

Levels of Cadmium, Lead and Zinc in Urine of Randomly Selected Smokers and Non-Smokers Residents of Abeokuta City, Nigeria

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Abstract: Urine samples of 200 male volunteers comprising 100 smokers and 100 non-smokers were analysed for levels of heavy metals using Perkin-Elmer atomic Absorption spectrophotometer model 4600. The levels of Cadmium (Cd), lead (Pb) and Zinc (Zn) in urine samples of non-smokers ranged from 0.34-0.65, 0.037-0.25 and 0.235-0.664 $\mu\text{g mL}^{-1}$, respectively while the corresponding range for smokers were 0.075-0.341, 0.076-0.297 and 0.488-1.976 $\mu\text{g mL}^{-1}$. Most smokers respondents had metal concentrations that exceeded the normal urinary levels for each metal. For the non-smokers in age groups 10-19, 20-29, 30-39 and 40-49, the average urinary excretion values of 0.046, 0.050, 0.054 and 0.051 $\mu\text{g Cd mL}^{-1}$; 0.152, 0.101, 0.094 and 0.138 $\mu\text{g Pb mL}^{-1}$; 0.433, 0.515, 0.551 and 0.561 $\mu\text{g Zn mL}^{-1}$ were respectively obtained, while for the smokers in age group 10-19, 20-29, 30-39 and 40-49, the average urinary excretion values of 0.110, 0.207, 0.216 and 0.330 $\mu\text{g Cd mL}^{-1}$; 0.145, 0.183, 0.203 and 0.182 $\mu\text{g Pb mL}^{-1}$; 0.563, 1.145, 1.089 and 1.718 $\mu\text{g Zn mL}^{-1}$ were obtained. Regression analysis show that a significant correlation ($r > 0.9$) exist between metal concentration (Cd and Zn) and duration of smoking period.

Key words: Cigarette smoking, toxic metals, cadmium, lead, zinc, environmental pollution

INTRODUCTION

Metals get into biological fluids from various sources apart from the direct consumption of food items that contains such metals. These sources include those of partially disintegrated particles of the containers in which food are stored, exposure to fine particles of metal waste in the metals extraction industries through ingestion (drinking) and from inhalation (tobacco smoke).

It has been shown that Environmental Tobacco Smoke (ETS) is a complex mixture of chemicals found in air as a specific result of smoking (side stream smoke that is released from the lit end of the cigarette and exhaled main stream smoke that is exhaled by the smoker after drawing on the cigarette) (Richard and Proctor, 1990). It has also been established that smoking is an important factor in the production of carcinoma of the lungs (Shaham *et al.*, 1996; WHO, 1990) and as such tobacco smoke can therefore lead to cancer (Daube *et al.*, 1997.)

The control of exposure to toxic metals has become an important part of most studies concerned with environmental pollution and environmental health hazards, although there does not appear to be a simple relationship between exposure to toxic metals and their unitary excretion (Nortrer *et al.*, 1997)

it has been reported that levels of these metals in urine are indicators of human exposure (Buchancova *et al.*, 1994).

The danger of smoking has long been realized in the developed countries with the promulgation of appropriate laws in 1962 (Farrly and Pybus, 1969) and more recently in Nigeria with the promulgation of Decree 28 of 1990 (Ajayi and Adekunle, 1991).

The presence of these metals in urine is regarded as a reliable index to the extent of recent metal intake and therefore determination of these metals in the diagnosis of incipient poisoning and in monitoring the working. This study discusses therefore the extent to which a relationship exist between smoking habit and the concentrations of Cd, Pb and Zn in urine.

MATERIALS AND METHODS

Twenty four hours urine samples were collected in plastic bottles from (200) male volunteers comprising (100) smokers and (100) non-smokers. The sample collection cut across different age groups and profession.

The plastic bottles had earlier been washed with detergent solution, rinsed with distilled water and 0.1 M HCl.

Few drops of 0.1M sodium azide was then added to the bottles before distribution to the sample donors. After collection of samples they were stored in the refrigerator at -18°C prior to analysis.

