Polybrominated diphenyl ethers (PBDEs) in serum from teenagers working in a waste disposal site, and in women with high consumption of fish in Nicaragua

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Introduction

Polybrominateddiphenyl ethers (PBDEs) have been extensively used as additive flame retardants since the 1970s. PBDE concentrations have been reported to increase with time both in humans and in wildlife from all environmental compartments [1-3]. Most published data originate from Europe, North America and the Arctic. There are also some reports from Australia, Japan, Korea, and Singapore. Information on human PBDE exposure from other regions in the world, except one report from Mexico[4], is entirely lacking. This is consistent with only few assessments of persistent organochlorine pollutants (POPs), pesticides and metals in the Southern hemisphere, over all.
The present study reports PBDE-levels in young Nicaraguans. Data on their serum levels of POPs has been reported earlier [5]. In general, the levels observed were higher than those reported from developed countries.

Material and methods

Setting: Managua, the capital of Nicaragua, is situated at the shore of LakeXolotlán. The lake, which is the second largest lake of Nicaragua, has been used as the recipient of domestic and industrial wastewater from the city, and receives the superficial run-off from its drainage basin, which is intensively cultivated.Fish from the lake is an important part of the diet, not only for the population living in rural fishing villages, but also for segments of the Managuan population.
The municipal domestic and industrial waste disposal site in Managua is located directly on the south shore of the lake, covering an area of 7 km^2.Approximately 1000 persons work at the city dump, collecting recyclable waste for selling. More than 50% of the workers are children under age 18. A thick cloud of smoke covers the area as the waste is burned to retrieve iron and other materials. The waste is not compressed, the sun is intense, and a constant breeze from the lake sweeps the area. Thus, substantial amounts of airborne dust are generated. In 2005, the mean level of particulate matter (PM2.5) in the city dump area was 710 µg/m^3, compared to 110 µg/m^3 in a nearby reference area, Acahualinca (Dr D Hernandez Romero, personal communication).
Study groups: We studied teenagers working in the city dump, and referents, all aged 12-15 and sharing the same underprivileged socio-economic situation. Forty eight percent were girls. Five serum pools were assembled in May 2002 (for further details see also Table 1): #1: teenagers living at the city dump, having worked there for 4 -10 years (median 6 years). Half of the teenagers had been living at the dump all their life, the other half between 5 to 11 years.#2: teenagers living in a near-by area, Acahualinca, having worked at the city dump for 4-12 years or more (median 6 years), #3 and#4: teenagers living in Acahualinca, not working at the dump #5: teenagers living in a remote urban area.
We also assembled another four pools to further study the influence of fish consumption: #A: women aged 15-17, living in fishermen´s families in San FransiscoLibre, a fishing village on the rural north-east side of the lake; #B: women aged 20-29 from another fishing village, Mateare, 25 km from the city of Managua. #C: women from urban Managua aged 18-25; #D: women from urban Managua aged 42-44. All were living in similar under-privileged socio-economic conditions. The serum sampling was performed in July, 2002.
Chemical analysis: The chemicals used, extraction of serum, lipid determination, partitioning with an alkaline solution, procedure and analysis have been described in detail elsewhere [6], except that n-hexane was replaced with cyclohexane. Lipids were removed from the extracts by sulfuric acid. Fractions containing both the neutral and phenol type substances were subjected to cleanup on sulfuric acid silica gel columns (1 g). The mobile phase for phenolic compounds was dichloromethane (10 ml). Additional cleanup was made for both fractions on an activated (300ºC, 12 h) silica gel column (1 g). The columns were conditioned with cyclohexane (6 ml) before the samples were applied. A first fraction was collected in cyclohexane (3 ml) and a second in dichloromethane (6 ml). The solvent in fraction 2 was reduced under a gentle stream of N_2 and replaced with n-hexane prior to gas chromatography mass

spectrometry (GC-MS) analysis. Reference compounds, synthesised in house, were used as standards. All solvents were of the highest available commercial grade.
Identification and quantification were performed using a GC-MS FinniganTSQ 700 (Thermoquest, Bremen, Germany) operating in electron capture chemical ionization (ECNI) mode, tracing the bromide ions (*m/z* 79 and 81). A DB-5HT column (15 m × 0.2 mm i.d. and 0.1 µm film thickness) from Supelco (Bellefonte, USA) was used with temperature program of 80ºC (1 min) – 15ºC/min – 300ºC – 2 ºC/min – 320ºC (2 min). On-column injections were performed using a septum equipped programmable injector fitted with a high performance insert. The injector temperature was 60ºC and increased with 150ºC /min up to 300ºC for each injection. Helium was used as carrier gas. The transfer line temperature was 290ºC and the temperature in the ion-source was 200ºC.

