Analysis of Mercury in Wastewater of some Dental Clinics in United Arab Emirates

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Abstract: The amount of mercury in the wastewater of three dental clinics from United Arab Emirates over a period of 3 to 17 days was quantified using cold vapour-atomic absorption spectrometry technique. The total Hg concentration in the wastewater of these clinics ranged from 25 to 146 $\mu g \ d^{-1}$. The Hg concentration in the wastewater samples collected from the outlets of the dental chairs after dental treatments varies depending on the type of dental treatment: the average Hg concentration in the samples of only amalgam restoration is 39 μg per sample (std. dev. 37, range 4-142); for samples with amalgam restoration plus other types of dental treatment is 24 μg per sample (std. dev. 24, range <MDL-77); and for sample with no amalgam restoration is 18 μg per sample (std. dev. 16, range <MDL-33).

Keywords: Dental amalgam; mercury; dental wastewater; United Arab Emirates

Introduction

Amalgam is the most commonly used dental filling material for more than 200 years (Arenholt-Bindslev & Larsen, 1996; Counter & Buchanan, 2004; Horsted-Bindslev, 2004). One of its major components, mercury, is of a particular concern due to its potential adverse effects on humans and the environment (Arenholt Bindslev & Larsen, 1996; Counter & Buchanan, 2004; Horsted-Bindslev, 2004; Hylander & Goodsite, 2006). The estimated annual mercury consumption for dental applications is 3-4 % worldwide (approximately 300 metric tons of mercury) (WHO, 1976; Mukherjee *et al.*, 2004; Vandeven & McGinnis, 2005). Even though the use of amalgam as a restorative material has declined recently, the removal of this material from patient's teeth and the subsequent discharge of it into the environment will continue as long as existing restorations remain in place and amalgam is continued to be used as a dental filling material. According to recent investigations, dental clinics appear to be responsible about appreciable amount (10-70 %) of the daily mercury burden that has been released into the environment via sewage treatment plants (Drummond *et al*., 2003; Adegbembo & Watson, 2004).

Mercury is known to bioaccumulate in fish and other living organisms and therefore can pose an environmental mercury burden on the entire food chain (Zhou & Wong, 2000; Berzas Nevado *et al.*, 2003; Kennedy, 2003; Hylander & Goodsite, 2006). Among the groups that are directly exposed to mercury are the dentists and their patients, where significant increases in their plasma mercury concentration have been reported compared to those of control groups (Tezel *et al*., 2001; Harakeha *et al*., 2002; Jones *et al*., 2007; Zolfaghari *et al*., 2007). On the other hand, the public and the environment are indirectly exposed to this element via mercury

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emissions from incinerators and mercury in wastewater from dental clinics and households (Berzas Nevado *et al.*, 2003; Mirlean *et al.*, 2003; Counter & Buchanan, 2004; Vandeven & McGinnis, 2005). Several studies have shown that exposure to mercury may lead to several health complications such as impairment of the developing central nervous system, pulmonary and nephritic damage, and impairment of osmoregulatory functions (Counter & Buchanan, 2004; Mutter *et al.*, 2004; Hylander & Goodsite, 2006). These complications are usually attributed to the strong affinity of mercury for sulphur and sulfhydryl groups inside the bodies of living organisms (Kennedy, 2003; Marchi *et al.*, 2004).

Increasing knowledge about the risk of toxic effects caused by anthropogenic mercury accumulation in ecosystems has resulted in a growing pressure for reduction of the discharge of mercury waste into the environment. Consequently, the mercury waste problems of dental clinics have been given increased attention, and therefore restrictions on handling and discharging of contaminated waste have been established in several countries. Current literature suggest that mercury emissions from dental clinics can be reduced by an improved design of the waste discharge system, use of high pressure water cleaning, and frequent replacement of amalgam separators and filters (Vandeven & McGinnis, 2005; Batchu *et al.*, 2006; Hylander *et al.*, 2006; Hylander *et al.*, 2006). For example, Arenholt-Bindslev and Larsen (1996) reported that the use of Hg separators has reduced the amount of Hg in the wastewater of some dental clinics from 270 mg Hg per dentist per day (range 65 to 842) to only 35 mg Hg per dentist per day (range 12 to 99). As a result, many countries such as Switzerland, Germany, Sweden, and Denmark have introduced a mandatory installation of amalgam separators in dental clinics (Arenholt-Bindslev & Larsen, 1996; Arenholt-Bindslev, 1998; Hylander *et al.*, 2006). However, use of such separators in UAE dental clinics is still uncommon. Additionally, no data have been reported in the literature about the mercury burden in wastewater in UAE or other GCC countries despite the fact that almost one third of the recycled wastewater is reused for irrigation in this region.