Fifty milliliter of the urine sample was digested by the method of (Hernandez *et al.*, 1989) and concentration of the metal determined with a Perkin-Elmer Spectrophotometer Model No. 4600.

RESULTS AND DISCUSSION

The results are presented in Table 1-5. Table 1 gives a summary of the biodata of some of the selected smokers (age-group, occupational status, type of cigarette smoked, estimated average number of cigarettes smoked per day and approximate years of smoking) along with the concentration of monitored metals. Table 2 gives a summary of the biodata of some of the selected non-smokers and the concentration of Cd, Pb and Zn in the samples.

Table 3 and 4 show the mean concentration of Cd, Pb and Zn in the urine samples of non-smokers and smokers according to age-group respectively.

Table 5 shows the correlation coefficient between the various biodata parameters and the concentration of Cd, Pb and Zn in the urine samples of smokers.

Trend in biodata of smokers and non-smokers: From Table 1 and 2 it was observed that the occupational status of the residents sampled varied widely from students to different categories of workers (trader, mechanic, carpenter, driver, clerk, painter etc.). However while students constituted about 16% of the smoking population sampled they also constituted a larger percentage of the non-smoking respondents, thus indicating that a smaller proportion of students at the University of agriculture, Abeokuta are involved in smoking. This was further confirmed from the questionnaire administered to the Year II students from which only 15% (120 out of 800) indicated having smoked at one time or the other and to date.

Students also constituted a greater percentage of the non-smokers within the age group 10-19 (60%), 40% for the age group 20-29, 33.3% for the age group 30-39 and 0% for the age group 40-49. This trend appears normal in that as expected the higher the age group, the lesser is the numerical strength of students expected in such age bracket. Similarly, the largest percentage of student smokers was found in the age group 20-29 (20%).

With respect to the type of cigarette smoked, the respondent engaged in smoking various types of cigarettes (Rothmans, Benson and Hedges, St. Moritz). It was also observed that the lowest estimated average

Table 1: Biodata of selected smokers and levels of trace metals (Cd, Pb and Zn) in urine samples

| Sample code | No. of sample | Age group | Occupational status | Years of smoking | Type of cigarette smoked | Estimated average No. of cig./day | Metal ion concentration (ppm) | | |
|-------------|---------------|-----------|---------------------|------------------|--------------------------|-----------------------------------|-------------------------------|-------|-------|
| | | | | | | | Cd | Pb | Zn |
| 1. | 4 | 10-19 | Carpenter | 6 | Rothmans | 3-4 | 0.171 | 0.139 | 0.620 |
| 2. | 4 | 10-19 | Student | 4 | All types | 2-4 | 0.089 | 0.076 | 0.488 |
| 3. | 4 | 10-19 | Bus conductor | 7 | All types | 5-8 | 0.101 | 0.245 | 0.631 |
| 4. | 4 | 10-19 | Unemployed | 5 | Benson, St. | 3-4 | 0.078 | 0.118 | 0.511 |
| Moritz | | | | | | | | | |
| 5. | 4 | 20-29 | Unemployed | 12 | Rothmans | 5-7 | 0.180 | 0.233 | 1.181 |
| 6. | 4 | 20-29 | Air Force Officer | 16 | Rothmans | >10 | 0.300 | 0.230 | 1.611 |
| 7. | 4 | 20-29 | Mechanic | 12 | SM | >10 | 0.255 | 0.297 | 1.282 |
| 8. | 4 | 20-29 | Carpenter | 13 | Ten-ten | 8-10 | 0.227 | 0.223 | 1.342 |
| 9. | 4 | 20-29 | Bricklayer | 14 | Rothmans | 7-9 | 0.241 | 0.189 | 1.233 |
| 12. | 4 | 20-29 | Labourer | 12 | Eric moore | 8-10 | 0.236 | 0.245 | 0.131 |
| 13. | 4 | 20-29 | Bricklayer | 13 | SM | 7-9 | 0.241 | 0.189 | 1.233 |
| 14. | 4 | 20-29 | Clerk | 14 | Benson | 8-10 | 0.262 | 0.213 | 1.355 |
| 15. | 4 | 20-29 | Student | 7 | Rothmans | 3-4 | 0.095 | 0.105 | 0.513 |
| 16. | 4 | 20-29 | Painter | 4 | Rothmans, | 6-8 | 0.075 | 0.113 | 0.656 |
| 555 | | | | | | | | | |
| 17. | 4 | 20-29 | Civil servant | 6 | Rothmans | 5-7 | 0.097 | 0.133 | 0.660 |
| 18. | 4 | 20-29 | Student | 11 | Rothmans, | 7-8 | 0.196 | 0.124 | 1.245 |
| St. Moritz | | | | | | | | | |
| 19. | 4 | 20-29 | Student | 11 | Rothmans, | 4-5 | 0.186 | 0.101 | 1.070 |
| St. Moritz | | | | | | | | | |
| 20. | 4 | 30-39 | Driver | 12 | Target | 5-8 | 0.265 | 0.265 | 1.170 |
| 21. | 4 | 30-39 | Baker | 14 | Benson | 8-10 | 0.301 | 0.211 | 1.586 |
| 22. | 4 | 30-39 | Painter | 8 | Target | 5-7 | 0.091 | 0.133 | 1.511 |
| 23. | 4 | 40-49 | Trader | 18 | Benson | 8-10 | 0.320 | 0.205 | 1.604 |
| 24. | 4 | 40-49 | Welder | 20 | Gold leaf | 8-10 | 0.340 | 0.158 | 1.831 |
| 25. | 4 | 50-59 | Driver | 22 | Benson | 8-10 | 0.302 | 0.124 | 1.976 |

