Abstract

Air pollution is a matter of great concern globally due to its adverse effects on health, environment, and climate. Urbanization, industrialization, mining, vehicular emission, biomass burning, and population growth are the main contributors to air pollution. Among them, the pollution caused by coal mining in India is a concern. The existing standard for air quality emphasizes the concentration of particulate matter with specific reference to PM_{10} and $PM_{2.5}$. The composition of particulate matter is important, and there is a need for a thorough investigation of particulate matter in terms of concentration and composition along with size characterization. The concentration, composition, and size play an important role in adversely affecting the environment and control measures of air pollution in coal mines. Composition of particulate matter along with concentration and size now portly considered. Only, Ni, As, and Pb elements are included in the recent notification of the national ambient air quality standard of India.

In opencast coal mines, airborne particulate matter, gaseous pollutants, and an air–suspended mixture of both solid and liquid particles in the atmosphere due to its adverse effects on human health, machinery and the environment are a major concern. Particularly, $PM_{2.5}$ and PM_{10} mass & NO_2 and SO_2 concentrations have been given special attention due to their impact on air quality and human health. The highly mechanized large mega–projects like Singrauli coalfield is facing environmental problems due to the presence of high concentrations of particulate matter in the atmosphere. Hence, a details investigation has been carried in the Singrauli coalfield of India.

The objectives of this work are as follow:

1) to assess air quality status in and around coal mining complex and thermal power plants,

2) to assess the variation in concentration of particulate matter of various sizes along with nitrogen dioxide and sulphur dioxide,
3) chemical characterization of particulate matter of various sizes in terms of major, trace, and radioactive elements,
4) determination of health risk assessment in and around the mining complex,
5) to quantify the contribution of various sources of particulate matter for air quality deterioration, and
6) mitigation of particulate matter.

This research work is focused on the monitoring of particulate matter of different sizes ($PM_{2.5}$, PM_{10}, and SPM) along with gaseous pollutants (NO_2 and SO_2) in the ambient air of Singrauli coalfield, India. This coalfield is one of the largest opencast coal mining complex of India and produced 100 million tonnes of coal in 2018–19. Standard advanced techniques were used to monitored the air quality and analyzed the elements in the collected samples of different sizes of particulate matter. Water–soluble inorganic ions, major and trace elements (Ag, Al, As, Br, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, Pb, Se, Si, Sr, Th, U, V, Zn, C, H, N, S, Br^-, Cl^-, F^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, Ca^{2+}, K^+, Mg^{2+}, Na^+, and NH_4^+) in airborne particulate matters of different sizes were also analyzed.
Air quality monitoring sites were selected, and field investigation was conducted for two consecutive years to observe the variation in concentration of particulate matter monthly and season wise also.

The annual average concentration of particulate matter of different sizes at Singrauli Coalfield area were varying from 66.4±37.3 μg m^{-3} to 81.3±38.9 μg m^{-3} of $PM_{2.5}$, 170.53±73.26 μg m^{-3} to 202.42±84.21μg m^{-3} of PM_{10}, and 365.30±140.46 μg m^{-3} to

391.29±158.08 μg m^{-3} of SPM. The annual average concentration of gaseous pollutants are ranging between 22.81±10.97 μg m^{-3} to 29.76±12.22 μg m^{-3} of NO_2, and 13.25±3.81 μg m^{-3} to 16.68±4.31 μg m^{-3} of SO_2 in 2016 and 2017, respectively. It has been observed that the concentration of particulate matter along with the nitrogen dioxide and sulphur dioxide in the winter season was ranging from 67.4 to 166.7 μg m^{-3} for $PM_{2.5}$, 174.4 to 351.2 μg m^{-3} for PM_{10}, and 389.7 to 771.9 μg m^{-3} for SPM. The gaseous pollutants are ranging from 30.1 to 40.8 μg m^{-3} of NO_2, and 15.0 to 24.4 for μg m^{-3} of SO_2, which is higher than the rest seasons. This may be due to temperature inversion, dry condition, and low humidity. The air pollutant levels are higher as compared to rainy and summer.

