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Blood plasma concentrations of endocrine disrupting chemicals in Hong Kong populations

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HIGHLIGHTS

- Over 150 human blood samples were analyzed for the presence of chemical pollutants.
- PFCs, BPA and phthalates were detectable over 90% of the blood samples.
- The mean plasma DEHP level was significantly higher in the young age group.
- PFCs were significantly higher in male than in female.

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ABSTRACT

In this study we report the human plasma concentrations of some common endocrine disrupting chemicals (EDCs) in the Hong Kong population. We have analyzed 153 plasma samples for the contaminants by methods involving labeled standards spiked into the samples. Quantification was performed using high performance liquid chromatography tandem mass spectrometry for bisphenol-A (BPA) and perfluorinated compounds (PFCs), and gas chromatography mass spectrometry methods for phthalates. We found BPA, several types of PFCs and phthalates in over 90% of the plasma samples. Perfluorooctane sulfonate (PFOS) was the dominant PFC, followed by perfluoroctanoic acid (PFOA) and perfluorohexane sulfonate (PFHxS). Eight out of ten phthalates were detected, with bis(2-ethylhexyl) phthalate (DEHP) as the most abundant, followed by bis(2-methoxyethyl) phthalate (DMEP) and dioctyl phthalate (DnOP). The levels of PFOS, PFOA, PFHxS and perfluorohexanoic acid (PFHxA) were significantly higher in the male plasma samples ($p < 0.05$), while the mean plasma levels of DEHP and n-butyl benzyl phthalate (BBP) were significantly higher in the young age group ($p < 0.02$). The presence of the selected EDCs in human blood plasma indicates common exposure routes among different population cohorts. Although the plasma levels of the EDCs were comparable to other countries, regular monitoring of human blood EDC contamination levels is necessary to provide a time-trend database for the estimation of exposure risk and to formulate appropriate public health policy.

1. Introduction

In the past century the relentless advance of industrialization and technology and the consequent rapid growth of human populations have impacted on the environment in a way that is unprecedented in human history. The production of large amounts of synthetic industrial and biomedical chemicals in addition to unwanted pollutants, has given rise to destructive consequences for our ecosystem and negative health effects on both wildlife and humans. A recent review has highlighted that about 40% of human deaths (62 million per year) is attributed to exposure to chemical pollutants. Some of the more worrying chemical contaminants are classified as endocrine disrupting chemicals (EDCs) because they are able to interfere with the synthesis, metabolism and action of endogenous hormones. They are known to exert different biological effects by means of diverse mechanisms. The adverse effects of EDCs have raised public concern due to epidemiological studies that correlate EDC exposure to many negative health outcomes in typical human populations, such as obesity, decreased fertility and immune dysfunction.

A considerable number of EDCs are produced and used widely in our daily lives. Bisphenol A (BPA) is present in plastic water

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Table 1
Summary of plasma PFC concentrations.

	PFOS	PFOA	PFHxS	PFNA	PFDA	PFUdA	PFHxA	PFDoA	PFBA
Mean	8.68	4.02	1.34	1.06	0.77	0.64	0.60	0.47	0.27
SD	5.91	2.70	1.14	0.42	0.31	0.37	0.48	0.24	0.06
Minimum	0.24	1.12	0.25	0.51	0.50	0.20	0.20	0.20	0.16
Maximum	44.77	18.92	7.43	3.05	2.44	2.89	4.23	1.71	0.49
Median	7.65	3.24	1.08	0.95	0.65	0.57	0.47	0.43	0.26
% of samples > LOD	100.00	96.08	83.66	87.58	58.82	96.08	96.73	64.05	47.71

Nine species of PFCs family were found in plasma of Hong Kong donors' blood samples and listed, according to the relative concentrations.

bottles, food packaging, thermal printer paper and market fish [1–3]; phthalates are used in the production of cosmetics and plastic containers [4,5]; and perfluorinated compounds (PFCs) are found in indoor/outdoor dust and market fish [6–8], thereby indicating that contamination is ubiquitous. In the past 30 years numerous studies have measured levels of EDCs in many different environmental samples. Although pathways of exposure to EDCs can be diverse, the identification of all possible exogenous exposure is not yet a feasible task; and it is this factor which highlights a major limitation of the measurement of external exposure to EDCs. We maintain that there is a need for a transformational change in the approach to contaminants in which more emphasis be placed on correlating population-based data to reveal human-environment interactions. By doing so, researchers will be able to develop better predictive models of human response to toxicants. In this study we analyze a dataset of human blood samples in order to provide a framework of accumulated concentrations of EDCs.

