1. EXECUTIVE SUMMARY

Environmental Change and Rising DOC Trends: Implications for Public Health

(ERA-EnvHealth call (FP7-ENV-2007-CSA-1.2.3-01))

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Context and objectives

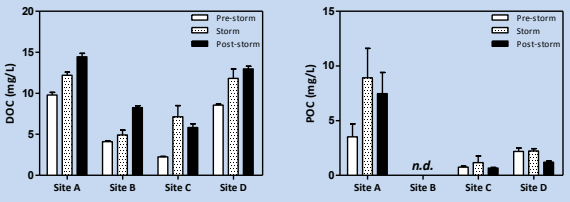
Environmental change could indirectly harm human health by driving a rise of dissolved organic carbon (DOC) in aquatic ecosystems used for potable water supplies, as this process can promote quantifiable increases in harmful pollutants and disinfection by-products following water treatment. The following objectives were set for the project: 1) Carry out extensive time series analysis of existing datasets in order to identify environmental variables driving changes in DOC quantity and quality. 2) Integrate effects of changes in climate with deposition driven changes in soil water chemistry, and with DOC generation and flux from these systems into a single model for the delivery of DOC and organic pollutants to water works. 3) Determine the impacts of modelled changes in DOC quality and quantity on the formation of disinfection by-products; and persistence through the treatment process of DOC-associated organic pollutants. 4) Determine the implications for human health (through drinking water) of changes in potentially toxic disinfection by products and other hazardous or emergent substances associated with increasing DOC. The project was divided in 6 work packages (WP).

Towards a better understanding of climate impacts on water quality (WP1)

Surface water quality was monitored on 4 small watersheds. One site experiences strong agricultural pressures in Brittany and is used for water production and distribution by a Small Scale Water Service (SSWS). The three other sites are located in Wales and represent a large variety of environments (agricultural and upland peat and mineral soils). Autosamplers were installed on site and allowed to sample at set time intervals. Sampling periods began just before the start of the rain, integrate the flow peak and extend a few days after the rain stops. The main experiments were conducted during spring rainfall events. Rainfall raised the concentration of DOC in all 4 streams; from the pre- to post-storm period the DOC increased by +47.7% for the Brittany agricultural site (site A), +51.6% for the UK upland peat site (Site D), +101.7% for the UK agricultural site (Site B) and +158.0% for the UK mineral site (Site C). POC increased two fold following a storm in Site A.

An experiment was conducted to investigate the influence of recovery from acidification on soil DOC. It demonstrated that that soil pH is an important factor in determining the size of the DOC pool liable to leaching into freshwaters, but there was no impact on Trihalomethane Formation Potential (THMFP). Therefore, as soils continue to recover from acidification it is expected that DOC export will increase but the propensity of this extra DOC to form DBPs will remain unchanged from current conditions on a per unit basis.

Figure 1. Impacts of storm event on water quality

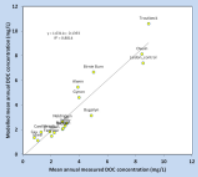


Predicting surface waters DOC in UK (WP2)

Long-term monitoring data from the UK Acid Water Monitoring Network (AWMN) has been used to determine variables controlling DOC concentrations in freshwaters in the UK and this has led to the development of two simple linear models that are highly effective in predicting dissolved organic carbon (DOC) concentrations and fluxes draining upland landscapes in the UK. The models are able to predict DOC loadings to water treatment plants now and in response to future environmental change and should provide significant economic benefits to the water industry by informing planning procedures. The simpler, spatial DOC concentration model is based on six predictor variables (mean site altitude, proportion of peat and peaty-gley soils in the catchment, effective rainfall, mean sulphate, mean chloride and mean non-marine base cation concentration). Model validation using a dataset representing mean 1995 concentrations at 18 independent sites produced an R^2 of 0.88 (Figure 2).

