

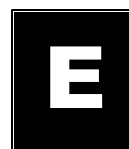


Waste Management and Research Center

Characteristics and Treatment of the Dental Waste Water Stream

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Characteristics and Treatment of the Dental Waste Water Stream

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ABSTRACT

Dental amalgam consists of approximately equal parts mixture of metallic mercury and an alloy powder consisting of silver, tin, copper and zinc. Amalgam has been used extensively as a tooth filling material, accounting for 75% of posterior restorations. The waste material from dental offices generated during restorative dental procedures contains amalgam. The uncontrolled discharge of this waste into the sewer system from a large number of dental units (i.e. dental clinics), will increase the mercury load to treatment facilities and could eventually contribute higher potential mercury exposure as well. The main objective of this project was to characterize the properties of the dental waste (DW) stream. This was accomplished by collecting more than 90 DW stream samples from various clinics and quantifying the mercury and silver content of their two major waste components: a) the solid waste (SW) retained on the in-line vacuum trap (also known as a chair-side trap), and b) the DW water (DWW) which has the potential to be discharged into the sewer system. On a conservative median basis, the DW stream has the potential to generate as much as 1,297 mg of mercury and 833 mg of silver per day per dental unit (i.e., chair). The majority of this toxic and recyclable waste material is generated at the in-line vacuum trap in the form of a solid waste (i.e., SW component). This waste has the potential to generate 799 mg of mercury per day per dental chair and 533 mg of silver per day per dental chair. The DWW component has the potential to generate 497.9 mg of mercury per day per dental chair and 300 mg of silver per day per dental chair. To assist the development of effective removal/recovery/reuse procedures for this waste stream, predictive regression models for the amount of mercury and silver generated from the major components of the DW stream were established.

The other major objective of this project was to assess the relative effectiveness of removal procedures for mercury and silver in the DWW component. The present study found that gravitational settling under quiescent conditions for a 24-hr period has the potential to remove more than 99% of the total mercury content of the DWW component. This operational, simple and cost effective procedure is recommended for providing the majority of mercury reduction by weight. Further reduction of the mercury content of the residual DWW (after settling), is accomplished by applying a coagulation-flocculation/filtration approach. The present study found that on a cumulative basis the overall mercury removal potential of a settling/coagulation-flocculation/filtration treatment approach for the DWW component is likely to be more than 99.9%.

Contaminant	SW: Solid Waste in Trap Median (mean \pm SD)	DWW: Dental Wastewater Median (mean \pm SD)	DW: Dental Waste DW= SW + DWW (median)
Hg, mg/day/chair	799 (1,069 \pm 913)	498 (708 \pm 661)	1,297
Ag, mg/day/chair	533 (716 \pm 633)	300 (525 \pm 543)	833

INTRODUCTION

In the United States 90 to 100 tons of amalgam are used yearly in dental restorative work (WHO, 1991). The composition of dental amalgam varies from manufacturer to manufacturer. However, the basic ingredients of amalgam, by weight, are silver (20-34%), tin (8-15%), copper (1-15%), other metals (0-5%), and mercury which comprises (42-52%) of the total mass (O'Brien, 1997).

Mercury is a major constituent of dental amalgam. Mercury is a heavy metal, which is toxic at certain levels and in different forms. Its release into traditional waste streams such as the municipal solid waste stream or the sewerage system and its potential discharge into the environment are becoming major concerns. Studies have found that the dental waste stream can contribute from 10 to 70% of the total daily mercury loading to wastewater treatment facilities (Berglund, 1999). Dental procedures generate a heterogeneous waste mixture of liquids and particles. A major component of this waste mixture is amalgam particles with sizes ranging from large visible particles to sub-micron colloidal size suspension. Arenholt-Bindslev (1992) classified the waste of dental operations into two categories, "Primary Amalgam Particles" and "Sewage". In the present study, more content specific terms have been adopted based on a material flow balance approach of amalgam particles generated during dental procedures.

Figure 1 presents a simplified schematic of the overall material flow related to an operational dental unit. The underlying operational assumption is that this unit has a high-speed evacuation (suction) system with the cuspidor discharge line connected to it. Based on the waste material flow approach (Figure 1), the following components are discerned:

- **Dental Waste (DW):** The aggregate waste generated during placement, removal and polishing of dental amalgam before this waste is discharged through the cuspidor or the suction hose. The DW is a heterogeneous mixture of particles (dental amalgam, dentine, enamel, oral tissues, pulp, bacteria, etc.) and liquids (water, oral fluids, blood and saliva, plasma, surfactants, mouthwash fluids, etc.).
- **Solid Waste (SW):** The solid waste which is retained on the in-line vacuum trap filter (also known as a chair-side trap). This trap is utilized to prevent clogging of the disposal suction lines and has a mesh size of approximately 700 μm .
- **Dental Waste Water (DWW):** The portion of the generated DW mixture which enters the disposal and suction lines (i.e., $DW = SW + DWW$).
- **Residual Amalgam (RA).** Excess amalgam is mixed to ensure that the dentist does not run out of amalgam. Excess amalgam is mixed to overfill the prepared tooth to allow proper finishing of the restoration. The amalgam particles that are not used during the placement and are not placed into the oral cavity are referred to as non-contact amalgam or excess amalgam. Based on common dental practices this quantity is contained outside the oral cavity and can be easily recycled since separation is not required.

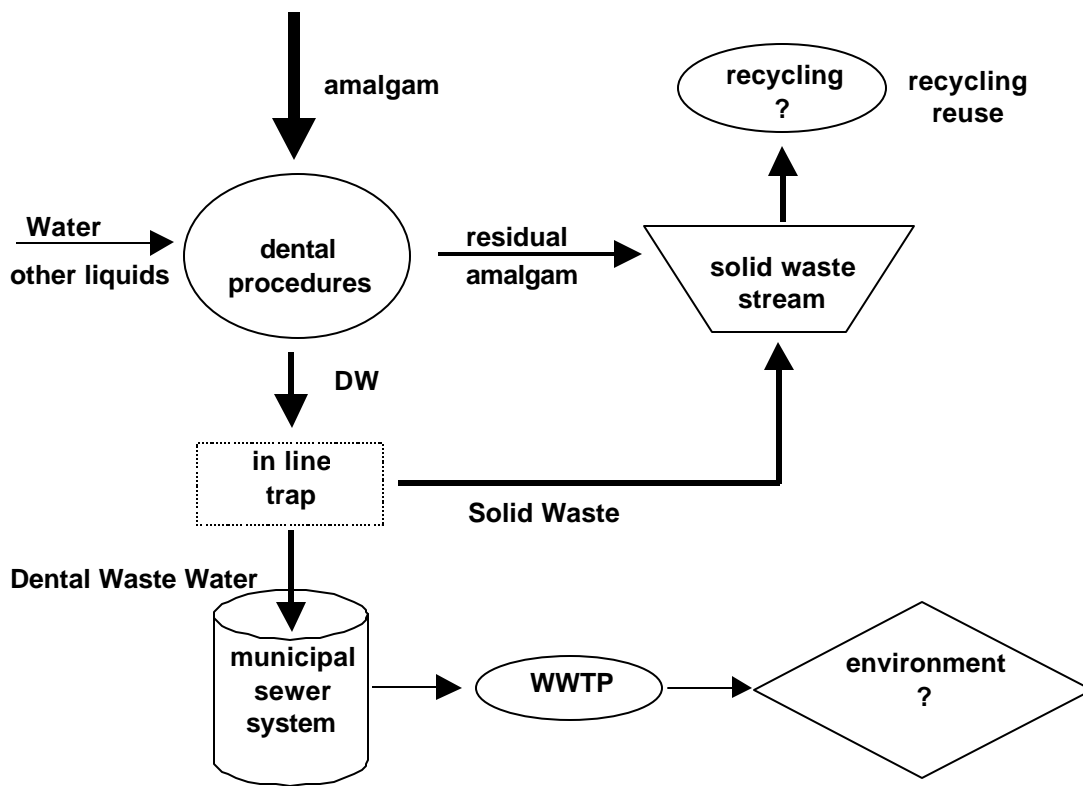


Figure 1. Flow chart of the dental waste stream

The DW stream and its two major components are the main focus of the present study.

Minor, or irregular, sources of dental amalgam have not been accounted for in the above material waste flow (e.g., instrument cleaning, spills, gloves, cotton swabs, and amalgam capsules). The largest percentage of dental amalgam, by weight, is retained on the in-line vacuum trap (i.e., SW). The remaining dental amalgam particles suspended in the liquid phase follow the flow of the DWW. The DWW mixture may be “treated” at the source for separation/recovery of its toxic solid constituents and proper disposal of its liquid portion, or it may be directly discharged into the sewer system.

In the United States, treatment at the source of the DWW stream is not yet mandated by local or federal agencies. However, approximately 6% of the major Publicly Owned Treatment Works (POTW) have to comply with mercury effluent permit limits which can reach as low as 1.3 ng Hg/L based on the Great Lakes Water Quality Guidance criteria for wildlife protection (USEPA, 1995), or as in the case of Maine, a proposed effluent limit of 0.2 ng Hg/L (Walker, 2002). The implementation of these low mercury effluent limits, as part of the permit requirements for many POTW will most likely expedite the implementation of “upstream” mercury pollution prevention and reduction strategies. The potentially toxic and recyclable components of the DW stream make it an ideal candidate for implementing treatment/collection at the source requirements in combination with a recycling program.

In Europe, concerns about the impact of mercury on aquatic ecosystems and the heavy metal content of the compost material generated from wastewater treatment sludge, has already resulted in mandatory treatment at the source (Arenholt-Bindslev, 1992).

Previous Studies of the DW Stream

Clinical dental operations include placement, removal, and polishing of dental amalgam. These operations generate a particle size distribution which contains amalgam, dentine, enamel, and other particulates. Although much work has been done on the characteristics of dental amalgam as a restorative material, very few studies have focused on characterizing the basic properties of the DW stream and its components. Amalgam has a density of approximately 9.50 g/cm³ (i.e., density of the amalgam standard). A commissioned study by DÜRR Dental GmbH & Co. KG, showed that the density of an amalgam and tooth matter mixture ranged from 2.81 g/cm³ to 6.43 g/cm³, with most values around 4 g/cm³ (Muschelknautz, 1992). This wide range indicates that amalgam and tooth matter combine to form a heterogeneous mixture during removal operations and consequently variability increases. Furthermore, these relatively high-density values suggest that gravitational settling of the particles in the DWW will be effective in removing a significant fraction of amalgam particulate.

Cailas et al. (1994) determined that particles between 10 µm to 700 µm in diameter contained more than 90% of the total mercury (particles greater than 700 µm in diameter were trapped by the in-line vacuum trap). The remaining 10% of the mercury content were found in the fine suspension containing particles less than 10 µm. Another important finding of this study is the dual phase settling pattern that DWW samples are likely to exhibit. In the first phase the particulate matter settles due to gravitational forces with velocities as high as 65.7 cm/hr (Cailas et al., 1994). Such velocities occur because of the high density of amalgam particles. During the

second phase electrostatic and microdynamic forces prevail. Consequently, a fine particulate suspension remains in the liquid phase. The mercury concentrations in this suspension reached levels of 4,011 ng Hg/mL (Cailas et al., 1994). This fraction is likely to evade traditional techniques of particulate removal based on sedimentation or centrifugation and eventually enter the sewer system. The mercury levels of this fraction are orders of magnitude greater than the discharge limits set by certain local wastewater treatment plants (WWTP) for small quantity generators (e.g., METRO Seattle, 200 ng Hg /mL, Dayton; Ohio, 2.5 ng Hg/mL; Pima County, Arizona, 50 ng Hg/mL; Norfolk, Virginia, 500 ng Hg/mL).