2. Materials and methods

2.1. Sample collection

A total of 153 whole blood samples (EDTA-treated) were collected between 2010 and 2011 from the Hong Kong Red Cross. Samples were separated equally into different groups by age (16–39 years and 40–63 years) and sex (male and female). The study was approved by the Hong Kong Red Cross and Hong Kong Baptist University and no personal information was disclosed. All whole blood samples were centrifuged at 3000 × *g* for 15 min to obtain the upper plasma layer. To minimize background contamination, all glassware and polypropylene tube were rinsed with methanol, n-hexane and ethyl acetate prior to use. All plasma samples collected were stored in sanitized polypropylene containers at −20 C until analysis. Aliquots of 500 μl plasma were thawed and transferred into a clean 15 ml polypropylene tube; thereafter the respective internal recovery standard was added (1 ng PFCs internal standard in methanol, 5 ng of deuterated-bisphenol A in methanol (d^{16}-BPA) or 5 ng of surrogate standards (diisooctyl phthalate in acetonitrile: THF (2:1)). Procedure blanks were tested every 10–15 samples to check for possible laboratory contaminations and interference.

2.2. Chemical materials for instrumental analysis

A mixture of standard solution of perfluoroalkylcarboxylic acids (PFCAs) and perfluoroalkylsulfonates (PFASs) in addition to a mass-labeled standard solution (used as the internal standard) were purchased from Wellington Laboratories (Ontario, Canada). Purities of the analytical standards were greater than 98%. Authentic standards of bisphenol A and bisphenol A-d^{16} (99% purities) were obtained from AccuStandard, CT, USA and Chiron, Trondheim, Norway. Methyl tert-butyl ether (MTBE), methanol, acetonitrile, and n-hexane were purchased from Tedia Company Inc. Pesticide grade ethyl acetate was purchased from LAB SCAN, UK. Tetrabutylammoniun hydroxide solution (TBA), sodium carbonate and sodium hydrogen carbonate were obtained from Sigma–Aldrich (MO, USA).

An Agilent 1200 liquid chromatography (Waldbronn, Germany) equipped with a quaternary high-pressure gradient pump and an automatic sample injector was used for LC–MS/MS analysis for PFC and BPA. Chromatographic separation was performed using an Agilent C8 (2.1 mm × 12.5 mm, 5-μm) guard column (ZORBAX Eclipse XDB-C8, Narrow-Bone) and a C18 ODS column (Agilent ZORBAX XDB-C18, 3.5-μm × 2.1 mm × 50 mm, 3.5-μm) for BPA and Zorbax Eclipse Plus C8 column (2.1 mm i.d. × 100 mm length, 3.5-μm; Agilent Technologies) for PFCs. Tandem mass detection was conducted by an Agilent 6410B Triple Quadrupole mass spectrometer system equipped with an Agilent Mass-hunter Workstation and an electrospray ionization source.

Table 2
Gender difference in plasma PFC concentrations (ng/ml).

	PFOS	PFOA	PFHxS	PFNA	PFDA	PFUdA	PFHxA	PFDoA	PFBA
Male									
Mean	9.59*	4.50*	1.65*	1.07	0.80	0.57	0.70*	0.46	0.27
SD	7.07	3.17	1.38	0.45	0.36	0.38	0.59	0.24	0.05
Minimum	0.33	1.27	0.25	0.51	0.50	0.30	0.20	0.20	0.20
Maximum	44.77	18.92	7.43	3.05	2.44	2.89	4.22	1.61	0.40
% of samples > LOD	100	94	90	83	51	94	96	61	57
Female									
Mean	7.63	3.50	0.92	1.07	0.75	0.71	0.48	0.48	0.27
SD	3.99	1.96	0.44	0.39	0.25	0.35	0.24	0.24	0.08
Minimum	0.24	1.12	0.31	0.57	0.50	0.24	0.20	0.20	0.20
Maximum	19.97	13.40	2.41	2.61	1.50	2.24	1.22	1.71	0.49
% of samples > LOD	100	99	76	90	68	99	97	68	38

The plasma samples were analyzed separately according to gender. Male plasma PFOS, PFOA and PFHxS were found to have significantly higher levels ($p < 0.05$, <0.03 and <0.001) while plasma PFHxA levels were higher in the female group ($p < 0.005$).

* Indicates significant differences among groups by analysis of variance (ANOVA) followed by Duncan's multiple range test (significance at $p < 0.05$) SPSS16.

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