



# Effect of iodine on mercury concentrations in dental-unit wastewater

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## KEYWORDS

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**Summary Objective.** This study was undertaken to determine whether iodine used to control bacteria in dental unit waterlines could increase mercury concentrations in dental wastewater.

**Methods.** The study was conducted in four parts. *Part 1.* Solutions containing iodine in concentrations ranging from zero (control) to 20 mg/L were mixed with ground and sieved dental amalgam and then allowed to equilibrate by settling. Cold vapor atomic absorption spectrometry was used to determine mercury levels in the settled supernatants at 24 h and at 7 days. *Part 2.* Deionized water was pumped through an iodine-releasing water-treatment cartridge, collected, and mixed with ground and sieved dental amalgam. Mercury levels in settled supernatants were measured at 24 h and at 7 days. *Part 3.* Iodine in water from two commercial iodine-releasing cartridges was measured using Inductively Couple Plasma Mass Spectrometry. *Part 4.* Baseline mercury levels in settled supernatants from wastewater collected from two dental chairs were compared to samples taken from chairs equipped with iodine-releasing cartridges.

**Results.** *Part 1.* A linear correlation between iodine and mercury concentration ( $r^2=0.9167$  and  $0.9459$ , respectively, both  $P<0.001$ ) was seen at both 24 h and 7 days. *Part 2.* Mean mercury levels in 24 h samples were 3.0 times higher than the controls (0.2864 mg/L compared with 0.0939 mg/L for the 24 h controls). Mean mercury levels in the 7-day samples were 5.9 times higher than the 7-day controls (0.2048 mg/L compared with 0.0348 mg/L for the 7-day controls). *Part 3.* The effluent from two iodine-releasing cartridges showed iodine concentrations averaging 3.2 mg/L ( $n=10$ ,  $SD=0.8$ ,  $range=2.5-4.6$ ). *Part 4.* Data from the clinical study showed a statistically significant 2.5-fold increase in mercury levels with iodine-containing samples compared to baseline (0.0853 mg/L,  $n=18$ ,  $SD=0.0441$  and 0.0345 mg/L,  $n=18$ ,  $SD=0.0145$ , respectively;  $P<0.001$ ).

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*Significance:* Data suggest that iodine can increase concentrations of dissolved mercury in dental unit wastewater.

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## Introduction

Biofilm in dental unit waterlines and the contamination of dental unit wastewater with mercury (Hg) are two recognized concerns in dentistry [1-6]. At first glance these issues appear disparate—the first centers on the ‘clean water’ side of the chair, the second on the wastewater—but in at least one large dental treatment facility, a possible connection was identified. Because of its history of exceeding local mercury discharge limits, the facility was required to install amalgam separators to limit the release of mercury into the publicly owned sewer system [3]. Subsequent to the installation of amalgam separators, the facility placed iodine-releasing systems on all dental chairs to control bacteria and biofilm levels in dental unit waterlines. These systems contain a proprietary resin that releases iodine at a claimed concentration of 2-6 mg/L. Since installing the iodine-releasing resin cartridges, dissolved mercury levels in wastewater discharged from the facility have increased almost 21-fold.

Iodine is one of five non-metallic elements called halogens (from the Greek *hals*, meaning ‘salt’, and *gennan*, ‘to form or generate’). Halogens readily share electrons in covalent bonds with other atoms to complete an octet of electrons in their valence shell. They are strongly electronegative [7,8]. Mercuric ions form exceptionally strong complexes with halide ions ( $F^{-1}$ ,  $Cl^{-1}$ ,  $Br^{-1}$ ,  $I^{-1}$ ), and this is particularly so with iodide (Table 1). The chemical stability of mercuric halogen complexes are:  $HgI_n > HgBr_n > HgCl_n > HgF_n$  [9], with the mercuric tetraiodide complex being the most stable. Depending on the availability of the halide, mercury can bind with more than one of the halide ions.

