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Assessment of Leachate Pollution Index and Greenhouse Gas Emission at MSW Dumpsites along Ganga River at Varanasi, India

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Authors' contributions

This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.

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ABSTRACT

Recent scientific attention has shown serious concern towards municipal solid wastes (MSW) as a source of greenhouse gases and concentrated leachate. We studied the leachate pollution index (LPI) and emission fluxes of two greenhouse gases (CH_4 and CO_2) at two municipal solid waste dumpsites situated along the Ganga River at Varanasi (India). The LPI is a quantitative tool by which the leachate pollution data of dumping sites can be reported uniformly. Concentration of nutrient ions (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, NO_3^{-}, Cl^{-}, PO_4^{3-}) and heavy metals (Cd^{2+}, Fe^{2+}, Cu^{2+}, Pb^{2+}, Ni^{2+} ,Zn^{2+}, Co^{2+}, Mn^{2+}) in leachate varied with season with values being highest in rainy season. Total dissolved solids, conductivity and salinity in leachate showed a similar trend. Leachate pollution index was found to be 87.19 and 82.56 at KZP and BPS sites respectively. The LPI was much higher than the permissible limit at both the sites indicating high contamination potential for surface and ground water and risk to human health. Among all the study metals, Pb was found in abundance at Site 1. The emission flux of CH_4 ranged from 10.73 to 96.74 mg m^{-2} h^{-1} and that of CO_2 from 17.28 to 321.89 mg m^{-2} h^{-1}. Emission flux of both the

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greenhouse gases increased with rising moisture and temperature. The rates were higher at young landfill site and between-site differences in the emission of CH_4 and CO_2 were significant. The study has relevance establishing landfill associated contamination to Ganga River and reducing uncertainties in greenhouse gas emission estimates in India.

Keywords: Climate change; Ganga River; greenhouse gases; Leachate Pollution Index (LPI); contamination potential; heavy metals.

1. INTRODUCTION

Management of solid wastes is a major problem being faced by the municipalities in India. Open dumping is one of the most common methods used to manage major part of municipal solid wastes (MSW) in our country [1]. Environmental problem associated with MSW include availability of space, public health and such issues as the emission of greenhouse gases (GHGs) and contamination by leachate drains from dumping sites. The GHGs contributes to rise in earth surface temperature, while leachate contaminates surface and ground waters [1,2] and has human health concern. The MSW in developing countries contain relatively higher percentage of organic wastes and, by implication, have high potential to emit GHGs per unit weight [2]. As water percolates through MSW, it generates high strength contaminated liquid, known as leachate. The leachate generated from open dumps and uncontrolled landfill sites can pose serious threat to surface and ground water and risk to human health [3,4]. Chemical composition of leachate varies depending upon the nature of waste at dumpsites, degree of compaction, age of landfills and environmental conditions.

Leachates draining from dumpsite/ landfills contain a complex mixture of organic and inorganic constituents including heavy metals [5,6]. The growing consciousness about the health risks associated with heavy metals has brought a major shift in our concern towards prevention of heavy metal accumulation in soil, water and living systems [7]. Heavy metals that percolate the soil layer of agricultural land near landfill sites may enter to food chain through bioaccumulation in plants [8]. During monsoon season, the leaching of heavy metals and inorganic nutrients from landfills is higher than in dry seasons due to rain water flow mechanisms. Heavy metals in leachate are routinely reported in low ranges [9], but such concentrations represent only a small fraction of the metals associated with the solid wastes. The chemical and physical affinity of metal ions and waste materials reduce their leachability under landfill conditions. In earlier studies, metal concentrations in landfill waste in Sweden were found to be four times higher than the concentrations measured in leachates [10]. The mobility of metals generally increased over time as the waste becomes more acidic and oxidizing conditions dominate [6]. Thus, time coupled-site-specific conditions are critical for formation of metal complexes with inorganic or organic ligands.

Methane is among the major greenhouse gases (GHGs) responsible for the rising global temperature. Studies have shown that landfills are among the largest anthropogenic sources of methane [3,11,12,13]. Of the total, over 70% of MSW generated globally is landfilled waste contributing to about 30-35 Tg methane (CH_4) annually to the world's total CH_4 emission of ~550 Tg/yr. Unlike wetlands and paddy fields, landfills function as a closed system and are rich in biodegradable organic materials. Age of the landfills, degree of compaction, composition of waste, moisture content, pH and the management practices all influence the production of GHGs in landfills. Despite the fact that the global warming

potential (GWP) of CH_4 is about 25 order of magnitude higher than that of CO_2, the contribution of the latter to overall greenhouse forcing is about four times higher. In summer 2013, the daily mean CO_2 levels at Mauna Loa, Hawaii crossed 400 ppm [14]. Large scale land use changes coupled with fossil fuel burning have been implicated for rising CO_2 levels [15]. However, a correct understanding of anthropogenic impacts on greenhouse gases requires information on contribution of other sources to overall emission scenario.

In India, the inventory estimates of emission of greenhouse gases from landfills show wide uncertainties due possibly to the paucity of data on *in situ* emission estimates. The *in situ* measurements therefore bear significance in not only reducing uncertainties in inventory estimates, but also exploring regional contributions to overall emission scenario. This study presents the results of emission fluxes of CH_4 and CO_2 at two dumpsites along the Ganga River at Varanasi from January to December 2013. The study further attempted to characterize the quality of leachate being generated from the dumpsites.

2. MATERIALS AND METHODS

2.1 Study Area

The present study was conducted from January to December, 2013 at two dumpsites (Fig.1; Table. 1) of Varanasi (25º 18′ N latitude, 83º 1′ E longitude and 76.19 m above mean sea level). The climate of the region is tropical. The year can be divided into three distinct seasons; winter (November to February), summer (April to mid- June), and rainy (mid- June to September). March and October represents transition months. Of the 1100 mm average rainfall, about 90% occurs in rainy season. During the study period, mean monthly maximum temperature ranged from 27.5 to 45.4ºC and minimum temperature ranged from 9.5 to 25.7ºC. Wind direction shifts from predominantly westerly and south-westerly in October through April to easterly and north westerly in remaining months. The soil of the region is alluvial fluvisol, highly fertile and light textured sandy loam with pH between 6.8 and 7.9.

Site 1. Kazzakpura (KZP)

The Kazzakpura disposal site occupies an area of about 25 acres and is located inside Varanasi city, along the Varuna tributary of Ganga River and surrounded by high population density. The dumping of waste started in 2011. It receives about 600 to 800 MT waste per day. The average depth of waste dumped is around 28m and aerobic composting and landfilling method were used for waste disposal. The wastes being dumped at this site consist of household wastes, animal wastes, street sweeping (mainly polythene, plastic material, foam, paper, packing materials, metals, cloths etc.), construction and demolition wastes and excavated soil.

