1 Minimization of the Cost Function in 4DEnVar

The minimization of the cost function follows the 4DEnVar processes. An ensemble of emission inventory is generated randomly using the prior emission vector f_h and the assumed emission error covariance $\mathbf{B}$:

$$[\boldsymbol{f}_1, \ldots, \boldsymbol{f}_N] \tag{S1}$$

An ensemble of GEOS-Chem model simulations then forward with the ensemble emission inventories in parallel:

$$[\mathcal{M}(\boldsymbol{f}_1), \ldots, \mathcal{M}(\boldsymbol{f}_N)] \tag{S2}$$

Denote the emission ensemble perturbation matrix by:

$$\mathbf{F}' = \frac{1}{\sqrt{N-1}} \left[\boldsymbol{f}_1 - \overline{\boldsymbol{f}}, \ldots, \boldsymbol{f}_N - \overline{\boldsymbol{f}}\right] \tag{S3}$$

and mean of ensemble simulation by:

$$\overline{\mathcal{M}(\boldsymbol{f})} = \frac{1}{N} \sum_{i=1}^{N} \mathcal{M}(\boldsymbol{f}_i) \tag{S4}$$

where f is the mean of the ensemble emission inventories. In the 4DEnVar assimilation algorithm, the optimal emission f is defined as weighted sum of the columns of the perturbation matrix $\mathbf{F}'$ using weights from a control variable vector $\boldsymbol{w}$:

$$\boldsymbol{f} = \overline{\boldsymbol{f}} + \mathbf{F}'\boldsymbol{w} \tag{S5}$$

The cost function could then be reformulated as:

$$\mathcal{J}(\boldsymbol{w}) = \frac{1}{2}\boldsymbol{w}^{\mathrm{T}}\boldsymbol{w} + \frac{1}{2}\left\{\mathbf{HM}'\boldsymbol{w} + \mathbf{H}\overline{\mathcal{M}(\boldsymbol{f})} - \boldsymbol{y}\right\}^{\mathrm{T}} \mathbf{O}^{-1} \left\{\mathbf{HM}'\boldsymbol{w} + \mathbf{H}\overline{\mathcal{M}(\boldsymbol{f})} - \boldsymbol{y}\right\} \tag{S6}$$

here $\mathbf{M}$ is the linearization of the GEOS-Chem ammonia simulating model required for cost function minimization, and is approximated by:

$$\mathbf{MF}' \approx \frac{1}{\sqrt{N}} \left[\mathcal{M}(f_1) - \overline{\mathcal{M}(f)}, \ldots, \mathcal{M}(f_N) - \overline{\mathcal{M}(f)}\right] \tag{S7}$$

with the uncertainty in emission transferred into the observations space, the minimum of the cost function in Eq.(S6) could then be directly calculated, and the posterior emission f subsequently be updated.