The objective of this work was to quantitatively assess the mercury burden in the wastewater of some dental clinics in UAE. The results of this project will contribute to the efforts of the Ministry of Health in reducing the mercury concentration in the wastewater by introducing new measures on handling and discharging of dental clinics' mercury-containing waste.

Materials and Method
Equipment
An atomic absorption spectrometer (Spectra AA 220 FS, Varian) equipped with a vapour generation accessory (VGA-77, Varian) and a T-shaped quartz absorption cell was used for mercury determination. The instrumental parameters used are listed in Table 1.

Reagents and Solutions
All chemicals were of analytical-reagent grade unless stated otherwise. All water used was obtained from a Milli-Q reagent system (resistivity 18.2 MΩ cm, Millipore, Bedford, MA, USA). All plastic and glassware was soaked in 4M nitric acid for a minimum of 12h, washed with distilled water and finally rinsed with Milli-Q water before use.

Nitric acid (68.0-70.0%) and sodium chloride (99.5%) were purchased from Panreac Quimica (Barcelona-Spain), sulfuric acid (GPR), hydrochloric acid (37.0%), hydroxyl amine hydrochloride (99.0%), and stannous chloride (98.0-103.0%) from BDH (VWR Int'l Ltd, England), potassium permanganate (99.5%) from Surechem products Ltd. (England), potassium persulfate (98.0%) from Fluka (USA), mercury (for calibration, 1001 ± 5mg/L solution in 2 mol/L HNO_3) from BDH (England), and CRM from High Purity Standards (20.0µg/L ±0.5% in 2% HNO_3, Charleston-USA).

Stannous chloride (25 % w/v) reducing solution was prepared by adding 25.00 g of stannous chloride to a 20 mL of conc. hydrochloric acid. The mix was heated to dissolve the stannous chloride then allowed to cool before diluting the solution to 100 ml with water and mixing.

Table 1. Instrumental parameters (CV-AAS)

Wavelength:	253.7 nm
Slit Width:	0.5R nm
Lamp Current:	4.0 mA
Measurement Time:	5.0 s
Background Correction:	BC On
Vapour Type:	Cold Vapour
Pre-Read Delay:	70 s
Sampling Mode:	Auto Mix
Calibration Mode:	Concentration
Measurement Mode:	Peak Area
Replicates Standard:	3
Replicates Sample:	3
Smoothing:	5 point
Calibration Algorithm:	Linear
Flow rate of reducing agent:	1.0 mL/min
Flow rate of samples:	7.0 mL/min

Samples Collection

Samples were collected in acid-washed plastic containers from three clinics. Samples No. 1-19 (1-10 were collected from clinic 1, samples 11-18 from clinic 3, and sample 19 from clinic 2) are the waste collected after amalgam restoration treatment. For samples 20-31, which have been collected from clinic 2, amalgam restoration plus other types of treatment has been undertaken (*e.g.* composite filling, root canal treatment, cavity preparation plus temporary filling, glasso ionomer filling, pulpotomy, scaling plus polishing, fissure sealant, and bridge cementation). For the rest of the samples (32-36, collected from clinic 2), treatments other than amalgam restoration have been carried out. Samples from clinic 1 were all collected directly from the outlets of the dental chairs into the collection containers at the end of each treatment. Samples from clinics 2 and 3 have all been collected from a single chair, but each of them belongs to one patient. Summary of samples details is shown in Table 2.

Samples Treatment and Analysis

Collected samples were preserved in HNO_3 (concentrated acid was added to each sample container to achieve a final acid concentration of 1%) and kept refrigerated at 4◦C until the time of analysis.

