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Workplace Air Quality at Explosive Material Manufacturing and Handling Units

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ABSTRACT

Worldwide, large quantities of explosives are manufactured for use in various types of ammunitions, arms, and mines. Toxic pollutants in the workplaces of three major activities, viz., explosive and solid propellant preparation facility, solid propellant shell assembling facility, and solid propellant shell proof firing facility, were studied. The suspended particulate matter (SPM) concentration in grinding room (13.9 mg/m^3) and sieving room (19.3 mg/m^3) of solid propellant preparation facility was observed to be two to threefold higher than the permissible limit. The SPM in the dentex preparation section was found to be significantly high (10.8 mg/m^3). The personal exposure was fourfold higher (21 mg/m^3) than the permissible limit. It was emerged that concentration of particulate is a major concern in all the processing sections. Since the chemical nature of these particulates is expected to be more toxic in nature, it requires greater attention. At firing point, carbon monoxide appeared to be a major concern.

Keywords: Explosives, solid propellant, workplace air quality, particulate matter, solid particulate matter

1. INTRODUCTION

Air pollution has become a topic of major concern in recent years in India. Till the end of 1970s, there was no specific law for air or environmental pollution control but only some provisions in various other laws were effective in the country[1]. After the environmental awakening by the 1972 Stockholm Conference, specific environmental acts were enacted with more stringent provisions. Though various provisions are in place to regulate, yet air quality in the workplace of various industrial premises is continuously deteriorating and affecting the health of personnel[2-6].

Apart from environmental factors which affect the general population, factory workers, in addition, are exposed to more severe environmental conditions of the workplace, which, if not managed appropriately, may lead to adverse health effects on the workers[7]. Worldwide, large quantities of explosives are manufactured for use in various types of ammunitions, arms and mines. Almost 80 per cent of the types of mines manufactured worldwide contain 2,4,6-TNT (trinitrotoluene), or mixtures of explosives containing TNT and sometime HMX (cyclo-tetramethylenetetranitramine), RDX (cyclotrimethylenetrinitramine) and tetryl are also used to enhance the impact[8]. Although the inherent physical properties of TNT, HMX, and RDX do not encourage these vapours to emanate in appreciable quantities into the air, yet sufficient quantities of explosive vapours and particulates are likely to be present in the workplace environment during handling and processing of the explosives and may pose

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threat to the safety and health of the personnel involved[9].

A number of studies were carried out to assess indoor pollutants, eg, in facility handling formaldehyde[10], impact of various volatile organic compounds in building materials[11], and carpet as an adsorptive resembling volatile organic compounds[12]. Similarly, particulates collected in the workplace of manual metal arc welding facilities have been characterised for their chemical nature[7]. Concentration of nitrate[13], sulphate[14], polycyclic aromatic hydrocarbons[15] (PAH), and PAN, PPN, PnBN[16] have also been monitored in specific emissions.

Both coarse and fine particulates are of health concern[17] and fine particulates are of much greater health concern because these are deposited into the alveoli of the lungs[18] of the human beings. The mortality rate is strongly associated with concentrations of PM2.5 than with the concentration of larger particles[19]. Problems assocoated with the inhalation of fine particulate matter and its serious health effects has been a matter of concern in India[20].

Inhalation of TNT particles may result in nausea, vomiting, toxic hepatitis and anaemia[21]. Significant increase in mortality due to circulatory diseases[22] and significant reduction in sperm counts in workers employed in munitions plants, have been reported. The dinitrotoluene (DNT) isomers, which are the intermediates of TNT, are absorbed through the gastrointestinal tract, respiratory tract, and skin in most species[23].

A number of studies were carried out to assess emissions and effluents from various defence establishments to remediate sites contaminated with explosive compounds in various developed countries[24-26]. In India, though a number of explosive production and research and development facilities exist, yet very scant data is available on the status of workplace environmental quality. Lack of these measures may result in quantifiable, immediate, and pronounced effects. As a result, environmental safety has not yet attracted such a serious concern, especially in India, possibly because the health effects of exposure are not immediately apparent and surface only after a prolonged period, but with irreversibility, in most of the cases. In India, no specific study has yet been carried out comprehensively to ascertain the environmental quality of workplace for these contaminants and its likely impact on the health of the personnel in explosive manufacturing facilities.

