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Determination of Perfluorooctanoic Acid and Perfluorooctane Sulfonate in Lake Victoria Gulf Water

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Abstract In this study we present a report of investigation from the screening of perfluorooctanoic acid and perfluorooctane sulfonate in Lake Victoria Gulf and in its source rivers. The first determined levels of perfluorinated alkylated substances in Lake Victoria ecosystem are presented. Variability in the concentrations of perfluorooctanoic acid or perfluorooctane sulfonate in river waters (range perfluorooctanoic acid 400–96,400 and perfluorooctane sulfonate <400–13,230 pg/L) was higher than for Lake waters (range perfluorooctanoic acid 400–11,650 and perfluorooctane sulfonate <400–2,530 pg/L respectively) suggesting generalized point sources such as domestic and industrial waste. The lowest limit of quantification was 400 pg/L for both analytes and limit of detection were 75 and 40 pg/L for perfluorooctanoic acid and perfluorooctane sulfonate respectively. Typical values for precision obtained were 0.14–3.7%, with concentrations range from 400 pg/mL to 1 μg/mL).

Keywords Perfluorooctane sulfonate · Perfluorooctanoic acid · LC/MS/MS · Lake Victoria

Perfluorocarboxylic acids, such as perfluorooctanoic acid and perfluorinated sulfates are used as water and oil repellants in the treatment of fabrics and leather, paper industry, personal care products and in many other industrial use (Kissa 2001; Martin et al. 2003; Berger 2004). According to Giesy and Kannan (2001) and Kannan et al. (2001), these compounds in general, and perfluorooctane sulfonate (PFOS) in particular, can elicit toxic effects in wildlife and humans. In recent years perfluorinated alkylated substances (PFAS) have appeared as a new class of global pollutant. Besides being an industrially important group of compounds, PFAS are regarded as highly toxic and extraordinarily persistent chemicals that pervasively contaminate human blood (Olsen et al. 2003; Hansen et al. 2001) and wildlife throughout the world (Gonza′lez-Barreiro et al. 2006; Lau et al. 2006; Abbott et al. 2007). They are therefore regarded as PBT (persistent, bioaccumulative, and toxic) chemicals (Gonza′lez-Barreiro et al. 2006) and cause diverse toxic effects in laboratory animals including primates (Biegel et al. 2001; Butebhoff et al. 2002). Studies have been carried out in other Lakes. As example, concentrations of PFOS and PFOA in the Great Lakes waters ranged from 21 to 70 and 27–50 ng/L, respectively (Boulanger et al. 2004). Simcik and Dorweiler (2005) obtained PFOS concentrations of upto 1.2 ng/L and from 2.4 to 47 ng/L in remote and urban surface water, respectively. Perfluorooctanoic acid concentrations ranged from 0.14 to 0.66 ng/L and from 0.45 to 19 ng/L in remote and urban surface waters, respectively, within Lake Michigan environments. Water analysis of PFOS and PFOA has been carried out with several methods. The most commonly used methods involve solid phase extraction (SPE) followed by HPLC-MS-MS. With the use of high-performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS), a method detection limit in the

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range of pg/L in water matrices can be achieved (Taniyasu et al. 2005). Generally PFOS and PFOA concentrations in ambient waters, with no point source of pollution, are less than 5 ng/L (Yamatisha 2004).

The management of Lake Victoria has for the last half century been largely focused on fish production and management. Very little attention has been paid to the ecological effects of pollutants on biodiversity. Judging by the very limited number of publications on persistent organic compounds studies done in Winam Gulf of Lake Victoria and its wetlands in recent years, the trend suggests the need for further research. Assessment of persistent organic pollutants (POPs) in Lake Victoria aquatic resources is critical, considering the ban almost a decade ago (in April 1999) following a report that pesticides had been determined in fish samples from Lake Victoria (Abila Richard 2003). This ban resulted in a 68% decline in fish exports (World Trade Organisation 2006; Abila Richard 2003). Surface water is the major source of drinking water in riparian states of East Africa that share Lake Victoria water. Therefore, it is important to monitor perfluorinated alkylated substances as a new class of global pollutant in Lake Victoria.

Materials and Methods

Sampling was done during the period of November 2006 to January 2007. Samples were collected in areas where the detection of PFOA and PFOS was most expected due to anthropogenic inputs. Sites selected included along rivers that flow near industries, residential estates and waste treatment facilities. Also sites were selected near places where various commercial activities are carried out within Lake Victoria. Control sites where selected as sites far away from these commercially active sites. Five field blanks were prepared in selected locations. Samples were collected in 1L polyethylene bottles, packed in coolers containing wet ice upon collection and shipped to the testing laboratory. In order to minimize the possibility of introducing PFOA and PFOS contamination into samples, fluoropolymer materials were avoided. Sampling in the open waters of Winam Gulf catchments were divided into locations (Fig. 1) and each location with a number of sampling points. Water samples were collected along rivers that drain into Winam Gulf of lake Victoria namely: Auji, Saka, Kibos and Kisat designated A, S, K and C respectively (see map in Fig. 1). Sampling was also done within Nyalenda Municipal Waste Treatment Ponds (MWTS) which is within the Kibos river catchment. Most rivers are largely located in the Kisumu and Nyando districts in the Nyanza Province of Kenya and all draining into the eastern part of the Nyanza Gulf of Lake Victoria (see Fig. 1).