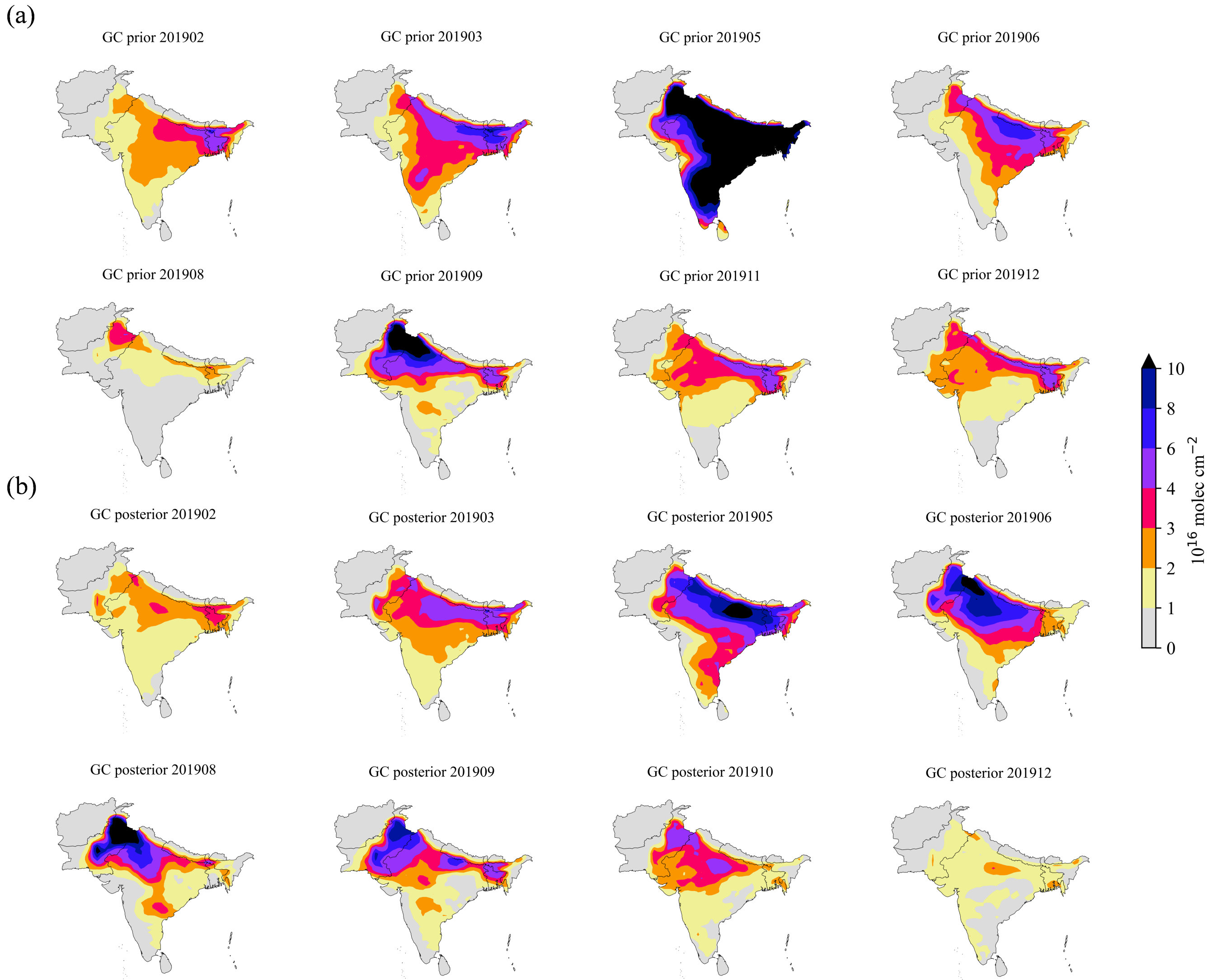

Figure S1. The distribution of the prior (a) and the posterior (b) ammonia total column for the remain months in 2019.