In this paper, an effort has been made to monitor and quantify the pollutant concentrations in the workplace of three major activities such as explosive and solid propellant preparation facility, solid propellant shell assembling facility, and solid propellant shell proof firing facility.

2. EXPERIMENTAL

2.1 Sampling Locations

Three major activities were considered for the study: (a) explosive and solid propellant preparation (b) propellant shell assembling, and (c) propellant shell firing. The sampling locations were selected in such a way as to represent the workplace quality of each processing activities. In explosive and solid propellant preparation activities, four processes namely (i) HMX preparation, (ii) solid propellant preparation, (iii) dentex composition preparation, and (iv) composite propellant preparation, were selected for the study. In each of these processes, few monitoring locations were identified based on the ingredients used in the processes and their environmental significance. The selected locations are listed in Table 1. At solid propellant shell assembling facility, three locations, namely centre, corner, and outside the processing room, were selected. In the firing point personal exposure, workplace air quality and downwash monitoring at various downwind directions were carried out. At least the following three sets of samples were collected for various pollutants:

- Particulate matter arising from handling of explosive materials as well as during preparation and assembling of solid propellant shell and proof firing.
- Volatile organic vapours namely (a) acetone vapours during recrystallisation of crude HMX and (b) toluene vapours during cleaning of vessels and moulds with toluene

Table 1. Pollutants concentration at various sections of explosive and solid propellant preparation facilities

Section	Location	Parameters	Workplace TWA for 8 h	Personal exposure	Permissible limit (NIOSH)	Remarks
HMX preparation	Nitration	*NO* (ppm)	0.01	ND	3.0	Open room, natural ventilation, manual feeding of hexamine
	Recrystalisation	Acetone (ppm)	796.5	ND	1000	
	Effluent neutralisation	Ammonia (ppm)	4.7	ND	25.0	
Solid propellant preparation	Sieving	Particulates (mg/m^3)	19.3	81.5	5.0	All rooms are closed and no forced ventilation, air conditioned in mixing casting room
	Grinding	Particulates (mg/m^3)	13.9	ND	5.0	
	Mixing	Toluene (ppm)	22.0	ND	100	
	Casting	Toluene (ppm)	101	ND	100	
Dentex composition	Mixing	Particulates (mg/m^3)	10.8	21.0	5.0	Manual feeding of ingredients and auto controlling of mixing, air conditioned
		TNT (mg/m^3)	0.14	BDL	0.5	
		RDX (mg/m^3)	0.04	0.018	1.5	
Composite propellant	Preparation	Particulates (mg/m^3)	8.12	8.25	5.0	Manual feeding of ingredients and auto controlling of mixing, air conditioned
		Toluene (ppm)	159	23	100	

BDL: Below detection limit; ND: Not done

- Gaseous pollutants, viz., carbon monoxide, ammonia, and nitrogen oxides, etc of HMX preparation, effluent treatment, and solid propellant shell proof firing facilities.

Within the workplace, the sampling locations were decided keeping in view the direction of air movement and workers position with reference to possible fugitive emission sources. The ventilation and operation aspect of each process details are given in Table 1.

2.2 Volatile Organic Vapour Sampling and Analysis

Toluene vapours were sampled using activated carbon (0.4 to 0.8 mm) in a two-stage sampling tube. The main adsorbing section contained 100 mg of activated carbon and the backup section contained 50 mg of activated carbon. The contents in the tubes were held in place with loosely packed silanised quartz wool. The samples were drawn at 200 ml/min flow rate. After sampling, the adsorbent sample tubes were sealed with teflon film and preserved at low temperature (4 °C ± 2 °C) till the analysis. The samples were desorbed in HPLC grade carbon disulphide and analysed using GC-FID (Nucon make) and SE-30 packed column as per the procedure outlined in the standard method[27]. Appropriate calibration standard was also run with $R^2 = 0.989$. Workplace samples were collected at 2 m from the process machinery and at 1.5 m height from the floor. For personal exposure, the adsorption tube was attached to the collar of the personnel moving within the processing room depending upon the requirement of the process operation.

Similar procedure was adopted to collect acetone vapours, with silica gel (0.4 to 0.8 mm) cleaned and dried in an inert atmosphere in place of activated carbon. The main adsorbing section contained 100 mg of activated carbon and the backup section contained 50 mg of activated carbon. The sample was desorbed in HPLC-grade water and analysed using GC-FID and porapack-Q packed column. Calibration standards were run at different concentrations with the $R^2 = 0.997$.