Perfluorooctanoic acid, perfluorooctane sulfonate and an internal standard perfluorononanoic acid (PFNA, $CF_3(CF_2)_7COOH$) (Wellington Laboratories, Canada), were dissolved in methanol at a concentration of 50 µg/mL. The stock solutions were prepared weekly. Methanol, (all suprasolv), Ammonium acetate (p.a.) and all other chemicals were obtained from Merck (Darmstadt, Germany). Ultrapure milli-Q water was prepared by a millipore-Q-system (Millipore, S.A. Molsheim France). For 1.1 L of sample, an internal standard was added to the water sample in the sample bottle prior to solid phase extraction. 1,000 mL sample was let to run through water Oasis HLB SPE cartridges (60 mg) previously conditioned, at a flow rate 3–6 mL/min. Cartridges were washed with 40% methanol (6 mL) and then completely dried. Target analytes were then eluted with 6 mL of methanol. The eluent was evaporated with a gentle stream of nitrogen gas to a final volume of 1,000 µl for analysis by HPLC-MS/MS. Liquid chromatography/Mass Spectrum analysis were carried out with HPLC (HP 1090) interfaced with an Ion Trap MS (Thermo LCQ-Duo). Solvent: A = 2 mmol/L Ammonium acetate in methanol and B: 1 mmol/L Ammonium acetate in water. Gradient program used: A 10% then increase to 30% at 0.1 min, increase to 75% at 7 min and from 7 to 10 increased to 100% where is kept at the level until 15 min, before reversion to original conditions. Flow rate was 0.3 mL/min. Separation was done by a Betasil C18 column. Mass Spectrum conditions: Type: quadruple, Ionization: ESl negative. The method was calibrated with spiked amounts of PFOA and PFOS water of concentration range 5–1,000 pg/L and then 1,000–2,00,000 pg/L. Eight calibration curve points from enriched standards gave a value of $r^2 = 0.997$ for both PFOA and PFOS was used for quantifications and were prepared routinely, to check for linearity. The limit of quantification (LOQ) of target chemicals was evaluated for each sample based on the average blank concentrations plus five times its standard deviation of ten blanks. Linearity of matrix matched those of standard calibration curves. With 10 µL of the final sample volume of 1 mL injected in the splitless mode, the LOQ was 4 pg (absolute amount) for HPLC/MS/MS method. It corresponds to a concentration of 400 pg/L for the HPLC/MS. The monitored ions in MS were m/e 371, 413 for PFOA and 499 for PFOS. Water samples were spiked and analyzed to test the precision of the method. Recovery range was 87.7%–104.6%. Results of accuracy and precision of analyses for the present investigation were found to be good. Reproducibility of the results done after every third day for (n = 4) number of times gave average absolute amounts (pg) 3,910 and percentage standard deviation 8.7%.