The addition of further parameters representing regional sulphur, hydrochloric acid and sodium deposition resulted in an even more robust model that was able to account for model deviations in sites representing a wide variety of altitudes, soil types, acid buffering capacity and levels of acid and seasalt deposition. By adopting regionally fixed deposition parameters there is little requirement for supporting site-specific chemical data, so that the influence of regional-scale drivers (i.e. deposition chemistry and climate) on fluxes and concentrations are essentially predictable across the UK uplands and should allow residual effects of within-catchment changes resulting from changes to land use and/or management to be better quantified.

Figure 2. Model validation using independent datasets



Water treatment issues (WP3)

THMFP tests were used to assess the impacts of rainfall events on the propensity of the DOC to form THM following chlorination. Water samples taken during the storm event (Figure 1) were used for this study. The increase in DOC during rainfalls did not significantly alter the THM concentration and speciation and revealed less of an impact than previously expected (Figure 3).

DOC from four raw water sources has been characterised using UV-Vis, fluorescence, Infra-red spectroscopy and size-exclusion chromatography. The samples were laboratory chlorinated and their THMFP determined. The formation of brominated THMs was highest for the Cwellyn as it has the greatest concentration of bromide in the raw water.

Analyses of soil pore water quality in samples collected from different habitats (beech, spruce, larch, pine, peat) in the catchment of the Alwen reservoir, UK, was conducted to investigate the potential impact on drinking water quality. Beech is likely to be the most appropriate tree species for planting in a drinking water reservoir catchment due to the relatively low DOC, THMFP and colour associated with pore water in this habitat (Figure 4).

Figure 3. Impact of storm event on THMFP

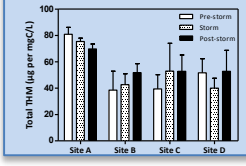
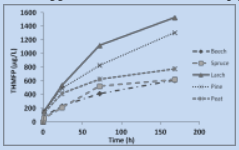


Figure 4. THMFP of leachate from different habitat types



Links between DOC & contaminants & expected health issues (WP4-WP5)

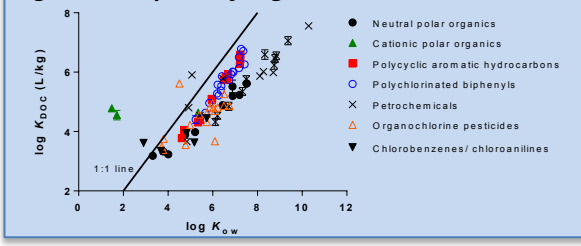
Incomplete removal of organic contaminants during drinking water preparation causes concern for potential health effects of residual contaminants. Increasing DOC concentrations may affect the mobility of contaminants in the environment and their fate during the production of drinking water.

Concentrations of total and freely dissolved polycyclic aromatic hydrocarbons (PAHs) and DOC were measured in water from the River Wyre, UK, which drains an upland peat-based catchment. Concentrations of the sum of total and freely-dissolved PAHs ranged from 2.7-18.9 ng/L and 2.6-16.8 ng/L respectively. PAH concentrations and fluxes increased downstream. A significant positive relationship was found between concentrations of DOC and PAHs containing five or more aromatic rings, suggesting that both are leached to the water together, probably after being released from the organic soils. No significant or a negative relationship was found for most PAHs with four or less rings. The concentrations of freely-dissolved PAHs can be estimated from total dissolved concentrations based on the octanol-water partition coefficients of the PAHs. Specific PAH concentration ratios show that the peat is a source of pyrogenically derived PAH, possibly from airborne deposition and the burning of heather. Increasing DOC concentrations may also result in increasing concentrations of dissolved heavy PAHs in raw water sources.

Besides this, DOC to water sorption coefficients (log K_{DOC}) of contaminants from 11 different sources were determined for 104 chemicals with a wide range of hydrophobicity (expressed as octanol to water partition coefficients, log K_{ow}). The log K_{DOC} values of neutral chemicals were linearly related to log K_{ow}, (Figure 5). The average log K_{DOC} values for each compound were used in the DSS of WP6 to calculate the risk of residual contaminant concentrations following water treatment. It was concluded that hydrophobic compounds with high log K_{ow} values will be removed after coagulation during water treatment, whereas hydrophilic compounds with low K_{ow} values may represent potential problems during the production of safe drinking water.

