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ORIGINAL ARTICLE

Evaluation of Metal Concentration (Hg, Zn, Cu, Co, Sn, Ag, Cr and Ni) in Influent & Effluent water of Dental Clinics' units

Mohammadreza Malekipour Esfahani¹, Farzaneh Shirani^{*2}, Maryam Ahmadi^{**3}, Shima Ghaderi⁴

¹Department of Operative Dentistry, School of Dentistry, Isfahan (Khorasgan) Branch, Islamic Azad University, Isfahan, Iran

²Dental Research Center, Dental Research Institute, Department of Operative Dentistry, School of Dentistry, Isfahan University of Medical Sciences, Isfahan, Iran 3 Post Graduate Student, Department of Paediatric Dentistry, Dental Students' Research Committee, School of

Dentistry, Isfahan University of Medical Sciences, Isfahan, Iran

⁴General dentist (DDS), School of dentistry, Isfahan (Khorasgan) Branch, Islamic Azad University, Isfahan, Iran

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KEYWORDS Atomic absorption spectrophotometry; Dental amalgam; Dental wastewater; Heavy metals; Water pollution **ABSTRACT:** Many contaminants can enter the environment via dentistry. Some of the materials including heavy metals may present some problems to the environment. Amalgam waste in dental clinics is the main source of mercury pollution in the environment. Apart from mercury, other amalgam constituents such as Ag, Sn, Co, Cu, and Zn in dental clinics' wastewater have just been reported in a few previous kinds of literature. This study aimed to measure the concentrations of mercury, cobalt, zinc, copper, tin, silver, chromium, and nickel in the influent and effluent of dental units of some dental clinics. Samples were collected over 6-month period from 5 dental clinics and three samples were collected from each clinic at the end of the working day, within a week as the effluent sample. Metal concentration was also detected in the influent of the dental units and samples were analysed for metals using the atomic absorption spectrophotometry (AAS) technique for statistical analysis. Data were analysed with Wilcoxon and Kruskal – Wallis tests within SPSS 18 software. The concentration of all the metals in influent water was at the level of the national standard in all samples. In comparing influent and effluent values, the P-values for Hg, Zn, Cu, and Sn (0.001) , Cu (0.003) , Ag (0.028) , Cr (0.007) , and Ni (0.016) as shown significant differences between influent and effluent values for all the sample. Based on the obtained findings from the study, wastewater has an undesirable level in terms of heavy metals. Thus, dental clinic wastewater might be considered hazardous waste that should be properly treated before it discharges into the environment.

INTRODUCTION

Heavy metals have always been in the natural environment at low concentrations. However, as a result of pollution from human activities, increase their concentrations and thus after getting into the human food chain, have an acute and chronic toxic effect on the body [1-2]. Heavy metals are not metabolized in the body; this

is one of the most fundamental issues [3-6]. They are deposited and accumulated in tissues such as fatty tissues, muscles, bones, and joints, and would several diseases in the body [6-9]. All around the world, the use of municipal and industrial wastewater in the irrigation of agricultural areas has become more common. The

*Corresponding author[: f_shirani@dnt.mui.ac.ir;](mailto:f_shirani@dnt.mui.ac.ir) ahmadimaryam1389@yahoo.com (F. Shirani; M. Ahmadi) DOI: 10.22034/jchr.2022.1959189.1555

main problem in the use of sewage for irrigation is the presence of heavy metals in wastewater, causing accumulation in the soil, and eventually absorbed by the plant [4-7]. Discharge of wastewater must be based on some standards that can be expressed as the maximum concentration of contaminants [10-14]. Compliance with these under the Environmental Protection Agency (EPA) has been required [8, 15-17]. Discharges of wastewater from dental clinics as an important part of urban wastewater is containing unacceptable amounts of metal such as mercury that must be treated before being discharged to the environment as well [15-25]. Amalgam is the most common dental restorative material that has been used for several decades. Amalgam contains about 43%-50.5% mercury is mixed with a powder of various metals consisting mainly of silver, tin, copper, indium, and zinc [10, 25-36]. Several studies have shown that exposure to these metals can cause defects in the internal organs and affect their function [19, 37-44]. Because of the importance of hygiene in heavy metals, it is essential to study the concentration of metals in the physical and biological environments and must be emphasized the way of absorption by humans as well as determine the incidence and prevalence of diseases associated with heavy metals [45-51]. All the previous research has studied just the risk of mercury in water, but evaluation of other metals used in dentistry could be important [51- 58]. This study aimed to evaluate the concentration of mercury, cobalt, zinc, copper, tin, silver, chrome, and nickel in the influent and effluent of dental units in Isfahan Schools of Dentistry and Isfahan dental clinics, to determine the values of these metals, compare with standard values and assess the effectiveness of dental treatment to change the metal concentration of effluent water.