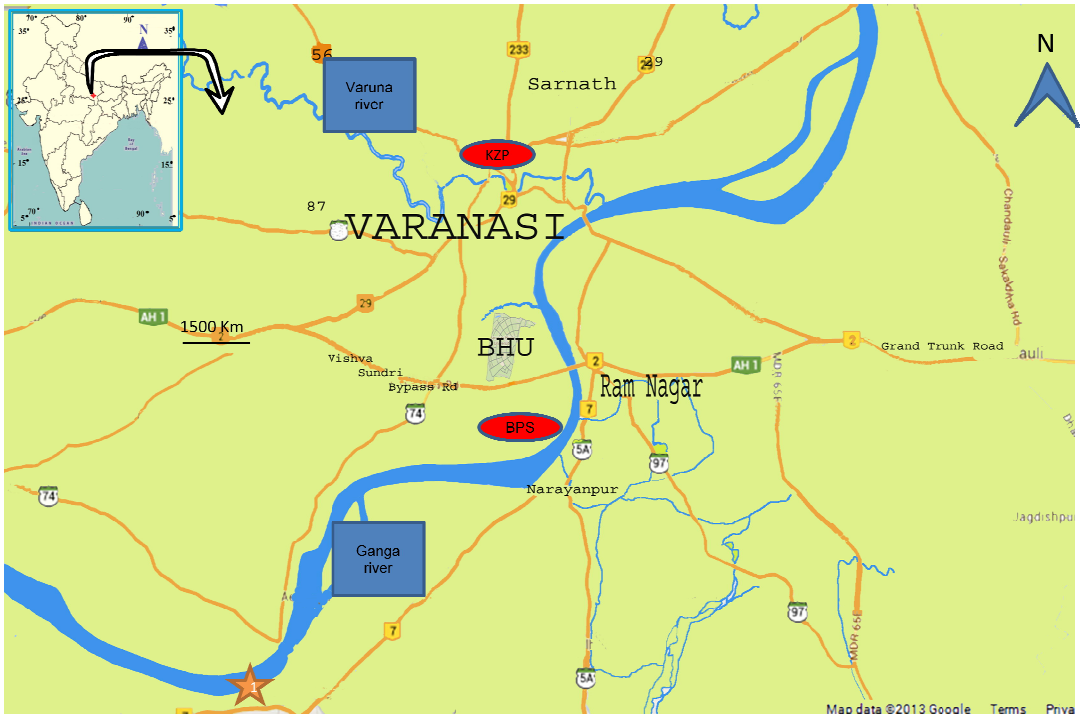

Fig. 1. Location map of the study area

Table 1. Characteristics of solid waste disposal sites of Varanasi

Characteristics	Kazzakpura (KZP)	Bypass (BPS)
Location	Inside the city, along the Varuna tributary of Ganga River (about 2 km away from Ganga River)	At the out skirt of the city and close to Ganga River bank
Year of operation	2011	2006 to 2012
Total area (acres)	25	20
Waste filled area	about 9 acres	About 5 acres
Disposal quantity (MT/day)	600 to 800	300 to 400
Average depth of waste dumped (m)	28	23
Waste disposal method	Aerobic composting and landfilling	Composting

Site 2. Bypass (BPS)

Bypass (BPS) site lies at out skirt of the city close to Ganga River bank. It occupies an area of 20 acres and receives about 300 to 400 MT waste per day. Dumping at this site is banned since 2012. Presently it looks like a hillock as it has been covered with soil and leveled. The composition of wastes dumped at Site 2 is almost similar to that of Site 1.

2.2 Experimental Design

The factorial design of the study consisted of two dumpsites, twenty one leachate quality variables and two greenhouse gases. The strategy was to evaluate the characteristics of leachate draining to Ganga River and to record source emission estimates of two most important greenhouse gases, CH_4 and CO_2.

2.2.1 Measurement of CH_4 emission

The *in situ* emission flux of CH_4 was measured at two dumpsites for the entire study period. Closed chamber technique was used for measuring CH_4 emission [16]. Steel chambers of 25 cm diameter were inverted and fixed penetrating the soil firmly to 6 cm deep. To ensure proper mixing of air inside the chamber a battery operated pump was used to circulate the air. Chamber was devised with a sampling pot on the top and a non-reactive silicon rubber septum. Samples were collected at 0, 15, 30, and 45 minute intervals in 10 ml air tight syringes fitted with three way top cork to prevent leakage of air samples. For each sampling event, eight air samples from each chamber were collected using air tight syringes. Concentration of CH_4 was measured in a gas chromatograph (Agilent Technologies 7820A, Germany) equipped with Thermal Conductivity Detector (TCD) and a Porapak Q Column (3 m). The carrier gas was N_2 with flow rate of 7 ml/minute. The detector and injector temperatures were set at 250ºC and 210ºC, respectively. The oven temperature was set at 60°C for 0 min and then ramped to 180ºC at 10ºC/min. Standard gas of 10 ppm and 100 ppm of NIST (National Institute for Standards and Technology, USA) were used for calibration. Concentration of gas was calculated from respective relative peak area from the standard gas of known concentrations obtained by running known volume of standard gas in GC. The concentration values, thus obtained, were used for computation of CH_4 flux.

2.2.2 Measurement of CO_2 emission

The emission flux of CO_2 was measured at both study sites using closed chamber technique. In this technique the gas in a closed perspex chamber is trapped as it leaves the soil surface which is then allowed to absorb in KOH within the chamber for a known period of time. The perspex chambers were inverted and fixed penetrating the soil firmly up to 6 cm deep. The CO_2 built– up inside the chamber was trapped in 0.5 N KOH and analysed volumetrically. The CO_2 emission flux was expressed in terms of mg m^{-2} h^{-1}.

2.3 Leachate Quality

The landfill leachates were collected from both the study sites and stored at 4ºC before analysis. The pH, conductivity, total dissolved solids (TDS) and salinity all were analyzed by multi-parameter tester of 35 series (Eutech PCSTESTR 35-01x441506 / Oakton 35425-10). Biological oxygen demand (BOD) was measured after 5 day incubation following standard method [17]. Nitrate-N was quantified using a brucine-sulphanilic acid method [18] and phosphate-P using ammonium molybdate method [17]. Chloride concentration was determined following Mohr's method [19]. For Na, K, and Ca, leachate samples were digested in concentrated HNO_3 and the concentrations determined using Flame Photometer (Systronics, India). For heavy metals, samples were digested with concentrated HNO_3 [17], and concentrations determined using Atomic Absorption Spectrophotometer (Perkin Elmer, model 2130, USA) with appropriate drift blank. The chemicals used were Merck analytical grade. Blank and drifts standards (Sisco Research Laboratory Pvt. Ltd., India) were run after

five readings to calibrate the instrument. Quality control measures were taken to assess contamination and reliability of data.

