Supporting Information

Speciation and Degradation of Triphenyltin in Typical Paddy Fields and its Uptake into Rice Plants

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Nutrient solution used for rice plants

For preparation of the Yoshida solution, the micronutrients shown in Table S1 were dissolved separately, then mixed with 100 mL of concentrated sulfuric acid and diluted with water to 2 L. Three aliquots of 1.25 mL of each of 6 solutions shown in Table S1 was combined with three different amounts of TPhT and filled up to 1 L resulting in 10, 100 and 1000 µg kg^{-1} TPhT Yoshida solution. The pH of the prepared solution was adjusted to 5.5 with NaOH. Separate trays were used for each plant. Each tray was filled with 50 ml of 50 TPhT Yoshida solution once a week, and filled up with water as necessary. Twice a week, only Yoshida solution (without TPhT) was added. Every week fresh Yoshida solution was prepared.

Table S1. Micronutrients used for preparation of Yoshida Solution.

	2L (g)	500 mL (g)	250 mL (g)
1. NH_4NO_3	182.8	45.7	22.85
2. $NaH_2PO_4.2H_2O$	80.6	20.15	10.075
3. K_2SO_4	142.8	35.7	17.85
4. $CaCl_2$	177.2	44.3	22.15
5. $MgSO_4.7H_2O$	648	162	81
6. Micro nutrient			
$MnCl_2$. 4H2O	3	0.75	0.375
$(NH_4)6HO_7O_{24}.4H_2O$	0.148	0.037	0.0185
H_3BO_3	1.868	0.467	0.2335
$ZnSO_4.7\ H_2O$	0.07	0.0175	0.00875
$CuSO_4.5H_2O$	0.062	0.0155	0.00775
$FeCl_3.6\ H_2O$	15.4	3.85	1.925
citric acid monohydrate	23.8	5.95	2.975

Mesocosm experiment

The total amount of TPhT added each mesocosm after seven weeks was calculated, as µg of Sn and is shown in Table S2.

TABLE S2. Total amount of TPhT (as Sn) added to each mesocosm after seven weeks.

Groups	Amount of TPhT added to each mesocosm, μg
Control	-
Low	8.0
Medium	72
High	373

Speciation of Sn compounds using GC-ICP-MS

After the extraction procedures used for soil and plant parts, the extracts were transferred to 2 mL autosampler vials and stored at -80 °C. For analysis by GC-ICP-MS, 1 μL was injected. The ICP-MS and chromatographic parameters are described in Table S3.

TABLE S3. GC-ICP-MS operating parameters.

Instrumentation	
GC	6890 GC
Inlet	On column
Detector	ICP-MS 7500c Agilent
Column	30 m x 0.53 mm id x 1.0 µm CPSIL-5CB
GC conditions	
Inlet temperature	300 ºC
Injection volume	1 µL
Carrier gas	nitrogen
Carrier gas pressure	60 psi
Transferline temperature	270 ºC
Oven temperature	60 °C/1 min, 40 °C min^{-1} to 250 °C, 60 °C min^{-1} to 350 °C, program hold for 3 min
ICP-MS conditions	
Power	1570 W
Carrier gas flow	0.60 L min^{-1}
Make up gas flow	0.60 L min^{-1}
Isotopes acquired	^{118}Sn, ^{120}Sn

Analyte recoveries using different extraction procedures are shown in Table S4. Chromatograms obtained for spiked soil and plant material are shown in Figure S1.

Table S4. Analyte recoveries, in %, obtained for extraction procedure A, B and C, in plant material (using procedure A and C) and soil samples (using procedures A, B and C). Uncertainties represent the mean and standard deviation of 3 extractions.

Specie	Procedure A		Procedure B	Procedure C	
	Soil	Plant material	Soil	Soil	Plant material
MPhT	73.7 ± 6.3	97.1 ± 4.9	94.0 ± 5.4	70.2 ± 6.8	76.8 ± 7.1
DPhT	84.9 ± 5.6	94.3 ± 5.2	98.1 ± 5.1	64.9 ± 5.7	80.2 ± 5.4
TPhT	85.4 ± 5.2	96.5 ± 6.6	97.0 ± 4.5	59.7 ± 8.0	61.3 ± 4.9