In the summer season, due to high temperature and high mixing height, the air pollutant concentrations were lower. The concentration of air pollutants ($PM_{2.5}$, PM_{10}, SPM, NO_2, SO_2) were lowest in the rainy season, perhaps due to coagulation and the removal of particulates during precipitation.

The frequency distribution of concentration of air pollutants were also studied to know the number of sampling sites showing higher or lower concentration than the prescribed permissible limit. In the distribution of $PM_{2.5}$ concentration, a peak observed between 60 and 100 μg m^{-3} at all air quality monitoring sampling stations. About, 41% of $PM_{2.5}$ concentrations were below 60 μg m^{-3}, 49% in a range of 60–100 μg m^{-3}, and 10% in range of 100–200 μg m^{-3} and around 59% of $PM_{2.5}$ sample exceeded the national ambient air quality standard of India of 60 μg m^{-3}. In the PM_{10} concentrations, the peaks were observed between 100 and 200 μg m^{-3}, 43% of PM_{10} concentrations were below 100 μg m^{-3}, and 57% of PM_{10} was above 100 μg m^{-3}. As far as SPM is concerned, the peak was observed from 360 to 500 μg m^{-3}, 35% of SPM concentrations were below 500 μg m^{-3}, and 18% of SPM was above 500 μg m^{-3}. Particulate matters (SPM, PM_{10}, and $PM_{2.5}$) were highly

correlated with NO_2 in the area, which R was in the range 0.45–0.85, reflecting their common origin.

The annual concentration of elements, i.e., As, Br, Hg, Pb, Cr, Ni, Th, U and Cd in $PM_{2.5}$ samples was found to be in the range of 0.72–10.52 (4.06±1.08) μg m^{-3}, 0.92–5.39 (1.62±0.39) μg m^{-3}, 0.005–7.46 (3.47±1.12) μg m^{-3}, 10.40–1061.42 (314.67±19.76) μg m^{-3}, 0.66–99.13 (19.92±4.33) μg m^{-3}, 0.03–18.75 (13.96±2.63) μg m^{-3}, 0.001–0.103 (0.061±0.024) μg m^{-3}, 0.0003–0.0194 (0.011±0.001) μg m^{-3} and 0.56–79.63 (7.29±2.46) ng m^{-3} respectively in the AQMS–03 in the year 2016. Out of the twenty–nine elements, the eleven elements Na, Mg, H, C, N, Ca, K, S, Fe, Al, and Si contribute more than 95 % of the total weight of the elements in $PM_{2.5}$, PM_{10}, and SPM samples at the area.

The most abundant water–soluble ions, i.e., NH_4^+, SO_4^{2-}, PO_4^{3-}, NO_3^-, Cl^-, F^- were among all collected samples in $PM_{2.5}$, PM_{10}, and SPM, followed by NO_2^-, Mg^{2+}, Na^+, K^+, Ca^{2+}, and Br^-. The water–soluble ions were 36.42 %, 22.00 %, and 18.40 % in the $PM_{2.5}$, PM_{10}, and SPM mass, respectively, in AQMS–01. The trend for the average concentration of water–soluble ions were as ($NH_4^+ > SO_4^{2-} > PO_4^{3-} > NO_3^- > Cl^- > F^- > NO_2^-$), ($NH_4^+ > SO_4^{2-} > NO_3^- > PO_4^{3-} > Cl^- > F^- > NO_2^-$), and ($NH_4^+ > SO_4^{2-} > NO_3^- > PO_4^{3-} > Cl^- > F^- > NO_2^-$) in $PM_{2.5}$, PM_{10}, and SPM samples, respectively.

The enrichment factor was also calculated. At the AQMS–03, the Ca, Mn, Ni, Na, Mg, K, and Cr of $PM_{2.5}$ have a low enrichment factor value ranging from <1 to 5 in the average enrichment factor, which indicates that elements mostly derived from the soil. The average enrichment factor values of cobalt, copper, bromine, arsenic, zinc, and hydrogen have ranged from 5 to 150, indicating that they are likely to be originated from anthropogenic emission sources. The higher enrichment factor of nitrogen and selenium in $PM_{2.5}$ may be indicated an industrial source, particularly from coal mining and coal yard.