2.4 Leachate Pollution Index

For comparing the leachate pollution potential of dumpsites, an index known as leachate pollution index (LPI) was calculated using Rand Corporation Delphi Technique. A complete description of Leachate Pollution Index is given in Kumar et al. [4]. The leachate pollution index (LPI) is an efficient tool to determine the detrimental effect the leachate can have if not treated properly. It is a quantitative measure of the leachate contamination potential and is calculated using the following equation:

$$LPI = \sum_{i=1}^{n} w_i p_i$$

Where, LPI = the weighted additive LPI,
Wi = the weight for the *i*th pollutant variable,
pi = the sub- index score of the *i*th leachate pollutant variable,
n = number of leachate pollutant variables used in calculating LPI,

$$\sum_{i=1}^{n} w_i = 1$$

However, when the data for all the leachate pollutant variables included in LPI is not available, the LPI can be calculated using the data set of the available leachate pollutants. In that case, the LPI can be calculated by the following equation:

$$LPI = \frac{\sum_{i=1}^{m} w_i p_i}{\sum w_i}$$

Where, *m* is the number of leachate pollutant variables for which data is available, but in that case, $m < 18$ and $\Sigma Wi < 1$ [4].

2.5 Statistical Analysis

Samples were collected as replicates and the values are presented as mean (n=4) ±SE. Between- site differences were tested using analysis of variance (ANOVA). The Mann-Kendall test with Sen's slope estimates were used for detecting trend direction and magnitude of seasonal change (XLSTAT 2013).

3. RESULTS AND DISCUSSION

Except pH that did not show a definite trend, all other variables including conductivity, TDS, salinity, BOD and concentrations of Cl^-, Na^+, K^+, Ca^{2+},Mg^{2+}, NO_3^- , PO_4^{3-} and heavy metals

(Cd^{2+}, Fe^{2+}, Cu^{2+}, Pb^{2+}, Ni^{2+} ,Zn^{2+} , Co^{2+} ,Mn^{2+}) showed values relatively higher at Site 1 (Tables 2 and 3). Between- site differences were significant at $p< 0.05$ for Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}, NO_3^{-}, PO_4^{3-} and BOD and at $p< 0.01$ for conductivity, TDS, salinity and Cl^{-}. Mann-Kendall test with Sen's slope statistics showed significant seasonality in BOD and concentrations of NO_3^{-} and PO_4^{3-} (Fig. 2). The trend in metal concentration at two study sites was not exactly similar. Overall trend in the concentration of heavy metals appeared as : Fe >Mn> Cu > Zn >Pb> Co > Cd > Ni at Site 1 and Fe > Cu > Zn > Cd >Pb>Mn> Ni > Co at Site 2 (Tables 2 and 3). Despite variability in overall concentration, metal concentration in leachate showed significant seasonality (Figs. 3 and 4). Leachate pollution index was found to be 87.19 and 82.56 at KZP and BPS site respectively (Table 4).

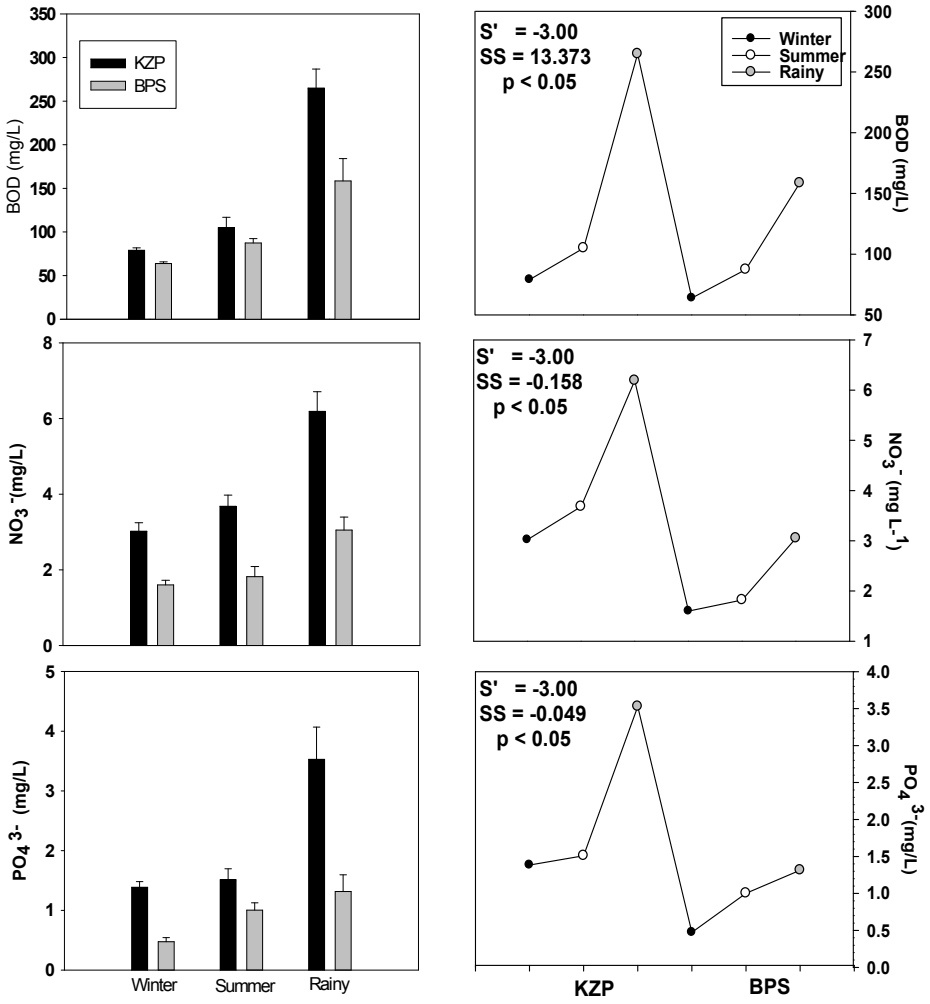

Fig. 2. Seasonal variation and Mann-Kendall test with Sens's slope statistics for concentration of NO3-, PO43- and biological oxygen demand (BOD) in leachate emerging from landfill sites at Varanasi