MATERIALS AND METHODS

In this study, the concentration of mercury, cobalt, zinc, copper, tin, silver, chrome, and nickel in influent and effluent water of dental unit has been analyzed. This study is an experimental study was conducted in three dental clinics in Isfahan city and two dental schools, (the Islamic Azad University of Isfahan and Isfahan Medical Sciences and Research) in 2016-2018. Ethical clearance was not necessary because this was not a human study.

Samples were collected with three repetitions in every of 5 dental clinics (n=15) in the interval 6 months in the sampling process. Effluent and influent samples were collected at the same time. The wastewater of these dental clinics is discharged directly into the city sewage system with no wastewater treatment. Therefore, comparing these values with data obtained from the allowable amounts of these metals in sewage is the goal. For each element, the certified reference material (CRM) standard solution with a concentration of 1000 mg l^{-1} as a standard solution for atomic absorption spectrometry (AAS) was prepared. Nitric acid solution 1%v/v was used to dilute and minimize the volume of each standard solution. To remove metal contamination, before sampling, two-liter containers including suction tanks for at least 12 hours were filled with 5% nitric acid, and after that washed with tap water and then with distilled water. Before each work shift, acid-washed tanks were replaced at the end of the work shift, and all effluent water was maintained in 10-litre containers. After sampling and before maintenance, the samples were filtrated immediately using filter paper. Immediately after the sampling, the pH of each sample was measured using a pH meter and the samples were kept by ISO -9886 ISIRI. Measuring the metals in input and output samples was made by using AAS using a Perkin Elmer Analyst800 model. The total mercury was measured by cold vapor atomic absorption (CV-AAS) using the standard method by ISIRI No. 17610. Cobalt, chrome, and tin were measured by graphite furnace, using the standard method ASTM No. D: 3558-08, INSO No. 19592 and ASTM standard No. D: 3919, respectively. Copper, zinc, and nickel were measured by the flame method using the standard method ASTM standard no. D: 1688-07, ASTM standard No. D: 1691-02 and ISIRI standard No.18201, respectively. Silver was measured by both the flame method and graphite furnace by using the standard method ASTM No. D3866-07. Calibration was done by a control solution and 3 to 5 standard solutions with a parallel distance of proper concentration range. Finally, T-test, Kruskal-Wallis, and the Wilcoxon test were done to analyze the data.

RESULTS AND DISCUSSION

Due to limitations in the laboratory measurement for nickel and cobalt measuring and trace amounts of this metal in the samples, all influent values were almost identical. Due to the non-homogeneity of data variance, to compare the difference between the studied Clinics, we use the nonparametric Kruskal-Wallis instead of the ANOVA test. The test shows that there are no significant differences between none of all dental clinics in terms of desired metals. Mercury (P-value= 0.639), cobalt (P-

value= 0.313), zinc (P-value = 0.076), copper (P-value= 0.122), Tin (P-value= 0.001), chrome (P-value= 0.007), nickel (P-value = 0.016), and silver (P-value= 0.028). Using the T-test analysis; by ISO-1053, in influent water, the averages of copper, zinc, mercury, and chrome were compared to 1 - 2 mg 1^{-1} , 3 mg 1^{-1} , 6 mg 1^{-1} , and 50 mg 1^{-1} , respectively. Table 1 indicated the total average and standard deviation of influent and effluent data by type of metals.

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Metal type Data		Сu $(mg l-1)$	Zn $(mg l-1)$	Co. $(\mu g I^{\mathsf{T}})$	Hg $(\mu g I^{\mathsf{T}})$	Ni $(mg l-1)$	Cr $(\mu g I')$	Ag $(\mu g I')$	Sn $(\mu g I^I)$
Influent data	Total average	0.09	1.33	2.14	1.27	0.1	22.77	81.26	122.93
	SD	0.02	1.71	0.54	1.01	0.049	17.225	83.995	76.922
Effluent data	Total average	1.73	32.90	11.21	223.62	0.30	44.84	231.85	3370.36
	SD	1.23	44.71	15.33	308.51	0.423	39.197	227.68	4357.24

Table1. Total average and standard deviation of influent and effluent data by type of metals.

The presence of different and higher than the standard concentrations of heavy metals is one of the major health problems in drinking water supplies and sewage systems that are re-used. Due to the chemical stability and strength accumulation of heavy metals in the bodies of living organs, environmental pollution is a health problem in the global environment. High levels of these metals cause morphological abnormalities and genetic effects on humans [51-57]. In dentistry, a variety of materials and equipment such as amalgam which contain silver, mercury, and other metals are used and can create challenges for the environment. Metals such as mercury, and silver at any concentration, although as a small amount can be detrimental and have long-term adverse effects [58-64]. As a dentist, we should know that some substances such as heavy metals, which are used to provide oral health services, can create challenges for the global environment. By knowing this it is possible to do voluntary actions to reduce the production of waste and the potential environmental impact of our actions [58- 64]. This data indicated that the difference between allowable values and obtained amounts from this study was significantly lower (P-value < 0.001, P-value = 0.003, P-value<0.001, P-value<0.001, respectively). However, the average concentration of nickel $(0.07 \text{ mg } l^{\text{-}1})$ was significantly higher than the standard value (P-value<

