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A validated analytical method for the determination of perfluorinated compounds in surface-, sea- and sewagewater using liquid chromatography coupled to time-of-flight mass spectrometry

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ABSTRACT

Perfluorinated compounds (PFCs), which are extensively used in a wide variety of applications because of their specific surfactant properties, have recently appeared as an important new class of global environmental pollutants. Quantitative analysis of PFCs in aqueous matrices remains, however, a challenging task. During this study, a new analytical method for the determination of 14 PFCs in surface-, sewage- and seawater was developed and validated. The target analytes were extracted using solid-phase extraction followed by liquid chromatography coupled to a time-of-flight mass spectrometer (LC–ToF-MS). The use of very narrow mass tolerance windows (<10 ppm) resulted in a highly selective MS-technique for the detection of PFCs in complex aqueous matrices. Validation of this analytical method in surface-, sewage- and seawater resulted in limits of quantification (LOQs) varying from 2 to 200 ng L^{-1}, satisfying recoveries (92–134%), and good linearity ($R^2 = 0.99$ for most analytes). Analysis of samples of the North Sea, the Scheldt estuary, and three harbours of the Belgian coastal region led to the detection of four different PFCs. Perfluorooctane sulfonate (PFOS) was found to be the most abundant PFC in levels up to 38.9 ng L^{-1}.

1. Introduction

Perfluorinated compounds (PFCs) constitute a large group of chemicals characterized by a fully fluorinated hydrophobic carbon chain attached to various hydrophilic heads [1]. The chemical class of PFCs includes the perfluoroalkyl carboxylates, the perfluoroalkyl sulfonates, the perfluoroalkyl sulfonamides, and related products. Their chemical and thermal stability and surface tension lowering properties make them very useful for a wide variety of applications and products: as additives in fire-fighting foam and food packaging, as fat and water repellents for textile, paper and leather treatment, as performance chemicals, and as polymerization aid for the production of fluorinated polymers such as polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF) [1,2]. Within the group of PFCs, perfluorooctane sulfonate (PFOS), the final degradation product of the frequently used sulfonated fluorochemicals, has been identified as the most important contaminant [2]. Moreover, PFOS fulfils the criteria of a persistent organic pollutant (POP) under the Stockholm convention [3]. As a result, EU legislation established the PFOS directive 2006/122/EC [4] which aims at ending the use of PFOS.

In general, PFCs have been reported as extremely persistent environmental contaminants with bioaccumulative and toxic properties [5,6]. Consequently, the concern about the environmental fate and prevalence of PFCs has increased in recent years. Recent monitoring studies have reported the widespread occurrence of PFCs in water [7], air [8], and biological matrices [9]. In surface water [10–12] as well as in wastewater [13,14], PFCs have generally been detected in the ng L^{-1} up to μg L^{-1} concentration range. Furthermore, PFCs have been found in seawater and open ocean waters, implying the transport of PFCs from surface water through estuaries to coastal regions and consequently to open oceans [15–17]. According to Van Leeuwen et al. [18], the quality of data obtained from analysis of PFCs in environmental matrices is a major issue of concern. The occurrence of branched isomers, matrix interferences, and cross contamination rendered quantitative analysis of PFCs in aqueous matrices a challenging task. To the best of our knowledge, the use of accurate mass high-resolution mass spectrometric tech-

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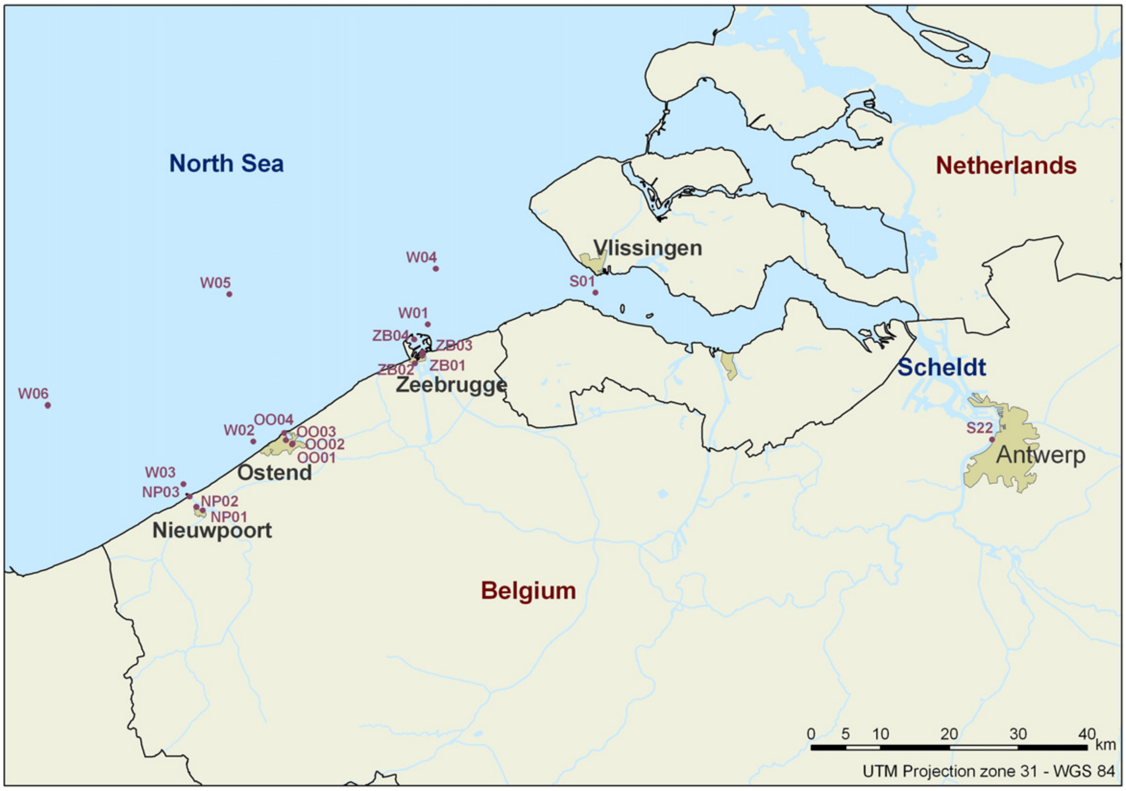