Value are mean (n= 4) ± 1 SE

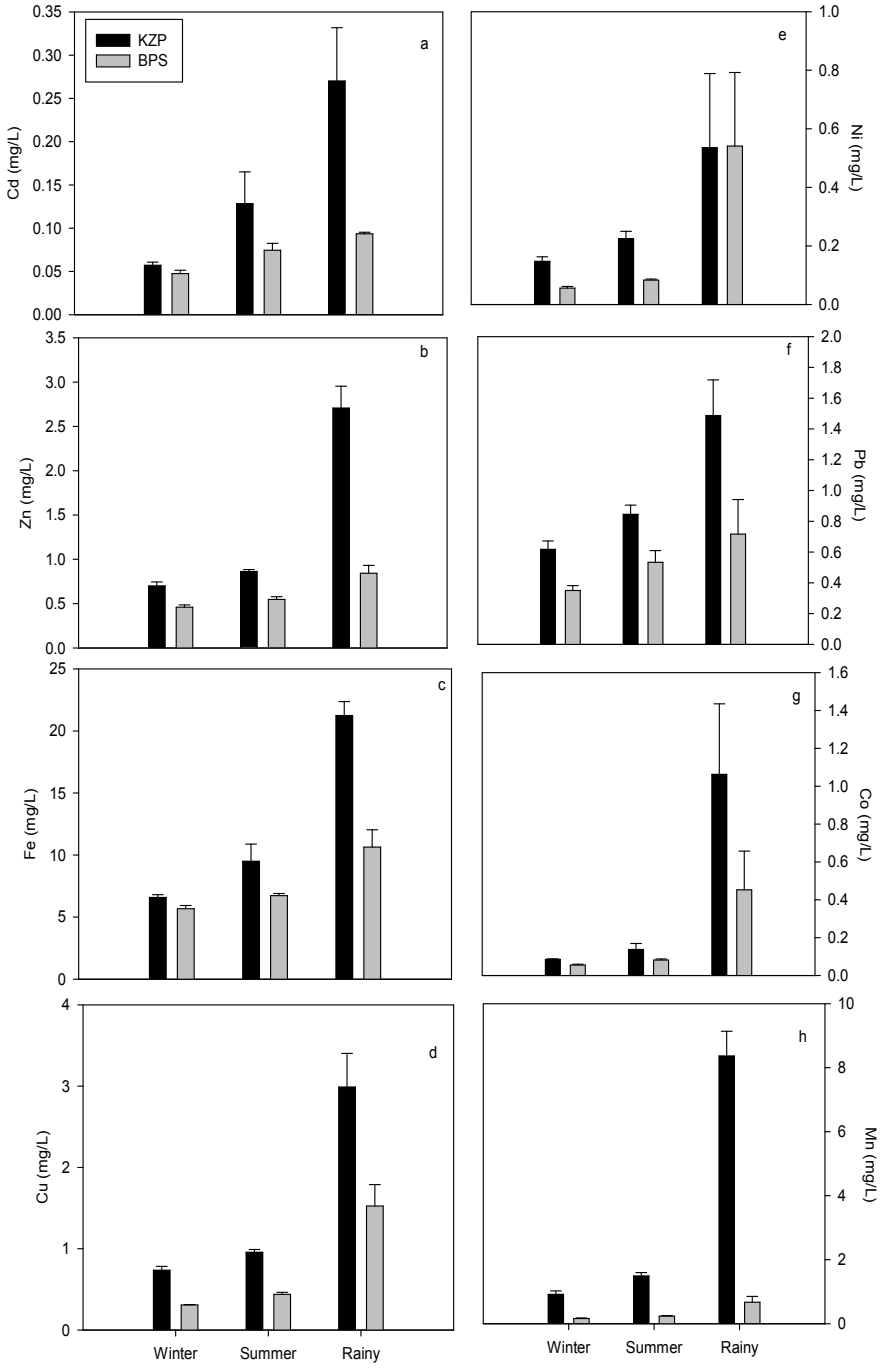

Fig. 3. Seasonal variation in the concentration of heavy metals in leachate emerging from landfill sites at Varanasi