and the WHO, the allowable concentration of cobalt, silver, and tin in drinking water is not defined, so that could not be compared with it. Metals of influent and effluent values were compared using nonparametric Wilcoxon and the differences between result was significant (P-value<0.05). In effluent data, there is no standard value for wastewater in Iran and WHO, so this is not possible to compare. In this study, the average amount of copper, zinc, and Chrome concentration in the influent water was less than the maximum allowable concentration of these elements in drinking by ISO-1053 standard and America's Environmental Protection Agency and WHO [23]. Thus, one can say that copper, zinc, and Chrome values in drinking water supplies are trusted sources. The average concentration of mercury in the input water was $1.27mg$ 1^{-1} . The maximum allowable concentration of this element in drinking water in standard 1053 of Iran is $6\mu g I^{-1}$ and based on the WHO and EPA drinking water standard is $1 \text{ mg } 1^{-1}$. Therefore, the average mercury value is more than the international standards, but the Iranian standard seems to be reviewed. Also, total average of Nickel was more than the maximum allowable concentration. The total average concentrations of Tin, cobalt, and silver in the influent water during this investigation were 122.93 mg 1^{-1} , 2.14

0.042). Given that in drinking water standards of Iran

 μ g l⁻¹, and 81.26 μ g l⁻¹, respectively as shown in Table 1. Table 1 shows the average effluent data by metal type, and it is clear that there is a difference between the influent and effluent data for all metals. The allowable concentration of these metals in drinking water in Iranian and WHO drinking water standards are not defined; therefore, one cannot compare these values [17, 62-71]. Shraim et al. [9] studied those discharges from dental clinics containing dangerous metals, especially Zn, Cu, Mn, Mg, Ba, Sn, and Hg which most of which are constituent elements of dental amalgam. The obtained results showed that the concentration of metals in influent water was very low, except magnesium and strontium concentration [67-70]. Similarly, the number of studied metals was less than standard except for Ni and mercury. Badrian et al. [26] reviewed the contamination of drinking water by heavy toxic and nontoxic metals in areas 15-11 of Tehran by using ABS. They concluded that the concentration of all metals was in the range of national standards, and in comparison, with international standards, only the concentration of arsenic in all areas was higher [26, 32-46]. Unfortunately, the national or international standards for sewage of Dental clinics are undefined and thus it is impossible to compare the values. Interestingly, all the articles studied the metal pollution of wastewater of Dental clinics have mostly focused on mercury but other metals used in dentistry have not been studied [46-57]. Only a similar study has been done and so the comparison is limited. Researchers considered based on 330 units of 155 dental clinics in Medina city and an average concentration for tin, chromium, silver, and nickel was 3,000 mg 1^{-1} , 450 mg 1^{-1} , 490 mg 1^{-1} and 0.38 $mg l⁻¹$, respectively [9]. These obtained values for tin and nickel are almost the same obtained results in our study. However, the obtained value for chromium and silver are higher than our study. The average values obtained from our study for Hg, Zn, Cu, and cobalt are less. The obtained results of our study are similar to results reported in the literature of Shraim et al., and Drummond et al. [27-36] which has been shown that unacceptable mercury is in wastewater in dental clinics. Stone et al. [29] consider the total amount of mercury in wastewater 3 clinics thoughout 18 months study. Batchu et al. [30] have shown that the release of mercury from dental

clinics to the environment could be significantly reduced by using amalgam separators, suction filters, and proper management, collection, and storage of mercurycontaining waste [30]. Adegbembo et al. [31] have shown that dental clinics are responsible for the significant amounts of mercury (10-70%) that are emitted daily to the environment by the sewage treatment plan. In this study, only 22% of dentists used amalgam separators. In this way, the dental share of mercury entering the sewage system was 27% and as all dentists used amalgam separators, the dental share of mercury entering the sewage system dropped to about 0.54 % [31].

CONCLUSIONS

The Metal concentration of influent water was less than standard values, except for Ni and Hg. For effluent data, no standard for sewage data to compare, but according to the analysis, it is clear that there is a difference between the influent and effluent data for all metals. Therefore, it could be concluded that dental treatments release a significant number of metals and must be properly treated before discharging into the environment. Dentist must be concerned about the environment as health care providers in addition to concerns about promoting human health. A rigid approach in our profession can lead to prosperity in an age where environmental concerns are increasing and environmentally-friendly regulations are in place. This is not only the dentist's legal obligation to provide dental services for the benefit of the community and with the least damage to the environment, but also it is a dentist's moral commitment. Thus, more studies are recommended to find out the link between dental treatments and environmental pollution.

Contribution

All authors have participated in (a) conception and design, or analysis and interpretation of the data; (b) drafting the article or revising it critically for important intellectual content; and (c) approval of the final version.

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Conflict of interests

None.

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