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Dental clinics: A point pollution source, not only of mercury but also of other amalgam constituents

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ABSTRACT

Current literature suggests that amalgam waste from dental clinics is a point-source of mercury pollution in the environment. However, apart from mercury, other amalgam constituents (e.g. Ag, Sn, Cu, and Zn) in dental clinics' wastewater have not been reported in the literature before. The objective of this study was to evaluate the concentrations of mercury and other metals in the wastewater of some dental clinics and the influent of a wastewater treatment plant in Al-Madinah Al-Munawarah (KSA). Samples were collected over a 2-month period from three dental clinics and analyzed for metals using ICP-MS. The mean concentrations of Hg, Ag, Sn, Cu, and Zn in the samples were 5.3 ± 11.1, 0.49 ± 0.96, 3.0 ± 10.7, 10.0 ± 14.5, and 76.7 ± 106 mg L^{-1}, respectively. Additionally, high concentrations of other metals such as Mg (14.4 ± 15.2 mg L^{-1}), Mn (3.0 ± 4.6 mg L^{-1}), Fe (3.0 ± 4.5 mg L^{-1}), Sr (1.6 ± 2.4 mg L^{-1}), and Ba (6.9 ± 10.3 mg L^{-1}) were also found. These values are much higher than the local permissible limits. Most of the metals of interest were also detected in the influent of the wastewater treatment plant. This renders dental clinics wastewater a hazardous waste which should be properly treated before it is discharged into the environment.

1. Introduction

Mercury amalgam has been used in dentistry for about 200 years. It is an alloy that is made from several metals including mercury, silver, tin, copper, and zinc (Desmet et al., 1984; Arenholt-Bindslev and Larsen, 1996). Dental amalgam is of concern because almost half of its mass is mercury; a metal that is very mobile in the environment, bioaccumulates in food chain, and has well documented health risks (neuro- and nephro-toxic) (Zhou and Wong, 2000; Berzas Nevado et al., 2003; Horsted-Bindslev, 2004; Hylander and Goodsite, 2006; Ismail, 2006; Needleman, 2006). Out of the 10 000 tons of mercury produced in 1973 worldwide and used by industry, approximately 300 tons were used in dentistry (WHO, 1978). Accordingly, dental clinics are considered as a major source of mercury discharges to the environment (Kummerer et al., 1997; Stone et al., 2003; Vandeven and McGinnis, 2005; Al Kawas et al., 2008; US-EPA, 2008).

Due to its hazardous nature, mercury was globally regulated. The US-EPA's maximum contaminant level of inorganic mercury in drinking water is only 2 μg L^{-1} (US-EPA, 2009). Whereas the maximum permissible value for mercury in the source water discharged into the public sewer is 50 μg L^{-1} and for treated wastewater intended for use in agriculture is only 1 μg L^{-1} according to the regulations of the Saudi Ministry of Municipal and Rural Affairs. As a consequence, several measures were adopted by dental clinics worldwide to reduce mercury discharge to the environment (e.g. use of amalgam separators and filters, improvement in the design of the waste discharge system, and use of high pressure water cleaning) (Vandeven and McGinnis, 2005; Batchu et al., 2006; Hylander et al., 2006b). But in Kingdom of Saudi Arabia (KSA), adoption of most of these measures, especially amalgam separators, is still unregulated.

Interestingly, all literature that dealt with metal pollution from dental clinics wastewater has concentrated only on mercury with no mention to any of the other metals comprising dental amalgam. The presence of such metals in wastewater may render it a hazardous waste. The aims of this study were to quantify the amount of soluble mercury in the wastewater of some dental clinics in Al-Madinah Al-Munawarah (KSA) and to examine if any of the other dental amalgam constituents is found in the clinics' wastewater.

2. Materials and methods

2.1. Chemicals and solutions

All glass- and plastic-ware used were soaked overnight in 10% nitric acid, rinsed with distilled water, and finally with reagent

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water (Milli-Q, 18.2 MΩ cm, Elix10, Millipore, USA) before use. Nitric acid from Riedel-de'Haën (65%, Puriss, Germany), L-cysteine from BDH (>98%, England), mercury standard solution from High-Purity Standards (20 μg mL^{-1}, Charleston, USA), ICP-MS multi-element standards from Agilent (10 μg mL^{-1}, Nos. 2A and 3, USA), certified wastewater from High-Purity Standards (CWW-TM-A and CWW-TM-D, Charleston, USA) and water from National Water Research Institute (TM-26.3, Environment Canada), respectively.