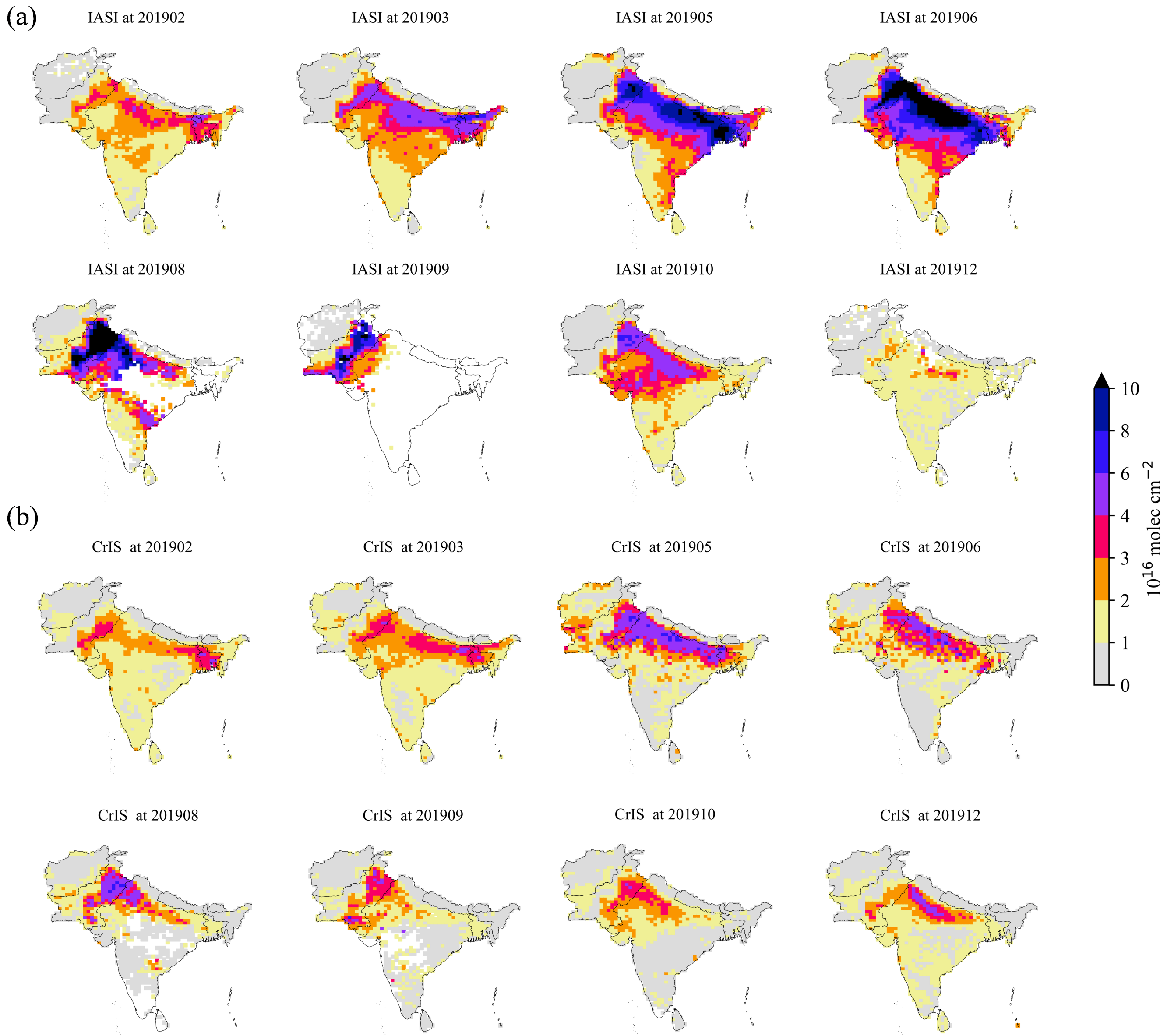

Figure S2. The distribution of the IASI-observed (a) and the CrIS-observed (b) ammonia total column for the remain months in 2019.