In a DW particle study using scanning electron microscopy and sieves as the instruments of detection, Letzel et al. (1997) determined that the amalgam particle waste followed a bimodal particle size distribution. Drummond et al. (1997) determined that these two methods of analysis were the least accurate and reproducible of the five techniques examined and that particle removal does not imply mercury removal.

Another source of dental amalgam waste generated during dental procedures is the residual amalgam (see Figure 1). This waste is considered easily recyclable since separation is not required and the particles are in a "pure" non-contact form. The environmental and economic aspects associated with the recycling of residual amalgam are adequately discussed in the available literature (ADA-CDMD, 1976; Rogers, 1989; Fan et al., 1992). Nevertheless, no exact data exists on what proportion of this amalgam is recycled in the United States.

Significance of the DW stream for Sanitary Districts

In recent years, many POTW's have had difficulties complying with the existing, or anticipated requirements of their National Pollutant Discharge Elimination System (NPDES) wastewater treatment plant permits concerning priority pollutants (USEPA, 2001). Unregulated small quantity generators, such as dental clinics, are likely to be one of the main sources causing these compliance problems. The Municipality of Metropolitan Seattle investigated the mercury content of the waste generated from dental clinics (Welland, 1991). The mercury concentrations in this waste stream were found to range from 12 to 480 mg Hg/L. In this case, the mercury concentrations exceeded the local discharge limits of 0.2 mg Hg/L. The POTW in the Seattle Metropolitan area estimated that the 1,650 dental offices in its service region contributed up to 14% of the total mercury load to the local WWTP (Welland, 1991). Although the database limitations and the lack of experimental design may be criticized, these findings signify the important contribution of small quantity generators to the heavy metal load of WWTP facilities. The results of similar studies indicate that the DW stream has the potential to contribute:

- on average 11% or 0.1 kg Hg per day (San Francisco; Barrucci, et. al., 1992; Rourke, 1993),
- a minimum of 10% or 0.046 kg Hg per day (Cohen et al., 1997),
- as much as 76% or 0.34 kg Hg per day (Minneapolis St. Paul; Berglund, 1999), and
- on average 56 mg Hg/dentist/day with a maximum of 98 mg Hg/dentist/day (Walker, 2002).

In addition, a Danish study produced an estimate for dental discharges of 100 to 200 g of mercury per year per office (Arenholt-Bindslev, 1992). Based on this study, and the average content of silver in the amalgam alloy, the expected amount of silver in dental discharges is likely to be within the range of 40 to 152 g per dentist per year.

Treatment of the DW stream

Because of the increasing concern over mercury pollution of the European waterways, the EC-Council directive of March 8, 1984 (No. L 74/49 of 17-3-1984) mandated the implementation of amalgam removal devices with a minimum efficiency of 95% (i.e., amalgam particle mass removal). This action provided fertile ground for the growth of European dental amalgam separator and recycling companies. In response to the requirement for separator installation by the dental professionals in Europe, companies in Sweden, Germany, and the Netherlands developed and marketed separator systems in a variety of designs. Five types of systems are available and marketed in the US: centrifuge, sedimentation, filtration, ejection, and other systems. However, as noted by Cailas et al., (1994) and Drummond et al., (1997), it is not known if such systems will be able to produce effluent which will satisfy the local discharge limits for small quantity generators.

The International Organization for Standardization (ISO), in an effort to standardize the evaluation of such systems, implemented a standardized procedure for assessing the efficiency of amalgam separators (ISO/DIS 11143; January, 1998). This procedure provided guidelines for the mass and particle size distribution fractions that will be used for separator evaluation. Regardless of these efforts to standardize the assessment procedure, a comprehensive evaluation of the removal efficiency of these devices has not yet been published.

In the US, treatment at the source of the DWW stream is not yet specifically mandated. The Palo Alto Regional Water Quality Control Plant, Palo Alto, California, the Metropolitan Council Environmental Services, St. Paul, Minnesota, and the Western Lake Superior Sanitary District (WLSSD), Duluth, Minnesota, implemented voluntary mercury pollution prevention and source control programs that did not require amalgam separators at dental offices. The sanitary districts implementing these programs found that the mercury effluent levels were not reduced below the Great Lakes Initiative Criterion of 1.3 ng Hg/L. In the case of WLSSD, the average effluent concentration was 4.7 ng Hg/L with a maximum of 18.3 ng Hg/L (Walker, 2002). The voluntary nature of these programs, as well as dental and residential discharges, were identified to be the likely cause of these high mercury levels (Walker, 2002).

The prevailing approach for sanitary districts seems to be the implementation of voluntary mercury pollution prevention and source control programs in collaboration with local dental associations (e.g., Duluth, Minnesota). To facilitate the implementation of DWW treatment devices to remove amalgam particles, the Seattle Sanitary district conducted a pilot evaluation of three DWW mercury separation devices (Welland, 1991). Among these methods, filtration and gravity settling removed more than 90% of the mercury content (i.e. filtration 93.4 to 98.8%, gravity sedimentation 99.3%, and ion exchange 79.0%). At present, there does not appear to be a prevailing mercury separation method employed in Europe or the US.

OBJECTIVES

The major objective of this project was to characterize the properties of the DW stream in terms of mercury and silver generation within each distinct component of this waste stream. The first component consists of the SW material retained on the in-line vacuum trap that has a mesh size of approximately 700 μm . The second component is the DWW passing through the in-line vacuum trap. This second component contains the particulate by-products generated during dental operations and suspended in the liquid phase. The DWW component can be further subdivided into three fractions: the settleable (SET), the suspended (SUP), and the soluble (SOL) fractions. The first objective of this project was to characterize this waste stream by quantifying the generation rates of mercury and silver in its various components and fractions. This objective was accomplished by randomly collecting a sufficient sample size of DW samples from various dental offices.

The second objective was to assess the recycling potential of the toxic material from this waste stream by estimating generation rates. The highly toxic and recyclable composition of the DW stream forms the basis to develop effective recovery and reuse procedures. The first step to achieve this objective was to develop predictive models for estimating the total amount of recoverable materials. This objective was accomplished by developing regression models for the amount of mercury and silver generated from the SW retained in the in-line vacuum trap and from the settleable fraction of the DWW.

The third objective was to assess the relative effectiveness of removal procedures for the mercury and silver content of the DWW. For this purpose the removal efficiency of settling was assessed. Treatment by settling alone was deemed insufficient to reduce the mercury levels of the residual wastewater to acceptable levels for discharge. Therefore, emphasis was placed on further reduction of the mercury content of the residual DWW by applying centrifugation/filtration and coagulation-flocculation/filtration.

METHODS AND MATERIALS

Waste Stream Component Characterization

In Figure 2, the processes of waste component characterization are presented. Based on the characteristics of the DW stream and a typical dental unit configuration, two basic components can be discerned: the first consists of the SW material retained on the in-line vacuum trap that has a mesh size of approximately 700 μm . From this waste material two generation variables were quantified (i.e., SW_{Hg} and SW_{Ag} ; see Figure 2). The second DWW stream component is the heterogeneous liquid suspension passing through the in-line vacuum trap. This component is further subdivided into two fractions formed from the DWW after 24 hours of settling: the SET and the SUP fractions (i.e., $DWW = SET + SUP$). In the present study the fine particulate suspension as well as the SOL fractions (part of the supernatant), are considered to be critical parameters since they are likely to evade traditional separation techniques and enter the sewerage system. The first objective of this project was to characterize the DW stream by quantifying the generation rates of mercury and silver in the various components of the waste stream (i.e., SW, SET, SUP, and especially SOL; see Figure 2). Ovsey (1995) noted that silver has been quantified only in the components and portions of the DW stream that yield a significant quantity (i.e., SW and SET).

Clinical Sample Collection

Dental waste samples were collected at the dental clinics of the Great Lakes Naval Base, and private dental offices and clinics at the University of Illinois at Chicago (UIC), College of Dentistry. Samples were collected in "BEMIS System I" 2000 cc and "BEMIS System II" 3000 cc graduated clinical vacuum canisters (see Figure 3). The major elements of the clinical sampling protocol were:

- Tubing: Smooth walled "Tygon" tubing was connected vertically between the dental unit and the collection vessel canister to prevent waste buildup.
- In-line vacuum trap: The large dental waste particles are retained on an in-line vacuum trap with a mesh size of approximately 700 μm (i.e., SW material). The contents of this trap were placed in a plastic bag and attached to the canister.
- Descriptive dental operations data: Each clinic collected and maintained a database describing the dental operations conducted during the working day on each dental unit. The data collected included as a minimum the following information: the number of patients per day per unit, the number of amalgam placements and removals per patient per day per unit (i.e., surfaces - one, two, three or more), any polishing operations, and other operations that may influence the properties of the dental waste water stream.
- Sample transport: Samples were transported from each clinic to the School of Public Health-Environmental Health Sciences (SPH-EOHS) Lab.
- Sample storage: Samples were stored at approximately 4°C to prevent evaporation and minimize microbial growth.