2.2. Equipment

ICP-MS (7500cx, Agilent, Japan) was used for metal content in samples. The operational parameters applied are listed in Table 1. For pH measurements, a pH meter (Hanna Instruments, USA) was used after calibration.

2.3. Samples collection and analysis

Wastewater samples were collected from the following three public dental clinics in Al-Madinah Al-Munawarah: Al-Azhari Health Centre (location 1), Al-Harrah Al-Sharqiya Health Centre (location 2), and King Fahd Hospital (location 3A and 3B from two dental nerve clinics and location 3C from a denture clinic). Samples were also collected from the water entering the dental chairs. The source of this water is onsite tanks fed by the mains water and is used as a mouth wash and a coolant during dental operations. This water is used without any treatment. Additionally, influent samples were collected from the wastewater treatment plant in Al-Madinah Al-Munawarah (location 4). Dental clinics samples were collected for 60 d (May to June, 2009), whereas influent samples of the wastewater treatment plant were collected between March and June, 2010. All wastewater discharged from the dental chairs was continuously collected in 5 L polyethylene plastic bottles, which were checked daily and replaced before being full. To minimize analytes loss during collection and storage, nitric acid solution (50% v/v) was added to the samples to maintain a solution pH below 2. Samples were then refrigerated at 4 °C and analysed within 28 d of collection. It was noticed that the wastewater of dental clinics in the study area is discharged directly into the main public sewer without treatment. But for some clinics, the wastewater is discharged improperly in their backyards. Relevant dental operations carried out in the clinics are summarized in Table 2.

Samples were analysed twice; once for Hg and once for other metals using different experimental parameters (e.g. washing time and dilution factor). Preliminary analyses were conducted to evaluate the extent of *mercury memory* effect and to establish proper dilution factors for the samples as follows: samples' bottles were took out from the refrigerator, shaken thoroughly, and left inside the preparation room to achieve temperature equilibration and to allow suspended matter to settle down. A known volume from the supernatant solution was then measured and diluted (100 times) with L-cysteine (0.5% in 2% HNO_3). Each subsample was introduced to the ICP-MS for 10 s and the counts were recorded. Washing solutions were run between samples for sufficient time to reduce the counts back to blank levels. Finally, a standard metals solution (10 μg L^{-1}) was introduced and processed in the same way. The approximate metals concentration in each sample was calculated and the obtained values were used to calculate the dilution factors needed for subsequent proper and accurate analysis, for which fresh subsamples were prepared with appropriate dilution factors.

2.4. Mercury memory effect

Memory effect associated with mercury analysis by ICP is very pronounced as documented in the literature (Harrington et al., 2004; Li et al., 2006; Zhu and Alexandratos, 2007). This effect is due to the nature of mercury where it accumulates inside the ICP sample introduction system and slowly released from there over time. This effect necessitates long washing times and produces non-linear calibration curves thus reduces the accuracy and reliability of the results. To reduce this effect, several washing reagents were investigated in the literature. Diluted solutions of nitric acid, Triton X-100/EDTA/ammonia, and 2-mercaptoethanol were investigated in the analysis of mercury by FI-ICP-MS (Harrington et al., 2004). The latest solution gave more reliable results and was therefore employed by the authors. In a similar study

Table 1
ICP-MS operating parameters.

Instrument	
Sampler	7500cx
Skimmer	Ni (standard)
Nebulizer	Ni (standard)
Plasma torch	Micromist (standard)
Integration time (s × points)	
Mg	0.05 × 3
Cr, Ni, As, Cd, Hg	1.00 × 3
Mn, Fe, Co, Cu, Zn, Rb, Sr, Ag, Sn, Ba, Pb	0.10 × 3
Se	5.00 × 3
Tune parameters	
RF power (W)	1500
Sample depth (mm)	7.6 (8.3 for Hg)
Carrier gas (L min^{-1})	0.95
Makeup gas (L min^{-1})	0.21
Extract 1 (V)	4.4
Extract 2 (V)	−89
Energy discrimination (V)	2
Reaction gas (He, mL min^{-1}): Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn, and As. off for Hg, Rb, Sr, Ag, Cd, Sn, Ba, Hg, and Pb	4
% Oxide (156/140)	1.84
% Doubly charged (70/140)	3.88
% RSD for *m*/*z*: 7, 59, 89, 205	<2
Spray chamber temperature (°C)	2
Nebulizer pump (rps)	0.1