

Polychlorinated Dibenzo-*p*-Dioxins and Polychlorinated Dibenzofurans in Sediments from Two Ethiopian Rift Valley Lakes

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Abstract

The aim of our study was to evaluate surficial sediments from two selected Ethiopian Rift Valley aquatic environments – Lake Awassa and Koka Reservoir, for the occurrence of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). The total concentration of target compounds resulted several times higher in the lake (270.39 pg/g dry weight) than in the reservoir (63.17 pg/g d.w.). Similarly, concentrations measured as WHO-Toxic Equivalent (WHO-TEQ) were 23.78 pg TEQ/g d.w. and 4.03 pg TEQ/g d.w., respectively.

Obtained results, in reference to the Canadian Sediment Quality Guidelines, exceed the limit of 0.85 pg TEQ/g d.w. in both lake and reservoir, as well as probable effect level (PEL) of 21.5 pg TEQ/g d.w. in lake sediment, and thus represent high pollution levels of analyzed samples.

Keywords: PCDD/Fs, sediments, Lake Awassa, Koka Reservoir, Ethiopian Rift Valley

Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) constitute a group of persistent, bioaccumulative, and toxic contaminants [1, 2]. They have been detected in soil, surface water, sediments, plants, and animal tissue in all regions of the earth [3-6]. Moreover, they have been recognized to have potential carcinogenicity, immunotoxicity, dermal toxicity, and adverse effects on reproduction, development, and endocrine functions in both animals and people. Furthermore, because of their low volatility and solubility in water, they easily interact with particles and eventually are accumulated in soils and sediments that serve as environmental reservoirs from which PCDD/Fs may be

released over a long period of time. In consequence, attempts to identify levels and sources of these contaminants in sediments of water reservoirs and lakes have recently intensified [7].

Ethiopia has been legally obliged to support research on persistent organic pollutants (POPs) since 2004, when the Stockholm Convention entered into force [8]. Nevertheless, lack of information regarding POP levels in this country is considered a key knowledge gap in understanding the overall environmental distribution and fate of PCDD/Fs [9]. As a consequence, this paper presents the results of a study into the levels of these contaminants in surficial sediments from two Ethiopian Rift Valley water bodies: Lake Awassa and Koka Reservoir. The environmental quality assessment is based on a limited data set that, nevertheless, can considerably enhance our knowledge on the situation in such Ethiopian aquatic environments.

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Materials and Methods

Study Area

Lake Awassa is located in the central part of the Ethiopian Rift Valley, 275 km south of the capital, Addis Ababa, at an altitude of 1680 m (6°33'-7°33'N and 38°22'-38°29'E) (Fig. 1) [10]. It has surface area of 90 km² [10] and maximum and mean depths of 22 m and 11 m, respectively (although these values are subject to seasonal variation). The catchment area is 1,250 km², in which 240,000 (1994) people reside [11]. The lake is topographically a closed basin, with no known outflow and it is primarily fed by a small river (Tikur Wuha, flow 1-12 m³/s) that flows from Shallo Swamp, and also from the ephemeral streams on the north and west caldera walls [11].

The Koka Reservoir (also known as Lake Gelila) is located in the Misraq Shewa Zone of the Oromia Region on the Awash River, near to the capital and largest city of Ethiopia, Addis Ababa (Fig. 1). The reservoir was constructed in 1960 and has an area of 180 km² with a capacity of about 1,840 Mm³. The Koka Dam is made of concrete and has a length of 458 m and a maximum height of 47 m. The head utilized is 32-42 m [12].

Sampling

Three sediment samples (10-25 cm thickness) were taken once during the dry season (November) of 2008 from each lake using sediment core samples. After collection, samples were placed into black jars (to avoid sunlight) and stored in an icebox at 4°C and transported to a laboratory where they were freeze dried (-40°C, 1 mba, 72 h; Edwards Freeze Dryer) sieved through a 2 mm mesh sieve, and mixed in proportion 1:1:1 to obtain one representative sample [13-16].