Table 2: Biodata of selected Non-smokers and levels of metals (Cd, Pb and Zn) in urine samples

| Sample code | No. of samples | Age group | Occupational status | Meta Ion concentration (ppm) | | |
|-------------|----------------|-----------|---------------------|------------------------------|-------|-------|
| | | | | Cd | Pb | Zn |
| 26 | 4 | 10-19 | Mechanic | 0.034 | 0.179 | 0.438 |
| 27. | 4 | 10-19 | Student | 0.037 | 0.104 | 0.317 |
| 28. | 4 | 10-19 | Student | 0.054 | 0.112 | 0.586 |
| 29. | 4 | 10-19 | Student | 0.054 | 0.037 | 0.571 |
| 30. | 4 | 10-19 | Student | 0.048 | 0.177 | 0.319 |
| 31. | 4 | 10-19 | Student | 0.043 | 0.173 | 0.599 |
| 32. | 4 | 10-19 | Mechanic | 0.043 | 0.187 | 0.511 |
| 33. | 4 | 10-19 | Painter | 0.045 | 0.194 | 0.243 |
| 34. | 4 | 10-19 | Painter | 0.065 | 0.188 | 0.409 |
| 35. | 4 | 10-19 | Student | 0.038 | 0.168 | 0.341 |
| 36. | 4 | 10-19 | Student | 0.041 | 0.057 | 0.563 |
| 37. | 4 | 20-29 | Petrol attendant | 0.065 | 0.251 | 0.576 |
| 38. | 4 | 20-29 | Trader | 0.050 | 0.038 | 0.660 |
| 39. | 4 | 20-29 | Student | 0.043 | 0.144 | 0.615 |
| 40. | 4 | 20-29 | Mechanic | 0.054 | 0.194 | 0.342 |
| 41. | 4 | 20-29 | Trader | 0.043 | 0.077 | 0.664 |
| 42. | 4 | 20-29 | Tailor | 0.048 | 0.038 | 0.488 |
| 43. | 4 | 20-29 | Student | 0.043 | 0.046 | 0.489 |
| 44. | 4 | 20-29 | Student | 0.054 | 0.123 | 0.235 |
| 45. | 4 | 20-29 | Student | 0.054 | 0.038 | 0.515 |
| 46. | 4 | 30-39 | Student | 0.048 | 0.048 | 0.502 |
| 47. | 4 | 30-39 | Teacher | 0.049 | 0.057 | 0.516 |
| 48. | 4 | 30-39 | Driver | 0.065 | 0.178 | 0.634 |
| 49. | 4 | 40-49 | Baker | 0.048 | 0.110 | 0.500 |
| 50. | 4 | 40-49 | Driver | 0.054 | 0.165 | 0.622 |