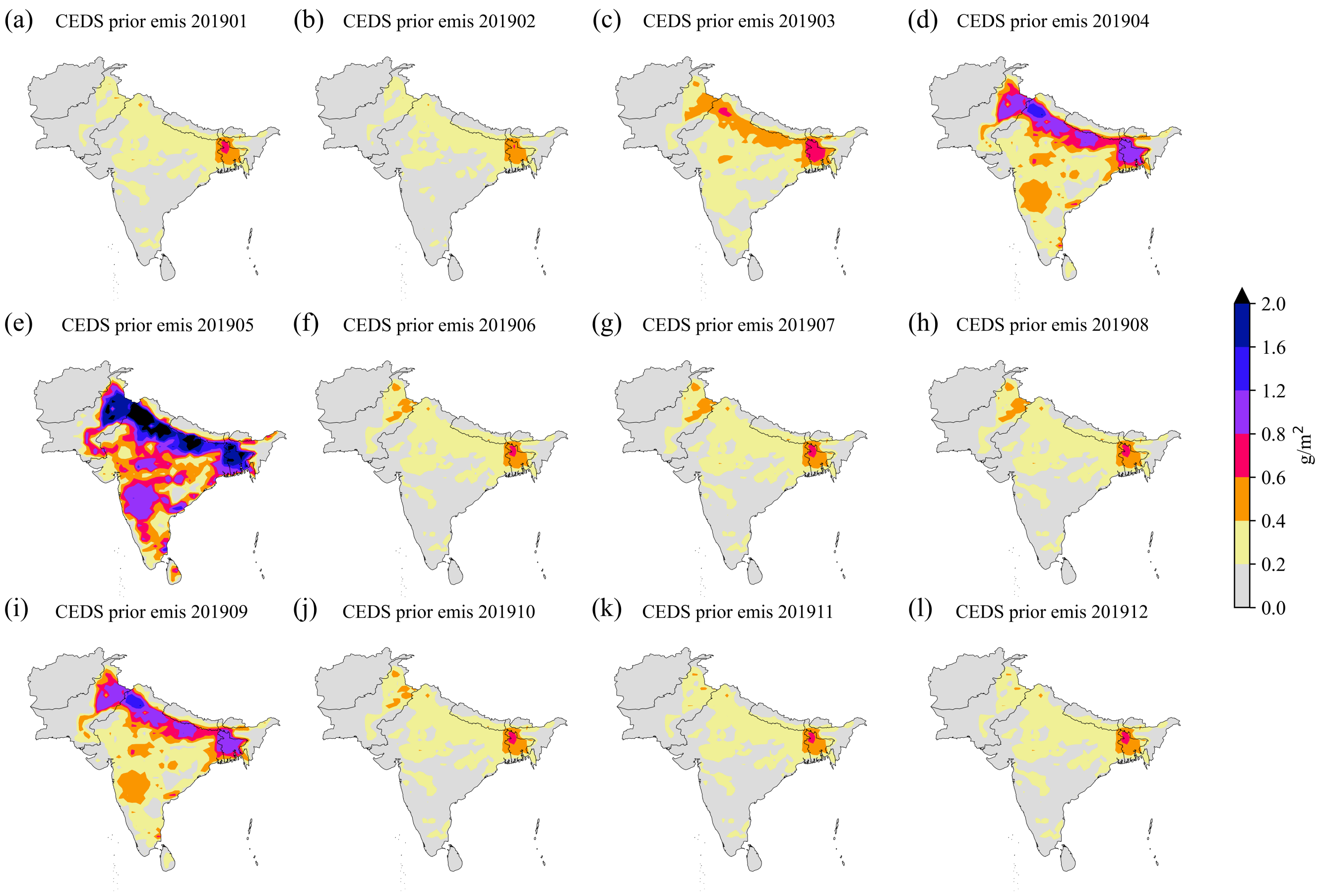

Figure S3. (a)-(l) represent the distribution of the prior inventory for each month from January to December in 2019.

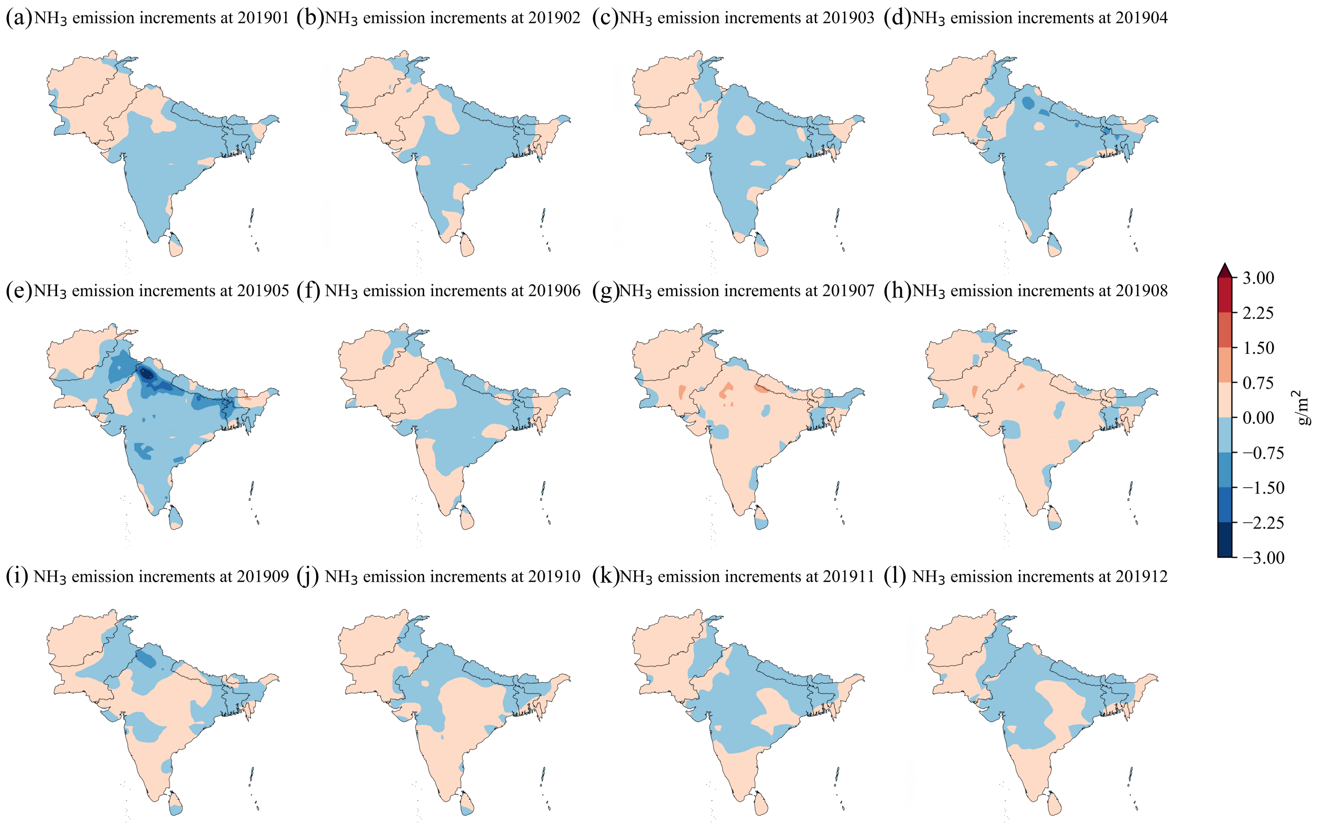

Figure S4. (a)-(l) represent the distribution of increments obtained by subtracting the prior inventory from the posterior inventory for each month from January to December in 2019.