Proton binding constants for natural organic matter

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Humic (HA) and fulvic (FA) acids are complex and heterogeneous assemblages of dominantly carboxyl (COOH) and phenol (ph-OH) polyelectrolyte groups issued from the breakdown of bacterial, algal, and/or higher plant organic material. The acid-base equilibria of these groups, which control their ion binding properties, is measured usually by potentiometric titration and expressed numerically by the two proton binding constants log $K_{H,COOH}$ and log $K_{H,ph\text{-}OH}$, and the two associated site densities $Q_{H,COOH}$ and $Q_{H,ph\text{-}OH}$. The mean intrinsic proton binding constants derived from titration curve fitting with the NICA-Donnan model are log $K_{H,COOH}$ = 3.09 ± 0.51 for HA and 2.65 ± 0.43 for FA, and log $K_{H,ph\text{-}OH}$ = 7.98 ± 0.96 for HA and 8.60 ± 0.83 for FA [1]. The high acidity of carboxyl groups and the differences between HA and FA either are real or within the uncertainty and accuracy of titration modeling. To address this question, average log K_{Hi} values were calculated semi-empirically from structure models of FA and HA, and then used to simulate titration data from *Sphagnum sp.* and *Carex sp.* peats. Predicted constants are log $K_{H,COOH}$ = 3.73 ± 0.13 for HA and 3.80 ± 0.20 for FA, and log $K_{H,ph\text{-}OH}$ = 9.83 ± 0.23 for HA and 9.87 ± 0.31 for FA, and reproduce data as well as the generic NICA-Donnan constants. Principal component analysis of 47 published proton titration curves shows that the dataset contains six independent parameters, while eight are optimized in the NICA-Donnan model. Results also show that the dataset can be fit using variable combinations of {log $K_{H,i}$, $Q_{H,i}$} numerical values. Therefore, differences in proton binding constants and site densities reported in the literature result partly from the use of loosely constrained data fits. An analytical procedure is proposed to increase the robustness of acid-base parameters derived from titration measurements for organic matter.

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Study on district level emission of carbonaceous aerosol from biofuels used in rural sector as energy over Indo Gangetic plain

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Indo Gangetic plain is major emitter of pollutants in India. To our best knowledge, for the first time, emission factor of carbonaceous aerosol from biofuels used by rural sector for energy, are presented at district level in all states (Punjab, Haryana, Uttar Pradesh, Bihar, Jharkhand, Utttarakhand, Himachal Pradesh, West Bengal, Delhi, Rajasthan) of Indo Gangetic Plain. Distribution of biofuels uses by rural sector as energy show that cow dung is mostly used as energy among other biofuels (fuel wood, crop residue). Emission factor are determined by total burning (pyrolysis, flaming and smoldering) of those biofuel samples in the laboratory. Cow dung represents major emitter of organic carbon in this region.

Samples were collected at district level from different rural areas of all states of IG plain to get the real picture of the biomass used in these areas by interrogating with local people. Demographic data were also collected to estimate the budget. Burning of those samples is being carried out in the laboratory and emission factor of carbonaceous aerosol are determined.

The study revealed that in the rural sector of north India cow-dung cake is the major biomass used as the fuel for cooking purpose. Uttar Pradesh has the largest variability among the biomass use. Further, *in situ* study of the biomass materials collected from the sampling locations will help to develop the mitigation strategy to reduce the atmospheric pollution. Contribution of dung cake in organic carbon is effectively more due to high emission factor (Table-1)

Fuel	EC (g/kg)	OC (g/kg)
Fuel wood		
Morus sp (Shahtoot)	~0.05	~0.51
Acacia sp (Keekar)	~0.07	~1.07
Brassica sp (Sarso)	~0.1	~4.48
Zizyphus sp (Ber)	~0.06	~0.95
Dung Cake	~0.07	~0.51

Table 1: Emission factor for OC and EC.