The radioactive elements were also analyzed, and significant concentration was observed.

The average activity concentration of ^{40}K, ^{210}Pb, ^{232}Th, ^{234}U, ^{235}U, and ^{238}U were 13.43, 9.88, 6.12, 10.13, 0.173, and 4.38 μBq m^{-3} in PM_{10} size, respectively. The same investigation has been made in suspended particulate matter and particulate matter of 2.5μm also. The $^{232}Th/^{238}U$ activity ratio in particulate matters was found between 0.20 to 1.54 with an average value of 0.9 ± 0.5, 0.25 to 1.10 with an average value of 0.8 ± 0.7, and 0.22 to 1.22 with an average value of 0.8 ± 0.8 in the $PM_{2.5}$, PM_{10}, and SPM, respectively. This range is in the average crustal ratio of 3.5, indicating that ^{232}Th activity concentration has not increased by coal combustion.

There is a good positive correlation between ^{232}Th and ^{238}U (0.60–0.70, p–value < 0.001), supporting the conclusion that they originated from the same source, mostly the crust, i.e., overburden and coal. The average calculated $^{232}Th/^{238}U$ ratio was 0.9 ± 0.5, 0.8 ± 0.7, and 0.8 ± 0.8 in the $PM_{2.5}$, PM_{10}, and SPM, respectively, which is close to the world average of unity. There is a good positive correlation between ^{232}Th and ^{238}U (0.60–0.70, p–value < 0.001), supporting the conclusion that they originated from the same source, mostly the crust not as a result of coal mining.

The gross α activity is ranging between 0.53×10^{-5} and 1.67×10^{-3} Bq m^{-3} with an average of $0.90 \times 10^{-4} \pm 0.31 \times 10^{-4}$ Bq m^{-3} and the geometric mean of 0.86×10^{-4} Bq m^{-3} in the $PM_{2.5}$ samples. In the PM_{10} samples, the gross α activities were found to range from $0.87 \times 10^{-5} – 2.44 \times 10^{-3}$ Bq m^{-3} with an average of $1.65 \times 10^{-4} \pm 0.51 \times 10^{-4}$ Bq m^{-3} and the geometric mean of 1.56×10^{-4} Bq m^{-3}. As for as SPM samples are concerned, the gross α activities was observed $0.93 \times 10^{-5} – 3.62 \times 10^{-3}$ Bq m^{-3} with an average of $2.36 \times 10^{-4} \pm 0.86 \times 10^{-4}$ Bq m^{-3} and the geometric mean of 2.18×10^{-4} Bq m^{-3}.

The activity concentration of gross β in $PM_{2.5}$, PM_{10}, and SPM samples were ranging of $0.86 \times 10^{-5} – 2.29 \times 10^{-3}$ Bq m^{-3}, $1.38 \times 10^{-5} – 3.18 \times 10^{-3}$ Bq m^{-3}, and $1.41 \times 10^{-5} – 4.07$

$\times 10^{-3}$ Bq m^{-3} with an average of $1.42 \times 10^{-4} \pm 0.37 \times 10^{-4}$ Bq m^{-3}, $2.23 \times 10^{-4} \pm 0.56 \times 10^{-4}$ Bq m^{-3}, and $2.58 \times 10^{-4} \pm 0.83 \times 10^{-4}$ Bq m^{-3} and geometric mean of 1.37×10^{-4}, 2.16×10^{-4} Bq m^{-3}, and 2.44×10^{-4} Bq m^{-3}, respectively.

The intake of elements inhalation was also calculated. The intake of heavy metals (Cd, Cr, Mn, Ni, and Pb) through inhalation exposure pathways attributable to $PM_{2.5}$ in the field was 164.9±56.8 ng d^{-1}, 450.4±100.1 ng d^{-1}, 2.7±1.1 µg d^{-1}, 315.5±60.8 ng d^{-1}, 6.8±0.4 µg d^{-1}, respectively. Similarly, In PM_{10}, the intake of Cd, Cr, Mn, Ni and Pb through inhalation exposure pathways owing were 238.1±49.0 ng d^{-1}, 759.3±182.7, ng d^{-1}, 3.2±1.0 µg d^{-1}, 400.9±124.5 ng d^{-1}, 8.81±1.5 µg d^{-1}, respectively. This may be noted that the WHO–recommended the tolerable daily intake values of 110.0 ng d^{-1} for Cd, 22000.0, ng d^{-1} for Cr, 666.0 µg d^{-1} for Mn, 22000.0, ng d^{-1} for Ni, and 11.1 µg d^{-1} for Pb. Therefore, the intake of elements in particulate matter is within the permissible range, and the air quality is posing no threat to the local population through inhalation.