The Overall Formation Constant,  $K$ , for chemical complexes relates to the strength of the covalent bond between the chemical species; the Standard Oxidation-Reduction Potential,  $E^\circ$ , provides a measure of the ability of a chemical compound to oxidize, or take up electrons from another compound. With a surplus of iodide (resulting from the reaction of iodine with compounds in the dental unit wastewater) and in the presence of  $Hg^{+2}$ , mercuric iodide complexes are formed with a neutral ( $HgI_2^0$ ) or a negative ( $HgI_3^{-1}$ ,  $HgI_4^{-2}$ ) charge. Elemental mercury ( $Hg^0$ ) is not oxidized to the mercuric ion ( $Hg^{+2}$ ) in the presence of iodine alone because  $Hg^0$  has a more positive Standard Potential,  $E^\circ$ , than iodine (+0.85 and +0.53 V, respectively, versus the Normal Hydrogen Electrode). Some relevant half-reactions [10] are presented in Table 2. Elemental mercury can, however, be oxidized by iodine in the presence of iodide, chloride or other halogens because the Standard Potential of the mercury couple is shifted more to the negative than the Standard Potential for the  $I_2/I^-$  couple with increasing chelator concentration (Table 2). In the process, elemental mercury is oxidized to  $Hg^{+2}$  and elemental iodine is reduced to iodide ( $I^-$ ), freeing it up to complex with other mercury ions. Iodine in the presence of other mercury complexing agents makes it an efficient instrument for solubilizing mercury [10-13] and provides the basis of a patent for removing mercury from contaminated soil [11]. The ability of iodine to both complex and oxidize mercury can also suppress the production of mercury vapor, hence, the inclusion of iodine in some mercury spill kits.

We hypothesized that iodine used to manage biofilm in waterlines can form stable and soluble complexes with mercury, resulting in elevated

**Table 1** Logarithm of Overall Formation constants,  $K$ , for aqueous species of various mercuric halogen complexes.

Number of available halide ions	Chloride	Log K chloride	Bromide	Log K bromide	Iodide	Log K iodide
1	$HgCl^{+1}$	6.74	$HgBr^{+1}$	8.94	$HgI^{+1}$	12.87
2	$HgCl_2^0$	13.22	$HgBr_2^0$	16.88	$HgI_2^0$	23.82
3	$HgCl_3^{-1}$	14.17	$HgBr_3^{-1}$	19.15	$HgI_3^{-1}$	27.49
4	$HgCl_4^{-2}$	15.22	$HgBr_4^{-2}$	20.90	$HgI_4^{-2}$	29.86

Large values of  $K$  indicate a favorable formation of the products of the reaction. (Values used in the table were obtained from Sillen LG and Martell AE. Stability constants of metal-ion complexes. Chemical Society (London) Special Publications No. 17, 1964 and No. 25, 1971).

**Table 2** Several relevant half reactions with their Standard Potentials,  $E^\circ$ . (Obtained from Bard AJ, Parsons R, Jordan J. Standard potentials in aqueous solutions. New York: Marcel Dekker; 1985).

Half Reactions	$E^\circ$ (versus Normal Hydrogen Electrode)
$\text{Hg}^{+2} + 2e^- = \text{Hg}^0$	+0.85
$\text{Hg}_2^{+2} + 2e^- = 2\text{Hg}$	+0.79
$2\text{I}^- + 2e^- = \text{I}_2$	+0.53
$\text{Hg}_2\text{I}_2 (\text{aq}) + 2e^- = 2\text{Hg} + 2\text{I}^-$	-0.04
$\text{Hg}_2\text{Cl}_2 (\text{aq}) + 2e^- = 2\text{Hg} + 2\text{Cl}^-$ (0.1 M KCL)	+0.33
$\text{Hg}_2\text{Cl}_2 (\text{aq}) + 2e^- = 2\text{Hg} + 2\text{Cl}^-$ (1.0 M KCL)	+0.28

dissolved mercury levels in wastewater. This study was undertaken in an attempt to test this hypothesis and help quantify the relationship between iodine and mercury in the dental unit wastewater stream.

## Materials and methods

*Part 1.* Five-gram samples of ground and sieved dental amalgam (Tytin™, Kerr Manufacturing, Romulus, MI, USA) with a particle size distribution of 105-710  $\mu\text{m}$  were exposed to iodine solutions at concentrations varying from 0 (control) to 20 mg/L. Samples were agitated by rotating them end-over-end at 30 rotations per minute for 10 min. Duplicate 125 mL aliquots of the settled supernatant were removed for analysis at both 24 h and 7 days. Mercury levels were determined utilizing US Environmental Protection Agency (USEPA) method 245.1 for cold vapor atomic absorption (CVAA) spectrometry.