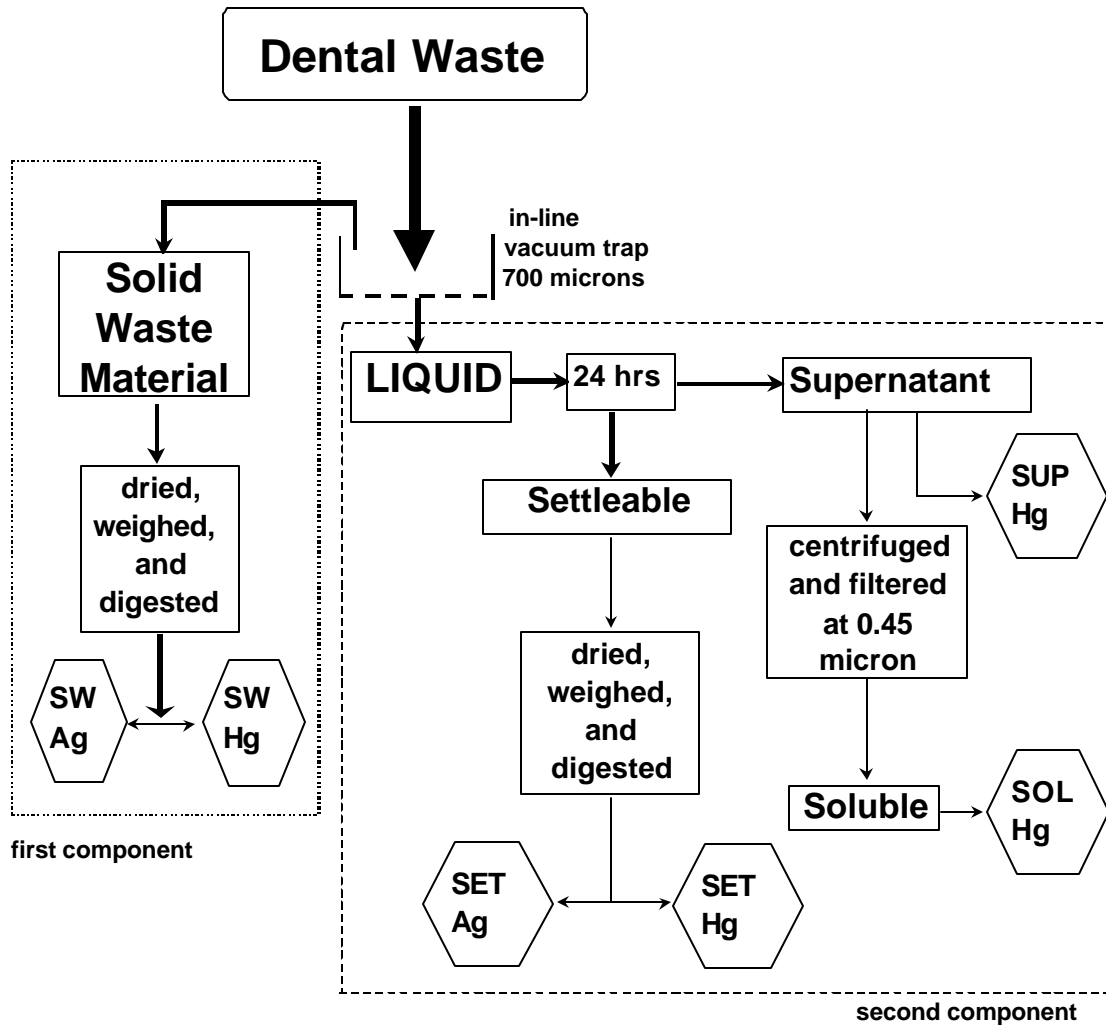


Figure 2. Flow chart of the waste component characterization procedures

Sample Processing

All samples were processed and analyzed in the laboratory no longer than three to four weeks after sample collection. SW materials from the in-line vacuum traps were transferred into clean, dry, weighed beakers. Any residual material attached to the plastic bag or on the in-line vacuum trap was removed with a sharp pair of stainless steel forceps and an anti-static brush, and then placed in the pre-weighed beaker. The beaker and its contents were dried in a Fisher Isotemp Model 501 oven (Fisher Scientific, Pittsburgh, PA) to constant weight at 30°C. After drying, the total weight of the solid component was determined using a Sartorius 1204 MP balance (Brinkmann Instruments, Des Plaines, IL). After drying and weight determination, these samples were digested on a hotplate using the nitric acid Standard Method 3030E (APHA, 1992).

Liquid heterogeneous suspensions of the DWW were mixed in the BEMIS vacuum canister (see Figure 3). A suction probe was inserted in the small sampling port and the container was then tipped at approximately 45 degrees to allow settling for a 24 hr quiescent period. The SET waste material accumulated on the bottom and the side opposite to the small sampling port (i.e., 1 mL glass volumetric pipette).

Two distinct fractions of the DWW formed during the 24-hr settling period which could be easily separated: the SUP and the SET material. Without disturbing the SET material, the waste container was placed in an upright position. The supernatant was suctioned from the container using a 50 mL syringe and Tygon tubing. A 4 mL aliquot of the supernatant was preserved with 4 mL of preservative solution [10 % HNO₃ (v/v) and 0.02 % K₂Cr₂O₇ (w/v)]. The preserved SUP samples were stored at 4°C for further analysis.

A fraction of the SUP was subjected to centrifugation and filtration to remove a fine suspension of particles. The SUP was decanted into a 50 mL centrifuge tube, and centrifuged for 10 min at 3,000 rpm. The resulting SUP was filtered with a 10 cc syringe equipped with a 0.45 µm filter into a 15 mL polypropylene tube. The filtrate was preserved and stored as described above for the SUP.

The SET fraction was transferred into a preweighed clean dry beaker. Deionized water was used to wash any solid residue from the waste container into the beaker. Stainless steel forceps and an ultrasonic bath were used to dislodge any attached solids from the walls of the container. The water content of the SET fraction collected in the beaker was evaporated at approximately 30° C in a Fisher Isotemp Model 501 oven. After evaporation, the weight of the dry solid waste that remained on the bottom of the beaker was determined. The sample was ready for preparation for the total mercury determination (Standard Method 3030E; APHA, 1992).

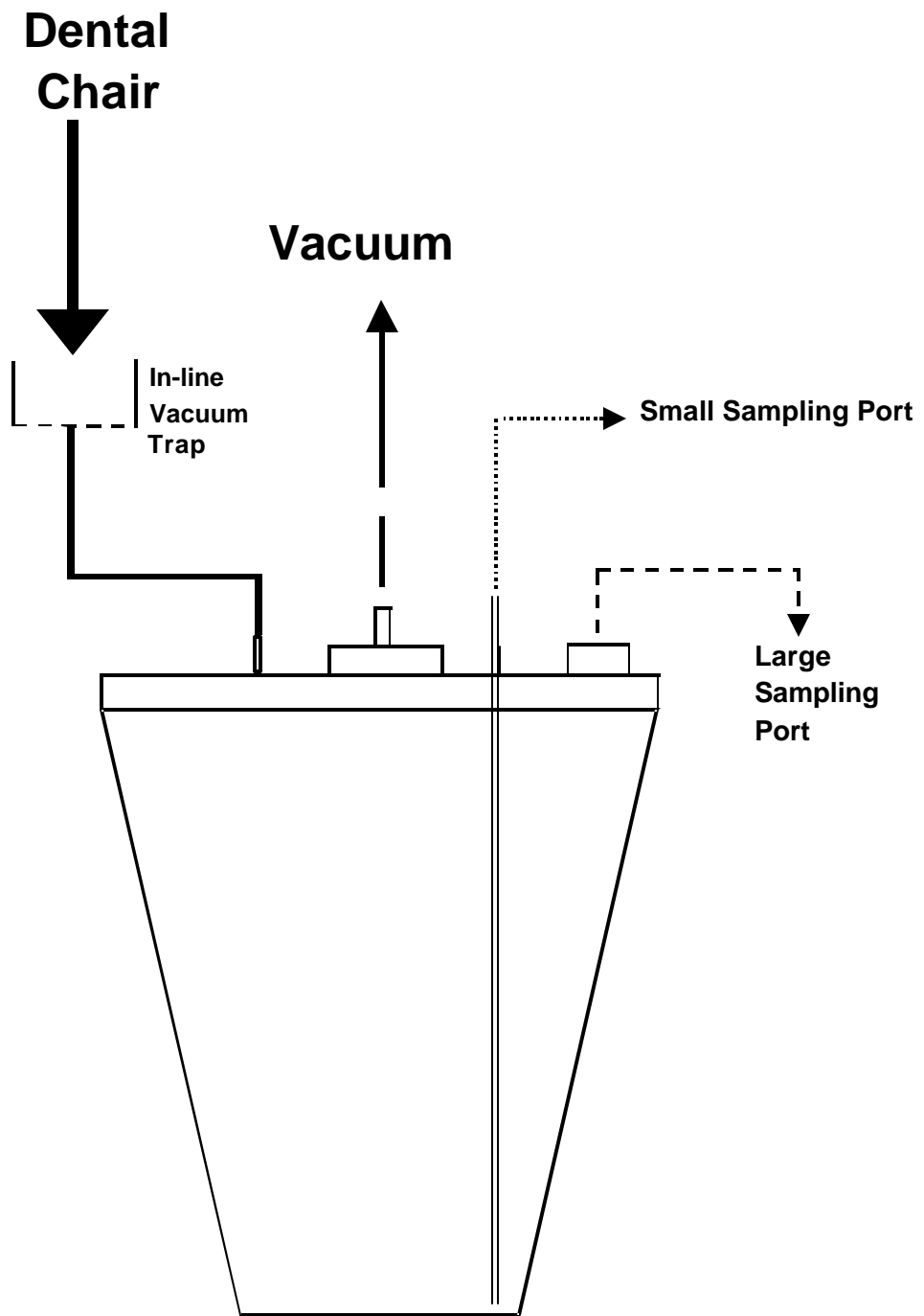


Figure 3. Schematic of the BEMIS vacuum sampling canister

TREATMENT STUDIES

The objective of this phase of the experimental procedure was to determine the relative effectiveness of competing removal techniques in removing mercury in the SUP portion of the DWW.

Centrifugation

Studies were designed to determine if centrifugation was a feasible approach for mercury reduction in the SUP of the DWW. Since this SUP portion settled for a 24 hr period, these centrifuge studies were actually aimed at assessing the performance of a dual treatment approach of the DWW supernatant (i.e., gravitational followed by centrifugal treatment).

The SUP sample was placed on a magnetic stirring plate and mixed gently. Two 4 mL aliquots of the SUP were sampled and preserved with 4 mL of preservative solution [10 % HNO₃ (v/v) and 0.02 % K₂Cr₂O₇ (w/v)]. Duplicate 50 mL centrifuge tubes were labeled. Using a 50 mL syringe, approximately 40 mL of mixed SUP was sampled and transferred into labeled 50 mL centrifuge tubes. Each pair of centrifuge tubes was weighed and balanced before they were centrifuged at the appropriate RPM rate for 15 minutes. After centrifugation, the samples were preserved as above and stored at 4°C in polypropylene bottles until analysis.

Coagulation and Flocculation

Coagulation and flocculation studies on the suspension were also conducted to assess mercury reduction in the SUP. Waste samples were tested using a Phipps and Bird six-paddle stirrer with a standard coagulation-flocculation jar test procedure (APHA, 1992). Aliquots (1000 mL) of each SUP portion of the DWW were dosed with coagulant, a 1% (w/v) ferric sulfate solution (SIGMA Chemical, MO). The solutions were stirred rapidly at 120 rpm for 1 min during coagulant addition, followed by a slower stirring at 25 rpm for 20 min. The pH was adjusted with phosphate buffer, caustic soda, or sulfuric acid, to selected values. After coagulation, the flocculants were added and the procedure was carried out with the same stirring regime and timing. At the end of each experiment, samples were removed and filtered before being analyzed by cold vapor atomic absorption spectroscopy.

Materials for Coagulation and Flocculation

- The following materials were used for the coagulation and flocculation experiments:
- Polyacrylamide with MW 5,000,000-6,000,000 nonionic water soluble polymer powder, poly(acrylamide/acrylic acid 60:40) with MW > 10,000,000 anionic powder / and polyethylenimine with MW 10,000 were used (Polysciences, Warrington, PA). Ferric sulfate was purchased from Sigma (St. Louis, MO).
 - Coagulant solution 1% (w/v): Dissolve 10 g of ferric sulfate in 100 mL of DDI water.
 - Flocculants solution 0.1% (w/v): Dissolve 0.1g of powder or liquid polymer in 100 mL of DDI water.
 - Buffer, Sodium bicarbonate (NaHCO₃).

Instrumentation

A Perkin-Elmer 5000 spectrometer was used to measure mercury concentrations by cold vapor atomic absorption. The absorption cell was mounted on the burner head. This cell was constructed from borosilicate glass with quartz windows (220 mm x 15 mm). The air pump was set to deliver a flow rate of 1.8 L air/min. The air pump could measure 1 to 5 L air/min. The aeration tubing was straight Teflon tubing (1/4" ID). "Tygon" tubing was used for all connections.

