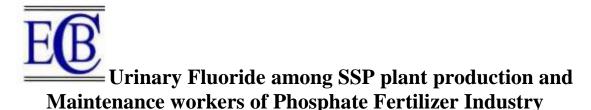
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ABSTRACT

In the phosphate fertilizer industry in Karnataka, India, 24 employees had their urinary fluoride concentrations reported. Using NIOSH technique 7902, gaseous fluoride particles were analyzed. Urinary fluorides were greater in fertilizer industry workers. As anticipated, particulate fluorides and respirable dust concentrations among the fertilizer industry personal monitoring showed a substantial significant positive correlation (r>0.36, p>0.01) between urine fluoride levels among exposed workers. These results suggest that there is a significant risk of fluoride exposure for phosphate fertilizer workers in India. For Indian phosphate fertilizer industries, it is advised that effective regulatory and protective measures be put in place to confirm the Occupational Safety and Health Hazards (OSHA) regulations or the Environmental Health & Safety (EHS) guidelines.

Keywords: Phosphate fertilizer industry, Urinary fluorides, and fluoride exposure.

INTRODUCTION

The implementation of environmental regulations that limit fertilizer use in many rich countries and a considerable increase in fertilizer demand in emerging regions as a result of Asia's extraordinary industrial boom are the key factors behind the change (Glasser, 1999). Fluoride is an inorganic, monatomic fluorine ion. All elements of the environment, including air, soil, rocks, plants, food grains, and water, generally include fluoride (D'Alessandro, 2006). Fluoride is typically ingested by humans and animals through water and plants. The government top priority is to boost farm production by employing chemical fertilizer to meet the demand for food due to the nation's limited resources for arable land and the burden of a growing population(Randive K, Raut T, Jawadand S.(2021); Chakraborty K. (2016)). Production of phosphate fertilizers depends on the mining of rock phosphate all over the world. Due to a lack of raw materials, our nation completely depends on imported high-grade rock phosphate. Dust from rock phosphate and phosphogypsum(Wang M et al., (2019)) contributes a significant amount of fluoride to the local phosphate fertilizer industry. The soil is exposed to the fluoride that is released into the air by the phosphate fertilizer industry through deposition, air, rain, and fluoride-contaminated plant residues(Dartan GU, Taspinar FA, Toroz I.(2017)). The total daily fluoride intake, urine fluoride, and other biomarkers were higher in fluoridated areas compared to non-fluoridated areas, according to fluoride exposure studies conducted in humans, particularly among children living in fluoridated and non-fluoridated locations(Idowu OS et al.,(2020)). Due to the retention of dietary fluoride in the body, residents in high altitude, low water fluoride areas had limited urine fluoride excretion and high fluoride concentrations(Sah O, Maguire A, Zohoori FV.(2020)). Fluoride exposure has been linked in several studies to nephrotoxicity in humans(Khandare AL et al., (2017); Jiménez-Córdova MI et al., (2018); Sayanthooran S et al., (2018); Malin AJ et al., (2019). The majority of studies on fluoride exposure are conducted in communities, however there are few studies done on the employees who are exposed while at work. Fluorosis occurrence and severity are influenced by the amount of fluoride that is present in the air, soil, food, and water. High sugar intake and appropriate fluoride exposure are the primary causes of dental caries in all nations Shekhar et al. 2006; Pandey, 2011 (WHO, 2010; 2015). According to Sharma and Thaker (2011), fertilizers are widely employed in our nation to increase food production and are crucial to maintaining food security in India. When it comes to ensuring global food security, which is essential for the Indian economy, the fertilizer sector is a significant one. According to Langer and Gunther (2001), soil microbial biomass and enzyme activities important indicators of soil fertility were significantly decreased by alkaline dust deposits from a phosphate fertilizer plant in Germany.

METHODOLOGY

STUDY DESIGN AND SAMPLE COLLECTION

24 male workers who were employed in the industry that produces phosphate fertilizer were included in this cross-sectional study. Each taking part employee provided their written approval. Before the shift began (pre-shift) and after it ended (post-shift), the workers' urine samples were taken and stored in a cold storage box in a 50ml sample container (Himedia) containing 0.2g of EDTA (Merck). Without delay, samples were brought to the lab for additional analysis.

An analysis of urinary fluoride was performed using the NIOSH-8308 protocol. Thermo scientific's ORION 4 STAR pH/ISE bench top meter was used to measure the amount of fluoride in the urine samples. Prior to the examination of the samples, the fluoride ion selective electrode was calibrated using five distinct working standards. The standards/samples and TISAB-II solution (Orion 940907) were maintained in a 1:1 ratio. The samples and standards receive consistent ionic strength from the TISAB-II solution. Both the standard and the samples were kept at the same temperature during the analysis. A 50ml plastic beaker was filled with the prestored urine samples and 10 ml of the total ionic strength adjustment buffer (TISAB-II) solution. The electrode was submerged in the solution while being stirred by a magnetic bar. Readings of fluoride concentration were taken in mg/L after stabilization. Every five samples, a blank and a standard were checked for quality control.