Results and discussion
The concentrations of selected PBDE congeners are given in Table 1. In all pools BDE-47 was the dominating PBDE congener, followed by BDE-99, BDE-100 and BDE-153. The teenagers working and living at the plant had by far the highest PBDE concentrations, followed by the city dump workers living in a nearby area.

Table 1. Concentrations of some PBDEs (pmol/g lipids) in teenagers working at a waste disposal site and referents (pool 1-5), and in women with varying fish consumption (pool A-D). For comparison, levels in Swedish men [7] and US blood donors [8] are also given.

GROUP	Fish meals/ month	Waste disposal area	BDE-47	BDE-100	BDE-99	BDE-153	BDE-183	BDE-203	BDE-209
Pool 1[1]	2 (0-8)	Work, live	640	110	310	46	2.4	0.86	5.4
Pool 2[1]	2 (0-8)	Work	70	18	19	18	2.4	0.70	3.6
Pool 3[1]	2 (2-8)	No	29	7.3	11	4.5	1.1	0.40	5.7
Pool 4[1]	0	No	11	2.0	4.6	2.2	2.6	0.47	7.3
Pool 5[1]	0	No	14	3.4	6.5	2.6	1.0	0.50	6.0
Pool A	4 (4-8)	-	20	4.2	11	2.2	1.8	0.63	4.5
Pool B	8 (8-16)	-	14	3.3	3.7	1.6	0.45	0.39	3.7
Pool C	0 (0-0)	-	86	15	14	12	0.79	0.61	4.1
Pool D[1]	0 (0-4)	-	68	11	26	5.4	0.48	0.46	3.0
Swedish men 2000[2]			*3.2*	*0.97*	*<0.1*	*0.89*	*0.16*	*<0.2*	*2.5*
US blood donors 2000-02[3]			*74*	*10*	*19*	*11*	*-*	*-*	*-*

[1]Mean of duplicate analyses, [2]Median values, [3]Median values of pooled samples

The teenagers living and working on the city dump had very high levels of low-medium brominated diphenyl ethers, higher than hitherto reported elsewhere. Obviously, the city dump is a source of exposure, and inhalation is the likely main route of exposure. Four of the teenagers in pool 1 had been living at the dump all their life. Thus, PBDE exposure in uterus had occurred; taken the presumed long half life of low-medium brominated PBDEs into account (several years [9]) this may partly contribute to their present levels.
PBDE-levels were higher among non-working teenagers eating fish from the lake, compared to the levels observed in non-consumers living in the same area. Thus, fish from the lake may also be a source of exposure to low-median brominated BDEs. This is in line with previous findings of a correlation of fish consumption and the level of BDE-47 [10].
However, factors linked to urban dwelling, whether dietary or others, were clearly much more important for the levels of low- to medium brominated PBDEs than fish consumption, as seen by the contrasts between pools C and D, *vs* pools A and B. Such a marked urban-rural gradient has not been reported before. We have no detailed dietary information for these subjects, but it is not likely that their diet, based on rice and beans, differs markedly expect for fish consumption. The levels of low- to medium brominated PBDE observed among young and middle aged urban Nicaraguan women were comparable to contemporary observations in US blood donors [8], whereas the urban teenagers not working at the dump had lower levels.
The city dump is not only a source of PBDE exposure, but also of other persistent organohalogens as PCB and pentachlorophenol [5]. Moreover, more than one third of the children and teenagers working at the dump had blood lead levels exceeding 100 µg/L, the action level recommended by US Environment Protection Agency (Cuadra, personal communication). Thus, in addition to the extremely harsh living and working conditions encountered by these children, their complex chemical exposure situation has to be taken seriously. A female teenager is also likely to be mothers in the near future – in 2001 as many as 21% of adolescent females in Managua were mothers or pregnant [11].

The present findings clearly call for the urgent necessity to monitor human PBDE exposure not only in the industrialized regions of the world, but also in developing countries and in underprivileged populations.

Acknowledgements
We gratefully acknowledge the cooperation of Dr Danilo Hernandez Romero, and the staff from “Dos Generaciones”, “Chateles project”, and health centers in the study areas during the field work. IoannisAthanassiadis skilfully performed the mass spectrometry analyses. The study was performed within the framework of a multidisciplinary co-operation project between Lund University and the National Autonomous University of Nicaragua (UNAN-Managua), funded by the Swedish International Agency for Research Cooperation with Developing countries, SAREC

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