Value are mean (n= 4) ± 1 SE

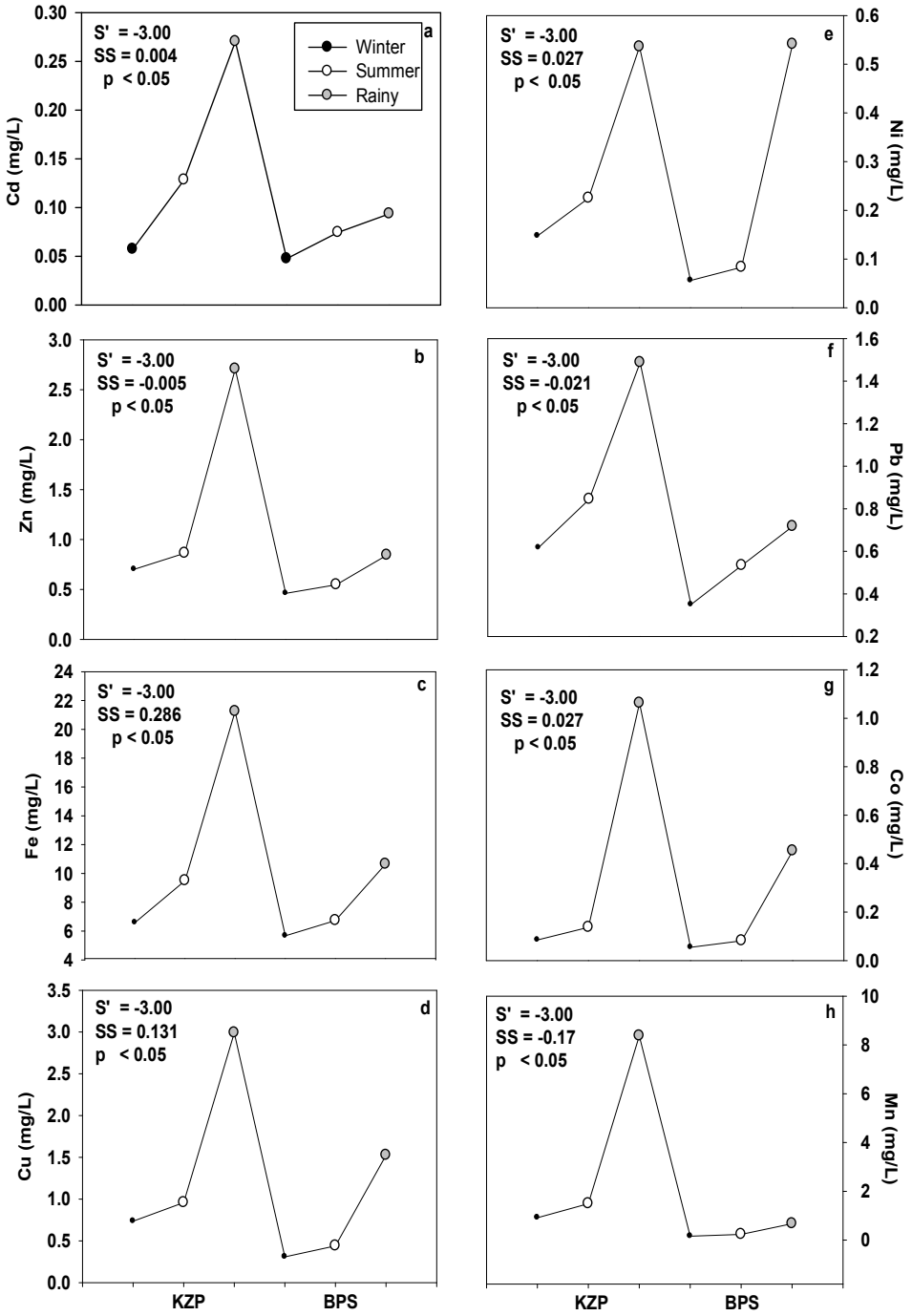

Fig. 4. Man-Kendall test with Sen's slope statistics for concentration of heavy metals in leachate at landfill site

Temporal trends in leachate quality showed a pattern similar to the previous studies [20]. Our observations showed a change in leachate quality across the year although the rates of such changes were lower than those reported for leachate emerging from wood wastes [21]. Earlier studies have shown that leachate generated from mature landfills has typically low biochemical oxygen demand (BOD_5) indicating resistance to biodegradability [22]. In another study, the young wood waste leachate showed higher oxygen demand than the older leachates [21]. We found higher BOD_5 in leachate generated in rainy season at Site 1 where the proportion of young wastes was relatively higher. The contribution of easily biodegradable fraction to total oxygen demand decreases rapidly overtime resulting in a more recalcitrant leachate and hence BOD declines with maturation of wastes. Microbial decomposition within the landfill reduces the availability of labile organic carbon with the age of the landfill. This merits attention in the present study as it regulates concentrations of dissolved organic carbon (DOC) in leachate and associated runoff added to the Ganga River.

One of the major problems associated with MSW is the production of massive amount of leachate which may enter the underground water and / or mixed with runoff and directly contaminate the surface waters [23,24]. The LPI values computed in this study are significantly higher than those reported for other metropolitan cities of India (Table 5). Significantly higher values of LPI of leachate emerging from both study sites indicated high contamination potential for surface and ground water. This suggests the need for proper treatment to ensure discharging leachate to the river. So far, these dumpsites do not have any base liner or leachate collection and treatment system. This invites serious concern of municipal authorities from a human health perspective. Landfill leachates are generally characterized as high strength waste water and BOD is often used as an important criterion for this purpose. In the present study, low BOD of older dumpsite leachate suggests that the anaerobic degradation predominate the degradation scenario producing CH_4, CO_2 and metabolic intermediates. Taylor and Carmichael [25] observed significant BOD reduction when leachate was stored in a catch basin under anoxic condition. Further, the anaerobic environment within the landfill could lead to a decrease in the concentration of nitrate as was evident in the present study. The biological treatment processes rely on a consortium of microorganisms and the nutrients supporting their growth. Aerobic biological system operates efficiently at a BOD_5: N: P ratio of 100: 5: 1 [26]. In the present study, the mean BOD_5: N: P ratio was 57: 2: 1 in winter, 70: 2: 1 in summer and 76: 2: 1 in rainy season at Site 1 and 135: 3: 1 in winter, 87: 2: 1 in summer and 120: 2: 1 in rainy season at Site 2. Thus, the BOD_5: N ratios of leachate in two study sites (ranged from 23:1 to 60:1) are significantly higher than those required for aerobic biological treatment. It seemed, despite very low BOD compared to leachate BOD in other metropolitan cities (Table 5), for the treatment of leachate draining from both the study landfills, the aerobic biological systems may not operate efficiently without N supplement [21].

The concentration of TDS showed characteristics synchrony with the concentrations of ions. In rainy season, high concentrations of inorganic constituents could be due to enhanced precipitation. The trend in metal concentration at two study sites was not exactly similar. The trend at Site 1 appeared as: Fe > Mn > Cu > Zn > Pb > Co > Cd > Ni and at Site 2 as: Fe > Cu > Zn > Cd > Pb > Mn > Ni > Co. This could be due to variability in waste composition at dumpsites, degree of compaction and environmental variables. Heavy metals in leachate are generally reported in low ranges [9]. Such concentrations however, represent only a small fraction of the metals associated with the solid wastes because the chemical and physical affinity of metal ions with waste materials reduces their leachability under landfill conditions. Possibly for this reason, metal concentrations in landfill waste remains several orders of

magnitude higher than the concentrations measured in leachates [10]. The mobility of metals generally increased over time as the waste becomes more acidic and oxidizing conditions dominate [6]. Thus, time coupled-site-specific conditions need to be considered for assessing heavy metal concentration relationships in landfill leachates. It may further be noted that the concentration of Pb in present study was significantly higher than those reported for other metropolitan of India except Kolkata (Table 5).

High moisture, rainfall and temperature in rainy season could enhance mobilization of inorganic constituents including heavy metals [27]. We found a mixed effect of moisture and temperature on leachate quality. Month-wise trends observed in the present study did support such a possibility as the concentrations of ions, nutrients and heavy metals were generally high in rainy season. Relatively higher moisture content in rainy season could enhance microbial activity and leaching of ions, heavy metals and soluble compounds. Despite a mixed effect of moisture and temperature, the effect of wet-winter was found sub-ordinate to summer temperature. A positive relation between temperature and concentration of ions and nutrients in leachate indicated the effect of climate variables on changing state of landfill leachate quality [28].

Emission fluxes of greenhouse gases increased consistently from January onward achieving a peak in July for CO_2 and in September for CH_4 (Fig. 5). Emission of both the gases declined sharply after September onward. Methane emission flux ranged from 12.39 to 44.61 mg m^{-2} h^{-1}in winter, 20.27 to 60.2mg m^{-2} h^{-1}in summer and 48.34 to 96.74mg m^{-2} h^{-1}in rainy season at Site 1.The respective ranges at Site 2 were 9.64 to 10.73mg m^{-2} h^{-1}in winter, 13.89 to 40.2 mg m^{-2} h^{-1}in summer and 37.63 to 77.49 mg m^{-2} h^{-1}in rainy season (Fig. 6). Between- site differences in the emission flux of both the gases were significant ($p<0.001$; ANOVA). Mann- Kendall test with Sen's slope statistics showed significant seasonality in the emission flux of both the gases (Fig. 6). Our observations indicate that Site 1 with relatively higher proportion of new wastes dominated the CH_4 emission flux during the study period. Although there were marked temporal and spatial variations, the CH_4 emission fluxes recorded in the present study are lower than those reported in previous studies. Börjesson et al. [29] reported methane emission flux ranging from 0.54 to 320 mg m^{-2} h^{-1} from landfill areas in Sweden. Chen et al. [30] observed methane emission ranging from 8.8 to 163 mg m^{-2} h^{-1} at landfills of Taiwan. Jha et al. [12] and Ankolkar et al. [31] estimated methane emission fluxes of 1 to 433 mg m^{-2} h^{-1} and 982.8 to 5972.4 mg m^{-2} h^{-1}at landfills of Chennai and Pune respectively. Chakraborty et al. [2] estimated methane emission fluxes of 1154.3 to 3617.5 mg m^{-2} $h^{-1}$from three landfills of Delhi. Similar ranges of methane emission flux were reported by Rawat et al. [32] Kumar et al. [33] and Mor et al. [34] from different landfill sites of India.

