presence of the mulch. Apparently, there is also no increase of the N_2O consumption in the soil, caused by reduced conditions created with increased microbial respiration by the mulch application, because CO_2 emissions of the all treatments were comparable (Figure 1). Solubility of N_2O (ca. 55 cm^3 per 100 cm^3 of water at 1 atm, and ca. 30°C, ref. 8) is ca. 40 times higher than that of N_2. Therefore, dissolved N_2O in the aqueous phase of the litter is first converted into N_2, which is then emitted immediately, thus litter degrading microbial activity acts as a naturally occurring enzymatic converter of N_2O.

When the mulch was autoclaved and vaseline-coated, the N_2O emission was lowered by ca. 90% (Figure 1). However, when the mulch was only autoclaved, the reduction in the emission was only ca. 10%. This is an interesting result where vaseline-coated mulch restricted gas permeability, possibly increasing the residence time of N_2O produced in the soil, which contributed to the completion of the conversion of N_2O to N_2. The implication of this is that mulches of leaves, etc. with a thick waxy cuticle that are only partially permeable to gas diffusion may contribute to this mode of mitigation of soil N_2O emission before their slow decomposition.

It is not known accurately to what extent this natural process contributes to control N_2O emission in managed and natural ecosystems. Further studies are therefore needed, particularly under field conditions to fully evaluate its effects and potential. By field measurements taken repeatedly over years of varying climatic conditions, trends would emerge on the N_2O emission and its suppression by the residues.

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Methane emission from community biogas plant at Masudpur, Delhi

Methane, a combustible gas, is exploited as a source of heat and light. Anaerobic digesters are used to generate CH_4 in the form of biogas by decomposition of biomass in the absence of O_2 (ref. 1). The conventional biogas digesters like floating gas holder-type installed by the Khadi Village and Industries Commission (KVIC) plant have exposed areas, from which CH_4 is emitted continuously to the atmosphere[2]. Methane is the second most important anthropogenic greenhouse gas after carbon dioxide[3,4], and contributes substantially to warming of the atmosphere, with the continuous increase in atmospheric carbon ratio[5]. Among the various identified CH_4 sources, emissions from community biogas plants have not been estimated. In this communication, we present the results of a quantitative analysis of CH_4 emission from the exposed areas of biogas plants, between the gap of floating gas-holder and digester wall and slurry drying pits.

The four biogas plants under study, each of 85 m^3, were located at Masudpur village, in the southwest fringe of Delhi, India. All the biogas plants were of floating gas holder-type (KVIC model), having a total installed capacity of 4×85 m^3 equalling 340 m^3. The plants cater to the need of the community as a whole and some institutions. The plants are fed with cattle dung procured from a nearby dairy. One of the plants is attached to a community latrine. Biogas generated is supplied to about 75 subscribers of the Masudpur village and Harijan Basti through a gas distribution network of 1.5 km. The digested slurry from the biogas plants is collected into four different slurry pits, each having an area of around 30 m^2, with depth varying between 20 and 60 cm.

The gas samples were drawn from the exposed area around the gas holder and the slurry drying pits using the closed-chamber technique described by Hutchinson and Moiser[6], with floatable cylindrical iron sheet chambers of 25 cm diameter and 30 cm height. Gas samples (5 ml) were drawn from the chamber in a 20 ml air-tight syringe at time intervals 0, 5 and 10 min. All the samples were collected in triplicate from each plant and slurry pit, once in a day between 11.00 and 11.30 h at weekly intervals, for studying seasonal variation. Diurnal variation in CH_4 flux was recorded every

two consecutive hours of the day, starting from 8.00 am until 6.00 am the next day, during the months of July and November.

Methane concentrations in the gas samples were quantified using a gas chromatograph (Shimadzu, GC-8A) fitted with Flame Ionization Detector (FID) and Poropak N column. The column, injector and detector temperature was maintained at 70, 130 and 130°C respectively. Carrier gas was nitrogen, with a flow rate of 20 to 25 ml/min. Hydrogen was used as the fuel gas and zero air as the supporting gas, having flow rates of 25 and 250 ml/min respectively. Concentration of CH_4 in a sample was determined by calculating from the peak area obtained by injecting standard gas mixtures containing known amounts of CH_4 under the same conditions. Primary standard used was 14.04 ppmV CH_4 in nitrogen for methane, which was procured from National Physical Laboratory, New Delhi. Methane flux was calculated using the equation[7]:

$$F = [(C_t - C_0)/t] \times H \times 42.857 \text{ mg m}^{-2} \text{ d}^{-1},$$

where C_0 is the CH_4 conc (ppmV) at '0' time, C_t is CH_4 conc (ppmV) after time 't', t is the time interval and H the head space height (in m).