Table 3: Mean concentration of Cd, Pb, Zn in urine samples of non-smokers according to age-groups

| Age group (years) | No. of samples | Cd | Pb | Zn |
|-------------------|----------------|--------------|-------------|-------------|
| 10-19 | 40 | 0.046±0.0094 | 0.152±0.05 | 0.433±0.128 |
| 20-29 | 40 | 0.050±0.0075 | 0.101±0.075 | 0.515±0.137 |
| 30-39 | 12 | 0.054±0.0078 | 0.094±0.059 | 0.551±0.059 |
| 40-49 | 8 | 0.051±0.003 | 0.138±0.028 | 0.561±0.061 |

The figures represent the means in µg mL⁻¹±SD

Table 4: Mean concentrations of Cd, Pb and Zn in Urine samples of Smokers according to age-groups

| Age group (years) | No. of samples | Cd | Pb | Zn |
|-------------------|----------------|-------------|-------------|-------------|
| 10-19 | 16 | 0.110±0.36 | 0.145±0.062 | 0.563±0.064 |
| 20-29 | 60 | 0.207±0.072 | 0.183±0.063 | 1.145±0.313 |
| 30-39 | 12 | 0.216±0.090 | 0.203±0.054 | 1.089±0.443 |
| 40-49 | 08 | 0.330±0.01 | 0.182±0.024 | 1.718±114 |
| 50-51 | 4 | 0.302 | 0.124 | 1.976 |

The figures represent the means in µg mL⁻¹±SD

Table 5: Correlation coefficients between duration of smoking, estimated average number of cigarettes smoked per day and concentration of metals in urine of smokers

| | Duration of Smoking | Estimated average No. | Cd | Pb | Zn |
|-----------------------|---------------------|-----------------------|------|------|------|
| Duration of Smoking | - | 0.76 | 0.93 | 0.41 | 0.95 |
| Estimated average No. | 0.76 | - | 0.77 | 0.59 | 0.81 |

number of cigarettes smoked per day was 2-4 with a highest estimated average value of 8-10 per day.

A trend of increasing age of respondent corresponding to increasing years of smoking was expected and this was as observed with the exceptions of respondent in the age group 20-29 who had been on the

smoke for 13, 14 and 17 years. Likewise, a deviation to this trend was also observed for the age group 30-39 with 8 years of smoking experience.

Trends in levels of cadmium, lead and zinc in urine samples

Cadmium (Cd): The concentration of cadmium present in the urine samples of non-smokers ranged from 0.034 to 0.065 µg mL⁻¹ and this is an indication that the Cd content of most non-smoker respondent conformed with the normal urinary concentration of 0.055 µg mL⁻¹ (Shaham *et al.* 1996). However it was observed that three samples had values, which exceeded the normal urinary concentration. These three respondents belonged to different age group of 10-19, 20-29 and 30-39 and had occupational status of Painter, Petrol attendant and Driver respectively. It is indeed likely that the higher levels associated with these groups of respondents may be related to their occupational status (Staessen *et al.*, 1996).

For the smokers the cadmium level in the samples ranged from 0.075-0.340 µg mL⁻¹ and in all cases the concentrations were higher than the urinary concentration of 0.055 µg mL⁻¹. The lowest concentration of 0.075 µg mL⁻¹ was obtained for a painter in the age group 20-29 with 4 years of active smoking. It was similarly observed that generally for smokers, 4 years of smoking experience represented the shortest duration of smoking (range of 4-22 years). The next to the lowest Cd concentration is that of an unemployed youth with 5 years of smoking with 0.078 µg mL⁻¹ (This is followed

