Letter to the Editor

Re: Stone et al.'s “Effect of iodine on mercury concentrations in dental-unit wastewater”

In their paper entitled “Effects of iodine on mercury concentrations in dental-unit wastewater” in the February 2006 issue of Dental Materials (2006 Feb;22(2):119-24), Stone et al. describe a 21-fold increase in mercury concentrations in dental waste water at a US Naval installation and argue that this increase is related solely to the use of waterline treatment cartridges based on an iodinated resin technology. Based on these findings, the authors state that: “... iodine used to manage biofilm in waterlines can form stable and soluble complexes with mercury, resulting in elevated dissolved mercury levels in waste water.” They further recommend against using iodine-containing devices for dental waterline bacterial control in naval dental clinics. We contend that these conclusions are not supported by the data presented in the article and offer alternative explanations for the reported mercury increase that were not adequately investigated by the authors.

Stone et al. state that the research project was initiated after a navy dental facility reported an almost 21-fold increase in dissolved mercury levels in dental unit wastewater. Stone et al. claim that the only significant change in that time was the installation of iodine releasing water purification cartridges. Alleged dissolved mercury levels in dental waste water rose from 0.37 to 7.61 mg/l following cartridge installation.

The quantitative results of testing from a dental operatory using the D365 Cartridge and a non iodinated control shown in Table 5 of the article however, show a mean difference of only 0.0508 mg/l (0.0345 in control and 0.0853 in treated water) of mercury present in the effluent. This is not sufficient increase to support the reported change of mercury at the Navy facility.

This minute increase in mercury release in the laboratory samples could therefore only cause a small fraction (approximately 0.0067%) of the increase in mercury release observed in the clinical setting that stimulated the author’s research. Furthermore, initial levels of Hg measured in waste water at the Navy clinical site averaged 0.37 mg/l prior to the installation of the iodinated cartridges. This is more than seven times the level of mercury that could be produced by the iodinated resin cartridge based on the laboratory data presented. Based on the data presented, the cartridges cannot produce enough iodine to have caused the increase mercury discharge reported from the dental facility.

The issue of increased mercury levels at Norfolk NAS was first raised in a letter from Cdr. Kuehne to the Navy Dental Command. MRLB International Inc., fully investigated the issue at Norfolk, and issued a report, a draft of which was forwarded to the authors in September of 2005.

While the author’s data showed that the amount of mercury produced with the DentaPure® cartridge could not have accounted for the increase in mercury at Norfolk, it is also physically impossible for the amount of iodine released by the cartridge to account for the increase.

Stone et al. found that the DentaPure® cartridges produced an average of 3.2 mg/l of iodine equivalent to 3.2 parts per million by weight. As water is sprayed into the mouth during treatment, iodine volatilizes out of solution reducing the amount of available iodine by as much as 70% and that passage through the suction tubing reduces available iodine by another 50%. Oral tissues, microbial biofilms and saliva further react with iodine to reduce the amount of iodine in suctioned fluids that is available to react with amalgam scrap containing mercury. Additional reaction with organic materials in the settling tank will also contribute to the reduction of available iodine.

Three tests run by MRLB International, Inc. to determine the volatility of iodine in solution in circumstances similar...
to those in the Naval dental facility showed that aeration of iodinated water reduced the level of iodine in the water by 70%. It also showed that running the iodinated water through tubing reduced the level another 50%. The total reduction of iodine level from the point of use to the container is therefore about 85%. Applying this measure to the averages obtained at Norfolk indicate that 0.98 x 15% = 0.15 ppm of iodine entering the dental wastewater collection tank 1. If that amount is then diluted by the cleaning solution, (50%) one would expect to find 0.07 ppm of iodine in the waste water at the collection point.