Toxicological Reference Values (TRVs) have been collected for 109 substances using 10 different international toxicological databases. This information have been crossed with predicted substances concentration (micropollutants and DBP) following water treatment for a given value of DOC, and time budgets of people to assess the human health risks. Ingestion is the main way of exposure studied and chronic effects are considered since toxic effects originating from water are almost always linked with long term exposure in European regions.

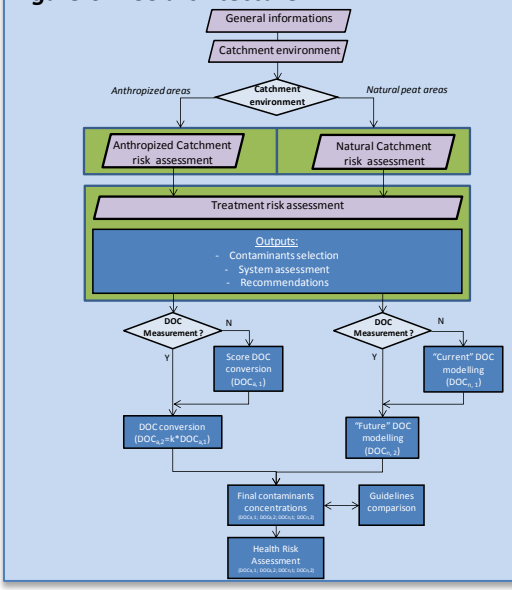
Figure 5. Sorption of organic chemicals to DOC



Decision Support System (WP6)

The architecture of the DSS followed a sequential approach based on: 1) Risk analysis of river basin characteristics, 2) Impact of water treatment (technical, operational, monitoring), 3) Recommendations, 4) Pollutants concentration after treatment & Health Risk Assessment. By considering the specific environments of the areas studied by the different teams of the consortium, two types of environments (natural for UK and anthropogenic for Brittany) were distinguished in the DSS. The DSS is composed of questionnaires and includes a statistical based model developed by the CEH Lancaster to predict long term trends DOC concentration for natural environments (Figure 6, cf WP2).

Figure 6. DSS architecture



Decision Support System (cont'd)

The DSS comprises three different questionnaires which are defined for the following purposes:

- Catchment environment: selection of the pressures occurring on the river basin (anthropogenic or natural).
- Anthropized catchment Risk Assessment (RA) or Natural Catchment RA: assessment of the vulnerability of the river basin catchment area.
- Treatment RA: assessment of the efficiency of the water treatment process, identification of the on-site monitoring tools and description of the treatment plant operation.

After identifying the main pressures on the water system, a system assessment is provided to the user allowing to identify the main critical point on the water system. A list of recommendations is proposed to the end users in order to lower the risk score and support decision making. These recommendations are related to catchment protection, river basin management, and to treatment work conception, maintenance and monitoring. Finally, the tool is also designed to model concentrations of substances potentially present after water treatment and assess the health risks related to these substances. The DSS provide this information for both current and predicted (on the basis of IPCC scenarios) DOC concentrations in water. Contaminants are selected from the substances list previously detailed on the basis of pressures identified on the catchment following users questionnaires answers.

What next?

- Having now established a baseline DSS, there is now a need for further work to validate and refine the system, with the aim of forming an even more robust tool.
- The work requires urgent expansion to include other EU states rather than just the UK, France and Netherlands, so as to ensure that the DSS is universally relevant.
- There is interest within our stakeholder communities for the development of bespoke versions of the DSS which consider only issues relevant to a given EU state or region

This project has led to 9 scientific papers published in peer-reviewed journals. Another 13 papers are actually in preparation, among which 4 common papers.