Factors such as temperature, moisture, composition and age of landfill and the degree of compaction all regulate the decomposition of MSW. The most conducive range of temperature for methane emission (30ºC- 40ºC) prevails for a major part of the year in tropical countries including India. Further, CO_2 emission is relatively rapid from easily biodegradable materials where the rate of decomposition is faster particularly if the temperature and moisture content is high. Under such condition, a major fraction of carbon is emitted as CO_2 rather than as CH_4 [12]. Varanasi is the cultural capital of India and therefore a major part of the waste generated in the city comprises of biodegradable materials. Due possibly to this reason, CH_4 emission fluxes were lower in present study compared to those recorded in other studies. In the present study, although CO_2 emission flux was higher than CH_4 emission flux, the CO_2 emission was relatively lower than those reported in other studies conducted at different landfills of India [12].

Table 2. Physico-chemical properties and heavy metal concentration in leachate emerging from landfillsat Site 1 at Varanasi

	Jan	Feb	Mar	Apr	May	June	July	Aug	Sep	Oct	Nov	Dec
Temp	21.4	25.1	29.6	39.9	43.6	48.7	37.9	33.6	33.2	30.8	23.9	18.6
pH	6.98	7.1	7.06	6.03	6.12	6.09	7.09	7.24	7.16	7.31	7.42	6.9
Cond	2678	2652	2870	4961	5248	5510	12569	10946	11468	8684	2743	2987
TDS	1728	1794	1910	2994	2968	3810	6743	5982	5472	4386	1765	1834
Salinity	994	986	1280	2748	2756	2872	4965	4187	3985	3852	893	1046
Cl^-	483.95	496.35	571.55	703.55	698.95	763.25	1094.19	1167.95	1132.46	864.35	364.93	398.87
Na^+	111.67	117.49	183.81	229.46	231.48	232.48	393.43	397.39	382.56	124.9	117.42	93.86
K^+	121.84	121.63	122.66	128.32	133.48	140.04	264.21	272.49	267.94	147.51	129.84	92.43
Ca^{2+}	97.36	105.73	112.7	27.62	30.84	32.23	518.46	662.2	538.59	492.26	102.57	109.43
Mg	54.59	62.59	64.83	65.11	73.39	75.47	113.49	117.64	129.98	84.83	64.59	59.59
NO_3^-	2.68	2.77	2.8047	3.9842	3.864	4.0761	6.84	7.09	6.04	4.79	2.96	3.67
PO_4^{3-}	1.12	1.57	0.96	1.69	1.63	1.76	4.18	4.05	3.97	1.91	1.38	1.47
BOD_5	86.32	73.28	78.92	102.38	102.46	136.22	296.38	307.49	218.91	236.8	76.82	79.56
Cd	0.06	0.063	0.074	0.094	0.108	0.237	0.29	0.34	0.36	0.091	0.047	0.059
Zn	0.756	0.794	0.813	0.837	0.895	0.906	2.94	3.06	2.85	1.98	0.615	0.639
Fe	6.87	7.04	7.18	7.32	10.6	12.9	20.06	23.17	23.09	18.64	6.12	6.31
Cu	0.769	0.853	0.932	0.916	0.927	1.056	2.77	3.42	3.83	1.94	0.639	0.683
Ni	0.13	0.19	0.16	0.23	0.23	0.28	0.023	0.96	0.98	0.18	0.12	0.15
Pb	0.57	0.49	0.69	0.87	0.84	0.98	1.49	1.73	1.89	0.84	0.73	0.68
Co	0.086	0.093	0.098	0.106	0.114	0.231	0.26	1.89	1.46	0.64	0.08	0.081
Mn	0.97	1.19	1.26	1.38	1.63	1.7	7.78	9.34	9.87	6.48	0.69	0.82

Values are in mg L-1 except temperature (^{0}C), pH and conductivity (μ S)

Table 3. Physico-chemical properties and heavy metal concentration in leachate emerging from landfills Site 2 at Varanasi

	Jan	Feb	Mar	Apr	May	June	July	Aug	Sep	Oct	Nov	Dec
Temp	20.8	23.5	27.9	38.3	39.4	42.6	31.9	28.2	30.06	27.4	23.81	18.7
pH	5.35	6.92	6.48	7.21	7.32	7.93	7.3	7.81	7.1	7.43	7.18	6.95
Cond	1294	1286	1320	1792	1731	1883	7634	10104	8412	6374	1273	1387
TDS	784	732	820	1432	1569	1620	4839	6072	4363	3978	732	864
Salinity	598	608	632	1132	1094	1190	3721	4543	3892	2653	579	634
Cl^-	173.5	186.3	195.25	276.3	298.5	308.8	549.29	523.9	550.5	431.6	169.6	193.65
Na^+	74.38	79.02	86.31	98.34	118.96	119.56	189.37	194.21	173.28	92.87	83.68	83.93
K^+	83.22	91.36	94.81	94.48	126.36	127.96	158.91	164.63	164.1	92.8	81.94	78.96
Ca^{2+}	76.32	76.81	81.12	99.41	99.94	121.8	197.4	203.8	192.6	187.9	59.38	81.47
Mg	33.83	34.09	34.17	54.63	59.84	65.36	113.83	114.62	164.91	64.57	53.04	33.46
NO_3^-	1.5321	1.5496	1.6902	1.9832	1.1648	2.4374	3.19	3.843	2.98	2.17	1.376	1.958
PO_4^{3-}	0.431	0.455	0.75	0.94	0.98	1.34	1.56	1.983	0.934	0.78	0.67	0.34
BOD_5	62.91	64.48	73.52	86.38	92.94	96.48	167.98	189.47	193.29	83.21	59.63	68.48
Cd	0.049	0.056	0.053	0.072	0.084	0.089	0.091	0.097	0.096	0.09	0.037	0.048
Zn	0.482	0.508	0.506	0.519	0.527	0.638	0.92	0.89	0.98	0.58	0.394	0.459
Fe	5.94	6.28	6.31	6.59	6.94	7.08	10.28	12.89	12.56	6.84	5.18	5.3
Cu	0.302	0.319	0.382	0.417	0.465	0.491	1.24	1.89	2.04	0.93	0.297	0.314
Ni	0.061	0.068	0.076	0.079	0.084	0.093	0.15	0.98	0.97	0.064	0.042	0.053
Pb	0.27	0.33	0.34	0.49	0.631	0.673	0.894	0.982	0.946	0.046	0.41	0.39
Co	0.053	0.068	0.069	0.076	0.089	0.093	0.14	0.78	0.83	0.061	0.047	0.051
Mn	0.173	0.203	0.198	0.224	0.227	0.294	0.548	0.946	0.981	0.213	0.113	0.159