Fig. 1. Sampling stations in the North Sea (W01–W06), the Scheldt estuary (S01 and S22) and in the harbour of Nieuwpoort (NP1–NP3), Ostend (OO01–OO04) and Zeebrugge (ZB01–ZB04).

niques for the quantification of PFCs in water samples has not been reported earlier [19].

Therefore, in this study, an analytical methodology was developed using liquid chromatography (LC) coupled to a time-of-flight mass spectrometer (ToF-MS). ToF-MS provides sensitive full scan data and allows the detection of the target PFCs by accurate mass measurements, resulting in a highly selective MS-technique. Fourteen environmentally relevant PFCs were selected, including four perfluoroalkyl sulfonates, nine perfluoroalkyl carboxylic acids and perfluorooctane sulphonamide. A validation study was carried out to demonstrate the applicability of this analytical approach. Finally, the developed method was applied to marine water samples from the North Sea and Scheldt estuary to examine the presence of PFCs in the Belgian marine environment.

2. Materials and methods

2.1. Study area and sampling

The study area is located in the three Belgian coastal harbours (Ostend, Nieuwpoort, and Zeebrugge), the Scheldt estuary, and the offshore coastal area of Belgium. An overview of the study area and sampling stations is depicted in Fig. 1. Ten sampling stations were selected in three coastal harbours; four in the harbour of Zeebrugge (ZB01–ZB04) and three in the harbours of Nieuwpoort (NP01–NP03) and Ostend (OO02–OO04) each. In each harbour, one sampling station was representative for the major freshwater inputs into the harbour, while a second sampling location represented the water at the harbour mouth, and at least one station between these points was sampled as well. An additional station was selected at the Sluice Dock in Ostend (OO01) since at this location aquacultural activities take place. Two stations were sampled in the Scheldt estuary: one station located at the river mouth near Vlissingen, the second more upstream near Antwerp. Six sampling stations were chosen in the Belgian coastal area: three (W01, W02 and W03) were located close to the harbour mouth of Ostend, Nieuwpoort and Zeebrugge; the remaining three (W04, W05 and W06) were situated more offshore. The sampling campaign was carried out in June 2009.

The 'Zeekat', a rigid inflatable boat, was used for sampling the harbour stations. North Sea and Scheldt estuary stations were sampled with the larger research vessels 'Belgica', 'Zeeleeuw', and 'Scheldewacht'. Water samples were collected at each sampling site using Go-Flo bottles® (General Oceanics Inc., Miami, Florida, USA) at a depth of 4–5 m. Go-Flo bottles® avoid sample contamination at the surface, internal contamination, loss of sample on the deck, and exchange of water from different depths. Samples were stored at 4 °C in the dark before analysis.

2.2. Reagents and chemicals

Fourteen PFCs were examined in this study: four perfluorosulfonates (potassium perfluoro-1-butane sulfonate, sodium perfluoro-1-hexane sulfonate, sodium perfluoro-1-octane sulfonate, and sodium perfluoro-1-decane sulfonate), nine perfluorocarboxylates (perfluoro-n-pentanoic acid, perfluoro-n-hexanoic acid, perfluoro-n-heptanoic acid, perfluoro-n-octanoic acid, perfluoro-n-nonanoic acid, perfluoro-n-decanoic acid, perfluoro-n-undecanoic acid, perfluoro-n-dodecanoic acid, and perfluoro-n-tetradecanoic acid) and perfluoro-1-octane sulfonamide. All analytical standards were purchased from Wellington Laboratories (Guelph, Ontario, Canada) with chemical purities of more than 98%. Six ^{13}C-labelled internal standards were used as well: sodium perfluoro-1-[1,2,3,4-$^{13}C_4$] octane sulfonate, perfluoro-n-[1,2-$^{13}C_2$] hexanoic acid, perfluoro-n-[1,2,3,4-$^{13}C_4$] octanoic acid, perfluoro-n-[1,2,3,4,5-$^{13}C_5$] nonanoic acid,