by a Cd concentration of 0.089 $\mu\text{g mL}^{-1}$ obtained from a student with 4 years of smoking experience). The highest concentrations of 0.340, 0.320 and 0.320 $\mu\text{g mL}^{-1}$ were obtained from the age groups of 40-49 and 50-59, respectively with 20, 18 and 22 years of smoking experience. In this case it was not necessarily the donor with the longest duration of smoking years that had the highest Cd concentration. (However in all cases an estimated average no. of cigarette of 8-10 per day was recorded for the three respondents). Other high concentrations of Cd observed might suggest a correlation between the years of smoking and concentration of cadmium as shown by the samples 6, 11 and 21 with Cd concentration of 0.300, 0.300 and 0.301 $\mu\text{g mL}^{-1}$, respectively 16, 17 and 14 years of smoking experience.

Lead: The lead content in the urine samples of non-smokers ranged from 0.037-0.251 $\mu\text{g mL}^{-1}$. Of a total of 100 respondents that were non-smokers, only respondent No. 37 had values higher than the normal urinary concentration of 0.2 $\mu\text{g mL}^{-1}$ (Ostapezuck and Valenta 1989). This sample (No. 37) belonged to the age group 20-29 with an occupational status of a petrol attendant and a Pb level of 0.251 $\mu\text{g mL}^{-1}$. Since only this non-smoker had a Pb level exceeding the normal urinary concentration, then it may be inferred that his Pb concentration must have been contributed mainly from occupational exposure, particularly in a country in which premium motor spirit additive is still lead. Biodata information on sample 37 further revealed that as at the time of sampling he had spent about a year at the pumps. In a similar manner occupational exposure may have contributed to the levels of Pb observed for samples 32, 33, 34 and 40 with job descriptions of mechanic, painter, painter and mechanic respectively and a Pb concentration of 0.187, 0.194, 0.188 and 0.194 $\mu\text{g mL}^{-1}$, respectively (Hernandez *et al.*, 1989).

A range of 0.076-0.297 $\mu\text{g mL}^{-1}$ was obtained for the smoking respondents. Of the total samples (25) about half had levels that exceeded the urinary Pb concentration of 0.2 $\mu\text{g mL}^{-1}$ (sample Nos. 3, 5, 6, 7, 8, 11, 12, 14, 20, 21 and 23). The lowest concentration of urinary lead was obtained from a student respondent with 4 years smoking experience. This result may not reflect a positive correlation in itself for concentration of lead and duration of smoking; though this may seem as an isolated case, other lead concentration particularly of those which exceed the normal urinary Pb concentration whom a relationship between job status, years of smoking and

concentration of Pb. Respondents 3, 7, 12 and 20 with Pb levels of 0.245, 0.297, 0.245 and 0.265 $\mu\text{g mL}^{-1}$ and a corresponding occupational status of Bus Conductor, Mechanic, Labourer and Driver had 7, 12, 12 and 12 years of smoking. This may also indicate occupational exposure as a probable contributor to source of Pb in the respondents apart from contribution from tobacco smoke (Hernandez *et al.*, 1989).

Also the highest Pb concentration of 0.297 $\mu\text{g mL}^{-1}$ obtained for a mechanic with an average of 10 cigarettes per day is also indicative of the possibility of a relationship between number of cigarette consumed daily and the eventual urinary Pb concentration.

Zinc: The levels of zinc found in the urine samples of non-smokers ranged from 0.235-0.664 $\mu\text{g mL}^{-1}$ and in all cases below the normal urinary level of 0.67 $\mu\text{g mL}^{-1}$ (Schuhmacher *et al.*, 1994b). No particular trend could be identified with respect to the zinc concentration, though respondent No. 37 conformed with the trend observed for other metals (Cd and Pb) in terms of having a high concentration for Zn (0.576 $\mu\text{g mL}^{-1}$) which had earlier been attributed to occupational status.