2.3 Particulate Matter Sampling and Analysis

Workplace particulate matter samples were collected using Envirotech make handy sampler (APM 820). A 37 mm teflon filter disc of Whatman make was used for sampling at 2 l/min flow rate and analysed gravimetrically as per the standard procedure[27]. For personnel exposure, particulate matter samples were collected using Envirotech make personal sampler (APM 800) with cyclone attachment to remove non-respirable fraction. Personal sampler was strapped on the waist of the personnel and the filter holder was clipped on the collar of the personnel during the operation. At solid propellant preparation process, only SPM was monitored since in this process only solid ingredients are put together to get a shell assembled with required composition and specification.

2.4 Characterisation of Particulates

Particulate matter collected on filter papers was then analysed for (i) size distribution using optical microscope with MOTIC software capability to measure the particle size in the respirable range (up to 10 μm) (ii) heavy metal content of the particulates using HNO_3 extraction and analysed by atomic absorption spectrometer (GBC-AAS) (iii) explosive constituents namely TNT and RDX of particulates were analysed using Perkin-Elmer HPLC with UV detector using C-18 column with 6:4 methanol-water as mobile phase.

2.5 Gaseous Pollutants Sampling and Analysis

For nitrogen oxides and carbon monoxide, a known quantity of air was sampled through self-indicating Dragger tube and on the spot results were obtained. Ammonia was sampled through dilute sulphuric acid solution and analysed colorimetrically using GBC (Cintra 1000) double beam UV-visible spectrophotometer as per the standard procedures[28]. Repetitive monitoring was carried out to get consistent results. For personal exposure, the Dragger tube was attached to the collar of the combat personnel while they were moving inside and outside the battle tanks for loading and firing.

3. RESULTS

3.1 Explosive and Solid Propellant Preparation Facility

The following details of the workplace air quality monitored at four different processing locations of the explosive and solid propellant preparation facility are:

(i) NOx concentration (0.01ppm) in nitration room and ammonia (4.7 ppm) of effluent neutralisation of HMX preparation facility were found to be well within the respective permissible limits. Acetone concentration (797 ppm) was found to be within but close to the permissible limit of 1000 ppm.

(ii) Total suspended particulate matter (SPM) concentration in grinding room (13.9 mg/m^3) and sieving room (19.3 mg/m^3) of solid propellant preparation divisions was observed to be two to threefold higher than the permissible limit of 5 mg/m^3. During cleaning of vessels, the toluene concentration in the mixing room was very low (22 ppm) and well below the permissible limit (100 ppm). However, in the casting room, the toluene vapours concentration (101 ppm) during the cleaning operation was just crossing the permissible limit. Personal exposure to particulates was exorbitantly higher (82 mg/m^3) than the permissible limit to the tune of 15-time than the permissible limit.

(iii) Suspended particulate matter (SPM) in the dentex preparation section was found to be significantly high (10.8 mg/m^3). The personal exposure was fourfold higher (21 mg/m^3) than the permissible limit. However, the individual chemical constituents, viz., TNT (0.14 mg/m^3) and RDX (0.04 mg/m^3) were well within the permissible limits. Since aluminium powder is added in the proportion of 18 per cent to the mass of composition[29], the particulate concentration might be due to the addition of this powder.

(iv) In composite propellant preparation section also total suspended particulate matter (8.12 mg/m^3) was found to be exceeding the permissible limit. Personal exposure to particulates too had almost similar value (8.25 mg/m^3). Toluene in the workplace was found to be 1.5-time higher than the permissible limit.

3.2 Solid Propellant Shell Assembling Facility

In this section, preprocessed ingredients of solid propellants are assembled in to a shell with the required specification and sent for proofing at firing point. The details of the processing of solid propellant assembling during the monitoring are given in Table 2. The results of the particulate matter monitored at this section are given in Table 3.

(i) SPM value observed outside this section was (0.059 mg/m^3) well within the suspended particulate matter permissible limit for workplace (5 mg/m^3), even lower than the ambient air quality standard limit of 0.200 mg/m^3. This might be due to local factors such as dense greenery and good wind speed (Table 2) blowing at 8-12 km/h from the sea side.