Reagents

1. Water: Double deionized (DDI) water was used for all purposes.
2. Sulfuric acid (H_2SO_4), concentrated: trace metal analysis grade.
3. Nitric acid (HNO_3), concentrated: trace metal analysis grade.
4. Hydrochloric acid (HCl), 2 N: Dilute 166.7 mL of reagent grade concentrated HCl to 1.0 liter.
5. Stannous chloride, 15% (w/v): Dissolve 178.5 g of trace metal analysis grade stannous chloride dihydrate in 1.0 liters of 2 N HCl.
6. Hydroxylamine hydrochloride, 12% (w/v): Dissolve 120 g of trace metal analysis grade hydroxylamine hydrochloride in 1.0 liters of DDI.
7. Potassium permanganate, mercury-free, 5% (w/v): Dissolve 50 g of trace metal analysis grade potassium permanganate in 1.0 liter of DDI.
8. Potassium persulfate, 5% (w/v): Dissolve 50 g of trace metal analysis grade potassium per sulfate in 1.0 liter of DDI.
9. Certified stock mercury solution: 1000 ppm (0.100%, w/v) of atomic spectral mercury.
10. Mercury working standards: Dilute stock mercury solution with 5% HNO_3 (v/v) and 0.01% $\text{K}_2\text{Cr}_2\text{O}_7$ (w/v), to obtain a series of standards containing 50, 30, 20, 10, and 0 ng/mL.

Sample Preparation

One mL of a homogenized, well mixed, preserved sample (or diluted sample) and 1 mL of spike standard (recovery of known additions) or dilution stock solution was added into a 150 mm x 25 mm glass test tube. The total amount of mercury in this test tube should not be greater than 50 ng. Two mL of concentrated H_2SO_4 , 1 mL of concentrated HNO_3 , 4 mL of potassium permanganate solution, and 2.5 mL of potassium persulfate solution were added to the test tube. This tube was then thoroughly mixed with a vortex. The test tube was placed in a heating block at 95°C. After two hours, the sample was cooled to room temperature. Using automatic dispensers, 0.5 mL of hydroxylamine hydrochloride solution was added to reduce the excess permanganate. The tube was then thoroughly mixed with a vortex. After the solution became clear, 1 mL of stannous chloride solution was added. The test tube was immediately attached to the aeration apparatus and analyzed for mercury (see Figure 4).

Standard Preparation

Mercury standards were prepared monthly at concentrations of: 50, 30, 20, 10, and 0 ng/mL and refrigerated at 4°C to prevent evaporation. As with sample preparation, one mL of each standard was used in calibrations.

Analysis

Samples were vortex mixed for 10 sec. during analysis. After 10 sec., the read button on the atomic absorption control panel was pressed, and the four-way flow switch was opened (see Figure 4). Mercury was carried by the airflow from the sample tube to the absorption cell and out to the scrubber. The absorbance reached a maximum within 10 seconds. The area of the peak was determined after 10 sec. of integration.

The aeration apparatus was detached from the sample tube and rinsed in DDI water. The four-way switch was closed. The airflow bypassed the aerator and was recirculated in the absorption cell closed loop. The closed loop reduced flow fluctuations, which insured that moisture and mercury-free air recirculated in the absorption cell. A calibration curve was constructed and the results were calculated. Dilutions of samples were obtained both before and after digestion to determine if this had any effect on the mercury results. Both approaches produced identical results, which are not presented here.

In addition to the above assessment of the two alternative methods, an inter-laboratory analysis was conducted. Two DWW samples were analyzed by both the UIC-EOHS laboratory and the Illinois Department of Public Health (IDPH), Department of Toxicology, Environmental Lead Unit. The summary of these results is provided in Table I. As evident from the low replicate percent difference (RPD) in Table I, the two laboratories produced comparable results.

Summary of Quality Control (QC) Procedure

This section provides a summary of the working standard operating procedure for data quality control assessment during this project. All quality control measures used in this study were consistent with that of standard mercury analysis procedures reported above (APHA, 1992). An outline of the QC protocol for mercury analyses is presented in Table II. A similar QC protocol was followed for silver analysis (Ovsey, 1995). Reagent checks were not performed because of the high quality of the purchased certified reagents. Although the detection limits for mercury and silver have been evaluated, analyses of such highly concentrated samples obviate the need for determining the method detection limits.

All samples were analyzed within 28 days in accordance with holding times specified by the USEPA for acid preserved (pH<2) samples (USEPA, 1979).

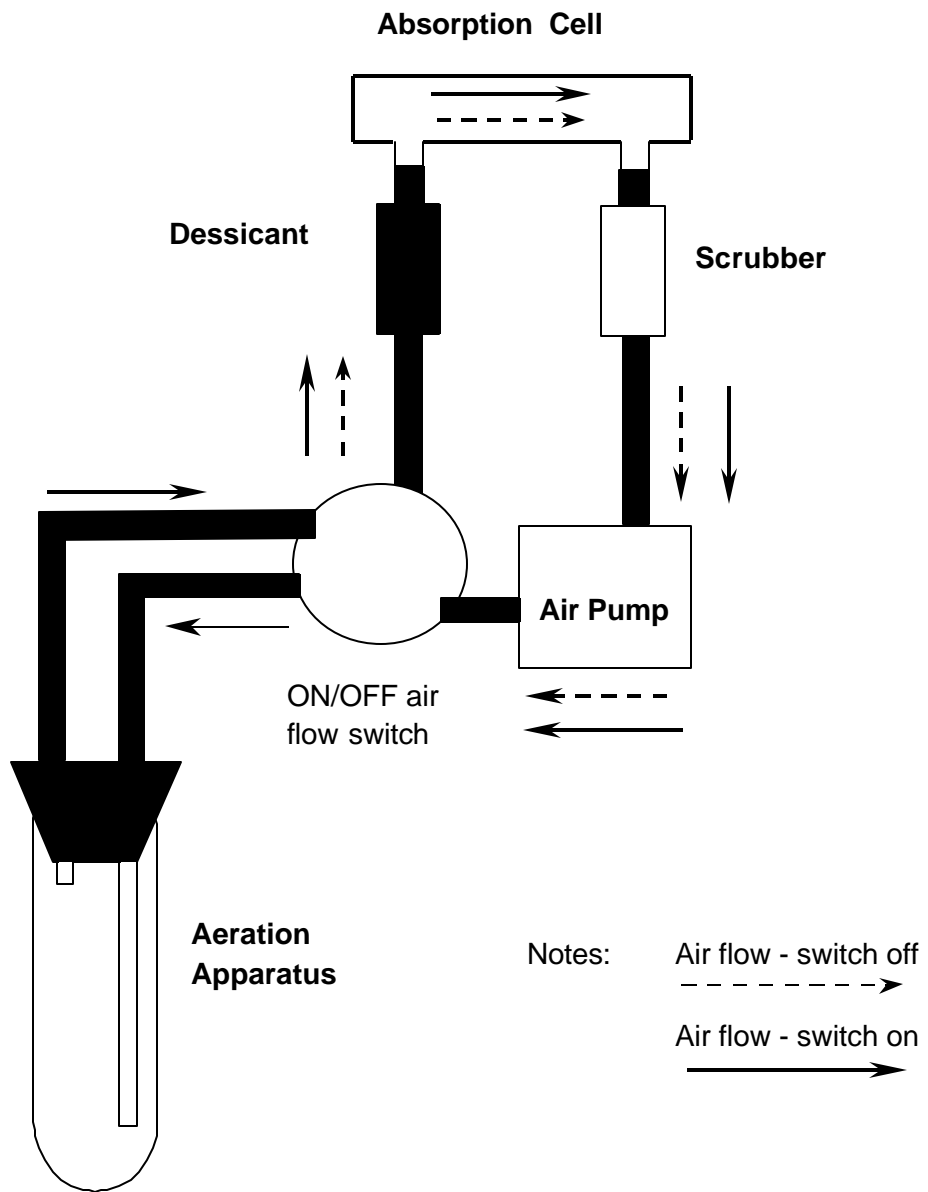


Figure 4. Cold-vapor assembly used for mercury analysis

TABLE I**SUMMARY OF UIC-EOHS & IDPH MERCURY ANALYSIS**

SAMPLE CODE	# DUP UIC / IDPH ^a	AVERAGE ng Hg/ml UIC	AVERAGE ng Hg/ml IDPH	UIC / IDPH CV%	RPD ^b %
B8	4 / 6	3,092,500	2,895,000	0.41 / 0.57	6.59

a # DUP UIC / IDPH identifies the number of duplicates performed by each laboratory.

b $RPD = (AVG. UIC - AVG. IDPH) * 100 / (AVG. UIC + AVG. IDPH) / 2$.

Calibration

Satisfactory instrument calibration with at least 4 standards and one blank was required to ensure reliable quantitative measurements. The calibration curve was deemed satisfactory if the correlation coefficient was greater than 0.995. Initial and continuing calibration confirmed that the instrument remained calibrated.

Blanks

Reagent blanks were analyzed to detect the existence and magnitude of contamination problems during the preparation process. No contamination was observed during this study. The laboratory control samples (LCS) served as a monitor of performance during the overall procedure (i.e., preparation, digestion, and analysis). All LCS had a recovery acceptance criterion of $100 \pm 20\%$. All LCS recovered within this range.

Duplicate/Replicate Sample Analysis

All samples were analyzed at minimum in duplicate. Duplicates provide an indication of precision based on each individual sample matrix (APHA, 1992). To evaluate duplicate data, the control limit for low level duplicates was 5% and 10% for high level duplicates.

Method of Standard Additions

A sample was selected at random for applying the method of standard additions (MSA) to evaluate the presence of matrix effect or interferences.

TABLE II

QC FRAMEWORK/SUMMARY FOR MERCURY ANALYSES

Sample Type	Frequency of Usage	Frequency of Preparation	Acceptance Criteria
Calibration Blanks ^a	Initially	As needed	
Calibration Standards ^b	Initially	4 Weeks	> 0.995
System Blanks ^a	Periodic	As needed	< low standard
Duplicates/Replicates ^c	2-4/Digestion	N/A	RPD <10%
LCS (ICV, CCV) ^{b, d}	10 Analyses	4 Weeks	Within $\pm 20\%$ of T.V. ^h
MSA ^e	10% or 1	During	Within $\pm 10\%$ of T.V. ^h
Spiked Samples ^f	See MSA	See MSA	
LCS(Method) ^g	2-4/Digestion	andom	R Within $\pm 10\%$ of T.V. ^h

^a Dilutions function as blanks.

^b Performed initially, or when the ICV or CCV fails.

^c For mercury each sample is digested two times.

^d Usually a mid range standard is used as ICV or CCV.

^e Method of Standard Additions (MSA) .

^f May be calculated from the known additions in MSA.

^g Performed at random to check the mercury digestion procedure.

^h T.V. = true value.

Detection Limits

All DWW samples were diluted to ensure that mercury was analyzed within the linear range. The instrument detection limit (IDL) and the lower level of detection (LLD) were evaluated for mercury analytical methods discussed in the previous sections, although they were not critical for this project. The recommended procedure by APHA (1992) was used. IDL was also determined for mercury. Seventeen blank samples were analyzed for mercury using the cold vapor technique. The standard deviation for these samples was 0.103 ng Hg/mL. Following the same calculation format, the IDL for mercury determination by cold vapor atomic absorption spectrometry using the Perkin-Elmer 5000 AA, was 0.169 ng Hg/mL and the LLD was 0.338 ng Hg/mL.

Silver Determination and Analysis

Ovsey (1995) presented details related to the silver content determination of the DW stream.

Data Analysis

All statistical data analyses and model development were performed by using the Statistical Analysis System (SAS), release 6.12 (SAS, 1997).