Applying a molar analysis to the results yields the following:

Using the actual numbers from the clinic, and the aeration reduction studies result in a more likely amount of iodine entering the tank as being (5.52 x 10) - 7 M. (0.07 ppm/1000/126.9) Therefore, again assuming that all of the iodine combines with mercury, we get:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Moles of compound</th>
<th>Atomic wt.</th>
<th>Total possible Hg (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HgCl₂</td>
<td>4.52 x 10⁻⁵</td>
<td>271.49</td>
<td>0.13</td>
</tr>
<tr>
<td>HgCl₁</td>
<td>9.03 x 10⁻⁵</td>
<td>236.04</td>
<td>0.18</td>
</tr>
<tr>
<td>HgCl₃</td>
<td>3.01 x 10⁻⁵</td>
<td>306.94</td>
<td></td>
</tr>
<tr>
<td>HgCl₄</td>
<td>2.26 x 10⁻⁵</td>
<td>342.39</td>
<td></td>
</tr>
</tbody>
</table>

These calculations suggest that chloramine would have contributed significantly to the increase in mercury levels from 0.37 to 7.67 ppm reported at the Naval dental facility. As confirmation to this theory, a unique opportunity presented itself at Norfolk.

Additional support for the causation by reaction of mercury with chloramine was provided by observations made when the HRSO “shocked” municipal water system with chlorine for three weeks in March of 2005 to improve disinfection. Norfolk NAS coordinated with MRLB International to take scoop tests of the unfiltered dental waste water in tank 1 at Norfolk NAS. Samples were collected during the week of Jan 31, 2005, before the change to chlorine, and then again on March 7 2005, after the chloramine shock had been completed. The result obtained are in Table 3:

<table>
<thead>
<tr>
<th>Average ppm Hg</th>
<th>S.D. (ppm)</th>
<th>Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Using chloramine</td>
<td>11.66</td>
<td>0.96</td>
</tr>
<tr>
<td>After chlorine shock treatment</td>
<td>6.39</td>
<td>0.42</td>
</tr>
</tbody>
</table>

Use of chlorine as a disinfectant over chloramine resulted in almost 45% reduction in combined mercury(11.66-6.39 = 5.27 ppm dissolved and suspended, i.e. unfiltered). T-test for difference = 0.0006. These data support the hypothesis that chloramine was responsible for the mercury increase reported.

1. **What about the alternative?—Chloramine?**

The authors claim that the only change related to the increase mercury levels was the addition of the DentaPure iodinated cartridges. However, in October of 2000, the Hampton Roads Sanitary District (HRSD) began using chloramine as a water disinfectant in place of gaseous chlorine. Chloramine, usually in the form of monochloramine or NH₂Cl is used by many municipalities as a substitute for chlorine. It’s claimed benefits are a reduction in disinfection byproducts, and a decrease in costs. However, it is not nearly as efficient as chlorine, so higher levels are used. It is also more persistent than chlorine, and is not removed by aeration. Chloramine is also more reactive with and has been implicated in increased lead levels in municipal drinking water.¹

Applying the same theoretical molar analysis to chlorine in the form of chloramine to the conditions reported at the Naval dental facility, we find:

First using 3.2 ppm for chlorine gives (9.03 x 10) - 5 M/l Cl (3.2 ppm/1000/35.45). Using a similar table gives the following for chlorine:


2. **What about the claim that iodine/mercury compounds are not removed by amalgam separation systems?**

Stone et al. suggest that neutral (HgI₂) and anionic mercuric iodide complexes (HgI₃⁻ and HgI₄⁻) are not removed by amalgam separators utilizing sorbents and ion exchange resins specific to the mercuric ion (Hg²⁺). For this to happen however, the iodide must be present in the form of iodide rather elemental iodine, and the sorbents and ion exchange resins must not be of a “mixed” nature, that is, containing anionic and cationic resins. Stone et al. admit that their test methods cannot verify if iodine species present in tested solutions are in the form of I₂ or I⁻.

Stone et al. further admit that there is no support for their proposition that the compounds found would not be removed by normal mercury recovery technology. Whether or not the mercury compounds created in their study could be removed by normal sorbents or ion exchange resins was not tested. Additionally, their claim that iodine is involved in the mobilization of mercury requires that the iodine be in the form of iodide. They admit that their testing cannot tell if the
iodine is I₂ or I⁻, so this conclusion can only be based on speculation, and is unsupported by their study. It seems that one simple way to evaluate their second hypothesis would have been to run the supernatant from their fourth condition through a mercury recovery unit containing sorbents or ion exchange resins as they described, but they chose not to do so. Because the authors have not demonstrated the presence of the appropriate complexing agents, there is no basis to conclude that such mercury/iodine complexes exist at significant levels. Their conclusions regarding the production of stable mercury iodine compounds must remain firmly in the realm of speculation, and should have been characterized as such.

