Science of the Total Environment 563–564 (2016) 293–301

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Rain pH estimation based on the particulate matter pollutants and wet deposition study

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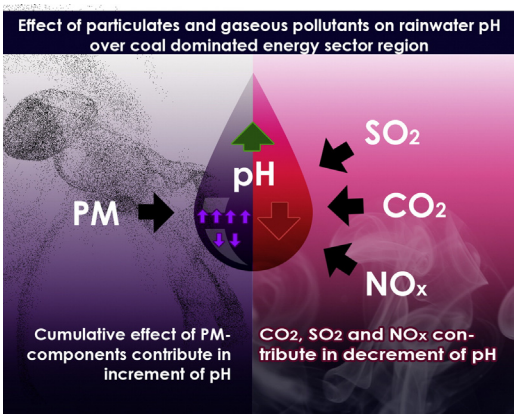
HIGHLIGHTS

- This study suggests not to use rain pH as the only indicator for acidic rain events.
- Observed rain pH were not representative of the high sulfate concentration found in rain.
- Theoretical prediction of pH was done with and without considering PM, with the former being more representative of real scenario.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 5 January 2016
Received in revised form 10 April 2016
Accepted 10 April 2016
Available online xxxx

Editor: D. Barcelo

Keywords:
Rain pH
Acid rain
Buffering of rain pH by PM
Ionic flux
Sulfates

ABSTRACT

In forecasting of rain pH, the changes caused by particulate matter (PM) are generally neglected. In regions of high PM concentration like Dhanbad, the role of PM in deciding the rain pH becomes important. Present work takes into account theoretical prediction of rain pH by two methods. First method considers only acid causing gases (ACG) like CO_2, SO_2 and NO_x in pH estimation, whereas, second method additionally accounts for effect of PM (ACG-PM). In order to predict the rain pH, site specific deposited dust that represents local PM was studied experimentally for its impact on pH of neutral water. After incorporation of PM correction factor, it was found that, rain pH values estimated were more representative of the observed ones. Fractional bias (FB) for the ACG-PM method reduced to values of the order of 10^{-2} from those with order of 10^{-1} for the ACG method. The study confirms neutralization of rain acidity by PM. On account of this, rain pH was found in the slightly acidic to near neutral range, despite of the high sulfate flux found in rain water. Although, the safer range of rain pH blurs the severity of acid rain from the picture, yet huge flux of acidic and other ions get transferred to water bodies, soil and ultimately to the ground water system. Simple use of rain pH for rain water quality fails to address the issues of its increased ionic composition due to the interfering pollutants and thus undermines severity of pollutants transferred from air to rain water and then to water bodies and soil.

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http://dx.doi.org/10.1016/j.scitotenv.2016.04.066
0048-9697/

1. Introduction

Rain is one of the major sources that replenish the water bodies and ground water system. These sources of fresh water provide humans water for drinking and other domestic uses. Any changes in the physical or chemical nature of this water will have adverse health impact on humans. The effect of rain on pollutant scavenging depends upon data on physical (rain drop size, rain amount and rain intensity) and chemical (ionic composition of rain water) properties of rain and data on sources of pollutants and their transport. The scavenging of atmospheric pollutants by wet deposition affects the rain pH (Al-Khashman, 2009). The quality of rain water in turn affects the rivers and other water bodies, soil and ultimately ground water system. Hence, for the assessment of input of materials brought by rain into terrestrial system, composition of rain water needs to be determined (Thornton and Eisenreich, 1982).

Unpolluted natural rain water has a pH value around 5.6, as atmospheric CO_2 gets dissolved in rain drops (Bayraktar and Turalioglu 2005). Any change in the pH, below or above this level, defines rain to be acidic or alkaline, depending upon the type of pollutants transferred to rain water. The growing energy demand of nations to fuel the ever increasing number of industries and transport activities, has led to emission of large amount of gaseous pollutants like oxides of carbon, sulfur, and nitrogen and PM from fossil fuel combustion. These oxides are precursors of major acids in rain water and lower down its pH. Cases of acid rain were reported and shown to have adverse effect on biosphere, building materials and visibility (Fujita et al., 2000; Tsuruta, 1989; Weng, 1993; Ayers et al., 2002; Hooper and Peters, 1989). Atmospheric CO_2 is reported to be continuously rising by Mouna Loa observatory. As per the report of IFCC, Intergovernmental Panel on Climate Change, 2007, CO_2 accounts for >80% of total greenhouse gas emission globally, primarily from the burning of fossil fuels. In 2010, energy sector contributed 41% of global CO_2 emissions (IEA, International Energy Agency, 2012). Despite the continuous rise in the emission of major pollutants in the form of SO_2, NO_x and PM, the same is not reflected in the observed rain pH.