*Part 2.* Deionized water was pumped through a commercial iodine-releasing waterline treatment cartridge (DentaPure DP-365, DentaPure/MRLB International, Fergus Falls, MN, USA) at a rate of 50 mL/min and collected in four 2 L, high-density polyethylene containers. Four deionized water samples containing no iodine were collected in identical containers to act as experimental controls. Five grams of ground and sieved amalgam particulate with a particle size distribution of 105-710  $\mu\text{m}$  were added to each container. The containers were agitated using end-over-end rotation at 30 rotations per minute for 10 min and then allowed to settle. Duplicate 125 mL aliquots were removed at 24 h and 7 days and analyzed for total mercury utilizing USEPA method 245.1 (CVAA spectrometry).

*Part 3.* To quantify the amount of iodine released by the commercial iodine-releasing cartridges used

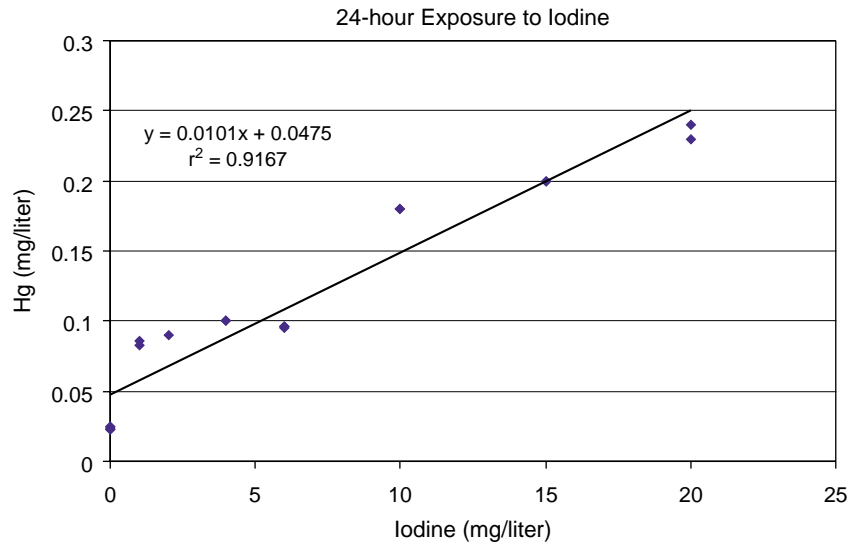
in this study, deionized water was pumped through two new cartridges at a rate of 50 mL/min and collected in high-density polyethylene containers. Samples were stored unpreserved and in the dark at 4 °C until analyzed by Inductively Couple Plasma Mass Spectrometry (ICP-MS). Analyses by ICP-MS were conducted after the manner of Fecher et al. [14] in which tetraethylammonium hydroxide was used in the carrier solution to minimize memory effects of iodine on the instrument's sample introduction system of the instrument. Total iodine ( $\text{I}_2$  and  $\text{I}^-$ ) as iodide was measured by ICP-MS at mass 127, the element's only naturally occurring isotope. The instrument technique is not able to distinguish between iodine ( $\text{I}_2$ ) and iodide ( $\text{I}^-$ ), except that the intensity of an iodine signal measured at mass 127 would likely be twice that of iodide. Iodine has two atoms that are available for ionization and measurement; iodide has one.

*Part 4.* Baseline mercury levels in the settled supernatant from two dental chairs were determined utilizing USEPA method 245.1. Commercial iodine-releasing cartridges then were installed on the chairs, and mercury levels were determined utilizing USEPA method 245.1. Eighteen baseline and 18 experimental samples were analyzed for total mercury.

## Results

Data from Part 1 (presented in Figs. 1 and 2) show a positive linear correlation between iodine levels and mercury concentrations at 24 h and at 7 days ( $r^2=0.9167$  and  $0.9459$ , respectively, both  $P<0.001$ ). In both 24 h and 7 day samples, increasing concentrations of iodine produced an increase in the concentration of dissolved mercury when compared to controls. At 24 h, a 9.9-fold increase in mercury levels was noted in the 20 mg/L iodine solution compared to the control (0.2350 and 0.0237 mg/L, respectively). At Day 7, the increase was 31.6 fold (0.5375 mg/L for experimental samples, compared with 0.0170 for controls).

