ENVIRONMENTAL ANALYSIS

# MONITORING OF BISPHENOL A AND ITS ANALOGUES IN ENVIRONMENTAL MATRICES USING THE AGILENT 6550 Q-TOF LC/MS

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## ABSTRACT

The use of the Agilent 6550 Q-TOF LC/MS enabled bisphenol A and its analogues to be determined in a variety of complex sample matrices, including effluents, sludges, leachates, sediments and biological samples, as part of a screening study for the Norwegian Environment Agency.


## INTRODUCTION

Bisphenol A (BPA) is a high-production volume chemical and is used as a monomer in the production of polycarbonate polymers and epoxy resins in many industries. Polycarbonate is used for a variety of applications, including food packaging such as drinks bottles and food storage containers. Residues of BPA are also present in epoxy resins used in protective coatings and linings for food and drinks cans. BPA can migrate in small amounts into food and drinks stored in materials containing this substance.

As BPA is recognised as an endocrine disruptor, there are concerns over its potential impact, particularly on the health of children and the environment. BPA is permitted for use in food contact materials in the European Union (EU) under Regulation 10/2011/EU [1].

In January 2011, the European Commission adopted Directive 2011/8/EU, which prohibits the use of BPA in the manufacture of polycarbonate infant feeding bottles [2]. Health Canada has also banned BPA use in baby bottles and the US FDA has prohibited its use in the coating of infant formula packaging. The European Food Safety Authority (EFSA) completed its first full risk assessment of BPA in 2006 and set a Tolerable Daily Intake (TDI) of 50 µg/kg bw/day, although in 2014, they recommended that this should be lowered to 5 µg/kg bw/day on a temporary basis. They state that the health risks for all population groups is low as exposure is well below this new proposed temporary TDI [3]. BPA is also used in a number of non-food related applications, including epoxy-resin based paints, medical devices, surface coatings, printing inks and flame retardants.

Recently, the restrictions on the use of BPA have forced the polymer industry to replace BPA with bisphenol S (BPS) in thermal paper and other products. Bisphenol F (BPF) and bisphenol B (BPB) are possible replacements in the production of epoxy resin and polycarbonate, and have already been detected in canned foods and soft drinks. In addition to these analogues, Bisphenol AF (BPAF) is used in the manufacturing of phenolic resins or fluoroelastomers. These bisphenols have a structural similarity to BPA and unfortunately, may also have the same health effects as BPA.

In 2013, the Norwegian Environment Agency initiated a screening program for contaminants of emerging concern that included new bisphenols. The overall objective of this program was to establish the occurrence and environmental impact of these new persistent organic pollutants in the Norwegian marine and freshwater environments, with particular focus on their potential to bioaccumulate. The study was conducted by the NILU – Norwegian Institute for Air Research and the NIVA – Norwegian Institute for Water Research [4]. In this study, bisphenol A (BPA), bisphenol F (4,4'-BPF and 2,2'-BPF), bisphenol AF (BPAF), bisphenol BP (BP-BP) and bisphenol S (BPS) were determined using the Agilent 6550 Q-TOF LC/MS in effluent, sludge, leachate, sediment and biological samples.

## ANALYTICAL TECHNIQUE

### Sample Preparation

Water Samples

Water samples were extracted using Agilent Bond Elut PPL SPE cartridges, which were preconditioned with 5 mL of methanol/acetonitrile (1:1) and 5 mL of MilliQ water. After extraction, the cartridges were washed with 5 mL of MilliQ water, dried for 30 minutes and eluted with 10 mL of methanol/acetonitrile (1:1) and 5 mL of acetone. The extracts were then combined, reduced to near dryness and reconstituted with 0.5 mL of methanol.

Sediment and particle samples

Wet sediment and sludge samples were mixed with diatomaceous earth and then extracted using Accelerated Solvent Extraction, followed by multimode SPE cleanup.

Biological samples

Biological samples were homogenised in dry $Na_2SO_4$ and extracted with dichloromethane by ultra-sonication. They then underwent a liquid-liquid partition extraction performed using n-hexane and acetonitrile, followed by Florisil and SampliQ PSA/C18 (dSPE) cleanup.