The ambient and slurry temperatures of the biogas plants were recorded 20 cm below the surface of the slurry using an ordinary mercury thermometer, at the time of sampling.

Data on CH_4 emission from the four plants, A–D and their slurry drying pits indicated variation of CH_4 flux due to changes in seasonal as well as diurnal temperatures. The highest rate of CH_4 emission was recorded during June, when the slurry temperature reached a maximum (32°C). Methane flux during June from the cattle dung-fed plants A, B and C was 235, 219 and 222 g m^{-2} day^{-1} respectively, and for the toilet-linked plant D it was 128 g m^{-2} day^{-1}. The differential nature of substrates led to a higher rate of CH_4 emissions from cattle dung-fed plants throughout the year compared to the toilet-linked (cattle dung + human excreta plant). The average mean CH_4 flux from the cattle dung-fed plants ranged between 68 and 230 g m^{-2} day^{-1}, while the corresponding CH_4 flux from the (toilet-linked) plant ranged between 15 and 128 g m^{-2} day^{-1} (Figure 1).

The CH_4 fluxes were considerably reduced during winter. The lowest rate of CH_4 emission occurred during December and January, when the ambient and slurry temperatures went down below 20°C. The mean emission of CH_4 per day per plant throughout the year for plants A–C, running on cattle dung, and toilet-linked plant-D (cattle dung and human excreta), amounted to 286.6 g and 138.9 g respectively. The correlation coefficient between the slurry temperature and CH_4 flux from the cattle-dung plants, toilet-linked plant and slurry pits was positive (0.964, 0.946 and 0.913 respectively) and significant.

In toilet-linked biogas plants, gas production is reduced due to excessive dilution, owing to larger volume of water discharge during flushing. This upsets the fermentation process and also reduces the total solids retention period and gas production. In excess dilution, methanogenic bacteria are restricted in nutrient uptake[8]. The excessive dilution

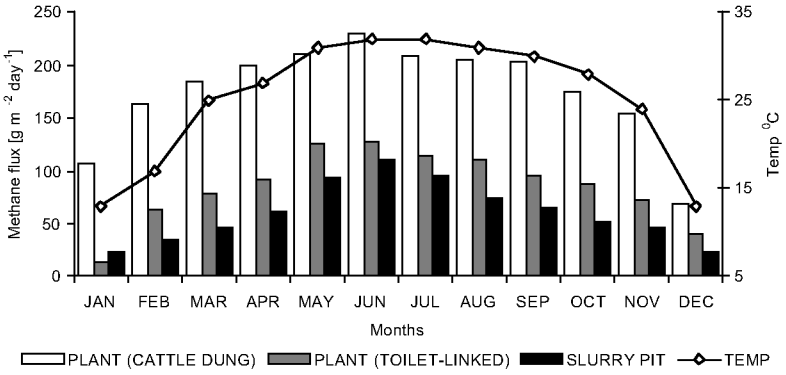

Figure 1. Seasonal methane flux from 85 m^3 biogas plant and slurry drying pit.

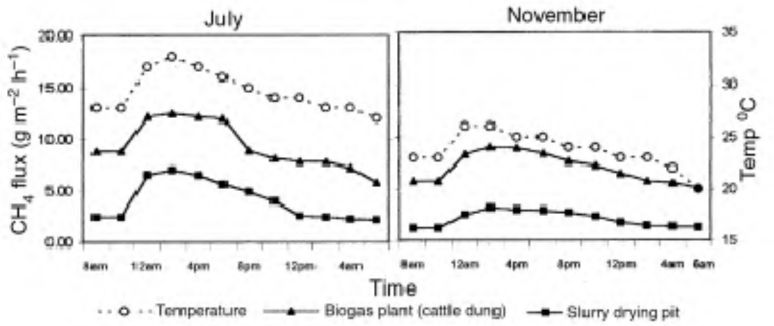

Figure 2. Diurnal methane flux from biogas plant and slurry drying pit.

coupled with the inferior feed material reduced CH_4 emission from plant-D.