In Part 2 of the study (Table 3), in which deionized water was pumped through an iodine-releasing cartridge, collected, and mixed with ground and sieved amalgam, mean mercury levels in the 24 h samples were found to be three times higher than the control samples (0.2864 mg/L compared to 0.0939 mg/L, respectively). Mean mercury levels in the 7-day samples were 5.9 times higher than in the 7-day controls



**Figure 1** 24 h Exposure of amalgam particulate to iodine.

(0.2048 mg/L for experimental samples compared to 0.0348 mg/L for the controls).

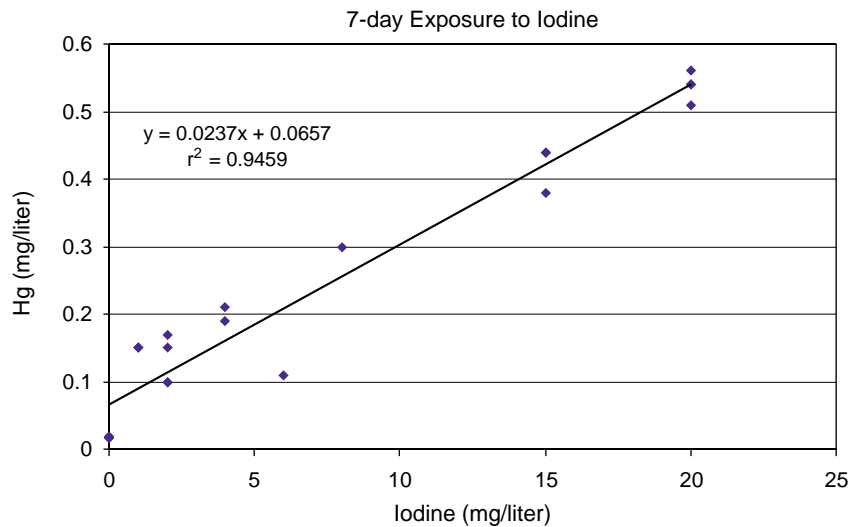
In Part 3 of the study, the concentration of total iodine in the water samples collected from the iodine-releasing cartridges were determined by ICP-MS (Table 4). Iodine levels averaged 3.2 mg/L ( $n=10$ ,  $SD=0.8$ , range=2.5-4.6 mg/L), which is consistent with the manufacturer's stated iodine output. The iodine level in a deionized water control was found to be less than the method detection limit of 0.02 mg/L.

Results from the clinical evaluation portion of the study (Part 4) show an increase in mercury levels in wastewater from the dental chairs with the iodine-releasing system in place (Table 5). The data show a statistically significant 2.5-fold increase in dissolved mercury with the iodine-

releasing systems compared to baseline samples (0.0853 mg/L,  $n=18$ ,  $SD=0.0441$  and 0.0345 mg/L,  $n=18$ ,  $SD=0.0145$ , respectively;  $P<0.001$ ).

## Discussion

This study examined the effect of iodine on mercury concentrations in dental unit wastewater. Our attention was first drawn to this issue with the observation of an increase in dissolved mercury levels seen in dental unit wastewater from a dental facility that installed iodine-releasing cartridges on all of its dental chairs. Prior to cartridge installation, dissolved mercury levels (obtained from wastewater samples processed through 0.45  $\mu\text{m}$



**Figure 2** Seven-day exposure of amalgam particulate to iodine.

**Table 3** Amalgam particulate exposed to effluent from a commercial iodine-releasing cartridge.

Sample type	Mean Hg (mg/L)	Standard deviation	Sample size
24-hour control	0.0939	0.0350	4
24-hour iodine	0.2864	0.0430	4
7-day control	0.0348	0.0090	4
7-day iodine	0.2048	0.0285	4

filters prior to analysis) averaged 0.37 mg/L. Some time after the installation of the iodine-releasing cartridges, mean dissolved mercury levels in dental unit wastewater measured 7.61 mg/L, an almost 21-fold increase.