(ii) SPM value measured inside the processing room (0.303–0.312 mg/m^3) was 5-10-time higher than that observed outside the room, especially the centre of the processing zone had higher values. This clearly indicates that the processing operation in the room generates particulates. However, the value was within the permissible limit. In view of the particulate matter emanating from the toxic propellant material handled in the room, prolonged exposure to even this concentration may lead to undesirable health effects[30].

(iii) The particle distribution [Figs 1 (a) and 1 (b)] shows that major fraction (> 90 %) of SPM generated inside the room is in the non-respirable range (>10 µm).

(iv) Lead, which is also used as one of the ingredients to provide lubrication in the pipe of gun and canons during firing, was found to be (1.14 µg/m^3) well within the permissible limit of < 0.1 mg/m^3.

Table 2. Processing of solid propellant assembling during the workplace air quality monitoring

Set of monitoring*	Activity during the monitoring	Type of monitoring	Location reference	Remarks
I set	120 mm tank ammunition and 13.5 kg round of 130 mm graphite propellant were being prepared.	Workplace	The samplers kept at corner, centre, and outside room. Particulate was monitored. Room dimension was 16 m x 12 m and had aircondition duct at one corner opposite to the monitored corner	Personnel's were involved in the preparation of propellant rounds with various ingredients. The wind was blowing from south and wind speed observed at the nearest observatory (1 km from the location) was 8-12 kmph during the monitoring period.
II set	41 number of 130 mm propellant of 13.5 kg charge, 53 numbers of 105 mm Indian field gun with 3.1 kg/round, 41 numbers of 120 mm graphite 5.0 kg/ charge were being prepared	Workplace and personal exposure		
III set	21 rounds of 105 mm IFG (Non-graphite), 7 rounds of 130 mm full charge (graphite), 11 numbers of 120 mm FSAPDS (non-graphite) ammunition, and 20 rounds of 125 mm FSAPDS (non-graphite) were prepared	Workplace		

* In each set, three parallel monitoring were carried out to ensure reproducibility.

Table 3. Workplace air quality at solid propellant shell assembling facility

Parameter	Location with reference to processing room			Permissible limit (NIOSH)
	Corner	Centre	Outside	
Particulate matter (mg/m^3)	0.307	0.648	0.059	5.0
Lead (µg/m^3)	1.14	0.69	BDL	<100 µg/m^3)
Lead (µg/mg dust)	1.65	2.57	BDL	