RESULTS AND DISCUSSION

In total, 24 employees participated in the survey. Depending on the nature of their work, two groups of employees production and maintenance at the SSP plant were divided. Urinary fluoride levels were discovered to be 2.14 mg/g and 2.42 mg/g, respectively, in pre- and post-shift urine samples collected from workers (Table 1). The concentrations of urine fluoride were higher in post-shift samples, despite the lack of a statistically significant difference. It appears that while they were working, the employees were exposed to fluorine on the shop floor.

Shifts	Average	SD	
Pre shift (n=24)	2.14	1.35	
Post shift (n=24)	2.42	2.02	

Table 1: Urinary fluoride concentration mg/g of crtn among workers.

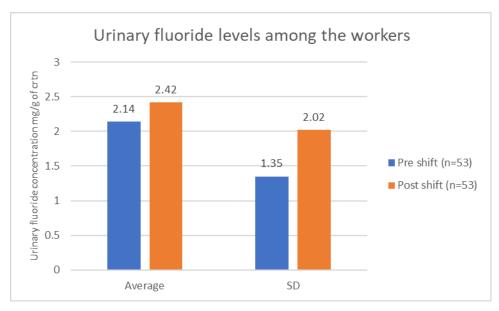


Figure 1: A graphical representation of urinary fluoride levels among the Department workers.

Source of						
Variation	SS	df	MS	F	P-value	F crit
Between						
Groups	0.354025	1	0.354025	2.685568	0.242928	18.51282
Within Groups	0.26365	2	0.131825			
Total	0.617675	3				

The pre-shift urinary fluoride levels $(2.14\pm1.35 \text{ mg/g of crtn})$ found in the current investigation were just a little bit higher than the pre-shift values $(1.31\pm0.77 \text{ mg/g of crtn})$ reported in workers at an aluminum smelter in the USA(Seixas NS, et al., (2000), (Figure 1). The post-shift urine fluoride levels in the current investigation, however, are comparable to the post-shift urinary fluoride levels $(3.02\pm1.87 \text{ mg/g of crtn})$ observed in the same aluminum sector workers in the USA ($2.42\pm2.02 \text{ mg/g of crtn}$). Pre- and post-shift urinary fluoride levels in Slovakian aluminum smelter workers were $0.455\pm0.353 \text{ mg/g}$ of crtn and $0.957\pm0.686 \text{ mg/g}$ of crtn, respectively, according to another study(Schwarz M, et al.,(2021)). Fluoride levels in the current study, however, were higher than those seen in Slovakian employees at aluminum smelters.

Table 3: Urinary fluoride levels among workers of SSP plant's production and maintenance in the pre-shift and post shifts

Shift	SSP plant production (n=09)	Maintenance (n=15)
Pre shift (n=24)	2.87	2.16
Post shift (n=24)	3.68	2.24

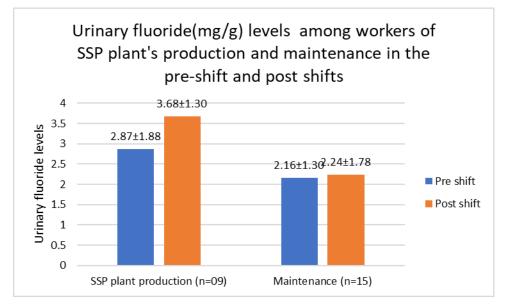


Figure 2: Urinary fluoride (mg/g)levels among workers of SSP plant's production and maintenance in the pre-shift and post shifts

Source of Variation	SS	df	MS	F	P-value	F crit
Between						
Groups	1.155625	1	1.155625	6.977358	0.118401	18.51282
Within Groups	0.33125	2	0.165625			
Total	1.486875	3				

Table 4: ANOVA: Single Factor

In the SSP plant's production and maintenance, the urinary fluoride concentration (mean \pm SD) in the pre-shift was 2.87 \pm 1.88 and 2.16 \pm 1.30 mg/g of crtn, respectively Table 3, Figure 2. The post-shift urine fluoride levels were similarly 3.68 \pm 3.00 and 2.24 \pm 1.78 mg/g of crtn. Due to the fact that SSP employees were directly exposed to fluoride on the factory floor, their urine fluoride concentration was compared to that of maintenance workers. Workers at the SSP factory were found to have higher urinary fluoride levels, with maintenance. The cause may be related to the SSP plant's digestion of rock phosphate, which exposes staff members in this division to excessive fluoride levels. Fluoride exposure levels are clearly linked to employment sources based on the higher amounts of urine fluoride seen in SSP plant employees.

Two department employees had their urine fluoride concentration tested both pre and post shift (ANOVA, F=2.68; p=0.24; ANOVA, F=6.97; p=0.11), and a significant difference was found as shown in Table 2,4. This outcome amply demonstrates the variations in fluoride sources based on the sorts of processes carried out in both departments and the exposure levels between the two departments. The maintenance department employees had lower urinary fluoride concentrations, which clearly shows that their work-related exposure was lower and that they were not directly exposed from process areas.