## INSTRUMENTATION

- Agilent 1290 Infinity UHPLC coupled with Agilent 6550 Q-TOF MS
- LC Conditions: Mobile phase: methanol/water, Column: Biphenyl, Run Time: 10 mins
- MS Conditions: Dual Jet Stream ESI, Negative Mode
- Internal Standard: $^{13}C$-bisphenol A
- Acquisition and Quantitation: MassHunter software

## RESULTS AND DISCUSSION

The study monitored bisphenol A (BPA), bisphenol F (4,4'-BPF and 2,2'-BPF), bisphenol AF (BPAF), bisphenol BP (BP-BP) and bisphenol S (BPS) in effluent, sludge, leachate, sediment and biological samples. Some of the results from this study are shown below:

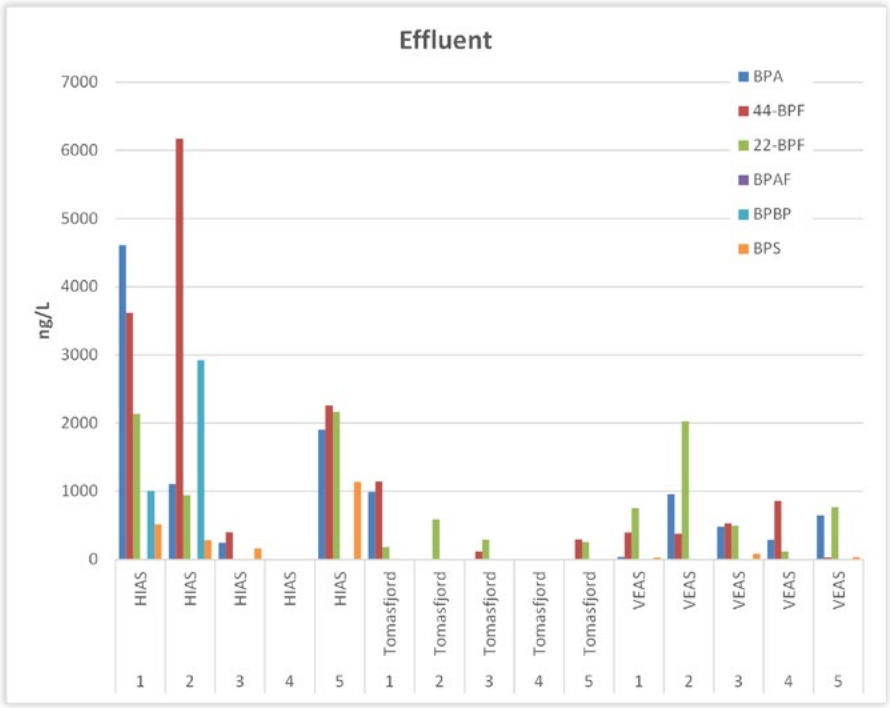


**Figure 1:** Effluent Samples - the study found that the effluent from waste water treatment works was a source of bisphenols.