All the values are averages of three sets monitoring; BDL: Below detection limit

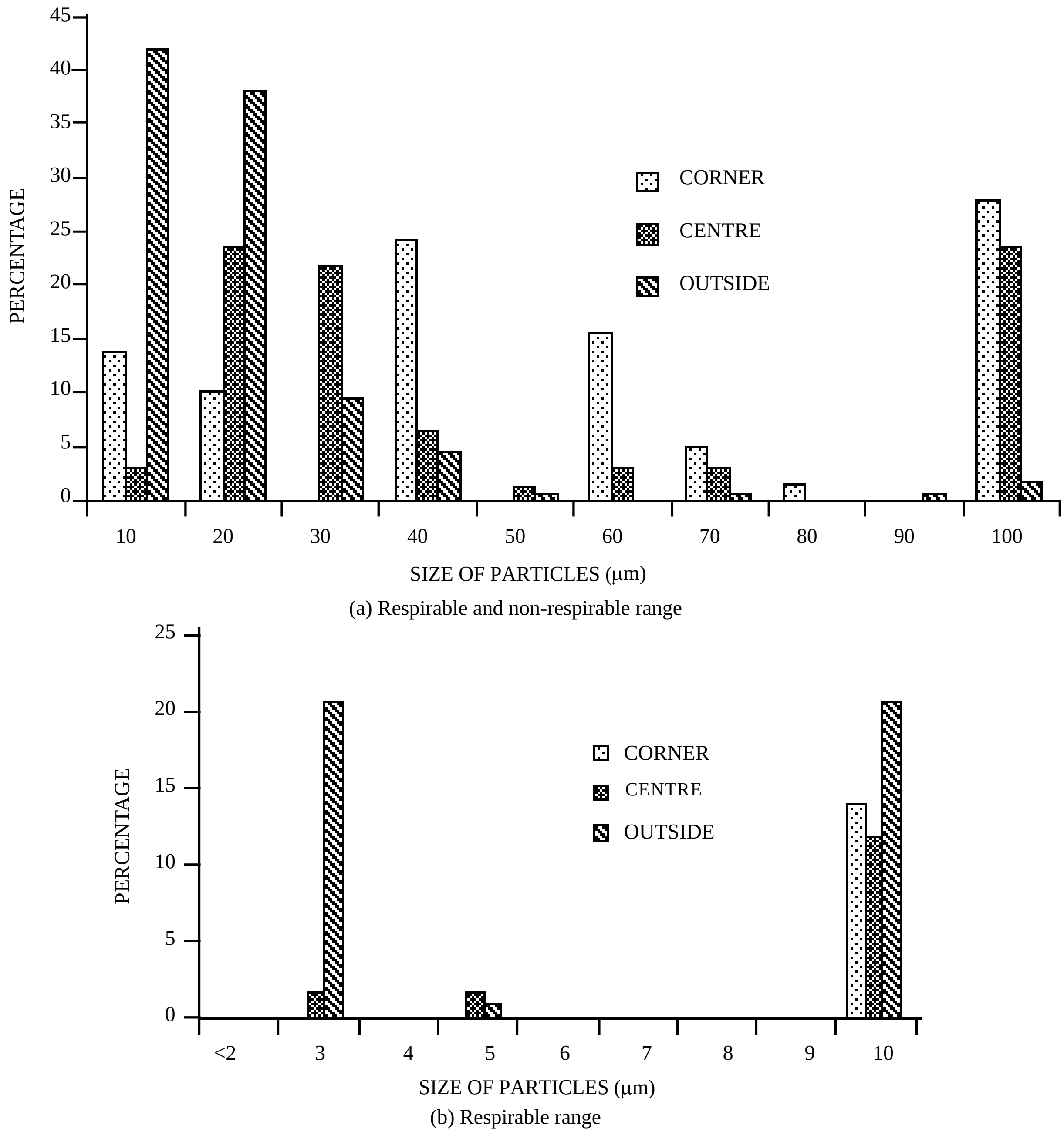

Figure 1(a) and (b). Size distribution of particulate matter in respirable (PM10) and non-respirable range at solid propellant shell assembling facility.

3.3 Solid Propellant Shell Proof Firing Facility

The solid propellant shell assembled in the assembling room is fired for proof in various guns and battle tanks. The details of the processing of solid propellant shell firing and climatic conditions during the monitoring period are given in Table 4. The results of particulate matter and gaseous pollutants during the monitoring period are given in Table 5.

(i) SPM concentration levels observed for personal exposure (2.551 mg/m^3) and workplace (1.191 mg/m^3) were found to be within the permissible limit. The concentration of lead was also very low (20.22 mg/m^3) in the personal exposure. This level is almost 18-time higher than in the propellant shell assembling room.

(ii) Particulates inside the battle tank were 1.901

Table 4. Details of the proof firing of solid propellant shell during the workplace air quality monitoring at firing point

Set of monitoring*	Firing activity during monitoring	Type of monitoring	Location reference	Remarks
I set	18 rounds of field arms of 130 mm	Personal exposure	The parameters measured were SPM, *CO* and nitrogen oxides	Personnel involved in loading the propellant shell in to the gun and tank and take shelter in nearby iron shield while firing. The wind was blowing from south and wind speed observed at the nearest observatory (1 km from the location) was 8-12 kmph during the monitoring period. No obstruction was in the way. Firing was carried on the seashore towards the sea.
II set	7 rounds of 130 mm and 24 rounds of 125 mm	Personal exposure and workplace		
III set	24 rounds (non-graphite) of 125 mm in T-72 tank 24 rounds of 130 mm in Doppler gun (graphite propellant)	Workplace	Handy samplers for SPM and *CO* measurement (one each was kept inside and outside T-72 tank)	
IV set	20 numbers of 125 mm NG/NC/ picrite propellant and 10 numbers of 125 mm in tank	Workplace	SPM was measured during firing at four distance namely near firing point, 10 m, 20 m and 35 m downwind from tank/gun location.	

* In each set, three parallel monitoring were carried out to ensure reproducibility.