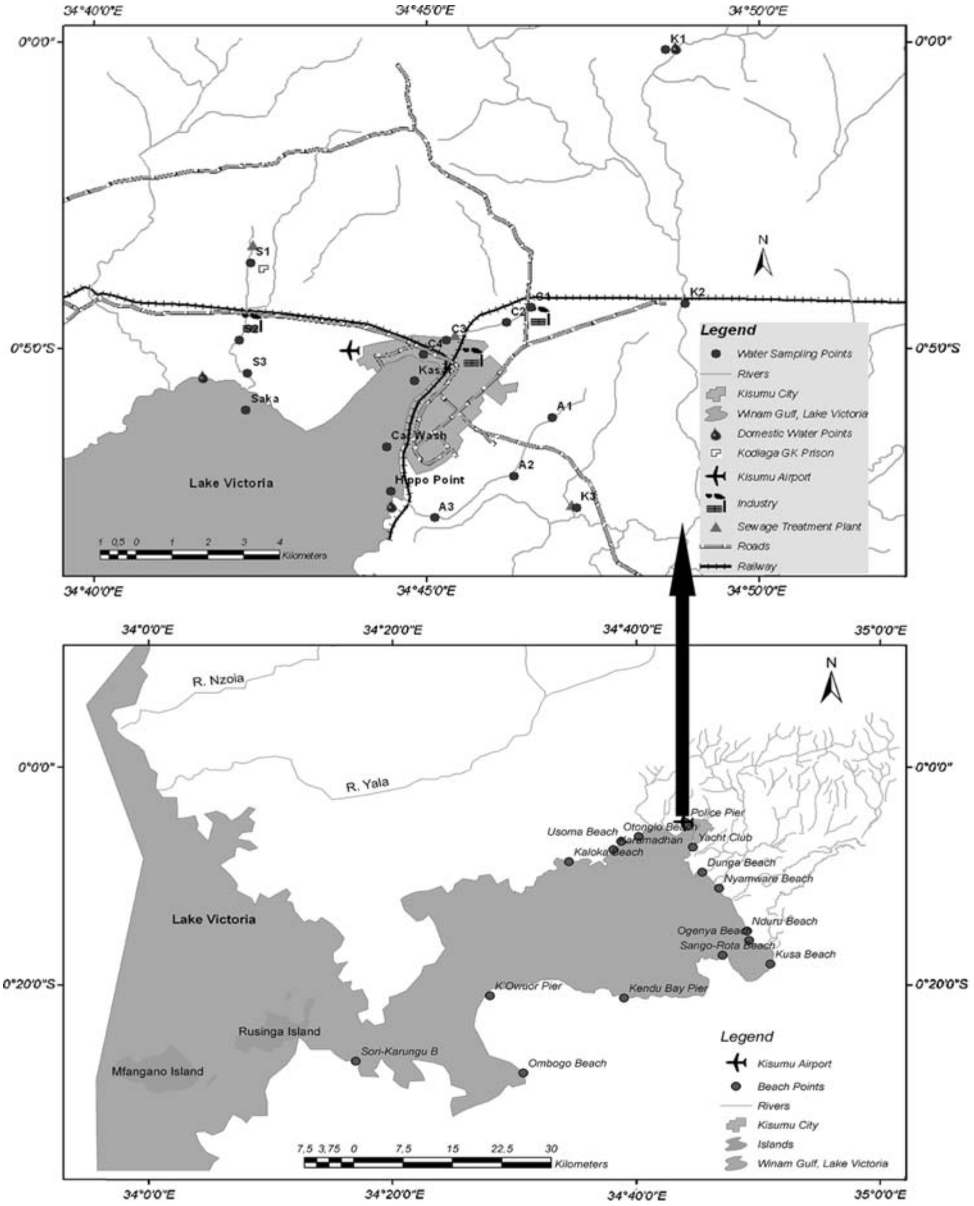

Fig. 1 A map showing sampling locations within Winam gulf of lake Victoria and sampling points along rivers draining into the gulf

Results and Discussion

Perfluorooctanoic acid was detected in most sampling locations in Winam Gulf of lake Victoria and within the rivers draining into Lake Victoria at Kisumu City. Figure 2 shows concentrations in pg/L of PFOA (black) and PFOS (white) represented by bars at each sampling points within Kisumu city region. Concentrations of PFOS less than 1,000 pg/L are not shown in the Figure. The maximum concentration of PFOA measured within the lake was 11,650 pg/L at the Dock/Car wash sampling location. These concentrations are approximately three orders of magnitude higher than those observed in other sampling locations in Lake Victoria. Many cottage industries and the main ship dock in Kenyas western region is located at this area that could provide a source for these elevated concentrations relative to PFOA concentration in ambient water (Yamatisha 2004). Relatively higher concentrations were also obtained along Auji river with an average of 17,000 pg/L at point A2 (see Fig. 2). Domestic waste from a Nyalenda slums and also inputs from the Kibos river catchment can be considered as the source of these perfluoroalkylated compounds along Auji river. Kibos and Auji rivers are interconnected within Nyakach swamp around the area. Auji river drains its water in Lake Victoria at Hippo point and Yatch club. This point is of interest because water for domestic use in Kisumu City is drawn near this point. The highest PFOA concentration was 96,400 pg/L (point K3) at Nyalenda Municipal Waste Treatment Ponds along the Kibos river catchment. This

