



Identification and quantification of linear and branched isomers of perfluorooctanoic and perfluorooctane sulfonic acids in contaminated groundwater in the veneto region



Alessandro Pellizzaro^{a,*}, Alessandro Zaggia^b, Massimo Fant^a, Lino Conte^b, Luigi Falletti^b

^a Acque del Chiampo S.p.A. – Servizio Idrico Integrato, Via Ferraretta 20, 36071 Vicenza, Italy

^b Department of Industrial Engineering, University of Padua, Via Marzolo 9, 35030 Padua, Italy

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ABSTRACT

Perfluoroalkylated acids (PFAAs) are ubiquitous xenobiotic substances characterized by high persistency, bioaccumulation potential and toxicity. They have generated global concern because of their widespread presence both in water and biota compartments. In the past four years, alarming levels of these pollutants have been found in both surface and groundwater collected in an area covering more than 150 square kilometers in the south-western part of the province of Vicenza (Veneto region, Italy). One of the sources of the contamination recognized by local authorities is a fluorochemicals production plant that produced PFAAs since late sixties by electrochemical fluorination involving the obtainment of a complex mixture of linear and branched isomers. Branched isomers account for a significant part of total long chain homologues (22%–35%). Because of the potential threat to public health and the absence of specific limits set for these pollutants by Directive 98/83/EC, local authorities have established the following performance limits for drinking water: 90 ng L⁻¹ for PFOA + PFOS, (reduced to 40 ng L⁻¹ in the most contaminated municipalities), 30 ng L⁻¹ for PFOS and 300 ng L⁻¹ for the sum of all other PFAAs. Given the non-negligible incidence of branched isomers, it appears very important to correctly identify and quantify their contribution to total PFAAs. A liquid chromatography-electrospray ionization tandem spectrometry LC–MS/MS method, coupled with solid phase extraction, was developed to identify and quantify 25 PFAAs including six branched isomers of PFOS and four branched isomers of PFOA. Expanded uncertainty, recovery and precision were determined and found to agree with the reference EPA method 537:2009. The quantification limit is comprised in the 1–5 ng L⁻¹ range.

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1. Introduction

In the past four years, high levels of PFAAs have been detected in both surface and underground water sampled in an area covering approximately 150 square kilometers in the south-western part of the province of Vicenza (Veneto region, Italy) [1]. Because of the potential threat to public health and the absence of specific limits set for these pollutants by Directive 98/83/EC, local Authorities have established the following performance limits for drinking water: 90 ng L⁻¹ for PFOA + PFOS, (reduced to 40 ng L⁻¹ in the most contaminated municipalities), 30 ng L⁻¹ for PFOS, and 300 ng L⁻¹ for the sum of all other PFAAs.

Surveys conducted by competent authorities identified one of the sources of contamination in a fluorochemical production plant that manufactured PFAAs since late sixties by electrochemical fluorination (ECF). Further investigations on both surface and groundwater sampled in the polluted area revealed the presence of significant quantities of branched and linear isomers for both PFOA and PFOS.

The PFAA production process must be considered when seeking to explain the presence of not negligible quantities of isomers. Electrochemical fluorination and telomerization are the major manufacturing methods used to produce both long and short chain PFAAs [2]. While telomerization produces primarily straight chain PFAAs, electrochemical fluorination produces a complex mixture of linear and branched isomers.

Electrochemical fluorination is an electrochemical reaction that replaces hydrogen atoms with fluorine atoms in an organic substrate (usually a fluoride or a chloride of an organic acid) dissolved

* Corresponding author.

E-mail address: pellizzaro@acquedelchiampospa.it (A. Pellizzaro).