Table 5. Workplace air quality at solid propellant shell proof firing facility

	Location	Pollutants			
		CO (ppm)	NO (ppm)	Pb (µg/m3)	Particulate matter (mg/m3)
Firing point	Workplace	100	1	BDL	1.191
	Personal exposure	10	1	20.22	2.551
T-72 tank	Inside the tank	10	< 1	5.12	1.901
	Outside the tank	< 2	< 1	4.73	0.782
Firing point downwash	Near firing point	< 2	< 1	15.2	1.191
	10 m downwind	< 2	< 1	11.8	0.782
	20 m downwind	< 2	< 1	5.6	0.451
	35 m downwind	< 2	< 1	3.71	0.212

All the values are averages of three parallel runs of two sets each; BDL: Below detection limit.

mg/m^3 and outside the battle tank were 0.78 mg/m^3. Both the values were well within the permissible limit. The battle tank has a very good exhaust system. These limits are prescribed for general SPM levels and do not account for the chemical and toxic nature of the SPM. It is known that Occupational Safety and Health Association toxicity limits of nitro-glycerine (0.1 mg/m^3), nitrobenzene (1 ppm), trinitrotoluene (1.5 mg/m^3), dinitrotoluene (1.5 mg/m^3) and toluene di-isocyanate (0.02 ppm) are much lower than the total SPM permissible limit. Prolonged exposure to these particulates is likely to cause health effects.

(iii) The generated particulate matter was found to be quickly dispersed by swift sea breeze as 1.191 mg/m^3 at firing point, 0.782 mg/m^3 at

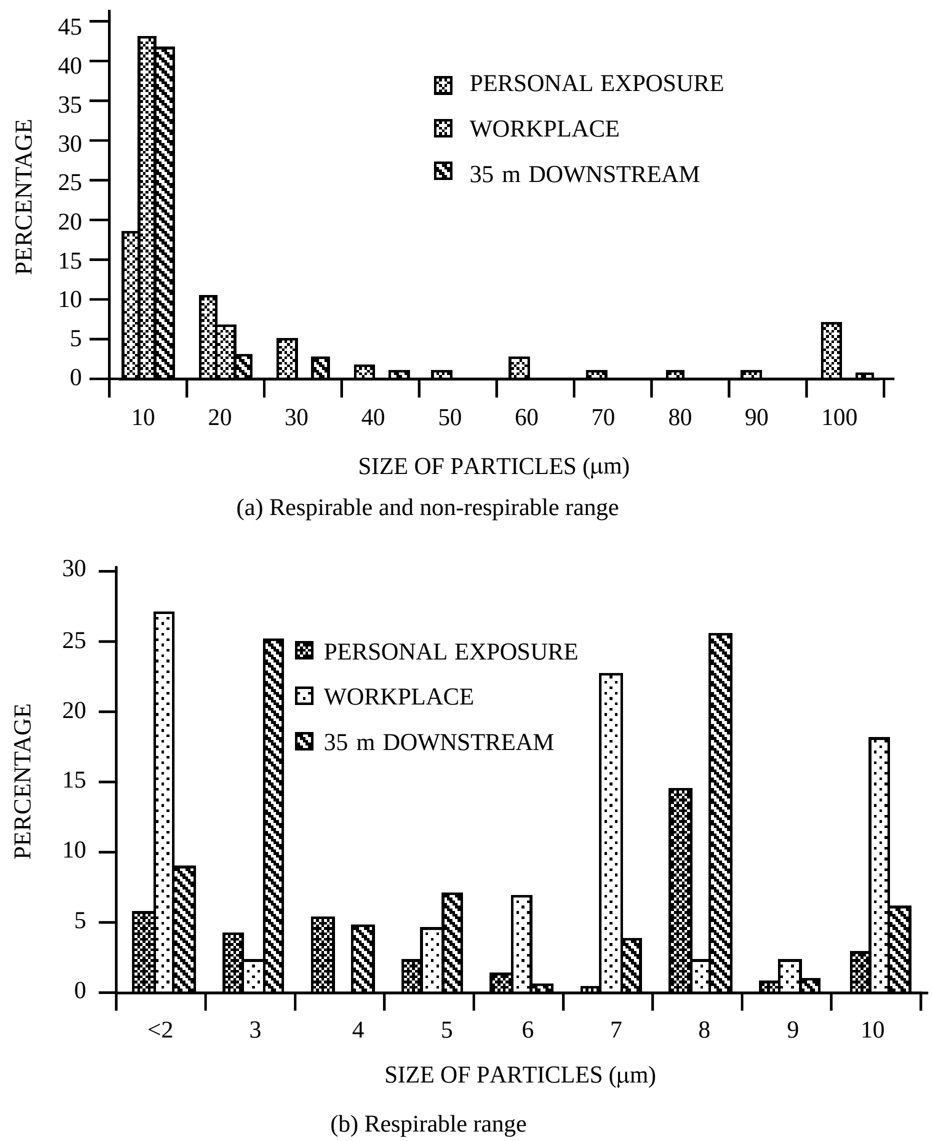

Figure 2 (a) and (b). Size distribution of particles in respirable and non-respirable ranges at solid propellant shell firing point.

