

OCCURRENCE OF PERFLUORINATED COMPOUNDS IN MILK PURCHASED FROM CHINESE MARKETS

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Abstract

This paper is devoted to a study of 9 perfluorinated acids and 2 fluorotelomer acids in milk purchased from Chinese markets in 2008-2009. In milk samples, PFHpA and PFNA were detected frequently, both in two third of samples. PFOS and PFOA were only observed in 36% and 46% of the milk samples, respectively. PFDA, PFUnDA and PFTA were found occasionally. Other PFCs were not observed in any samples. The mean concentration of total PFCs was 183 pg/ml. It is noteworthy that the data of this study indicated a significant correlation ($P < 0.01$) between concentration of total PFC and the packaging of milk.

Introduction

Perfluorochemicals (PFCs) is a class of synthetic perfluorinated compounds that are served as a kind of surfactant used in a variety of consumer and industrial applications for more than 50 years due to their oleophobic and hydrophobic properties¹. In May 2009, perfluorooctane sulfonate (PFOS), the most common PFC, was listed under the Stockholm Convention as persistent organic pollutants in Sweden. PFCs are widely distributed in the environment and have been detected in water, soil and air². In recent years, the concentration of PFCs have been extensively measured and studied for human exposure and risk evaluation. Various PFCs have occurred in human blood and milk from North America^{3,4}, Europe^{5,6} and Asia^{7,8}.

So far, a great number of studies focus on the sources of human exposure to PFCs. There was a report indicating that food, drinking water, air and indoor dust were several potential sources of human exposure to PFCs⁹. Generally, dietary ingestion is considered as the main route of exposure to PFCs even though there is no sufficient evidence^{9,10}. In recent years, the levels of PFCs in a series of normal foods have been investigated in several countries such as the United States³, United Kingdom¹¹, Canada^{9,10}, Germany⁶ and Spain¹⁰. However, few study focused on Chinese dietary. Milk and dairy products as a class of basic foods are consumed by human. Moreover, PFCs have been found in milk or dairy products in several countries^{10,12}. However, to our knowledge, there is no report yet on the occurrences of PFCs in milk and dairy products from Chinese market.

The purpose of the present study was to investigate the levels of 9 perfluorinated acids and 2 fluorotelomer acids in a variety of milk purchased from Chinese markets.

Materials and Methods

From August 2008 to February 2009, milk (n=84) samples were purchased randomly from markets in China. Milk samples are divided into three groups on the basis of different packaging: Bailey, Tetra Fino Aseptic and Tetra Brik Aseptic. All the samples are kept in their original packaging at 4°C and analyzed in their shelf life.

The extraction method described by Tittlemier⁹ was used, with some modifications. Samples were taken and placed in a polypropylene (PP) centrifuge tube, precleaned with MeOH. Internal standards were added into the tube, followed by 4 mL MeOH. Samples were mixed well on vortex before sonicated for half an hour. After centrifuged, the supernatant was transferred into precleaned PP tube and the extraction was repeated with another 4 mL MeOH. Supernatants were combined and concentrated to 1mL with a gentle stream of N₂. The samples was loaded onto Waters Oasis® WAX single-use cartridge (6 cc/150 mg) previously conditioned with 4 mL MeOH and 4 mL water. SPE cartridge was washed with 4 mL acetate buffer solution and 4 mL MeOH and eluted with 2% NH₄OH in MeOH (target fraction). The eluate was concentrated to 1 mL under nitrogen for injection. The samples were analyzed for 9 perfluorinated acids and 2 fluorotelomer acids, including Perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluorododecanoic acid (PFDoDA), perfluorotetradecanoic acid (PFTA), perfluoroundecanoic acid (PFUnDA), perfluorohexane sulfonate (PFHxS), perfluorooctane sulfonate (PFOS), Perfluorooctyl ethanoic acid (FOEA), and 2H-Perfluoro-2-decenoic acid (FOUEA) with a high performance liquid chromatography equipped with an electrospray ionization tandem mass spectrometer (API 3200; Applied Biosystems/MDS SCIEX, US) (HPLC-ESI/MS/MS). Sodium perfluoro-1-[1, 2, 3, 4-¹³C₄]octanesulfonate (MPFOS) and perfluoro-n-[1,2,3,4-¹³C₄] octanoic acid (MPFOA) were used as the internal standards. Spearman's correlation analysis was applied to examine the relationship between the packaging of milk and PFC concentrations.