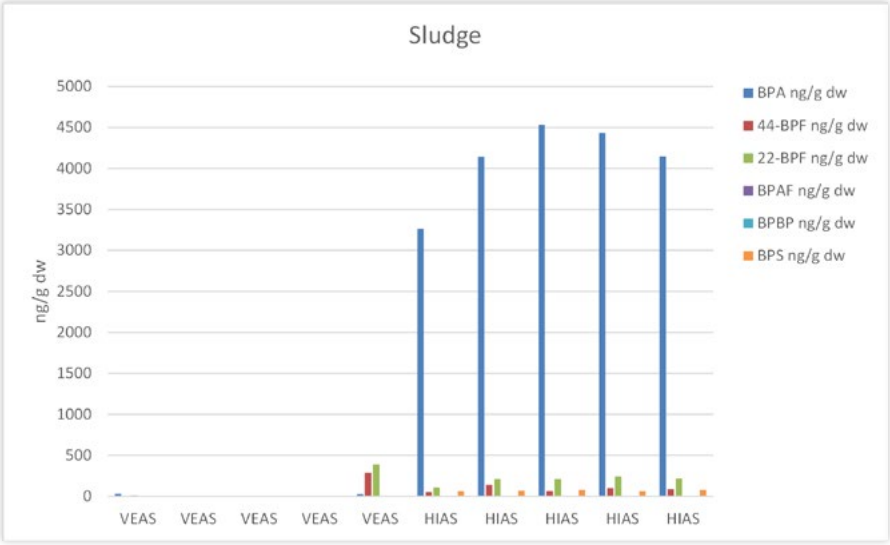


**Figure 2:** Sludge Samples from waste water treatment works were also found to be a source of bisphenols.

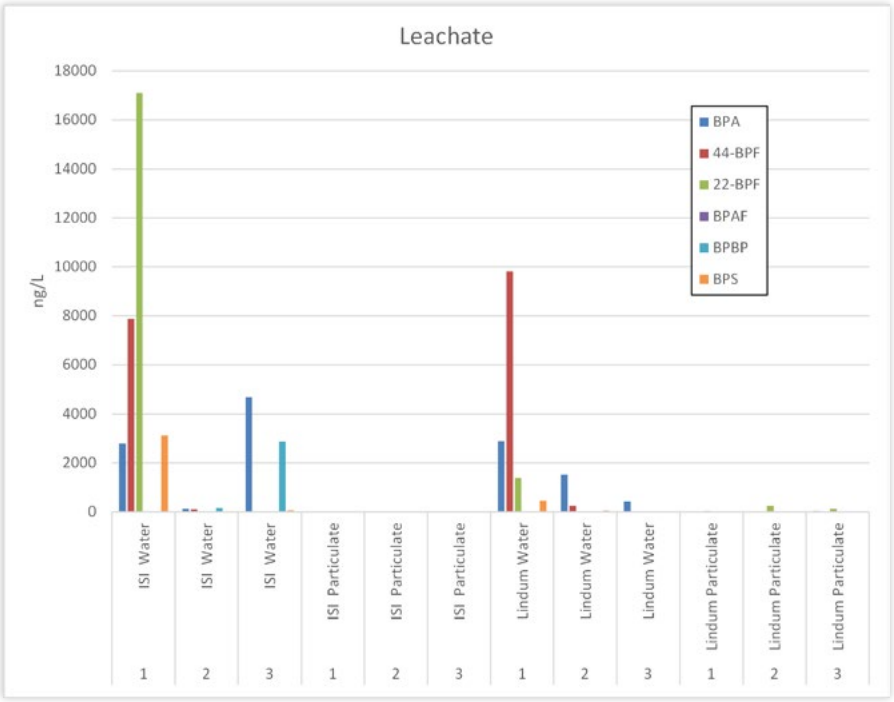


**Figure 3:** Bisphenols in leachate samples from landfill sites, in particular BPA, BPF, BP-BP and BPS.

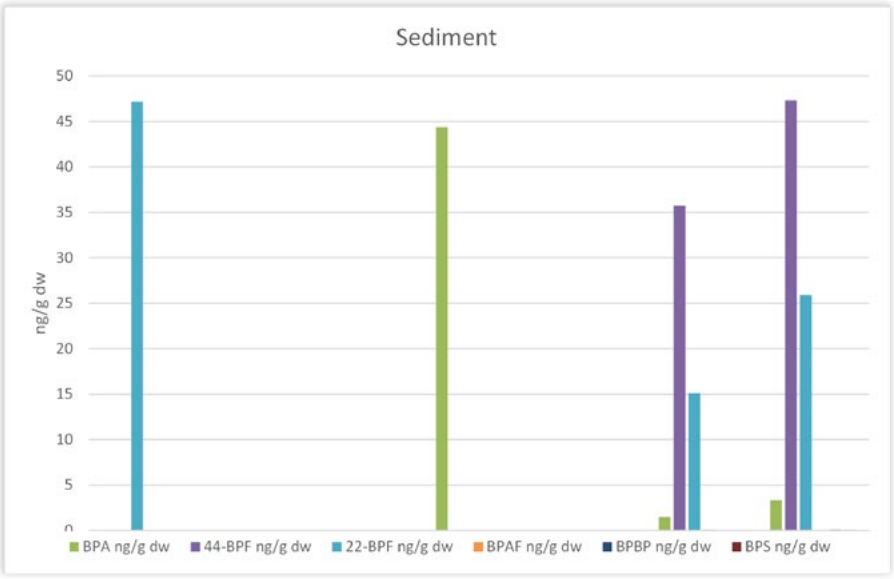


**Figure 4:** Bisphenols in marine (Oslofjord) and freshwater (Lake Mjøsa) sediment samples. BPF and BPA were found to accumulate in both marine and freshwater sediments receiving treated wastewater.