PCDD/Fs Analysis

Extraction and Clean-Up

Sample pretreatment was carried out according to PN-EN 1948-3 [17] and EPA Method 1613 [18]. Sediment samples were spiked with 20 µL of isotopically ¹³C-labeled PCDD/Fs standards (EDF-8999, Cambridge Isotopes Laboratories, USA) prior to toluene extraction using ASE (accelerated solvent extraction) 200 Dionex. Extracts were eluted through multilayer silica columns (packed with SiO₂/AgNO₃, SiO₂/H₂SO₄ and SiO₂/KOH) with 200 mL of

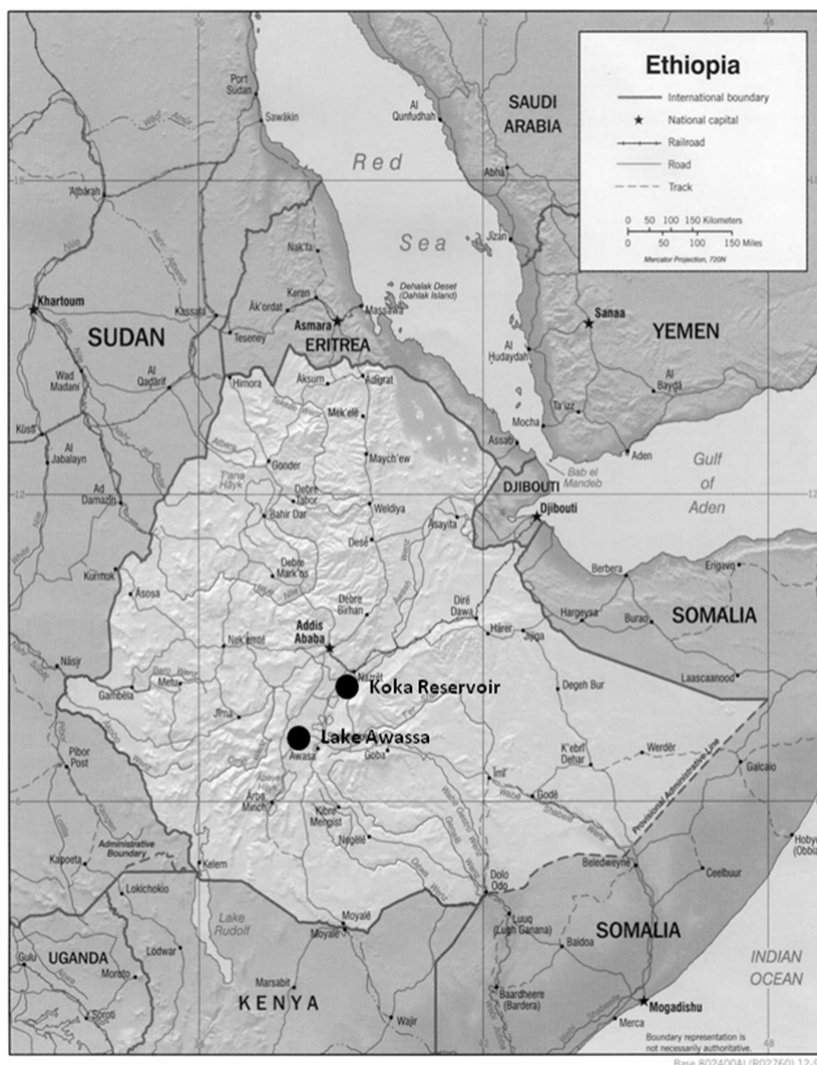


Fig. 1. Location of the study areas.

hexane. The hexane extracts were further evaporated to 5 mL and concentrated to 100 µL under a gentle stream of nitrogen, replacing the *n*-hexane to *n*-nonane.

Identification and Quantification

Identification and quantification of PCDD/Fs were performed by a HRGC/HRMS: HP 6890N Agilent Technologies coupled to a high-resolution mass spectrometer (AutoSpec Ultima). The HRMS was operated in the splitless injection mode and the perfluorokerosene (PFK) was used for a calibration reference. For separation, a DB5-MS column (60 m x 0.25 mm i.d., film thickness 0.25 µm) was used. Monitored masses were those proposed by EPA 1613 [17, 18].

The oven temperature program was 150°C held for 2 min, 20°C/min to 200°C held for 0 min, 1°C/min to 220°C held for 16 min, and 3°C/min to 320°C held for 3 min. The injector temperature was 270°C. The MS was operated under positive EI conditions: 34.8 eV electron energy at a resolving power of 10,000, with an iron source temperature of 250°C. Helium was used as carrier gas at a 1.60 mL/min flow rate. Samples were quantified with an isotopic dilution technique [17, 18].