The carcinogenic element chromium has observed the highest percentage of total average daily dose both in $PM_{2.5}$ and PM_{10} samples. On the whole, average daily dose values decreased in the order of Pb > Zn > Mn > Cu > Cr > Ni > Hg > Cd > As in $PM_{2.5}$ and PM_{10} in male demographic groups. The risk levels for the carcinogenic elements occurred in the following increasing order of As < Cd < Ni < Cr in both the particulate matter ($PM_{2.5}$ and PM_{10}), respectively. Thus, a similar fluctuation has been found in the female and children demographic groups.

The risk level of the carcinogenic elements for exposure through the respiratory system have been found to be 1.05×10^{-11} $year^{-1}$ and 2.09×10^{-08} $year^{-1}$ in $PM_{2.5}$ and 6.66×10^{-12} $year^{-1}$ and 3.31×10^{-08} $year^{-1}$ in PM_{10} for all demographic groups, which is lower than the average risk acceptance of 10^{-6} $year^{-1}$.

The elemental oxides in particulate matter in study area is mainly of aluminum silicate (Al_2SiO_5), silicon dioxide (SiO_2), aluminum oxide (Al_2O_3), ferric oxide (Fe_2O_3), Calcium oxide (CaO), ammonium sulphate ($(NH_4)_2SO_4$), potassium chloride (KCl), potassium oxide (K_2O). The shape of the particulate matter was also studied under a scanning electron microscope (SEM). The SEM microphotograph of particulate matter collected on filter paper showed that most of the particles possess rectangle, and irregular rectangle structures. The EDS analyses also show that the dominant mineral phase in the particulate matter samples is silica, along with a trace amount of Al, Fe, and Si.

The source marker calculations also confirmed that K^+, Cl^-, Si, Se, Pb, and As are useful markers for coal combustion and traffic–related emission.

A principal component analysis result showed that the contribution of the coal combustion is ~30%, traffic–related emission ~25%, soil dust ~13%, biomass burning ~9%, and resuspended road dust ~7%. The other remaining percentage (~16%) is unknown sources of the total particulate matter. The major role of coal combustion and traffic–related emission was also supported by statistical analysis. The elements extracted in the particulate matter have been a major contribution of particulate matters by coal combustion and traffic–related emission.

The positive matrix factorization results showed that the contribution of the coal combustion and mining activity (~23%), traffic–related emission (~17%), resuspended road and soil dust (~16%), secondary inorganic aerosols (~15%), biomass burning (~12%), and mixed emission (~17%) are sources of particulate matter at the both observational area.

A laboratory investigation was conducted to study the impact of soap bubbles on the particulate matter of different sizes for minimization of dust ambience of the mining complex. The effect of soap bubbles reducing the $PM_{2.5}$, PM_{10}, and TSPM was

concentration levels 51.0±1.0 to 37.0±0.8 μg m^{-3}, 90.2±1.0 to 62.2±1.0 μg m^{-3}, and 112.0±1.5 to 75.0±1.2 μg m^{-3} at 1.0 km h^{-1} wind speed, respectively. The method is a low–cost technology and the environment–friendly. The result mentioned above is valid within the present experimental range. A more detail study is required before applying this technique in the field.

The findings of this study will be useful in designing to assess the virulency of particulate matter in one place and effective air pollution abatement measures in an area on the other place. Component of a mixture of chemical species and phases and existing in a variety of shapes and sizes, atmospheric aerosols are complex and can have dangerous effects on human health, the environment, and the climate. To understand the effect of aerosols on local to regional scales, detailed monitoring and measurements of the physical and chemical properties of ambient particles are essential.