Results and Discussion

PFHpA, PFOA and PFNA were the predominant compounds found in all milk samples (Figure 1). PFHpA and PFNA were both detected in 68% of the milk samples, followed by PFOA in 46%. PFOS, the most familiar perfluorochemical, was only observed in 36% of the milk samples. PFDA, PFUnDA and PFTA were found occasionally. PFHxS, PFDoDA, FOEA and FOUEA were not observed in any samples. The mean concentration of total PFCs was 183 pg/ml. The PFC levels found in the milk are similar to or somewhat higher than those found in several previous studies^{10, 12, 13}. Ericson¹⁰ determined PFC levels in 36 composite samples from the Catalan (Spain) Market. Only three PFCs (PFOS, PFOA and PFHpA) were detectable. The total concentrations of PFCs were 71pg/mL in whole milk and 121 pg/mL in dairy product. Another study showed that PFCs were also not observed in the formula based on milk from the United States except a few samples¹³.

The composition profile of relative levels of PFHpA, PFOA, PFOS, PFNA and PFDA is performed using mean concentration values. In milk samples, PFHpA and PFNA contributed up to 29% and 37%, respectively, of the total composition, while PFOA and PFOS only accounted for 27% together. In whole milk from Spain¹⁰, PFOS was not detectable. The proportion of PFHpA was lower than PFOA in whole milk from Spain, which was different from that in milk from China.

No significant correlation was found between levels of PFC and company brands. In addition, there were many kinds (such as whole and skimmed milk) and tastes (such as chocolate and fruits) in the milk and yoghurt samples and no difference in concentrations of these samples was observed. However, the concentrations of total PFC associated with the packaging of milk strongly ($P < 0.01$). Among three packaging, the levels of PFC in milk packaged with Bailey are notably higher than the levels with other two packaging. The total PFC concentrations in some samples exceed 600 pg/ml. PFC levels in milk with Tetra Fino Aseptic are similar to the levels with Tetra Brik Aseptic. The total PFC concentrations in all the samples with Tetra Fino Aseptic and Tetra Brik Aseptic are below 300 pg/ml. There were some reports^{9, 10, 14} suggesting that food packaging might serve as a source of PFCs and perfluorooctanesulfonamides, used as repellents of water and grease, in food. So we think that the difference of PFCs concentration may be related to the milk packaging or processing.

Acknowledgments

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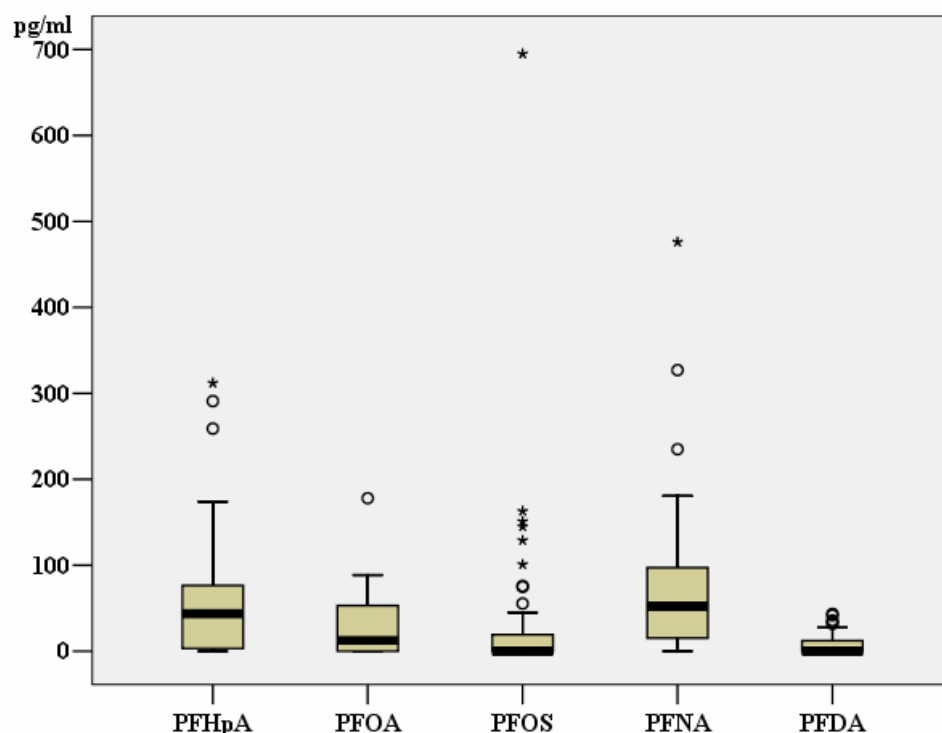


Figure 1. PFC concentrations (pg/g) in milk samples from Chinese Markets

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