. In addition samples are being taken at the treatment plant, before membrane filtration, after membrane filtration and at a domestic house on the network.

Williamstown PWS experiences periodic THM exceedances and is situated in a catchment area with extreme groundwater vulnerability. Williamstown PWS abstracts its water from Springfield Spring, Co. Galway. The spring located in a secluded forested area and surrounded by agricultural land. The spring is part of a much larger spring system and a comprehensive ZOC has not to date been attempted for the spring system. Potential swallow holes in proximity to varying land management uses, i.e. agriculture, municipal effluent, peat harvesting and forestry, have been identified and are being monitored. Samples are been taken at the Williamstown treatment plant pre-ozone, post-ozone treatment and post -GAC filtration. Additionally three scour valves at remote locations on the network are also being monitored.

Sampling program

Sampling commenced on the 25th of August 2014 and will continue on a monthly basis. 250 ml water samples are taken at 42 locations across the three study sites over a two day period. Samples are collected in sterile plastic bottles and stored in the dark on ice in cool boxes for analyses on the third day. Analyses are carried out in laboratories across the NUIG campus. Dissolved Total Organic Carbon is measured using a Biotector (TOC-TN-TP analyser); Soluble Reactive Phosphorus, Nitrogen and Total Oxidised Nitrogen are tested using a Konelab (nutrient analyser). UV254 is measured using a UV-Vis. THMs are tested using a Hach-Lange spectrophotometer with kits provided by Hach-Lange. The Biotector, Konelab and UV-Vis

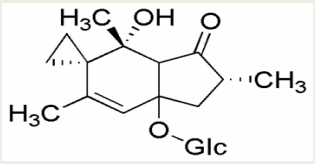
are located in the Environmental Engineering Laboratory.

Samples are taken to the Martin Ryan Building for Florescence spectroscopy analysis. Professor Peter Croot, Earth and Ocean Sciences Group will help us generate Fluorescence Excitation Emission Matrices using an Horiba Scientific Aqualog housed in their lab. Fluorescence spectroscopy can be used for organic matter characterization and assessment of TOC removal in drinking water treatment.

"No one knows where it comes from and no one knows where it goes to." On problematic East Galway drinking water supplies.

Martin Lavelle, Senior Engineer, Galway

Trip to Food and Environment Research Agency, York



The chemical structure of ptaquiloside (Pta)

On Monday the 28th of July 2014 I travelled to the UK for a ptaquiloside training week with Dr. Carmel Ramwell, FERA. On my arrival in Skipton we set off to visit one of Carmel's study sites in neighbouring Skipton. The site was located in a catchment with extensive bracken cover. There was a large treatment plant which included coagulation and rapid gravity filtration. Carmel sampled the raw and treated water. We continued on to the Lake District the following morning to collect samples from another of Carmel's study sites. A catchment with extensive visible bracken cover. The samples were taken in amber glass bottles and kept on ice until we arrived later that day in the FERA buildings in York. The samples were refrigerated for analyses on Wednesday. On Wednesday morning the samples were put through solid phase extraction (SPE). Following SPE replicates of the Pta were converted to Ptb using acid and an autoclave. The samples were then ready for testing with the LC-MS. Each sample took approximately 8 minutes. On Thursday morning Wendy van Beinum gave a tutorial on ptaquiloside focus modelling using Pearl software to round off the trip.

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