WHO-TEQ Concentration

WHO-TEQ is an acronym for 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) equivalents. It is a means of expressing the net toxicity of a complex mixture of different PCDD/Fs. The WHO-TEQ term was used therefore to estimate the toxicity of a collected sediment sample due to these contaminants. Each of 7 individual congeners of PCDD and 10 congeners of PCDF have been assigned a toxic equivalency factor (TEFs) based on its toxicity relative to that of 2,3,7,8-TCDD, which is universally assigned a TEF of 1. Multiplication of the concentration of 7 congeners of PCDD and 10 congeners of PCDF by its assigned TEF gives its concentration in terms of WHO-TEQ calculated for all 17 PCDD/F congeners [19].

Chemicals

The hexane, nonane, and toluene used for extraction and clean up of sediment samples were obtained from Bujno Chemicals (Warszawa, Poland). The H₂SO₄, AgNO₃, KOH, and SiO₂ were obtained from the Sigma-Aldrich Co. (Poznań, Poland). All solvents were pesticide residue analysis grade. The PCDD/F standards were all purchased from LGC Promochem, CIL Cambridge (Łomianki, Poland).

Quality Assurance/Quality Control

The analytical method used for PCDD/F analysis was properly validated on the basis of internal reference materials, and the analytical laboratory involved in 2005 and 2009 successfully passed the accreditation procedure.

Table 1. PCDD/F method detection limits [MDL].

PCDD/F congeners	MDL [pg/kg]
2,3,7,8-TCDD	0.41
1,2,3,7,8-PeCDD	0.84
1,2,3,4,7,8-HxCDD	0.45
1,2,3,6,7,8-HxCDD	0.28
1,2,3,7,8,9-HxCDD	0.31
1,2,3,4,6,7,8-HpCDD	0.83
OCDD	0.42
2,3,7,8-TCDF	1.03
1,2,3,7,8-PeCDF	0.3
2,3,4,7,8-PeCDF	0.11
1,2,3,4,7,8-HxCDF	0.15
1,2,3,6,7,8-HxCDF	0.42
1,2,3,7,8,9-HxCDF	0.64
2,3,4,6,7,8-HxCDF	0.19
1,2,3,4,6,7,8-HpCDF	0.51
1,2,3,4,7,8,9-HpCDF	0.26
OCDF	0.38

All glassware and bottles used in field and laboratory were cleaned with detergent rinsed with ultra-pure water, followed by heating at 450°C overnight. Before use, the glassware was rinsed with acetone and hexane. The teflon jar caps were also cleaned with detergent, rinsed with ultra-pure water, and before being used rinsed again with acetone and hexane. The same system was used to clean the stainless steel cells of the Dionex ASE 200. Moreover, before each environmental sample extraction the empty cells were extracted to clean them and thus avoid cross-contamination.

Each analytical batch contained a method blank, a matrix spike, and duplicate samples. A reagent blank was used to assess artifacts and precision was verified by duplicate analyses. Sample spikes were used as an additional check of accuracy. Analyte recoveries, ranging between 70 and 120%, were determined by analyzing samples spiked with isotopically ¹³C-labeled PCDD/F standards. Additionally, Standard Reference Materials were used to assess method correctness [20]. The PCDD/F method detection limits (MDL) are presented in Table 1.

Statistics

All data were subjected to statistical analysis using "Statistica" software for Windows. The Kolmogorov-Smirnov Test was used to compare treatment levels in analyzed reservoirs. The statements of significance were based on a probability level of $p \leq 0.05$.

Table 2. Concentrations of total PCDDs, PCDFs, PCDD/Fs, and WHO-TEQ in sediments from Lake Awassa and Koka Reservoir.

	Lake Awassa	Koka Reservoir
Total PCDD concentrations [pg/g d.w.]	120.84±17.75	37.29±9.80
Total PCDF concentrations [pg/g d.w.]	149.56±9.79	25.88±3.01
Total PCDD/Fs [pg/g d.w.]	270.39±12.40	63.17±6.56
Total WHO-TEQ [pg TEQ/g d.w.]	23.78±1.70	4.03±0.55

Results and Discussion

The total concentrations of PCDD/Fs, as well as WHO-TEQ concentrations in studied reservoirs, are listed in Table 2 and show that the Lake Awassa presented higher levels of total PCDD/Fs than the Koka Reservoir (270.39 and 63.17 pg/g d.w., respectively). The same situation was observed for the sum of PCDDs (120.84 and 37.29 pg/g d.w.) and sum of PCDFs (149.56 and 25.88 pg/g d.w.). These results indicate that Lake Awassa has about 4 times higher levels of total PCDD/Fs than Koka Reservoir, and about 6 times higher for PCDF. Moreover, the concentration measured as WHO-TEQ was also about 6 times higher in Lake Awassa (23.78 vs. 4.03 pg TEQ/g d.w.) (Table 2).