RESULTS AND DISCUSSION

Descriptive Statistics

The descriptive statistics for the generation variables describing the properties of the two major components of the DW stream (SW and DWW) and its various fractions (SET, SUP and SOL) are presented in Table III (see also Figure 2). More specifically, from the DW samples the following generation variables have been defined:

- The mercury and silver content of the SW material retained on the in-line trap (SW_{Hg} and SW_{Ag}),
- The mercury and silver content of the settleable waste (SET_{Hg} and SET_{Ag}),
- The mercury content of the supernatant (SUP_{Hg}), and
- The mercury content of the soluble fraction in the supernatant which passes through a 0.45 μm filter, (SOL_{Hg}).

The histograms for the two critical mercury generation variables (SUP and SOL) are presented in Figure 5. The histograms and the descriptive statistics indicate that all distributions were highly skewed. The estimated median generation rate for the SW_{Hg} fraction was 799 mg Hg per day per chair, while the SET_{Hg} rate was 498 mg Hg per day per chair. On a conservative median basis, silver generation from the SW_{Ag} fraction reached 533 mg Ag per day per chair, whereas from the SET_{Ag} fraction reached 300 mg Ag per day per chair (see Table III and Ovsey, 1995). In Table III, the SW component and the SET fractions of the DWW contain the vast majority of the targeted heavy metals (i.e., more than 99% of the total generation rate; see Table III). The other fractions of the DWW generate less than 1% of the total DWW mercury. This implies that gravitational forces are likely to remove at least 99% of the particulate mercury content of the DW. The median generation rate for the SUP_{Hg} fraction was 0.42 mg Hg per day per chair (1,213.5 ng/mL), whereas for the SOL_{Hg} fraction 0.121 mg Hg per day per chair (367.7 ng/mL). The highly skewed distribution of this portion (SUP) indicates that its generation rate can reach 1.26 mg Hg per day per chair, or 3,276 ng/mL, with a relative high frequency (75th percentile of the distribution, see Table III and Figure 5). This quantity is orders of magnitude greater than the discharge limits set by certain local POTW (e.g., 200 ng Hg/mL for the Seattle district). A further alarming find is that the total generation rate is a multiple of the above rates since each dental office is likely to have more than one operational unit.

The adequacy of the DW sample size, which has been used to estimate these generation rates, was examined. The mean, median, and the 25% upper quartile statistics of the SUP_{Hg} and SOL_{Hg} variables were used. The sequential estimate of these statistics facilitated the identification of a stabilization range. Beyond this range, the analysis of additional DW stream samples does not have a significant effect on the generation rate estimates. For the present study the stabilization range was reached with 60 DW stream samples.

TABLE III**DESCRIPTIVE STATISTICS FOR THE DW STREAM GENERATION VARIABLES**

Statistics	SW_wt	SET_wt	SW	SET	SUP	SOL	SW	SET
			Hg	Hg	Hg	Hg	Ag	Ag
Mean	2,211	2,118	1,069	708	1.22	0.62	716	525
N	96	99	96	99	112	112	96	90
SD	1,838.8	1,672.4	913.4	660.5	1.92	1.22	633	543
Skewness	1.09	1.31	1.19	1.61	3.15	3.46	1.10	1.29
Median	1,590	1,630	799	497.9	0.42	0.121	533	300
75%	3,230	2,910	1,649	1,010	1.26	0.29	1,077	832
25%	715	793	326	199	0.22	0.07	210	92
Max	9,050	8,200	4,758	3,299	11.92	7.94	3,198	2,309
Min	55	280	11.5	20	0.05	0.008	3.1	1.8

Notes:

All units are in mg per day per dental chair unless other specified.

SW_wt : dry weight of solid waste

SET_wt : dry weight of settleable particles

SW : particles on in-line trap (> 700 μ m), total dry weight

SET : settleable portion (24hr. settling)

SUP : supernatant portion

SOL : soluble portion (< 0.45 μ m)

TABLE III (continued)**DESCRIPTIVE STATISTICS FOR THE DW STREAM GENERATION VARIABLES**

Statistics	vol_d	SUP	SOL	SurRem	SurPlc	Caps	pH	Patnt
	ml	Hg(ng/mL)	Hg(ng/mL)					
Mean	522.6	5,558.5	3,193.0	2.01	8.21	11.3	6.43	5.73
N	125	112	112	115	117	113	23	117
SD	423.5	12,590	8,018.9	2.19	6.79	11.3	1.13	3.10
Skewness	1.45	3.71	3.70	1.21	1.37	1.25	-0.35	0.96
Median	340	1,213.5	367.7	1.5	6	7	6.77	6
75%	753	3,276.1	1,466.3	3	12	20	7.5	7
25%	225	601.9	188.7	0	3	3	5.24	3.5
Max	2,150	80,400	50,640	8	33	48	7.97	18
Min	75	75.2	7.6	0	0	0	4.22	1

Notes:

All units are in mg per day per dental chair unless other specified.

SUP : supernatant portion

SOL : soluble portion (< 0.45 microns)

vol_d : volume per day (ml)

SurRem : surfaces removed

SurPlc : surfaces placed

Caps : amalgam caps used

Patnt : patients

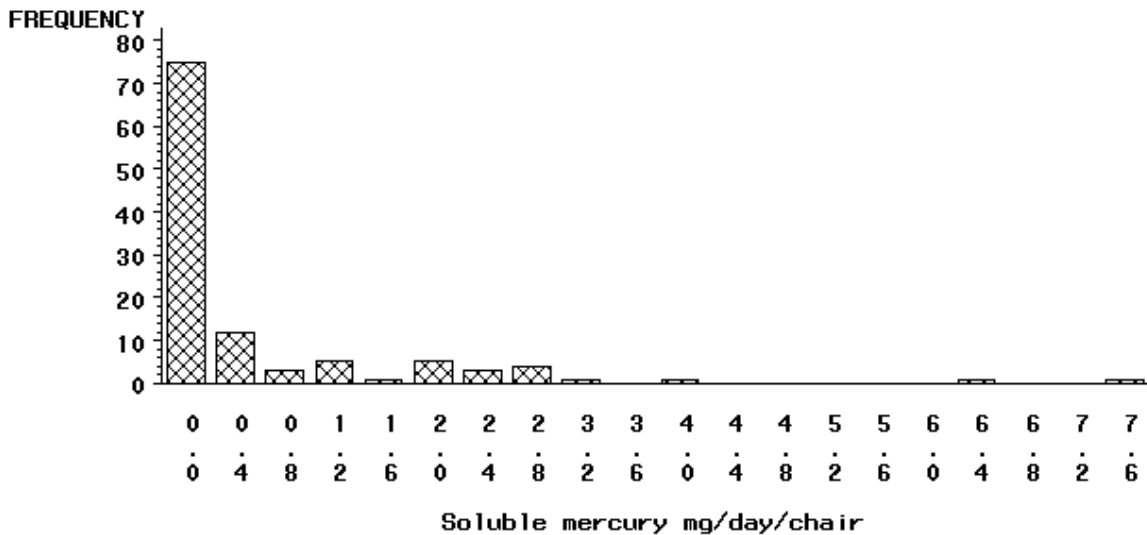
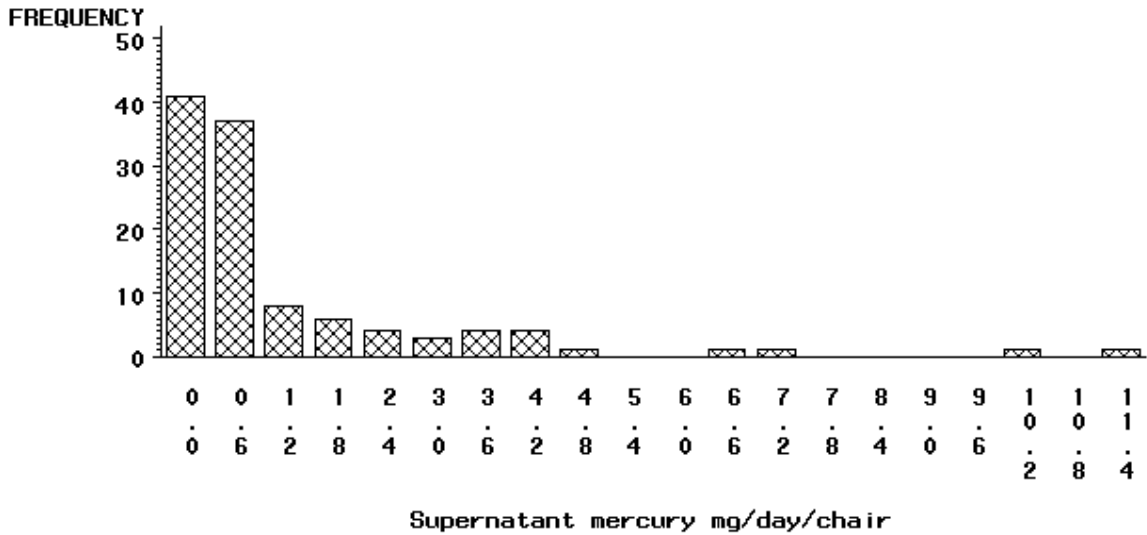


Figure 5. Midpoint Frequency distribution of critical DW fractions

Descriptive Statistics for the Explanatory Variables

A number of variables related to the DW stream generation process have been measured and analyzed, such as the dry weights of the SW material (SW_{WT}) and the SET waste material (SET_{WT}). These variables are likely to be useful in predicting the mercury generation rates from the DW stream samples because they represent more than 99% of the generated mercury mass. In addition, the number of amalgam surfaces-placed, amalgam surfaces-removed, amalgam-capsules consumed, and the wastewater volume have also been measured and analyzed. The descriptive statistics of these variables are in Table III. From this table it can be seen that all these variables are highly skewed as well. Consequently, correlation analysis of all these variables was performed with the Spearman rank correlation coefficient (Sprent, 1993).

Predictive Models

Predictive models of mercury generation have been developed as a function of easily measured independent (or explanatory) variables. Similar models have been developed for silver generation (Ovsey, 1995). The purpose of developing predictive models was to quantify the recycling potential of mercury in the DW stream as a function of easily measured independent variables. For this reason the associations between the dependent and explanatory (independent) variables were examined using the Spearman rank correlation coefficient (Sprent, 1993).

The correlation coefficient estimates, the probability estimate, and the number of samples used to estimate the coefficient are presented in Table IV. The mercury generation variables were highly correlated with the dry weight variables (i.e., probability values less than 0.01% and coefficients $\cong 1$). In addition, operational parameters such as the amalgam surfaces-placed and the number of consumed amalgam-capsules, are correlated with the mercury generation variables (i.e., even at a 0.01% level). Conversely, the volume of the generated DWW and some other operational parameters such as the number of patients or amalgam surfaces removed, did not suggest a significant association. Furthermore, the correlation analysis revealed that the mercury content of the SOL and SUP (fine particles) are not correlated to the operational variables. An interesting finding of this analysis is the fact that the fine suspension and the soluble mercury content variables (i.e., SUP and SOL) are not associated with the SET mercury content variable). This implies that the generating "mechanism" of the fine particulate is different from the mechanism generating the other amalgam components (i.e., highly correlated with each other and with the operational variables). This finding, in combination with the distributional properties of these DWW fractions (SUP and SOL) can lead to the suggestion that a soluble mercury content is generated at the source (as opposed to amalgam particulate which contains mercury).