Ren et al. (2011) in their work on buffering capacity of PM, have discussed the neutralization of rain water acidity by PM. PM can be acidic or alkaline depending upon the characteristics of the source from where they are emitted. Here it is important to state that unlike gases, PM is very much site specific. It is an aggregation of several kinds of trace elements, primary and secondary pollutants, therefore overall effect of these pollutants decides whether PM will increase or decrease the acidity of rain. Acidic PM can add on to the acidity caused by the gaseous pollutants and hence more acidic rain. Alkaline natured particles can mask the severity of acidic components in rain, and therefore their adverse effects may go unnoticed. Considering only the gaseous precursors of acid rain, leaves a major fraction of impact unexplained and hence requires an understanding of the nature of PM being released in the environment. This will also help in the back estimation of emission of pollutants in emission inventory studies. Here it is important to mention that the study does not take into account NH_3 gas or NH_4^+ aerosols in neutralization of rain acidity, as in the present study region, where coal combustion is predominant, sources of NH_3 is meager in comparison to those of SO_2, NO_x and PM.

On the basis of the research gap identified, the purpose of present work is i) observation of rain pH along with major ions and ii) theoretical estimation of rain pH based on the site specific acidic gases and PM. Theoretically estimated pH values of rain are compared with the observed values to study the impact of PM on rain pH.

2. Materials and methods

2.1. Description of study area

Dhanbad, one of the major districts of Jharkhand state in India, covers an area of 2861 km^2 and is actively associated with mining activities for more than a century. Its climate is typical hot and tropical type with three distinct seasons i.e. summer, monsoon and winter. The summer season is hot and dry from March–June, with maximum temperature ranging from 46 to 48 °C. Rainy season continues from July to October with the average annual rainfall recorded to be 1280 mm. The south-west monsoon lasts from July to October and this monsoon season gets >85% of the annual rainfall. Monsoon season is followed by cool and dry winter season from November to February, with lowest recorded temperature in the range of 5–7 °C. Dhanbad, well known for its coal mines, coal washeries, coke oven distillation units and power plants, adds high amount of gaseous pollutants as well as PM into its atmosphere. As per the estimation of Inventory of Geological resources of Coal in India (Coal resource report, 2015), Jharkhand has the most abundant reserves of the coal resources of country (81048.77 Million tonnes). On account of a number of active and abandoned coalmines, vehicular activities in and around the city, PM pollution is prevalent over here. While mines generate only coarser particles, vehicular activities, burning and thermal power plants give rise to finer particles as well. The acidic precursors present in the released gases negatively affect the rain pH. Higher the dissolution of gases in rain, lower will be the rain pH. As per the temperature dependence of Henry's constant and gas solubility in the liquid; the lower the temperature, the higher the solubility of gas in the liquid and higher the concentration of saturation of a soluble gas in a rain droplet (Elperin et al., 2011). On this basis, if only acidic gaseous precursors of rain are considered, pH of rain will be lowered most in the winter season. Besides gases, PM also plays major role in deciding the acidity or alkalinity of rain (Ren et al., 2011). It can either decrease the rain pH if PM is acidic or it can buffer the rain pH if it is alkaline natured.

2.2. Method for physico-chemical analysis of rain

Physical characteristics of rain involve pH, conductivity and TDS whereas chemical characteristics involve analysis of cations and anions present in it. Event wise sampling was done to collect bulk rainwater sample, using polyethylene trays during late monsoon month of 2013, winter and monsoon months of 2014. Samples were collected at terrace of the three-storey building of Environmental Science and Engineering department of Indian School of Mines, Dhanbad. The collectors were deployed as soon as the rain began and were retrieved immediately after the rain stopped to avoid further interference of dry deposition. Rainfall data were downloaded from www.mosdac.gov.in.

In total 52 rain water samples were collected for the entire study duration with 5, 20 and 39 samples for post monsoon 2013, winter 2014 and monsoon 2014 respectively. Immediately after collection, rain water samples were analysed for pH, conductivity, and total dissolved solids (TDS). Out of the total 39 samples collected in monsoon, only 27 were analysed for ions due to insufficient volume of other samples. Four major cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) and three major anions (Cl^-, NO_3^-, SO_4^{2-}) were analysed based on the methods mentioned in APHA (2005).

The load of the pollutants brought by rain to earth is estimated by wet deposition flux. It gives the rate at which pollutants are transferred from atmosphere to earth per unit area. Wet deposition flux for an element is given by (Baeyens et al., 1990):

$$F = \dot{P} \times C_{wet} \quad (1)$$

where, F = wet deposition flux of an element (meq.m^{-2}.$month^{-1}$ or meq.m^{-2}.$year^{-1}$), $\dot{P}$ = precipitation (mm.$month^{-1}$ or mm.$year^{-1}$), C_{wet} = measured concentration of element in rain (meq.L^{-1}).

2.3. Measurement of CO_2, SO_2 and NO_x

Theoretical prediction of rain pH requires concentration of acidic precursor gases like CO_2, SO_2 and NO_x. Reports suggest that the