10 m downwind, 0.451 mg/m^3 at 20 m downwind, and 0.212 mg/m^3 at 35 m downwind direction was observed (Table 5). The similar trend was observed in the case of lead concentration also.

(iv) Carbon monoxide (100 ppm) was significantly higher than the permissible limit (35 ppm for 8 h). However, the personal exposure was only 10 ppm as the personnel move around the firing point during loading and firing operations.

(v) The number size distributions of all the fine particulate observation [Figs 2 (a) and 2 (b)] show that a large fraction (42-85 %) of particles are in the finer range (<10 μm), which are important from the personnel inhalation point of view. This is likely to have definite impact on the health of personnel involved in the operation.

4. DISCUSSIONS AND RECOMMENDATIONS

From the above results and discussion, it has been emerged that particulate matter is a major concern in most of the processing sections, which have been observed to exceed the permissible limit. At some sections, though the observed values are low compared to the value of the permissible limit, since the chemical nature of these particulates is expected to be more toxic in nature, it should be treated with caution. The fineness of the particulate and the manual handling enhance the possibility of personnel getting exposed. At firing point, carbon monoxide appears to be a major concern. However, the wind speed in the area is quite high most of the time, and hence, causes quick dilution. Excessive quantities of toluene used for cleaning of mixing, casting, conditioning moulds, and other processing vessels in explosive and solid propellant preparation facilities, result in toluene vapour concentration in the workplace exceeding the permissible limit. To control these excesses and ensure healthy and conducive workplace environment for the personnel involved, following steps need to be considered

(i) Utmost care must be taken while handling ingredients during mixing, grinding, and sieving processes in all the rooms in the explosive and solid propellant preparation sections. Though the personnel involved are provided face filter masks, they should strictly adhere and make it as a practice to use these. Action should be taken to minimise manual involvement to reduce exposure and also sieving and grinding operations in various sections of explosive and propellant preparation shall be revamped to reduce dust emanation. Design improvement should be considered to reduce personnel involvement in grinding, mixing, sieving operations.

(ii) All personnel involved in such operations must wear protective filter masks, cloths, glows, etc as per the requirement. Periodic inspection of adoption of safety procedures must be carried out to assess the safe practices. Periodic health checkups for the personnel involved should also be made mandatory.

(iii) Proper ventilation must be provided to give appropriate air changes in the hazardous materials handling processes section. Even the redesign of the process rooms should be taken to ensure the health of personnel.

(iv) Periodic monitoring must be carried out to keep track of the workplace quality. This would help planning the safety regulations.

(v) While cleaning the moulds and mixing vessels, it must be ensured to have adequate air changes by providing forced ventilation, besides taking other factors in to consideration. Usage of toluene in the cleaning process should be reduced to a minimum required quantity.

(vi) Design improvement should be considered to reduce personnel involvement in grinding, mixing, sieving operations. Ventilation of the processing room in all sections should be scientifically done to ensure optimum air changes during the operation.

5. CONCLUSION

The study was carried out to initiate environmental awareness and safety enforcement in the explosive material manufacturing and handling units. The main problem observed was the particulate matter emanating during handling of explosives and solid propellant. In addition, carbon monoxide emanating from the solid propellant proof firing operations appeared to be of concern at firing point. The study was carried out at relatively small units. However, in the ordnance factories, where the operations are on a much larger scale and where the quantum of material manufacturing and handling is manifold, the problem is likely to be more, and hence, require a though understanding to ensure workplace air quality through management measures. The workplace air quality management has been a grey area so far and leads to risk of health of the personnel working in such environment. The findings reflect and expose only the tip of the iceberg of a large-scale problem in the explosive processing factories in the developing countries, especially in Asia.

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