Samples were digested according to USEPA Method 245.1, but with slight modifications. In summary: the samples' containers were vigorously shaken before taking subsamples for analysis. 50.0 mL of filtered sample (gravity filtration using Schleicher & Schuell 595 filter papers) was placed in a 150 mL clean plastic bottle followed by the addition of 5.0 mL conc. H_2SO_4, 2.5 mL conc. HNO_3, 5.0 mL $K_2S_2O_8$ (5 %), and 5.0 mL $KMnO_4$ (5 %). Then, the samples were kept inside an oven for 2.0 hours at 95 ◦C. After cooling to room temperature, hydroxyl amine hydrochloride (12% in 12% NaCl) was added drop wise to each bottle until the colour of $KMnO_4$ disappeared. More hydroxyl amine hydrochloride was added if the $KMnO_4$ colour reappeared before the elapse of 15 min after the 1st addition. Approximately 1 mL of hydroxyl amine hydrochloride was found to be enough to completely reduce any excess

KMNO$_4$. Finally, water was added to each bottle to obtain a volume of 100.0 mL. All calibration solutions, blanks, and CRM have been treated in the same way. Total mercury was determined using Cold Vapour-Atomic Absorption Spectrometry (CV-AAS) (see Table 1 for details of necessary parameters).

Table 2. Mercury concentration (µg/L and µg) in dental clinics wastewater samples collected from various clinics in UAE along with the type of treatment undertaken.

Sample No.	Type of treatment	Sample volume, ml	Hg, µg/L	Hg, µg/treatment
1	*a*	1500	94.7	142
2	*a*	380	94.2	36
3	*a*	580	17.8	10
4	*a*	240	15.6	4
5	*a*	1030	22.7	23
6	*a*	430	18.0	8
7	*a*	1330	12.0	16
8	*a*	50	124.0	6
9	*a*	350	23.1	8
10	*a*	2550	6.5	17
11	*a*	1100	53.9	59
12	*a*	940	51.2	48
13	*a*	1050	22.4	24
14	*a*	1480	75.2	111
15	*a*	1100	25.5	28
16	*a*	1100	30.4	33
17	*a*	2000	27.1	54
18	*a*	2010	40.0	80
19	*a*	2530	14.4	37
20	*a, b, c, d*	5100	3.1	16
21	*a, b, c, d, e, f, g*	4100	12.8	52
22	*a, b, c, d, h*	5900	1.3	8
23	*a, b, c, d, i*	6000	3.7	22
24	*a, b, c, d, h*	4100	3.9	16
25	*a, b, k, f*	7800	9.9	77
26	*a, b, d, f*	3700	0.8	3
27	*a, b, c, e, k*	4100	10.9	45
28	*a, b, c, h*	6700	6.4	43
29	*a, b, c, g, j, l*	7020	<MDL	<MDL
30	*a, b, c, d*	3300	<MDL	<MDL
31	*a, b, c, m*	3800	2.8	10
32	*b, g*	4050	8.0	33
33	*b, c, d, g, j*	6900	4.0	28
34	*b, c, d, g*	7200	3.8	27
35	*b, d, h, f*	4700	<MDL	<MDL
36	*b, c, d, m*	3900	0.6	2

* Samples no 17 and 24 are spiked with 20.0 µg/L Hg. CVC-1 (20.0 µg/L) and CVC-2 (50.0) are calibration verification checks prepared from solutions other than those used for calibration.
a: Amalgam restoration. b: Composite filling. c: Root canal treatment (irrigation with NaHCl solution + temporary restoration). d: Cavity preparation + temporary filling. e: Tooth extraction. f: Glasso ionomer filling. g: Pulpotomy. h: Scaling & polishing. i: Post & amalgam restoration. j: Reinforced zinc oxide eugenol. k: Fissure sealant. l: Bridge cementation. m: Replacement of amalgam with composite.

Results and Discussions

To ensure that the obtained results are of high quality, several quality control measures have been undertaken. The accuracy of the calibration curve was checked by "calibration verification check" (CVC) concept, where a 20.0 and 50.0 µg/L Hg solutions were prepared from the stock standard solution but using different working solutions from those used to construct the calibration curves. Results of these CVCs, as shown in Table 2, are 20.0-21.0 µg/L (n=3) and 52.3 µg/L, respectively. The method detection limit, which was calculated from "3 times the standard deviation" of 9 blank replicates, is 0.2 µg/L. CRM was analysed after every 10 runs and the accuracy was better than 96.4%. The accuracy of the method was also checked by spiking two of the wastewater samples each with 20.0 µg/L Hg and the spike recovery was between 106 and 112% (see Table 2).