Regression analysis of all these variables was performed. The model parameter estimates and basic regression diagnostic statistics are presented in Table V. The regression diagnostic statistics indicate that all the examined models have a reasonable predictive performance with model 1 being the "best" in terms of performance statistics (Montgomery and Peck, 1992). For this reason practical criteria were considered as well. The recommended predictive model should serve two purposes: a) to facilitate recyclers in predicting the amount of recoverable mercury from the waste material retained on the in-line vacuum trap, and b) to serve as a tool for performing cost-benefit analyses and pollution prevention planning. By considering these two

model objectives, model 1 and 3 will apparently be more appropriate for recovery purposes, since these two models require only the dry weight of the waste material. Models 2 and 4 are likely to have a very useful analytical application as well. They have the potential to provide estimates of mercury generation based on the amount of silver. From an analytical point of view, the silver content of the DWW samples is relatively easier to assess and is prone to less interference. Similar conclusions were drawn for both of the mercury retained on the in-line vacuum trap and the SET waste material (see Table V).

TABLE IV**SPEARMAN CORRELATION COEFFICIENT BETWEEN
MERCURY GENERATION AND EXPLANATORY VARIABLES**

Spearman Correlation Coefficients / Prob > |R| under Ho: Rho=0 / Number of Observations

	SWWT	SWHG	SWAG	SETWT	SETHG
SWWT	1.00000 0.0000 96	0.98809 0.0001 96	0.96829 0.0001 96	0.48099 0.0001 80	0.46374 0.0001 80
SWHG	0.98809 0.0001 96	1.00000 0.0 96	0.96984 0.0001 96	0.45408 0.0001 80	0.44122 0.0001 80
SWAG	0.96829 0.0001 96	0.96984 0.0001 96	1.00000 0.0 96	0.52187 0.0001 80	0.50006 0.0001 80
SETWT	0.48099 0.0001 80	0.45408 0.0001 80	0.52187 0.0001 80	1.00000 0.0 99	0.96947 0.0001 99
SETHG	0.46374 0.0001 80	0.44122 0.0001 80	0.50006 0.0001 80	0.96947 0.0001 99	1.00000 0.0 99
SETAG	0.50343 0.0001 80	0.47612 0.0001 80	0.54613 0.0001 80	0.95367 0.0001 90	0.97632 0.0001 90
CAPS	0.79300 0.0001 85	0.78217 0.0001 85	0.83122 0.0001 85	0.75596 0.0001 84	0.73612 0.0001 84
VOL	-0.11826 0.2589 93	-0.13392 0.2006 93	-0.19592 0.0598 93	-0.05830 0.5665 99	-0.08718 0.3909 99
SUPHG	-0.05878 0.5800 91	-0.04526 0.6701 91	-0.05513 0.6038 91	-0.19476 0.0600 94	-0.18474 0.0747 94
SOLHG	-0.06418 0.5456 91	-0.04068 0.7018 91	-0.05807 0.5846 91	-0.23733 0.0213 94	-0.22644 0.0282 94

TABLE IV (continued)

**SPEARMAN CORRELATION COEFFICIENT BETWEEN
MERCURY GENERATION AND EXPLANATORY VARIABLES**

Spearman Correlation Coefficients /Prob > |R| under Ho: Rho=0/ Number of Observations

	SETAG	CAPS	VOL	SUPHG	SOLHG
SWWT	0.50343 0.0001 80	0.79300 0.0001 85	-0.11826 0.2589 93	-0.05878 0.5800 91	-0.06418 0.5456 91
SWHG	0.47612 0.0001 80	0.78217 0.0001 85	-0.13392 0.2006 93	-0.04526 0.6701 91	-0.04068 0.7018 91
SWAG	0.54613 0.0001 80	0.83122 0.0001 85	-0.19592 0.0598 93	-0.05513 0.6038 91	-0.05807 0.5846 91
SETWT	0.95367 0.0001 90	0.75596 0.0001 84	-0.05830 0.5665 99	-0.19476 0.0600 94	-0.23733 0.0213 94
SETHG	0.97632 0.0001 90	0.73612 0.0001 84	-0.08718 0.3909 99	-0.18474 0.0747 94	-0.22644 0.0282 94
SETAG	1.00000 0.0 90	0.77658 0.0001 77	-0.18437 0.0819 90	-0.19804 0.0644 88	-0.23085 0.0305 88
CAPS	0.77658 0.0001 77	1.00000 0.0 113	-0.31847 0.0007 110	-0.06751 0.5112 97	-0.06512 0.5263 97
VOL	-0.18437 0.0819 90	-0.31847 0.0007 110	1.00000 0.0 125	-0.01204 0.8997 112	-0.17342 0.0675 112
SUPHG	-0.19804 0.0644 88	-0.06751 0.5112 97	-0.01204 0.8997 112	1.00000 0.0 112	0.91214 0.0001 112
SOLHG	-0.23085 0.0305 88	-0.06512 0.5263 97	-0.17342 0.0675 112	0.91214 0.0001 112	1.00000 0.0 112

TABLE V

PREDICTIVE MODELS FOR MERCURY AND SILVER GENERATION

		Explanatory variables		Performance statistics			
Dependent Variable	Intercept	Dry Weight ^a	Silver Content of the Solid ^b	F-value	R ²	PRESS	Model
SW _{Hg}	-19.7	0.49	-----	3,911.6	0.980	1,493,410	1
	56.8	-----	1.4	1,282.6	0.943	4,239,190	2
SET _{Hg}	-100.6	0.39	-----	1,641.9	0.955	1,903,430	3
	121.7	-----	1.2	1,565.3	0.953	1,962,200	4
SW _{Ag}	21.5	0.33	-----	1,602.5	0.954	1,615,330	5
SET _{Ag}	-153.7	0.31	-----	913.8	0.921	2,083,168	6

Notes:

a Dry weight refers to SW_{WT} for SW_{Hg} and SET_{WT} for SET_{Hg}.

b Silver content of the solid refers to SW_{Ag} for SW_{Hg} and SET_{Ag} for SET_{Hg} (Ovsey, 1995).

TREATMENT STUDIES

Centrifuge Studies

A series of rotating speeds (0, 1000, 2000, 3000 rpm) were used in this study. Relative gravity (G) was calculated as follows:

$$\text{Relative gravity } (G) = r H (\text{rpm})^2, H = \text{universal constant}$$

Where: $r = 15.22\text{cm}$ for swinging bucket rotor, and universal constant = $1.12 * 10^{-5}$

Table VI and Figure 6 present the results for six DWW supernatant samples treated by various centrifugal forces. The results indicate that the remaining mercury concentration is inversely proportional to the exerted centrifuge force. However, the results from this study indicate that the SOL mercury concentration for each treated sample (i.e. the amount of mercury found in the sample after the centrifuged sample passes through a $0.45 \mu\text{m}$ filter), is likely to be independent of the exerted force. The results are strongly influenced by the initial mercury SUP concentration. In Figure 6, DWW samples with a low initial SUP mercury concentration are likely to yield low removal efficiencies, whereas samples with a high initial mercury concentration are likely to yield high removal efficiencies.

Coagulation and Filtration Studies: Coagulant Dose and pH Range

Previous studies indicate that after a 24 hr settling period the remaining DWW contains particles with diameters less than $53 \mu\text{m}$ (Cailas et al., 1994). Mercury laden waste particles of such magnitude are likely to behave as a colloidal suspension. The coagulation-flocculation study was performed to identify the operational parameters that yield optimum mercury removal rate. The SUP portion from more than 10 DWW samples was combined to form a composite SUP sample. The first level of treatment for the composite sample was filtration. Figure 7 presents the mercury removal results of a composite SUP sample having an initial mercury concentration of $1,051 \text{ ng/mL}$ (i.e., "mix"). Mercury levels remain stable for filter sizes larger than $53 \mu\text{m}$. Significant mercury removal rates are only achieved for filter sizes less than $2.5 \mu\text{m}$.

The $1,051 \text{ ng/mL}$ SUP composite sample was also used to assess the performance of the coagulation-flocculation removal approach. The remaining mercury concentrations for four different dosages of ferric sulfate coagulant (1g, 2g, 3g and 4g per 1,000 mL of DWW) and nine pH values (3 to 11) were examined. Figure 7 presents the mercury reduction pattern as a function of filter size and pH (3 to 7 range) for a fixed dosage. This figure indicates a high removal region for filter sizes less than $20 \mu\text{m}$ and pH values close to 4. A better visualization of the mercury reduction pattern as a function of dosage and pH is presented in Figure 8. This figure presents the interpolation surface of the experimental results as a function of dosage and pH (SAS/Graph Software, 1990). The optimum removal range of mercury is achieved for pH values close to 4 and a ferric sulfate coagulant dosage greater than 2.5 g/L . Within this optimum range the mercury removal efficiency is greater than 98%. The residual mercury concentration was 11.42 ng/mL after passing through an $11 \mu\text{m}$ filter.

TABLE VI**SUPERNATANT AND SOLUBLE TOTAL MERCURY CONCENTRATION
AT DIFFERENT RPM**

RPM	Force (G)	Supernatant Conc. (ng/mL)	Supernatant Removal Efficiency (%)	Soluble Conc. (ng/mL)
Sample 1				
3,000	1,534.2	603.0	90.22	238.0
2,000	681.9	649.0	89.47	245.0
1,000	170.5	719.0	88.34	243.0
0	1	6,165.0	0	260.0
Sample 2				
3,000	1,534.2	233.7	76.75	102.0
2,000	681.9	262.4	73.90	102.2
1,000	170.5	277.8	72.37	102.2
0	1	1005.0	0	102.5
Sample 3				
3,000	1,534.2	198.1	76.86	82.9
2,000	681.9	229.8	73.16	83.9
1,000	170.5	258.0	69.85	85.9
0	1	855.95	0	88.5
Sample 4				
3,000	1,534.2	179.2	75.69	76.3
2,000	681.9	198.5	73.07	76.5
1,000	170.5	252.7	65.72	78.1
0	1	737.1	0	82.7
Sample 5				
3,000	1,534.2	124.9	72.06	87.3
2,000	681.9	133.2	70.20	88.0
1,000	170.5	150.7	66.29	90.8
0	1	447.0	0	92.8
Sample 6				
3,000	1,534.2	80.0	69.81	30.0
2,000	681.9	99.0	62.64	31.0
1,000	170.5	116.0	56.23	32.0
0	1	265.0	0	32.0