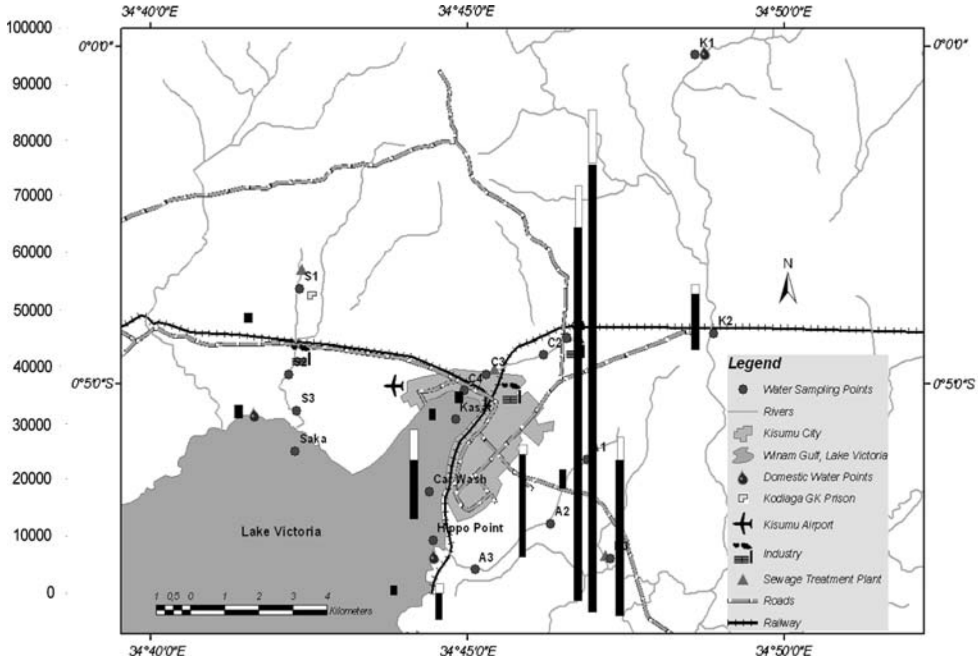

Fig. 2 Concentrations in pg/L of PFOA (black) and PFOS (white) represented by bars at each sampling points within Kisumu city region in Kenya. Concentrations of PFOS less than 1,000 pg/L are not shown in the map in the figure

Table 1 Concentrations range and mean (in brackets) in pg/L of PFOS and PFOA obtained from various sampling locations

Sampling location	*N*	PFOS	PFOA
Kisat	9	<400–450 (420 ± 28)	410–730 (580 ± 120)
Auji	6	1,200–1,720 (1,330 ± 230)	3,760–4,560 (4,060 ± 300)
Kibos	8	1,340–8,250 (3,870 ± 2,400)	7,970–32,500 (17,660 ± 8,550)
Saka	5	<400–750 (560 ± 230)	450–920 (710 ± 180)
Nyalenda MWSP	11	5,670–13,230 (8,880 ± 2,730)	44,890–96,400 (65,700 ± 13,900)
Pipeline	6	<400	<400–600 (410 ± 190)
Dock/car wash	6	<400–2,530 (2,000 ± 670)	<400–11,650 (5,100 ± 4,900)
Hippo point/Yatch club	4	<400–650 (550 ± 140)	440–1,050 (750 ± 250)
Dunga beach	5	<400–950 (540 ± 90)	<400–1950 (840 ± 93)
Nyamware beach	5	<400	<400–1550 (820 ± 95)
Nduru beach	6	<400	<400–950[a] (805 ± 100)
Ogenya beach	3	<400	<400–850[a] (680 ± 90)
Songa-Rota beach	3	<400	<400–800[a] (640 ± 80)

[a] Only one to three samples are above the limit of quantification. Values below LOQ are donated by '<'. Values below the limit of detection were not included in the estimation of the mean

high concentration can be attributed to Municipal Waste which is drained into the Kibos river catchment at these point (see Fig. 2). Relatively low concentrations of PFOA and PFOS were obtained along Kisat river with mean of 580 pg/L. A municipal sewage treatment plant is located in the final part of Kisat river before it discharges into Kisumu bay of the Winam Gulf. There are several industries and a textile mill located in this area which may provide a source for these concentrations. Saka river system flows through a residential populated area, and along it is a molasses industry and small cottage industries. Lower concentrations of PFOA were determined along Saka river with mean of 710 ± 180 pg/L. Table 1 shows the results of concentration range of analytes and mean (in brackets) obtained from each locations. Results obtained from the other sampling locations not presented in Table 1 were generally below the limit of quantification. Perfluorooctanoic acid was the predominant fluorochemical found in all the samples analysed in this study. Variability in the concentrations of PFOA or PFOS in River waters samples of Kibos, Kisat, Auji and Saka was higher than for Winam Gulf water samples, suggesting generalized point source such as domestic and industrial waste. Lake water samples showed the presence of all investigated perfluorinated compounds at pg/L levels while most samples from river waters studied are in parts per trillion range for PFOA concentrations. Both concentrations of PFOA and PFOS in the Lake are several orders of magnitude lower than concentrations at the outlets of the rivers studied into the Lake Victoria waters. These lower values appear to be the background values in pg/L levels for remote Lake water far from local sources. These can be represented by range of values and mean concentration (in brackets) obtained at the following locations; Nyamware Beach < 400–1,550 (820 ± 95), Nduru beach < 400–950 (800 ± 100), Ogenya Beach < 400–850 (680 ± 90), Songa-Rota beach < 400–800 (640 ± 80) pg/L. Perfluorooctane sulfonate concentration values were < 400 pg/L for samples from these locations.

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