**Supporting information for:**

**The effects of fertilization treatments and agricultural practices on long-term dynamics and spectroscopic characteristics of dissolved organic matter in paddy soil**

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**Methods for determining chemical properties of soil samples (Table S1)**

1. The pH was measured at a soil-to-water ratio of 1:2.5 using a glass electrode pH meter (F-52, Horiba, Japan).
2. The EC was measured at a soil-to-water ratio of 1:5 using a EC meter (CM-30V, TOA corp., Japan).
3. Exchangeable cation K+ was extracted with 1M ammonium acetate solution (pH 7.0) and determined by Inductively coupled plasma atomic emission spectrometer ICP-AES (SPS 3100, Hitachi, Japan).
4. Available nitrogen was determined by incubation method (Bundy and Meisinger, 1994). Soil was adjusted its maximum water holding capacity to 60% and incubated in a UM glass sample bottle at 30℃ for 4 weeks. Available Nitrogen was difference in the amount of inorganic nitrogen between before and after incubation using an ion chromatograph (IC2001, TOSCH crop., Japan).
5. P2O5 was determined by the ascorbic acid method (Murphy and Riley, 1962). Soil was extracted by water at a soil: liquid ratio of 1:40. Then suspension was filtered and measured absorbance using a V-630 UV-visible spectrophotometer (JASCO, Japan). The working standard solutions were also measured absorbance which were used for making calibration curve. The P concentration of soil solution corresponded to the value on the calibration curve.

**References**

Bundy, L. G. and J. J. Meisinger. 1994. "Nitrogen availability indices." *in* *Methods of Soil Analysis: Part 2—Microbiological and Biochemical Properties*. 951-984.

Murphy, J., and J. P. Riley. 1962. "A modified single solution method for the determination of phosphate in natural waters." *Analytica chimica acta* 27: 31-36.

**Table S1.** chemical properties of the paddy soil samples

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  |  | pH (H2O) | EC  (mS cm-1) | TC  (%) | TN  (%) | C/N | Exchangeable cation K+  (cmol c kg-1) | Available nitrogen  (mg 100 g-1) | P2O5 (mg 100 g-1) |
| 1976 |  | - † | - | 1.73 | - | - | - | - | - |
|  | CHE | 6.0 | - | 1.94 | 0.15 | 12.93 | 0.2 | 12.8 | 29.8 |
| 1980 | CHE＋ORG | 5.6 | - | 1.97 | 0.12 | 16.41 | 0.2 | 12.8 | 22.3 |
|  | MAN | 5.9 | - | 2.02 | 0.15 | 13.47 | 0.2 | 14.4 | 22.9 |
|  | INT | 6.5 | - | 1.86 | 0.14 | 13.28 | 0.3 | 12.6 | 41.2 |
|  | CHE | 5.9 | - | 1.70 | 0.12 | 14.17 | 0.2 | 6.7 | 29.2 |
| 1984 | CHE＋ORG | 5.9 | - | 1.88 | 0.13 | 14.46 | 0.3 | 6.1 | 23.5 |
|  | MAN | 5.7 | - | 1.95 | 0.14 | 13.92 | 0.2 | 7.1 | 23.5 |
|  | INT | 7.0 | - | 1.77 | 0.13 | 13.62 | 0.2 | 6.1 | 48.1 |
|  | CHE | 5.6 | 0.05 | 2.06 | 0.16 | 12.875 | 0.4 | 11.6 | 18.0 |
| 1991 | CHE＋ORG | 5.4 | 0.05 | 2.33 | 0.17 | 13.70 | 0.6 | 13.9 | 18.0 |
|  | MAN | 5.4 | 0.05 | 2.66 | 0.19 | 14 | 0.9 | 13.8 | 24.8 |
|  | INT | 6.3 | 0.08 | 2.00 | 0.15 | 13.33 | 0.6 | 11.9 | 27.5 |
|  | CHE | 5.6 | 0.14 | 1.95 | 0.15 | 13 | 0.2 | 13.3 | 18.0 |
| 1995 | CHE＋ORG | 5.3 | 0.17 | 2.24 | 0.17 | 13.18 | 0.3 | 17.3 | 14.7 |
|  | MAN | 5.6 | 0.15 | 2.56 | 0.20 | 12.8 | 0.4 | 22.2 | 18.1 |
|  | INT | 6.1 | 0.15 | 2.12 | 0.16 | 13.25 | 0.3 | 13.7 | 26.6 |
|  | CHE | 5.9 | 0.10 | 1.79 | 0.15 | 11.93 | 0.2 | 11.4 | 18.3 |
| 2001 | CHE＋ORG | 5.8 | 0.09 | 1.87 | 0.15 | 12.47 | 0.3 | 11.5 | 16.3 |
|  | MAN | 5.8 | 0.12 | 2.05 | 0.16 | 12.81 | 0.3 | 12.6 | 19.3 |
|  | INT | 6.7 | 0.11 | 1.83 | 0.14 | 13.07 | 0.3 | 11.4 | 28.7 |
|  | CHE | 5.9 | 0.10 | 1.74 | 0.15 | 11.6 | 0.2 | 11.8 | 21.2 |
| 2006 | CHE＋ORG | 5.7 | 0.11 | 1.96 | 0.17 | 11.53 | 0.3 | 12.5 | 18.5 |
|  | MAN | 6.0 | 0.13 | 2.28 | 0.18 | 12.67 | 0.3 | 12.8 | 22.8 |
|  | INT | 6.6 | 0.11 | 1.86 | 0.16 | 11.625 | 0.2 | 12.8 | 34.5 |
|  | CHE | 5.9 | 0.08 | 1.92 | - | - | - | - | - |
| 2010 | CHE＋ORG | 5.7 | 0.09 | 2.08 | - | - | - | - | - |
|  | MAN | 6.1 | 0.12 | 2.34 | - | - | - | - | - |
|  | INT | 6.7 | 0.09 | 1.98 | - | - | - | - | - |
|  | CHE | - | - | 1.65 | - | - | - | - | - |
| 2015 | CHE＋ORG | - | - | 2.00 | - | - | - | - | - |
|  | MAN | - | - | 2.24 | - | - | - | - | - |
|  | INT | - | - | 1.58 | - | - | - | - | - |