The results also showed that all analyzed PCDD/F congeners were found in Lake Awassa, with concentrations spanning from 2.12 (for 2,3,7,8-TCDD) to 54.91 pg/g d.w. (for OCDD) (Fig. 2); whereas in Koka Reservoir concentrations ranged from below detection limit (for 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, 2,3,7,8-TCDF and 1,2,3,7,8-PeCDF) to 27.17 pg/g d.w. (for OCDD) (Fig. 2). The Kolmogorov-Smirnov Test used to compare the concentrations of PCDD/Fs between Lake Awassa and Koka

Reservoir samples also showed the statistically relevant differences with $p > 0.001$.

WHO-TEQ levels were highest for 1,2,3,7,8-PeCDD (6.38 and 2.33 pg TEQ/g d.w. for Lake Awassa and Koka Reservoir, respectively), 2,3,4,7,8-PeCDF (4.50 pg TEQ/g d.w. for Lake Awassa) and 2,3,4,6,7,8-HxCDF (0.31 pg TEQ/g for Koka Reservoir). This is due to the high TEF values of these congeners, especially 1,2,3,7,8-PeCDD (TEF=1.0) and 2,3,4,7,8-PeCDF (TEF=0.3) [19]. The differences between WHO-TEQ concentrations in analyzed samples were proved by statistical analysis with $p < 0.01$ (Kolmogorov-Smirnov Test).

Obtained results, in reference to Canadian Sediment Quality Guidelines, exceed the limit of 0.85 pg TEQ/g d.w. in both lake and reservoir. The probable effect level (PEL) of 21.5 pg TEQ/g d.w. was exceeded in Lake Awassa and thus represents high pollution levels of those samples.

The PCDD/Fs congener profiles in collected sediments revealed a predominance of OCDD (20.31% and 43.01% of the total PCDD/Fs in Lake Awassa and Koka Reservoir, respectively) and OCDF (13.02% and 14.55% of the total PCDD/Fs in Lake Awassa and Koka Reservoir, respectively) (Table 3). This type of profile with higher contribution of octachlorinated congeners has been shown in other lakes worldwide, where the major input was thought to be atmospheric [21]. As reported Rose and McKay [21], homologue profiles dominated by OCDD are observed in many environmental media, including sediments, soil, and sewage sludge. Koester and Hites [22] have shown that atmospheric processes tend to favour the deposition of OCDD in the environment. Rappe [23] demonstrated that photochemical degradation of lower chlorinated PCDD/F congeners may be responsible for enhanced OCDD/F concentrations in the atmosphere and thus this process may be one reason for their high relative contribution. Furthermore, Koka dam is constructed on the Awash River, which transports contaminants from Addis Ababa – the largest and the biggest city in Ethiopia. Studies investigating inputs to household waste and sewage treatment work effluent have indicated a predominance of higher chlorinated PCDDs, especially OCDD, in their profiles [24-31]. Thus, the pollution level in Koka Reservoir may also be considered as a result of disposal of municipal sewage to the Awash River.

Lake Awassa, in turn, is a closed basin with no known outflow, therefore OCDD/F loads reaching the system with the Tikur Wuha River (polluted by textile industry contaminants) are almost entirely retained in lake sediments. As

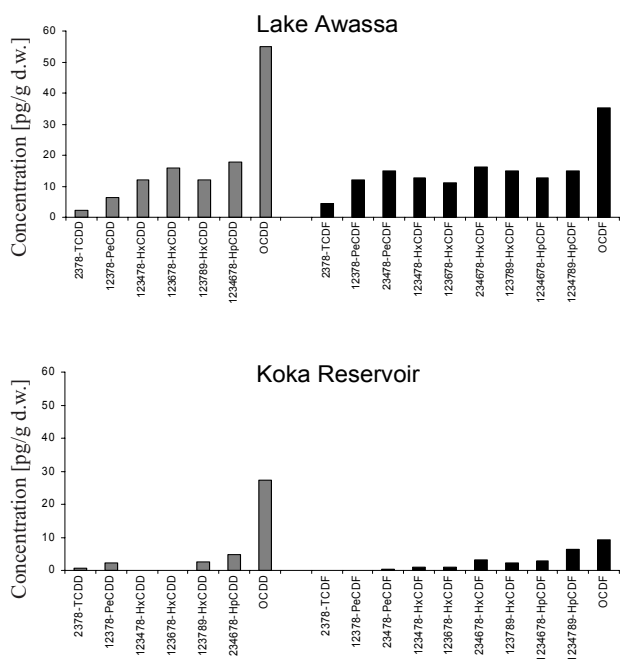


Fig. 2. PCDD/Fs congener profiles in sediments from Lake Awassa and Koka Reservoir.