Iodine-releasing cartridges are marketed as a method to disinfect dental unit waterlines with a vendor-claimed release of iodine at 2-6 mg/L. ICP-MS verified this level from two separate cartridges. Although iodine is a good disinfectant and control agent for biofilm [15], this study demonstrates its ability to mobilize mercury from amalgam particulate in both laboratory and clinically generated wastewater samples. The result is the creation of neutral ( $\text{HgI}_2^0$ ) and anionic mercuric iodide complexes ( $\text{HgI}_3^{-1}$  and  $\text{HgI}_4^{-2}$ ) that are not removed by amalgam separators utilizing sorbents and ion exchange resins specific to the mercuric ion ( $\text{Hg}^{+2}$ ). While technical limitations prevent us from directly measuring the concentrations of mercury iodide complexes, equilibrium studies with modeling software predict the formation of these stable and soluble iodide complexes.

Although there are benefits in utilizing iodine-releasing systems to control biofilms (primarily by obviating the need for technician intervention in the disinfection process), the mobilization of mercury from dental amalgam makes the deployment of these systems problematic. It should be noted, however, that in the setting used for the clinical phase of this study, amalgam restorations were both placed and removed; the study did not differentiate between iodine interactions with the mercury in unset, freshly triturated amalgam (i.e. amalgam

**Table 4** Iodine levels from commercial iodine-releasing cartridges.

Sample type	Mean iodine (mg/L)	Standard deviation	Sample size
Deionized water control	Non-detect (<0.02)	—	1
Iodine samples	3.2 (range =2.5-4.6)	0.8	10

**Table 5** Mercury levels before and after installation of commercial iodine-releasing cartridges.

Sample type	Mean Hg (mg/L)	Standard deviation	Sample size
Without iodine-releasing cartridge	0.0345	0.0145	18
With iodine-releasing cartridge	0.0853	0.0441	18

being placed as a new restoration) and that bound in existing amalgam fillings (e.g. existing amalgam fillings removed at chairside). Further research is necessary to determine if iodine-containing biofilm-control products affect the wastewater mercury levels in practices that do not use amalgam as a restorative and only remove amalgam restorations.

Another factor not addressed in this study is the effect of the chloramines used by some municipal water treatment facilities to keep the public water supply safe from microbial contamination. More stable than free chlorine, chloramines (chlorinated amides) provide longer lasting, residual activity and result in lower concentrations of hazardous disinfectant byproducts such as trihalomethanes and haloacetic acids [16]. However, because chloramines remain in the water supply much longer than the chlorine traditionally used to disinfect public water supplies, there may be greater potential for interaction between these halogen-containing compounds and amalgam in dental wastewater. A research protocol is currently being drafted to explore this possibility.

It should be noted that a number of commercially available biofilm-control products do not contain halogens [5,17]. In light of iodine's effect on mercury levels in dental wastewater, these options may be a better (and sometimes less expensive) choice for maintaining the microbiological quality of treatment water in practices that use amalgam as a dental restorative material. Of course, any waterline treatment protocol selected should be effective, reliable, cost-effective, and consistent with the dental unit manufacturer's recommendations [18].

## Conclusion

Iodine, used to help control biofilm and bacteria in dental unit waterlines, can mobilize mercury from amalgam particulate in dental unit wastewater,

resulting in higher levels of mercury in wastewater. Additional studies are indicated to:

- (1) Confirm these results and determine whether iodine mobilization of mercury is a risk in clinical settings where amalgam is only removed from existing restorations (and not used to restore decayed teeth).
- (2) Assess the effects of chloramines in the public water supply on mercury discharge levels in clinical dental settings.
- (3) Examine the effects of other halogen-containing waterline treatment products on dissolved mercury levels in wastewater.
- (4) Identify, develop, and test sorbents to remove halogens and/or dissolved mercury in dental wastewater.
- (5) Identify safe, reliable, and cost-effective biofilm-control products, protocols, and strategies that protect patients and dental team members without adverse environmental impact.

To help ensure that dental practices are not exceeding mercury discharge limits set by local municipally owned wastewater treatment facilities. Practices using amalgam as a dental restorative material may wish to consider alternatives to halogen-containing products to control biofilm and the bacteria in water used for dental procedures.

## Disclaimer

The views expressed herein are those of the authors and do not necessarily reflect the official policy or position of the Departments of the Navy or Defense, nor the US Government. The authors have no financial interests or consulting agreements in any company or product related to dental unit waterline disinfection and/or biofilm removal. The use of commercially available products does not imply endorsement.

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