Furthermore, respondents 33 and 34 both painters, had varying zinc levels of 0.243 and 0.409 $\mu\text{g mL}^{-1}$ showing variations in Zinc levels and occupational status. However there seems to be a more positive relationship between occupational status and zinc level for trades (respondents 38 and 41) engaged in selling of galvanized iron sheets with a highest zinc concentration of 0.660 and 0.664 $\mu\text{g mL}^{-1}$, respectively. Similarly respondent No. 48 a driver engaged in supplying with galvanized sheet and a high level of zinc (0.634 $\mu\text{g mL}^{-1}$).

For the urine samples collected from smokers, the zinc levels ranged from 0.488 to 1.97 $\mu\text{g mL}^{-1}$ and out of a total of 25 samples analysed, 17 had urinary zinc conc. Higher than the urinary conc. of 0.670 $\mu\text{g mL}^{-1}$.

The lowest zinc concentration was obtained for a respondent that had not only the least years of smoking experience (4 years) but also belonged to the age group of 10-19. The highest level of zinc was found in the respondent belonging to the age group 30-39 years with 22 years of smoking experience indicating a relationship between concentration zinc and duration of smoking. An important observation is that the type of cigarette smoked does not seem to have any relationship whatever with the level of metal concentrated.

Comparison of mean concentration of Cd, Pb and Zn in urine samples.

For the non-smokers, the mean concentration of cadmium 0.046, 0.050, 0.054 and 0.051 $\mu\text{g mL}^{-1}$ which were found for the age group 10-19, 20-29, 30-39 and 40-49, respectively were in agreement with the average urinary excretion value of 0.05 $\mu\text{g mL}^{-1}$ reported by Statesmen *et al.* (1996).

Similarly the mean concentrations of lead and zinc for all the age groups also below the normal urinary excretion value of 0.2 and 0.67 $\mu\text{g mL}^{-1}$, respectively.

For the smokers, the mean concentrations of 0.110, 0.207, 0.206 and 0.330 $\mu\text{g mL}^{-1}$ which were found for age groups 10-19, 20-29, 30-39 and 40-49, respectively were greater than the average normal excretion value of 0.05 $\mu\text{g Cd mL}^{-1}$. Also the average concentration values of 0.145, 0.183, 0.200 and 0.182 $\mu\text{g Pb mL}^{-1}$ found for age groups 10-19, 20-29, 30-39 and 40-49 similarly exceeded the average normal urinary excretion. This trend was also observed for the zinc concentrations for the different age groups. In general for the smoking respondents, there is elevation of metal concentration caused by smoking activity and confirming the report of previous workers that smoking increase the concentration of trace metals in urine (Buchancoval *et al.* 1994; Lin *et al.*, 1995; Schumacher *et al.*, 1994b).

Correlation coefficient analysis: The results obtained from analysis of urine samples donated by smokers were subjected to a simple regression analysis to show if there was any correlation between the concentration of trace metals, duration of smoking and estimated average number of cigarettes consumed per day.

It was observed that in general a positive correlation coefficient was obtained for all the parameters. For duration of smoking and the concentration of Cd and Zn, a regression coefficient of 0.93 and 0.95 were obtained indicating the dependence of these metals on the duration of smoking.

However for the concentration of lead, either for the duration of smoking or the average number of cigarettes per day the regression coefficient ($r = 0.41$, $r = 0.59$) were not significant.

Similarly a significant correlation exist between the estimated average number of cigarettes per day and the concentrations of Cd and Zn, though not as significant as that of the duration of smoking and concentration of Cd, Zn. That correlation exist between the concentration of metals in urine as a function of source (smoking) has been reported (Schumacher *et al.* 1994b).

CONCLUSIONS

Analysis of urine sample of (200) smokers and non-smokers show that in general the levels of concentration of cadmium, zinc and lead in the urine samples of smokers are relatively higher than those values obtained for non-smokers. Within the smoking and non-smoking donors, concentration of metals was also dependent on the occupational status of the respondent.

Regression analysis show a positive correlation between the level of metal concentrated and the length of time that the donor had been involved in smoking.

In conclusion this report shows that smokers are more prone to exposure of heavy metals and that occupational status can elevate the concentration of heavy metals.

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