Based on age groups, no significant differences in urine fluoride levels were found in our analysis (ANOVA, p>0.05) (Table 2,4). Renal clearance rates did not change with age in adults or children. However, older persons (those over 65) have significantly lower renal clearance of fluoride due to age-related glomerular filtration rate declines, with the majority of fluoride remaining in the body's bones and teeth (Khanoranga KS. (2019)).

In general, temporary employees are required to work in all areas, and their working hours may be longer than those of permanent employees. On the other side, the permanent staff will work during the designated times in the prescribed places. Additionally, it was observed that permanent employees used respiratory protective equipment more frequently than temporary employees. Therefore, it is strongly advised that temporary workers be educated on the value of employing safety equipment. The management should also give these personnel with all necessary safety equipment, taking into account their ability to afford to do so.

Fluoride is not considered to be a necessary component for human growth and development, but it is considered to be helpful in preventing dental caries(European Commission, 2011). According to a number of studies, excessive fluoride exposure can have harmful effects such as dental and skeletal fluorosis as well as non-skeletal fluorosis (Mandinic Z, et al.,(2009)). According to earlier research, fluoride levels are high in industrial worker environments as a result of anthropogenic activity, and this has a negative impact on the health of those who live nearby industries and fluoride endemic areas(Khanoranga KS. (2019). There aren't many studies in India comparing pre-shift and post-shift urine fluoride as a biomarker of workplace fluoride exposure in phosphate fertilizer sector workers. The current study's findings were contrasted with the exposure limits recommended by several agencies(World health organization (1996)).

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In our study, 9 out of 24 (37.50%) participants had pre-shift urine fluoride levels that were higher than allowed. Although there are several complicating factors, Koç E, et al., (2018), including lifestyle and nutritional consumption, urinary fluoride in pre-shift urine samples may be due to these factors in addition to occupational exposure, which is the main cause of urinary fluoride in post-shift urine samples. The chemical makeup of the fluoride intake affects how much of it is absorbed by the body. The body absorbs around 90% of the fluoride it contains into the blood, with the remainder being released in the feces. Fluorapatite is created when absorbed fluoride reacts with tissues that are calcifying. The kidneys filter and excrete about 45% of the blood's fluoride in the urine. Other bodily fluids including sweat, breast milk, and saliva release very little fluoride. Furthermore, some fluoride that has built up in the body's soft tissues affects the functioning of enzymes and is absorbed by the pineal gland, which may calcify(European Commission, 2011; Limeback H, (2012)).

Hydrogen fluoride (HF), a byproduct of fluoridation, is frequently present in the stomachs of both humans and animals. The blood transports the HF throughout the body when it is absorbed from the digestive system. Although the amount of urinary fluoride reflects the level of exposure from diverse sources, past studies, European Commission, 2011; Zheng Y. et al.,(2002) have shown that occupational exposure to fluoride at work is clearly indicated by the high amount of fluoride found in urine after a shift. Between three and ten hours is the usual short-term plasma fluoride half-life. Urinary excretion is the main route through which fluoride is expelled from the body. Blood fluoride ions are filtered before being partially reabsorbed in the kidney. The excretion of urinary fluoride may be influenced by many factors, including glomerular filtration rate, urine flow, and urine pH, European Commission, 2011; Zheng Y. et al.,(2002). In order to decrease the exposure to fluoride at sources, personal protective equipment (PPE) at the workplace is crucial.

CONCLUSION

The current study measured fluoride levels in urine samples taken from employees of the fertilizer industry pre and post shifts. Workers at the SSP manufacturing plant pre-shift 2.87 ± 1.88 and post-shift 3.68 ± 3.00 mg/g of crtn had greater urinary fluoride levels than those at the maintenance (pre-shift 2.16 ± 1.30 and post-shift 2.24 ± 1.78 mg/g of crtn, respectively). The SSP plant produced the majority of the rock phosphate (raw material) digestion process. This

could be the main cause of the SSP plant's urinary fluoride levels being greater than those of the maintenance. Because they could not be exposed continually at one location, prolonged exposure time was shorter in maintenance; this may account for the reduced urine fluoride levels. Urinary levels taken after a shift clearly show that people may be exposed to greater fluoride at work.

The focus of this study's limitations is on occupational exposure, however the human body absorbs fluoride through a combination of dietary, environmental, and occupational exposure. Consequently, our recent study suggests concentrating on other aspects of exposure pathways in further research. Fluorosis has no cure, thus the only option is to prevent it. The ideal practice is to monitor worker health status and fluoride levels in bodily fluids in order to understand the current situation at work. The results of the current study will assist the employer in developing a policy and intervention aimed at lowering the risk of possibly harmful consequences of long-term exposure to excessive fluoride in the industry. To prevent potential exposure to fluoride in the workplace environment, industrial workers should undergo routine fluoride testing. To reduce exposure levels among workers in the fertilizer industry, an information program about workplace dangers, their health impacts, and safety precautions such wearing gloves, shoes, safety goggles, appropriate clothing, helmets, masks, and earplugs should be conducted.

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