The lowest rate of CH_4 emission during a day was observed in the early morning hours at 6.00 am, when the ambient and slurry temperatures were lowest (Figure 2). Emission rates were observed to be highest (12.45 and 9.04 g $m^{-2} h^{-1}$) during early afternoon at 2.00 pm. Diurnal variation of CH_4 flux was more pronounced in the slurry pit compared to the exposed area of a plant.

The results of the study revealed that changes in seasonal and diurnal temperature affect CH_4 emission from biogas plants to the atmosphere. Methane emission was maximum around 2 pm during summer months, and decreased to a minimum around 6 am during winter months. Taking into account the exposed surface areas around the floating gas holder in a 85 m^3 biogas plant (1.63 m^2) and slurry pit (30 m^2), the annual contribution to global CH_4 budget from a cattle dung-fed biogas plant, a toilet-linked biogas plant and the slurry pit would amount to 104.6 kg, 50.9 kg, and 667.9 kg respectively.

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Pyrrhotite inclusions in sphalerite

Barton and Bethke[1], while discussing the nature of chalcopyrite inclusions in sphalerite wondered, '... why we have not observed pyrite blebs of similar origin forming in a Cu-deficient environment...?' In this communication, we report the presence of pyrrhotite blebs in sphalerite from the Rampura–Agucha Zn–Pb sulphide deposit in Rajasthan. The Rampura–Agucha deposit is a sedimentary exhalative type of deposit hosted by graphite–mica–sillimanite schist[2]. The predominant country rocks are granite gneiss and garnet–biotite–sillimanite gneiss with intercalated bands of calc-silicate rock and amphibolite. The mineral assemblages in the country rocks suggest upper-amphibolite facies metamorphism at peak *P–T* conditions of about 6.2 kb and 650°C (Pradeep Kumar, T.B., unpublished; Sharma[3]). The rocks also underwent intense deformation, manifested by the tight mega- and mesoscopic folds[4] and numerous microstructures in the ore and rock sections[5].

Independent equidimensional beads and chains of ellipsoidal beads of pyrrhotite are found in sphalerite of Rampura–Agucha. This phenomenon is comparable with the chalcopyrite disease in sphalerite[1,6]. The present communication discusses the nature of pyrrhotite beads in sphalerite. Polished ore slabs were studied in reflected plane polarized light and polished thin sections were studied in transmitted plane polarized light.

Sphalerite in Rampura–Agucha is classified into three types: (i) sphalerite in contact with iron-sulphide minerals (pyrite and/or pyrrhotite); (ii) sphalerite not in contact with iron sulphides and, (iii) sphalerite veins.

Only type-2 sphalerite includes blebs of pyrrhotite. Pyrrhotite occurs in two forms: (i) in association with pyrite, sphalerite and galena, and (ii) as inclusions in sphalerite.

These inclusions occur in two forms: (i) equidimensional inclusions within single grains of sphalerite (Figure 1 *c* and *d*), and (ii) chains of ellipsoidal beads along grain boundaries (Figure 1 *a*,*b* and *d*), which, in three dimensions, look like a grain of sphalerite covered with small beads of pyrrhotite. In other words, they resemble a 'sphalerite cell' carrying numerous small 'parasitic cell' of pyrrhotite on the surface.

Sphalerite has a bluish-grey colour and an average reflectivity percentage of 17.8. No internal reflections were observed. In transmitted light, with increasing Fe content the colour of sphalerite changes from yellow to red and brown, and opacity increases. Pyrrhotite is pinkish-yellow and strongly anisotropic in reflected light, whereas it is opaque in transmitted light. When the polished thin sections were studied, it was found that surrounding each of the pyrrhotite inclusions in sphalerite, there is a yellow-coloured area due to low Fe content, gradually changing to brownish-red colour due to high Fe content away from the inclusion. The chemical composition of the inclusions and sphalerite around these inclusions is given in Table 1. It can be seen from the data that sphalerite is deficient in sulphur ions relative to total Zn and Fe, while pyrrhotite contains excess sulphur. The relative deficiency of sulphur can be either due to vacant anion sites in the