3. **Finally, is the amount of mercury mobilized by iodine excessive to the point where iodine should not be used as a waterline biocide, as the authors suggest?**

Given Stone et al.'s admission that the DentaPure cartridge is an effective, efficient dental unit waterline biocide, does it increase the mercury emission to a point where it should not be used? Data from Stone et al.'s study show a definite relationship with the concentration of iodine used and the amount of mercury in the resultant solution. Given the molar analysis contained supra, there is certainly a relationship between the concentration of halogens, and the resultant mercury concentration. The question then, is whether or not given the actual clinical levels of iodine produced, the mercury released should be considered excessive.

For example, if ordinary water causes an increase in mercury release greater than the DentaPure cartridge, there is no reason to restrict the deployment of DentaPure, particularly given it's effectiveness as a waterline biocide. Water is the ubiquitous dental solvent, and is used in nearly every dental operatory.

Studies concerning “normal type of concentrations of mercury” in the presence of cleaners and disinfectants of mercury do exist. This is born out by a study also published by the Navy researchers in JADA. In the JADA article, the authors found that different surface disinfectants caused differing levels of mercury concentration in resultant supernatant. Similarly, the current authors compared the mercury release to deionized water.

<table>
<thead>
<tr>
<th>Sample type</th>
<th>(mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deionized water 24 h¹</td>
<td>0.0939</td>
</tr>
<tr>
<td>Deionized water 7 days¹</td>
<td>0.0348</td>
</tr>
<tr>
<td>Water in clinical use¹</td>
<td>0.0345</td>
</tr>
<tr>
<td>DentaPure in clinical use (includes water portion)¹</td>
<td>0.0853</td>
</tr>
<tr>
<td>Distilled water³</td>
<td>1.048</td>
</tr>
<tr>
<td>Tricide (triphenolic)⁵</td>
<td>0.852</td>
</tr>
</tbody>
</table>

(Continued)

<table>
<thead>
<tr>
<th>Sample type</th>
<th>(mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bleach 5.25% (chlorine)²</td>
<td>38.380</td>
</tr>
<tr>
<td>Compliance (peroxide)²</td>
<td>1.415</td>
</tr>
<tr>
<td>Microstat (bromide)²</td>
<td>5.536</td>
</tr>
</tbody>
</table>

NIDR’s studies show that distilled water caused 10 times the amount of mercury to be released as was released during the clinical application of DentaPure.

4. **Conclusions**

1. Iodine based products, and particularly the DentaPure DP 365 continue to be highly efficient in controlling dental unit waterline bacterial contamination.
2. The paper clearly shows that the DentaPure cartridges do not cause a significant problem in mobilizing mercury. In fact another study out of NDBRI shows that distilled water mobilizes 1.00 ppm of Hg 20 times more than the DentaPure cartridges.
3. Chloramine is more likely to have produced the large scale increase mercury levels than iodine from DentaPure cartridges and should be fully investigated.
4. Iodine (I₂) is unlikely to have been responsible for the 21-fold increase in Mercury at NAS Norfolk.
5. There is an obvious relationship between the concentration of halogens used, and the concentration of mercury released. It is therefore recommended that the minimal concentration of any biocide be used, consistent with good infection control practices and procedures. DentaPure cartridges meet this recommendation.

Barry Hammarback*  
MRLB International, Inc., DentaPure, N8351 818th Street,  
River Falls, WI 54022, United States

Shannon Mills  
University of Nevada School of Medicine, Las Vegas,  
Nevada, United States

Roger Johnson  
Novation Environmental Technologies, Inc., Reno,  
NV 89503, United States

* Corresponding author. Tel.: +1 715 425 2191;  
fax: +1 715 425 5699.  
E-mail address: barry@hammarback.us

14 August 2006  
© 2007 Academy of Dental Materials.  
Published by Elsevier Ltd. All rights reserved.  