The mercury concentration in the wastewater of the three involved dental clinics is listed in Table 2. This table also includes the types of treatment provided to each patient. The dental treatment undertaken is classified into 3 deferent categories: 1st "only amalgam restoration"; 2nd "amalgam restoration plus other types of treatment"; and 3rd "no amalgam restoration." The average, standard deviation, and range for Hg concentration in the samples versus the type of treatment are shown in Table 3. It is clear from Tables 2 and 3 that the wastewater samples of the 1st and 2nd categories contain, relatively, higher Hg than those of the 3rd one. This can be simply explained by the release of Hg from the amalgam itself during the dental treatment or afterwards from amalgam particles that have been deposited inside the drainage tubes. On the other hand, the samples of the 3rd category are not supposed to contain any Hg because no amalgam treatment has been carried out. However, the presence of Hg in these samples may be due to some amalgam particles from previous treatments that have sedimented inside the tubes and continued to release Hg. Similar findings and explanations have been reported by other investigators (Arenholt-Bindslev & Larsen, 1996).

Table 3. The average, standard deviation (*std. dev.*) and range of Hg mass in samples vs. type of dental treatment

Samples No.	Type of treatment	Hg concentration, µg		
		Average	*Std. dev.*	*Range*
1-19	amalgam restoration	39	37	4 – 142
20-31	amalgam restoration + others	24	24	<MDL – 77
32-36	no amalgam restoration	18	16	<MDL – 33

To explain the variations in samples' Hg concentration, there are several variables that are responsible for these differences. The main variable is the size of the treated cavity, which determines the size of the amalgam fillings to be used and hence the amount of Hg. Other variables may include the design of the amalgam capsule, (Stone *et al.*, 2002; Okabe *et al.*, 2003) the number of fillings per patient, and other operations that may influence the properties of the dental wastewater stream such as polishing (Drummond *et al.*, 2003).

Table 4 shows the amount of Hg produced by each clinic. The total Hg burden in the wastewater of the 1st, 2nd and 3rd clinics over the whole study period is 270, 418, and 438 µg, respectively (no of days: 5, 17, and 3, no of samples: 10, 18, and 8). It is obvious that the variation in Hg burden is dependent on the total number of treatments undertaken per day or over the whole period of study as well as the type and number of treatments performed. The burden of Hg per clinic per day (range 25-146 µg) appears to be insignificant when compared to the burden reported for other clinics worldwide (Desmet *et al.*, 1984; Munaf *et al.*, 1990; Arenholt-Bindslev & Larsen, 1996; Brown & Sherriff, 2002; Sweeney *et al.*, 2002; Drummond

et al., 2003; Stone *et al.*, 2003; Adegbembo & Watson, 2004; Al-Khatib & Darwish, 2004; Barregard, 2005; Vandeven & McGinnis, 2005; Hylander *et al.*, 2006). For example, Arenholt-Bindslev and Larsen (1996) reported a mean value of 270 mg Hg per dentist per day (range 65 to 842) in the wastewater of 20 Danish dental clinics without amalgam separator. The reason for the lower Hg content released per clinic in the present study is the small number of treatments carried out in the participating clinics per day, which is mainly due to the fact that these clinics are not yet fully operational.

Table 4. Total mass of mercury in teeth

Clinic	Hg, total mass (µg)	Total number of samples	Total number of days
1	270	10	5
2	418	18	17
3	438	8	3

A more detailed study involving larger number of fully operational clinics has to be performed before an accurate assessment of the extent of Hg release from dental clinics in UAE can be made.

In conclusion, the concentrations of Hg in the wastewater of investigated dental clinics, although small, re-emphasise the fact that dental clinics are considered as a source of Hg pollution in the environment. In order to control the emission of Hg from dental clinics, it is recommended that local authorities introduce new regulations concerning the release of Hg into the environment including the installation of amalgam separators in all dental clinics.

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