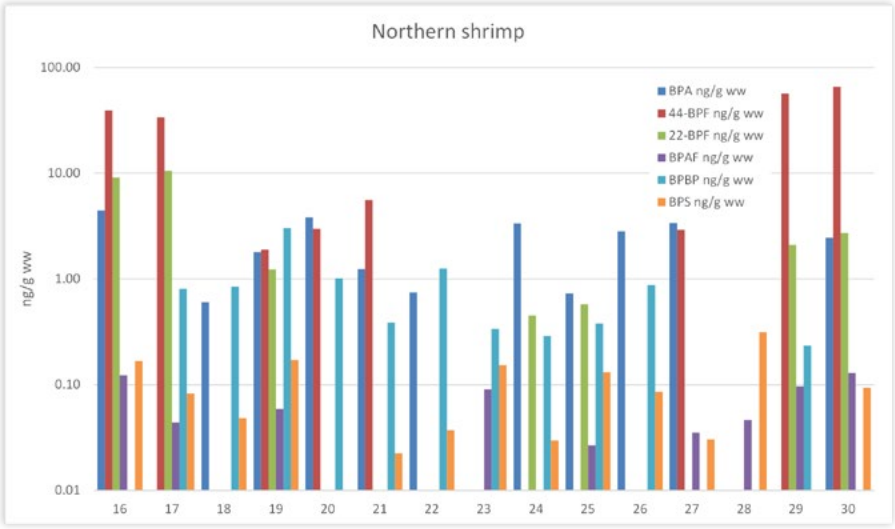


**Figure 5:** Accumulation of BPA, BPF, BPAF, BP-BP and BPS in Northern shrimp from Oslofjord.

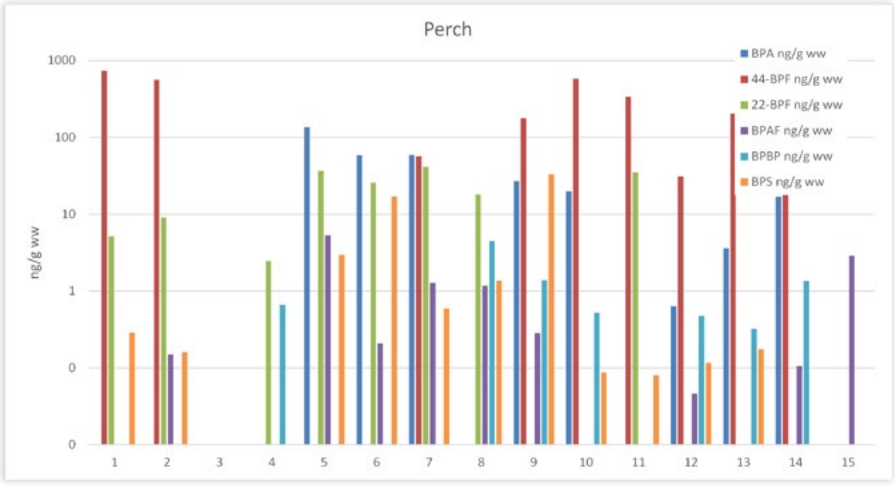


**Figure 6:** Accumulation of BPA, BPF, BPAF, BP-BP and BPS in Perch from Lake Mjøsa.

## CONCLUSIONS

The Agilent 6550 Q-TOF LC/MS proved to be a sensitive and robust tool in the monitoring of bisphenols (BPA, BPF, BPAF, BP-BP and BPS) in a variety of complex sample types, including effluents, sludges, leachates, sediments and biological samples. There is also the added benefit that analysis using the Q-TOF system with accurate mass measurements allows retrospective analysis to be performed. This could be especially useful, as there is the potential to determine new bisphenols in historical samples.

## REFERENCES


1. Commission Regulation (EU) No 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food.

2. Commission Directive 2011/8/EU of 28 January 2011 amending Directive 2002/72/EC as regards the restriction of use of Bisphenol A in plastic infant feeding bottles.

3. EFSA Press Release, Bisphenol A: EFSA consults on assessment of risks to human health, 17 January 2014.

4. Screening Program 2013: New bisphenols, organic peroxides, fluorinated siloxanes, organic UV filters and selected PBT substances, Kevin Thomas (NIVA), Martin Schlabach (NILU), Kathrine Langford (NIVA), Eirik Fjeld (NIVA), Sigurd Øxnevad (NIVA), Thomas Rundberget (NIVA), Kine Bæk (NIVA), Pawel Rostkowski (NILU) and Mikael Harju (NILU), Norwegian Environment Agency, Report M-176/2014.


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