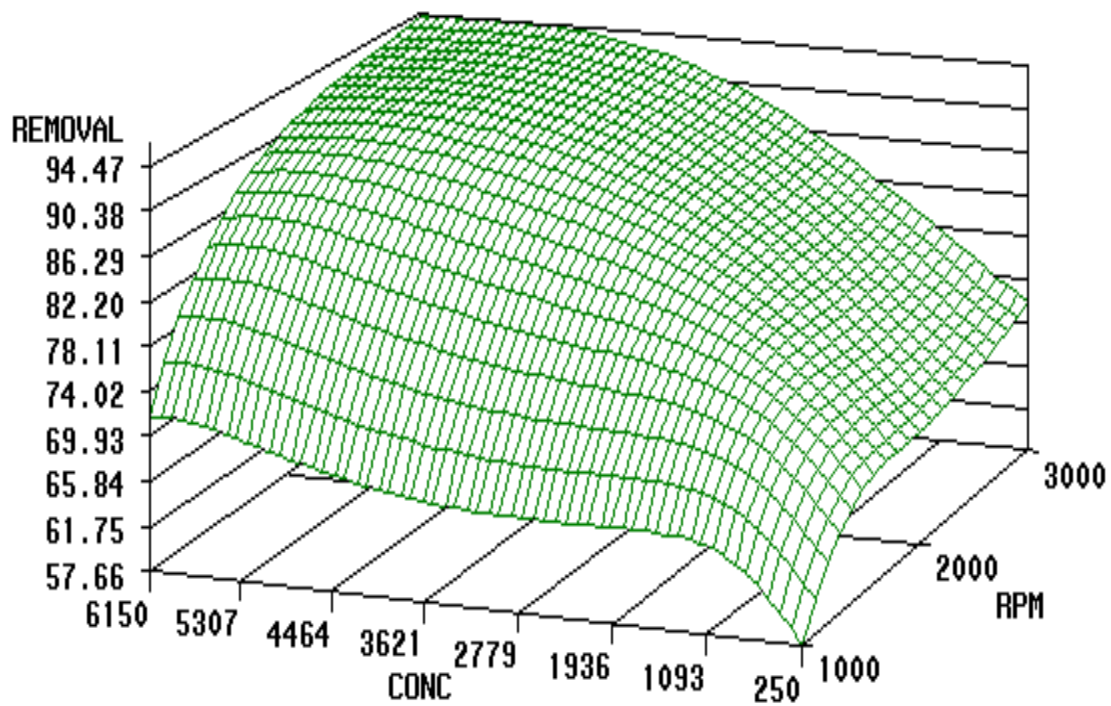
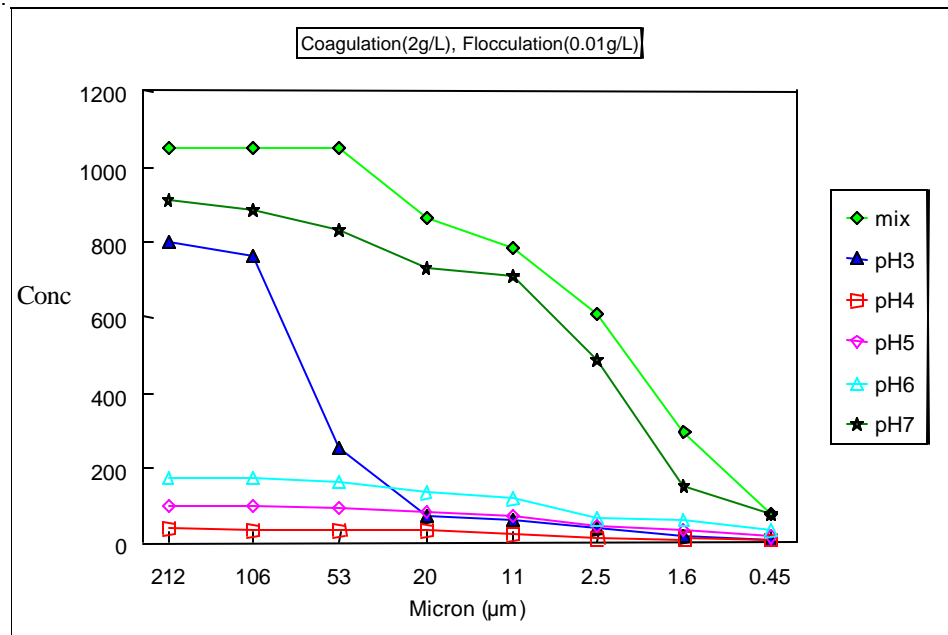


Figure 6. Removal efficiency as a function of initial supernatant DWW Hg concentration and rpm



Note: Initial concentration = 1,051 ng/mL

Figure 7. Remaining mercury concentration (ng/mL) in filtrate as a function of pH and filter size (µm)

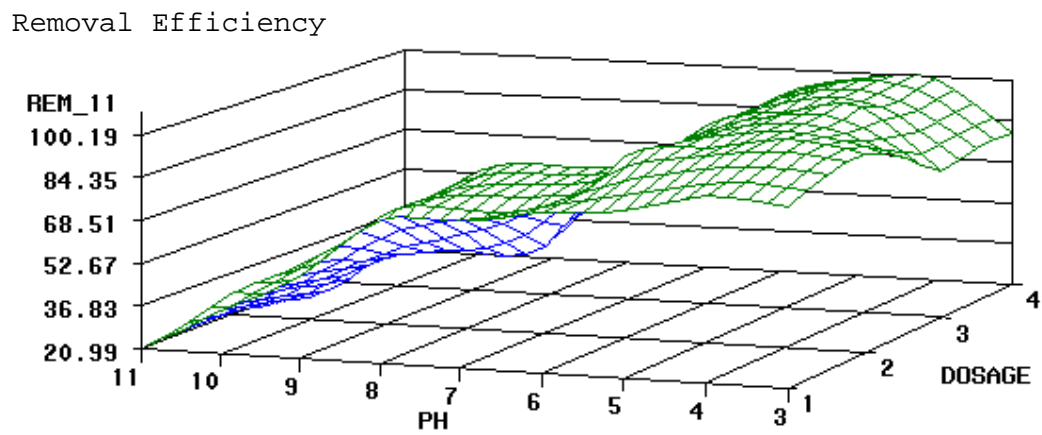
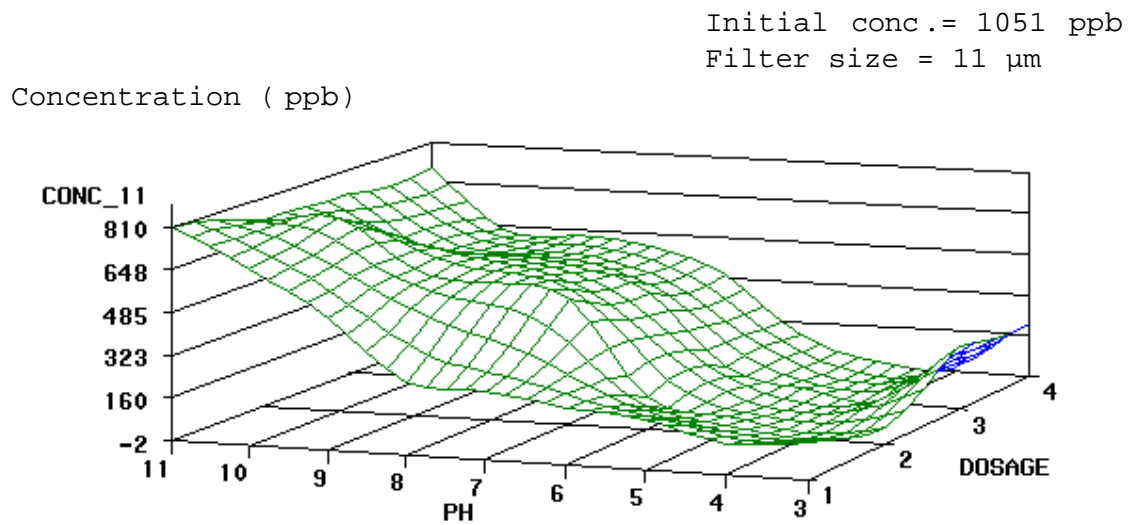
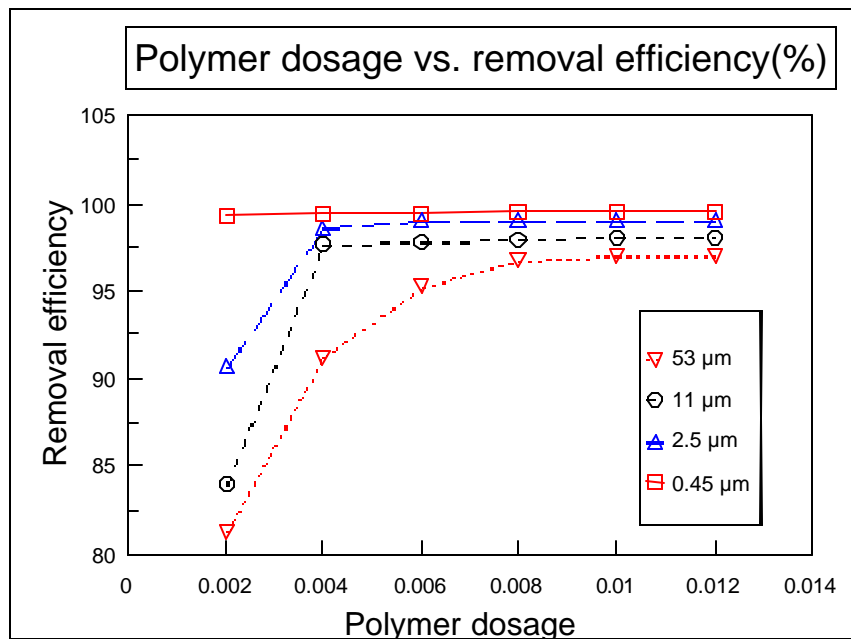


Figure 8. Spline interpolation surface for mercury concentration and removal efficiency as a function of pH and coagulant dosage

TABLE VII**TREATMENT OF COMPOSITE SUPERNATANT SAMPLE:
OPTIMIZATION OF FLOCCULANT DOSAGE**

Residual Mercury Concentration (ng/mL)				
Polymer Dosage (g/L)	53 μm Filter	11 μm Filter	2.5 μm Filter	0.45 μm Filter
0.002	197.16	168.70	98.63	7.47
0.004	92.27	23.94	14.94	6.81
0.006	39.32	23.50	10.20	6.37
0.008	34.64	21.09	10.10	5.05
0.010	31.53	20.21	10.10	4.83
0.012	31.51	19.99	9.98	4.83
Polymer Dosage (g/L)	Removal Efficiency (%) @ 53 μm	Removal Efficiency (%) @ 11 μm	Removal Efficiency (%) @ 2.5 μm	Removal Efficiency (%) @ 0.45 μm
0.002	81.24	83.95	90.62	99.29
0.004	91.22	97.72	98.58	99.35
0.006	95.31	97.76	99.03	99.39
0.008	96.70	97.99	99.04	99.52
0.010	97.00	98.08	99.04	99.54
0.012	97.00	98.10	99.05	99.54



Note: Initial concentration = 1,051 ng/mL.

Figure 9. Removal efficiency as a function of polymer dosage

A similar approach was applied for two more SUP composite samples with initial mercury concentrations of 589.7 ng/mL and 878.9 ng/mL. For both cases similar mercury removal patterns were observed with optimum removal ranges defined at:

- 99% mercury removal efficiency (residual mercury of 22.93 ng/mL through an 11 µm filter) for dosage above 3 g/L and pH close to 3.8 (SUP composite with initial concentration of 587.9 ng/mL).
- 96% mercury removal efficiency (residual mercury of 9.7 ng/mL through an 11 µm filter) for dosage above 3 g/L and pH close to 3.5 (SUP composite with initial concentration of 878.9 ng/mL).

The above residual mercury concentrations indicate that the effluent from this treatment approach is suitable to be discharged in most cases. Further reductions are achieved by reducing the filter size to a 0.45 µm filter.

Flocculant Dosage

After the coagulation process, the effect of the flocculant concentration on the removal of mercury was investigated. Flocculant material was added to the treated composite SUP sample with an initial mercury concentration of 1,051 ng/mL. Anionic water-soluble acrylamide polymer (0.1% w/v) was selected as the flocculant in this study. Polymer dosages from 0.002 g/L to 0.012 g/L were tested based on the optimum pH range established by the response surface analysis. The optimization results are presented in Table VII and Figure 9. The results indicate that maximum mercury removal is achieved for a polymer dose higher than 0.006 g/L. Similar results were obtained for the other two composite SUP samples (i.e. initial concentrations of 589.7 ng/mL and 878.9 ng/mL).