Values are in mgL-1 except temperature (^{0}C), pH and conductivity (μ S)

Table 4. Calculating Leachate Pollution Index (LPI) for the two study sites

LPV	Wi	Ci	Pi	Wi.Pi	Ci′	Pi′	WiPi′	Ct	Pt	Wi.pt
Cr	0.064	NA	NA	NA	NA	NA	NA	2	9	0.58
Pb	0.063	0.98	95	5.99	0.53	98	6.17	0.1	5	0.32
COD	0.062	NA	NA	NA	NA	NA	NA	250	10	0.62
Hg	0.062	NA	NA	NA	NA	NA	NA	0.01	6	0.37
BOD	0.061	149.63	82	5	103.23	77	4.7	30	6	0.37
As	0.061	NA	NA	NA	NA	NA	NA	0.2	5	0.31
CN	0.058	NA	NA	NA	NA	NA	NA	0.2	6	0.35
Phenol	0.057	NA	NA	NA	NA	NA	NA	1	5	0.29
Zn	0.056	1.42	82	4.59	0.62	98	5.49	5	6	0.34
pH	0.055	6.87	72	3.96	7.08	79	4.34	5.5-9	5	0.28
TKN	0.053	NA	NA	NA	NA	NA	NA	100	6	0.32
Ni	0.052	0.31	98	5.1	0.23	98	5.1	3	10	0.52
TCB	0.052	NA	NA	NA	NA	NA	NA	No standard	NA	NA
NH3	0.051	NA	NA	NA	NA	NA	NA	50	7	0.36
TDS	0.05	3448.83	90	4.5	2317.08	81	4.05	2100	7	0.35
Cu	0.05	1.56	96	4.8	0.75	68	3.4	3	18	0.9
Cl	0.049	728.36	78	3.82	321.43	73	3.58	1000	8	0.39
Fe	0.045	12.44	93	4.18	7.68	64	2.88	No standard	NA	NA
Total	0.716			41.94			39.94			6.67
										7.378
LPI for KZP	87.19									
LPI for BPS	82.56									

LPV - Leachate variables, Wi - Variable weight, Ci - Average Pollutant Concentration at KZP, Pi - Pollutant sub index value at KZP, Wi.Pi - Aggregation at KZP, Ci'- Average Pollutant Concentration at BPS, Pi'- Pollutant sub index value at BPS, WiPi'- Aggregation at BPS, Ct- Leachate disposal standards, Pt- Treated leachate Sub Index Value, Wi.Pt- Aggregation Treated Leachate

Table 5. Comparison of MSW leachate of some landfill sites in India

Sites	pH	TDS	BOD5	Fe	Cu	Ni	Zn	Pb	LPI	Ref.
Kolkata	8.18	9798	8980	9.8	1.43	2.0	3.53	6.94	52.79	[37]
New Delhi	8.4	21040	1848	108	4.25	NA	3.28	0.72	39.37	[4]
Mumbai	7.8	7251	645	3.82	0.167	0.633	0.231	0.313	11.81	[37]
Ludhiyana	9.3	5693	495	NA	NA	NA	NA	NA	26.45	[38]
Bangalore	8.37	6970	1090	13.15	3.116	0.316	4.97	0.155	NA	[37]
Pune	7.62	NA	6891	78.75	1.47	2.72	1.91	0.84	NA	[37]
Nagpur	6.97	2560	NA	8.87	0.124	0.268	0.395	0.785	NA	[37]
Varanasi	7.81	6743	307.49	23.17	3.83	0.98	3.06	1.89	87.19	Present study

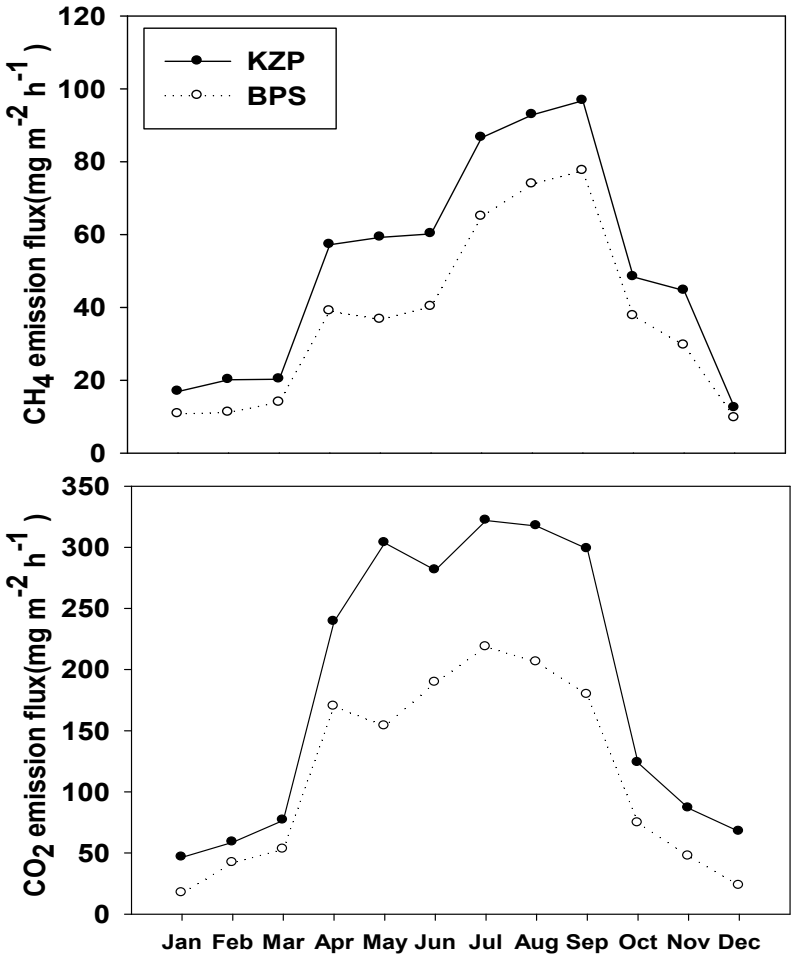

Fig. 5. Month-vies variation in methane and carbon dioxide emission flux at two landfill sites of Varanasi