† Not analyzed

**Table S2.** Kruskal–Wallis test by ranks of the effect of independent factor “Fertilization treatment” on soil TC (%), DOM/TC (%), DOM, HS, HS/DOM (%), SUVA254, HIX, FI, and BIX.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | TC | DOM/  TC | DOM | HS | HS/  DOM | SUVA254 | HIX | FI | BIX |
| *P* value | 0.002\* | 0.204 | 0.062 | 0.222 | 0.100 | 0.124 | 0.006\* | 0.009\* | 0.006\* |
| Pairwise comparison by Dunn’s test with Bonferroni Correction | | | | | | | | | |
| CHE vs. CHE+ORG | NS | NS | NS | NS | NS | NS | NS | NS | NS |
| CHE vs. MAN | 0.04 | NS | NS | NS | NS | NS | NS | NS | NS |
| CHE vs. INT | NS | NS | NS | NS | NS | NS | NS | 0.007\* | NS |
| CHE+ORG vs. MAN | NS | NS | NS | NS | NS | NS | NS | NS | NS |
| CHE+ORG vs. INT | NS | NS | NS | NS | NS | NS | NS | NS | NS |
| MAN vs.INT | 0.016\* | NS | NS | NS | NS | NS | 0.005\* | NS | 0.005\* |

TC=total carbon; DOM= dissolved organic matter concentration; HS= water extractable humic substance concentration, SUVA254 =specific UV absorbance at 254 nm; HIX= humification index; FI = fluorescence index; BIX= biological or autochthonous index.

\* Significantly different at the 0.05 level.

“NS” Not significantly different at the 0.05 level.

**Table S3.** Kruskal-Walls Test by ranks of the effect of independent factor “Fertilization treatment” on Fmax proportion in ∑Fmax (Cp).

|  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | Cp1 | | Cp2 | | Cp3 | | Cp4 | | Cp5 | | | |
| P | | 0.008\* | | 0.059 | | 0.061 | | 0.028\* | | 0.532 | |
| Pairwise comparison by Dunn’s test with Bonferroni Correction | | | | | | | | | | |
| CHE vs. CHE+ORG | NS | | NS | | NS | | NS | | NS | | |
| CHE vs. MAN | NS | | NS | | NS | | NS | | NS | | |
| CHE vs. INT | NS | | NS | | NS | | NS | | NS | | |
| CHE+ORG vs. MAN | NS | | NS | | NS | | NS | | NS | | |
| CHE+ORG vs. INT | NS | | NS | | NS | | NS | | NS | | |
| MAN vs.INT | 0.004\* | | NS | | NS | | 0.028\* | | NS | | |

Cp1–Cp5: the proportion of Fmax of each fluorescence component.

\* Significantly different at the 0.05 level.

“NS” Not significantly different at the 0.05 level.



**Fig. S1.** Boxplots for different fertilization treatments of(a)dissolved organic matter (DOM) concentration (mg C Kg-1 soil), (b) humic substances (HS, mg C Kg-1 soil), (c) HS/DOM ratio (%), (d) total carbon (TC, %), (e) DOM/TC (%) and (f) SUVA254 of the paddy soil samples. (CHE: chemical fertilization; CHE+ORG: CHE + organic fertilization; MAN: cattle manure compost fertilization; INT: CHE + ORG + soil amendment materials (fused phosphate and calcium silicate)



**Fig. S2.** Loadings of excitation and emission spectra of the identified PARAFAC components (*overall-ex* and *overall-em*) and the result of the split-half analysis (*Split1–6*). The dotted and solid curves represent excitation and emission spectra, respectively. C1, humic-like component; C2, humic-like component; C3, microbial humic-like component; C4, tyrosine-like component; and C5, tryptophan-like component.