Response Surface Analysis of the Composite DWW Supernatant Samples

The results of mercury removal in this study were further analyzed by estimating the response surface of the three composite SUP samples as a function of pH and dosage (filter size of 11 microns). Such an analysis yields a response surface with the following overall structure:

$$Z = A + B * X + C * Y + D * X^2 + E * Y^2 + F * X * Y$$

where:

- Z = Mercury removal efficiency, %
- X = pH levels
- Y = Coagulant dosage
- XY = Interaction term (pH and Coagulant dosage)

The response surface analysis of the combined removal data was used to identify an "overall" removal pattern for the SUP of the DWW and identify the operating conditions that can yield a "maximum" removal. The regression diagnostic results from the response surface analysis are presented in Table VIII (Myers, 1971). The regression diagnostic statistics indicate a well-established removal pattern, which can be described by a response surface model with linear and quadratic terms (see partial F-test and F-test for overall [total] regression results). The t-test in this model indicates that pH may be the most critical parameter, whereas the interaction term can be ignored. Canonical analysis of the results yield negative Eigenvalues (i.e. -0.81 and -34.75). This implies the existence of a maximum stationary point. Although these results are based on three composite SUP samples, the response surface analysis of the combined mercury removal data indicated a consistent pattern which yielded a theoretical maximum removal of 94.7% at a pH value of 5.7 and a ferric sulfate coagulant dosage of 6.98 g/L (Figure 10). This finding signifies the potential use of this procedure for removing approximately 95% of the mercury content of the SUP with a recommended operational range of pH close to 5, a coagulant dosage above 3, and a polymer dose higher than 0.006 g/L.

Four random samples were selected and treated at the theoretical maximum removal stationary point (i.e. pH = 5.7 and coagulant dosage of 6.98 g/L). Table IX present the results for these four samples. As seen from Table IX, the removal efficiencies are 95.26%, 96.11%, 98.06%, and 99.26%, respectively. These results confirm the optimum range, which has been theoretically identified.

TABLE VIII

RESPONSE SURFACT ANALYSIS RESULTS

Parameters	Estimates	t-test	Prob.	Partial F-Ratio Test (Prob.)
A	8.2386	0.390	0.6994	2.591 (0.0917)
B	24.5354	4.834	0.0000	
C	4.7361	0.384	0.7035	16.017 (0.0000)
D	-2.1717	-5.657	0.0000	
E	0.0417	0.054	0.9577	
F	-0.3606	-0.161	0.8735	0.003 (0.9577)
$R^2 = 0.554$, F-value = 27.16 [total regression], Prob. =0.001				

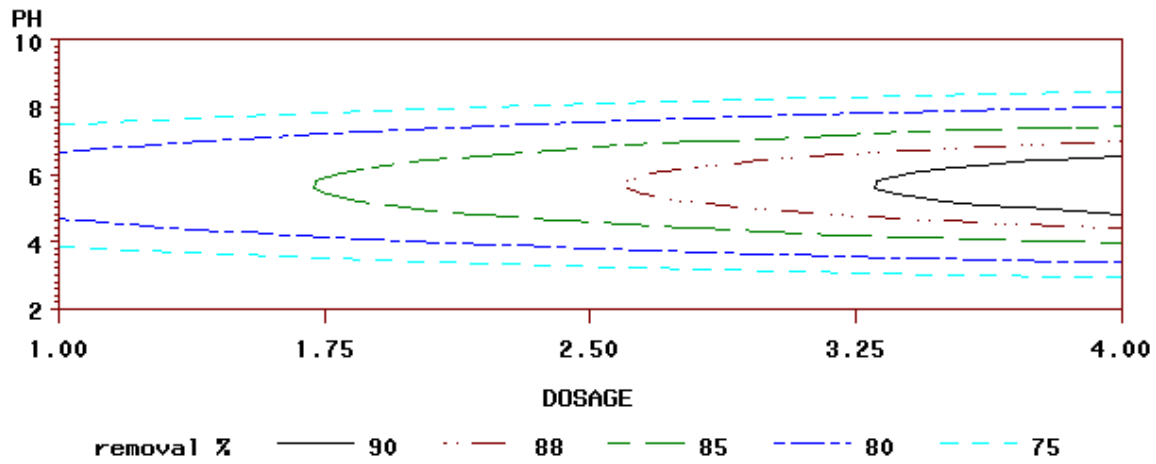
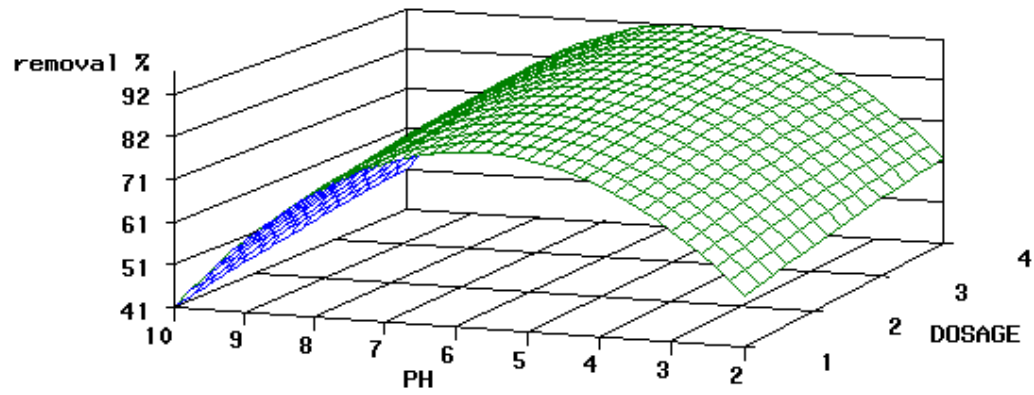


Figure 10. Response surface for mercury concentration and removal efficiency as a function of pH and coagulant dosage

TABLE IX**STATIONARY POINT TREATMENT RESULTS**

Sample	A	B	C	D
Volume (mL)	630	800	460	960
Surface removal	4	2	3	3
Surface placement	4	8	4	7
Amalgam caps used	4	8	3	6
Supernatant conc. (ng/mL)	581.98	304.56	1436.51	729.13
Solid waste (mg)	407	1016	387	1522
Settleable waste (mg)	510.1	342.0	201.7	435.2
After treatment conc. (ng/mL)	27.58	11.85	27.87	5.42
Treatment efficiency (%)	95.26	96.11	98.06	99.26
Cumulative removal efficiency (%) ^a	99.9981	99.9993	99.9978	99.9997
Cumulative removal efficiency (%) ^b	99.9966	99.9972	99.9937	99.9988

Notes:

a: including the solid waste portion.

b: not including the solid waste portion.

Units are in mg or mL per day per dental chair unless other specified.

Summary of Alternative Treatment Procedures for the DWW Stream

The lack of pertinent regulations implies that for the majority of dental clinics, the DWW is likely to be discharged into the sewerage system. In this context, DWW is the heterogeneous liquid suspension generated during various dental operations. The discharge of this waste has the potential to increase the mercury load on local POTW's. In addition, mercury will eventually enter the environment through one of the known mercury contamination pathways (i.e., direct discharge into the waterways as part of the effluent, mercury release into the atmosphere during waste water sludge incineration and deposition, etc.). For this reason the implementation of effective treatment procedures is essential.

Proper treatment of the DWW implies removal/recovery of the particles containing mercury and silver and proper recycling/reuse of this recovered waste material. The potential for proper treatment of this waste stream is further enhanced due to the silver content of the DWW. One of the objectives of this project was to assess effective treatment procedures in terms of mercury removal.

Settling under quiescent conditions for a 24-hr period has the potential to remove more than 99% of the mercury content of the DWW. This simple and cost effective procedure has the potential to provide the majority of mercury reduction by weight. Regardless of this significant reduction, the residual wastewater is likely to contain elevated levels of mercury (i.e. SUP and SOL portion). For this reason emphasis has been given to this portion of the DWW.

Centrifugation and filtration has the potential to remove more than 80% of the mercury content of the SUP and SOL portion of the waste. The initial content of mercury in the waste (see Figure 6), and clogged filters are some limiting factors to this procedure. The coagulation-flocculation filtration approach seems to provide the most effective procedure to remove more than 90% percent of the mercury content of this waste. Under optimum conditions this procedure has the potential to achieve over 99% mercury removal. On a cumulative basis the overall removal potential of a settling/coagulation- flocculation/filtration treatment procedure for DWW is greater than 99.9%.

CONCLUSIONS AND RECOMMENDATIONS

The results from this study illustrate that the DW stream has a relatively high concentration of mercury. The mercury concentration is likely to be found in two distinct components of the waste. The first component consists of the SW material retained on the in-line vacuum trap filter that has a mesh size of approximately 700 μm . The second component is the DWW which passes through the in-line vacuum trap filter. This heterogeneous component contains the particulate by-products generated during dental operations. The DWW component can be further subdivided into three fractions: the SET, the SUP, and the SOL fraction. The main objective of this project was to characterize this waste stream by quantifying the generation rates of mercury and silver in its various components and fractions. This objective was accomplished by collecting randomly more than 90 DW samples from various clinics and quantifying the mercury and silver content of its various components and fractions.

The SW material retained on the in-line vacuum trap filter has the potential to generate 799 mg of mercury per day per dental chair and 533 mg of silver per day per dental chair (median estimates for both generation rates). The SET fraction of the DWW has the potential to generate 497.9 mg of mercury per day per dental chair and 300 mg of silver per day per dental chair (median estimates for both generation rates). The SUP and SOL fraction of the waste contributes approximately 0.5 mg of mercury per day per dental chair. Thus on a conservative median basis, the dental waste stream has the potential to generate as much as 1,297 mg of mercury and 833 mg of silver per day per dental chair. The highly toxic (mercury) and recyclable (silver) composition of this waste signifies the need to develop effective removal/recovery/reuse procedures. A first step for achieving this objective is to develop predictive models for estimating the total amount of recoverable materials. This objective was accomplished by developing regression models for the amount of mercury and silver generated from the dental waste retained in the in-line vacuum trap filter (SW), as well as for the amount of mercury and silver generated from the SET portion of the DWW. The independent variables in these models were easy to quantify based on the dry weights of the corresponding waste materials.

Unregulated DWW discharges into the sewerage system have the potential to increase the mercury load on local POTW's, as well as to the surrounding environment. For this reason, the other major objective of this project was to assess basic and cost effective removal procedures for DWW mercury and silver removal. The present study found that settling under quiescent conditions for a 24-hr period has the potential to remove greater than 99% of the total mercury content of the DWW. This operational, simple and relatively cost-effective procedure is recommended for providing the majority of DWW mercury reduction by weight.

For many POTW's, treatment by settling alone will not suffice in reducing the mercury levels of the residual wastewater to acceptable levels for discharge in to the sewer system. The emphasis is to further reduce the mercury content of the residual DWW. Treatment by centrifugation and filtration was assessed on a number of residual (SUP) waste samples. Results of this study indicate that this combined treatment approach has the potential to remove greater than 80% of the mercury content of the residual DWW, and that the limiting factors for this

treatment procedure are the initial content of mercury in the waste, as well as filter clogging problems. The coagulation-flocculation/filtration approach appears to provide the most effective treatment procedure for removing greater than 95% of the mercury content of this residual waste. Optimization of this procedure has the potential to yield greater than 99% mercury removal. On a cumulative base, the present study found that the overall removal potential of a settling/coagulation-flocculation/filtration treatment approach for the DWW is likely to be close to 99.9%.

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