On temporal scale, CH_4 emission fluxes were lower in winter months and increased consistently in summer months. Similar trends were reported by Jha et al. [12] at landfill sites of Chennai, Ankolkar et al. [31] at landfill sites of Pune and by Chakraborty et al. [2] at landfill sites of Delhi. Although CH_4 emission flux and moisture content did not show significant correlation, yet the impact of moisture content was clearly evident in winter month. Trankler et al. [28] showed that methane oxidation in tropical landfills was a function of moisture content. We observed that the moisture content of both the landfills were higher by 10-20 % in winter months relative to summer. Interestingly however, despite the influence of moisture, CH_4 emission fluxes were higher in summer months indicating the influence of temperature. For easily biodegradable materials, where rate of decomposition is faster, the CO_2 emission is relatively rapid. This is favoured further by high temperature and moisture content and consequently, a major fraction of carbon is emitted as CO_2 instead of CH_4 [2].

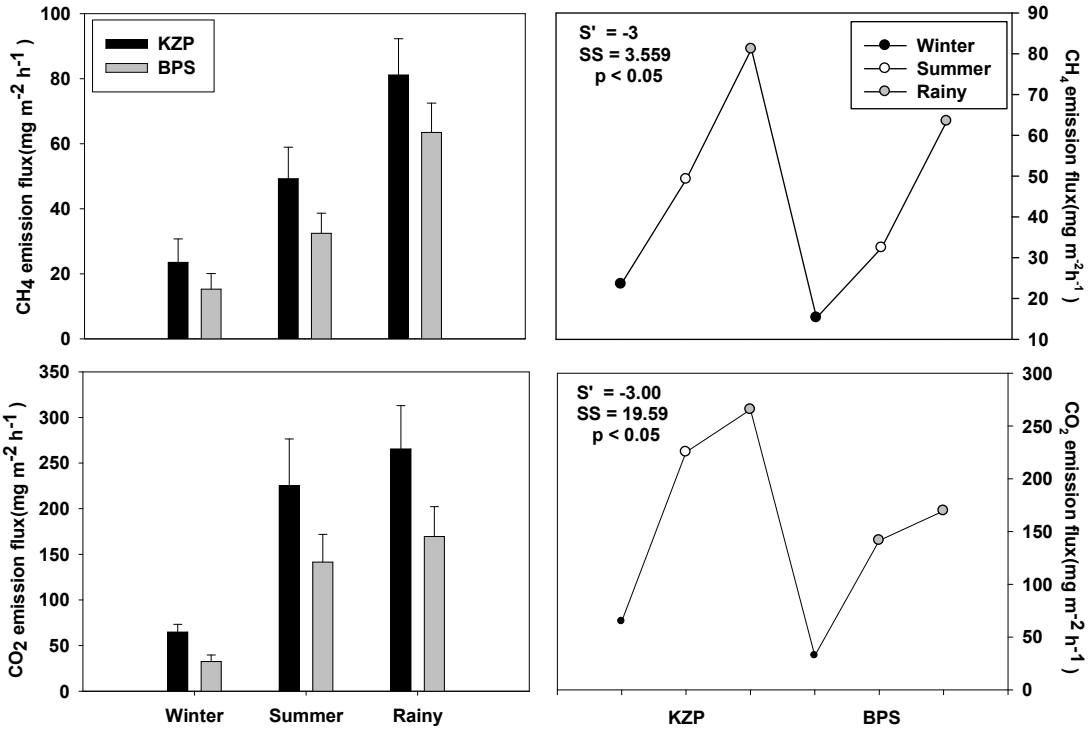

Fig. 6. Seasonal variation and Mann-Kendall test with Sens's slope statistics for methane and carbon dioxide emission flux at landfill sites of Varanasi
Value are mean (n=4) ± 1 SE

The MSW undergoes five stages of decomposition. These include acclimation, transition, acidogenesis, methanogenesis and maturation [35]. Young dumpsites are in acidogenic phase and contain large amount of biodegradable organic matter which undergoes anaerobic fermentation resulting in the production of volatile fatty acids (VFA). As the landfill matures the methanogenic phase starts and methanogenic microbes develop in the waste, converting the VFAs to methane and carbon dioxides. In due course, the organic fraction of the leachate becomes mostly non-biodegradable and rich mainly in humic and fulvic substances. Climate/seasonal weather condition also influences this outcome (Fifth Assessment Report, IPCC 2013) [36]. During rainy season the moisture content of landfills is increased. Since moisture content enhances the anaerobic fermentation of organic matter, biodegradability in the rainy season will be faster than in dry season [37,38]. Thus, a hot and humid climate which favours microbial activity generates more leachate and biodegrades organic matter more rapidly than hot and dry climate. Also, in dry season evaporation reduces the moisture content and consequently, decreases the leachate production and microbial release of gases.

Within-site variations observed in this study could also be attributed to the age and composition of waste and percentage of degradable organic matter [2]. Further, the landfill management practices including the type of covering materials, degree of compaction also influence methane and carbon dioxide emission fluxes. Variations observed in the emission

fluxes of CH_4 and CO_2 could also be linked to management practices. For instance, landfills covered with excavated soil or construction and demolition wastes show relatively lower emission of methane due probably to the soil being a strong sink of methane. Under such condition the process of oxidation transforms methane to carbon dioxide [2,39].This merits attention and can be suggested as a management practice for mitigating methane emission if it is not being translated in a usable energy source.

4. CONCLUSION

The landfills are important cause of concern due to their contribution to greenhouse gas emission and release of harmful leachate. The BOD_5: N: P ratios of landfill leachate recorded in this study indicate that the aerobic biological degradation may not operate successfully without supplemental nutrients for leachate treatment. From human health perspectives, it is the Ganga River that is of greatest concern as the river receives concentrated leachate draining from the dumpsites especially in rainy season. In addition to other toxicants, leachate draining from both the landfills contains high concentration of heavy metals generally flushed to Ganga River through rain-driven run-off. Leachate pollution index (LPI) at both the dumpsites exceeds the permissible limit and marks a serious concern for surface and ground water along the Ganga River and a threat to ecosystem and human health. The emission flux of CO_2 was about five orders of magnitude higher than that of the CH_4. The methane emission flux reported in this study was lower than those reported from other landfill sites in India. Emission of both the gases varied over time and showed effect of temperature and moisture content. Although more exhaustive data sets are needed, the data generated in the present study will help reducing uncertainties in greenhouse gas emission estimates.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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