For more information: http://www.era-envhealth.eu/servlet/KBaseShow?sort=-1&cid=23174&m=3&catid=23184

Project summary

The main outcomes of the project could be summarized as follows:

- The design of innovative experimental monitoring protocols in diverse catchment types (agricultural, peat, mineral) and on agricultural plots during intense rainy events has been conducted. Impacts of heavy rainfall events (about 20mm) on runoff sources and river water quality have been characterized. A DOC increases ranging from +47.7% to +158.0% in rivers sampled have been measured.
- Historical data of water quality from several British and French water bodies has been used with the aim at improving our knowledge of how dissolved organic carbon (DOC) varies quantitatively and quantitatively in response to climate. Results show negative relationships between DOC, acidity and altitude (British sites) and between TOC and nitrates (Brittany sites). Moreover, a distinct relationship between TOC fluxes and normalised flow rate has been observed.
- Two simple linear models have been consequently developed and are highly effective in predicting dissolved organic carbon (DOC) concentrations and fluxes draining upland landscapes in the UK using climate and acid deposition data.
- From the heavy rainfall event experiments, it was found that the DOC propensity to form disinfection by-product (DBP) is not different to pre-storm conditions on a per unit DOC basis althought an increase in concentration of DBPs precursors in freshwaters.
- The experiments conducted on soil pH shows that as soils continue to recover from acidification it is expected that DOC export will increase but the propensity of this extra DOC to form DBPs is not expected to be different to current conditions on a per unit basis.
- The study of the impact of habitat type (beech, spruce, larch, pine and peat) on DOC, THMFP and treatability which have shown that beech is likely to be the most appropriate tree species for planting in a drinking water reservoir catchment due to the relatively low DOC, THMFP and colour associated with pore water in this habitat.
- A significant positive relationship was found between concentrations of DOC and polycyclic aromatic hydrocarbons (PAHs) containing five or more aromatic rings, suggesting that both are supplied to the water together, probably after being released from the organic matter-rich soil. No significant or a negative relationship was found for most PAHs with four or less rings. Heavy PAHs appear to be released into the water mainly together with organic matter as this dissolves and forms DOC; therefore soils appear to act as an important reservoir supplying heavy PAHs to the water. This implies that increasing DOC concentrations may also result in increasing concentrations of dissolved heavy PAHs.
- The experimentation of various drinking water treatments such as UV irradiation, ozonation, granular activated carbon (GAC) filtration-adsorption and coagulation ($Al_n(OH)_mCl_{3n-m}$, $Al_2(SO_4)_3$, $Fe_2(SO_4)_3$ and $FeCl_3$) has been realized. The experiments showed that each of the simulated coagulant treatments were more effective in reducing THMFP than the existing treatments combined.
- The DOC samples were also treated individually with chlorine, ozone, UV radiation, or UV/H_2O_2 advanced oxidation. The largest change in DOC properties was observed after chlorination and ozonation. Negligible changes in DOC properties were observed for the treatments with UV and UV/ H_2O_2. After ozonation, DOC was partly mineralized, leading to TOC concentrations of about 79-82% of the original concentration, whereas the TOC concentrations for the other treatments did not change.
- Sorption of contaminants to DOC was determined for different chemical groups such as polar organics (*N*=19), PAHs (*N*=13), polychlorinated biphenyls (PCBs; *N*=18), petrochemicals (*N*=22), organochlorine pesticides (*N*=18), and chlorinated benzenes/anilines (*N*=12). The average log K_{DOC} values for each compound were calculated for a direct use in the Decision Support System to calculate the risk of residual contaminant concentrations following water treatment.
- A Toxicological Reference Values (TRVs) database has been built up by summarizing existing information on these contaminants and DBPs (THM and haloacetic acids). Ingestion is the main way of exposure studied and chronic effects are considered.
- The Decision Support System has been developed by distinguishing the specific environments of the areas studied by the different teams of the consortium (natural for United Kingdom and anthropized for Brittany). The DSS is composed by questionnaires and includes the DOC linear model. The tool is also designed to model concentrations of substances potentially present after water treatment and assess the health risks related to these substances. The DSS provide these informations for the current and predicted (on the basis of IPCC scenarios) DOC concentrations in water.