Table 3. Percentage (%) contribution of PCDD/F congeners in sediments from Lake Awassa and Koka Reservoir.

	Lake Awassa	Koka Reservoir
2,3,7,8-TCDD	0.78	0.76
1,2,3,7,8-PeCDD	2.36	3.68
1,2,3,4,7,8-HxCDD	4.43	n.d.
1,2,3,6,7,8-HxCDD	5.81	n.d.
1,2,3,7,8,9-HxCDD	4.47	3.86
1,2,3,4,6,7,8-HpCDD	6.53	7.71
OCDD	20.31	43.01
Sum	44.69	59.03
2,3,7,8-TCDF	1.62	n.d.
1,2,3,7,8-PeCDF	4.49	n.d.
2,3,4,7,8-PeCDF	5.55	0.67
1,2,3,4,7,8-HxCDF	4.71	1.59
1,2,3,6,7,8-HxCDF	4.13	1.34
2,3,4,6,7,8-HxCDF	6.01	4.85
1,2,3,7,8,9-HxCDF	5.57	3.30
1,2,3,4,6,7,8-HpCDF	4.69	4.68
1,2,3,4,7,8,9-HpCDF	5.51	9.97
OCDF	13.02	14.58
Sum	55.31	40.97

n.d. – concentration below method detection limit (MDL).

reported by Yusuff and Sonibare [32], the major sources of contaminants in textile works are primarily associated with wet processes such as sizing, fabric preparation, dyeing, printing, and finishing. During these processes, chemicals are used and produced, such as heavy metals and POPs. The main OCDD/Fs sources in the effluents can be related to processes of bleaching, which require the use of Cl₂ and dyeing and printing in which pigments containing high amounts of PCDD/Fs are used [33, 34]. As reported by Allock and Jones [33] and Bostian et al. [34], pigments like chloranil, or dyes produced on the basis of chloranil may contain from 300.00 to 2900.00 and from 2.00 to 200.00 µg TEQ/kg of PCDD/Fs, respectively. In consequence, the contamination level observed in this lake can be due to the waste released from the textile industry.

Conclusions

Our findings show that the higher potential to PCDD/F accumulation is seen in the reservoir situated in the closed basin subjected to industrial impact (Lake Awassa) in comparison to the large reservoir receiving domestic effluents (Koka Reservoir).

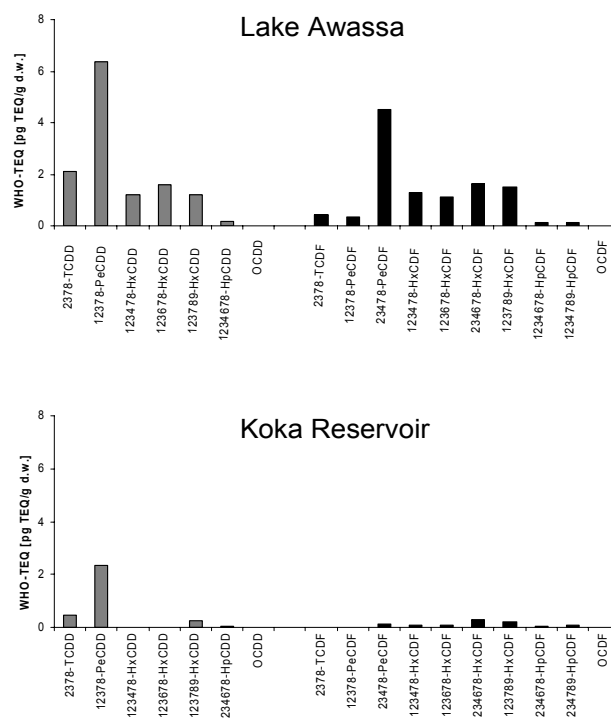


Fig. 3. WHO-TEQ congener profiles in sediments from Lake Awassa and Koka Reservoir.

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