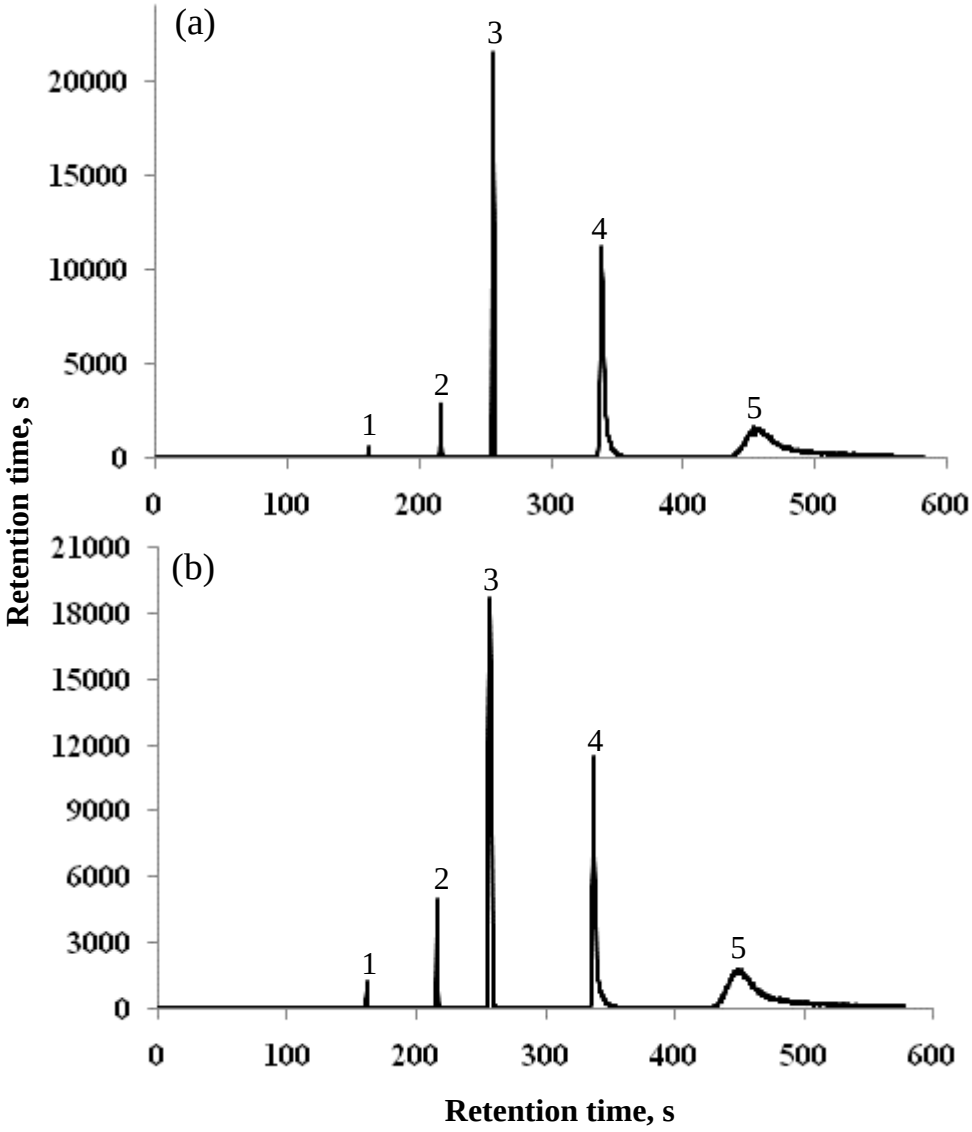

FIGURE S1. Chromatograms obtained by GC-ICP-MS for enriched soil (a) and plant material samples (b). Peak 1: inorganic Sn; 2: TPrT; 3: MPhT; 4: DPhT; 5: TPhT.

Analysis of commercial TPhT hydroxide

According to Brazilian legislation,[1] TPhT hydroxide can be used as biocide in several crops, including rice. Before speciation analysis of soil obtained from a natural rice field, the commercial product Mertin 400 was analysed. A sample was diluted by a factor of 4000000, derivatized using $NaBEt_4$ and 1 µL was injected into GC. The results obtained for phenyltin species are shown in **Table S5**.

Table S5. Concentration of phenyltin species in commercial TPhT hydroxide. Results represent the mean and standard deviation for 3 diluted samples.

Specie	Concentration, g L^{-1}
MPhT	< 0.001
DPhT	1.12 ± 0.03
TPhT	365 ± 8

Unidentified tin species

A correlation of boiling point or number of carbons *versus* retention time of chromatographic separation of standards can be used to assign unknown species.[2] A good correlation (R^2 = 0.99) was obtained from correlation of retention times of inorganic tin, TPrT, MPhT, DPhT and TPhT (160, 219, 257, 339, 450 s, respectively) *versus* their respective number of carbons (8, 11, 12, 16, 20, respectively), as can be observed in Figure S2.

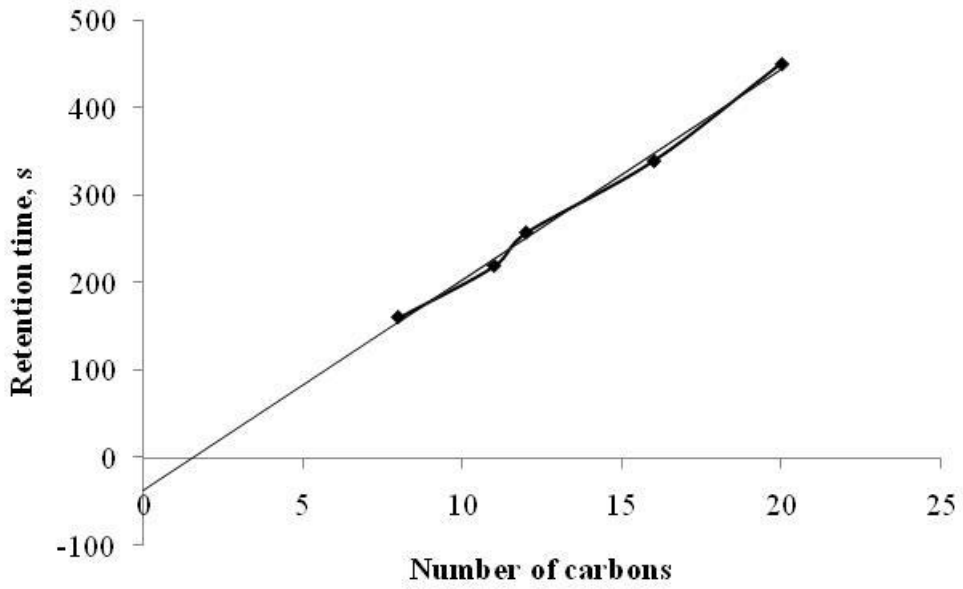

Figure S2. Retention time (RT) *versus* number of carbons (NC) of tin species (RT = 24.10*NC – 38.01; R^2 = 0.9954).

The equation obtained from correlation shown in Figure S2 was used to calculate the number of carbons of unknown tin species observed in chromatograms obtained from soil and roots of rice plants exposed to TPhT. From the number of carbons obtained, tin species were suggested, as described in Table 4.

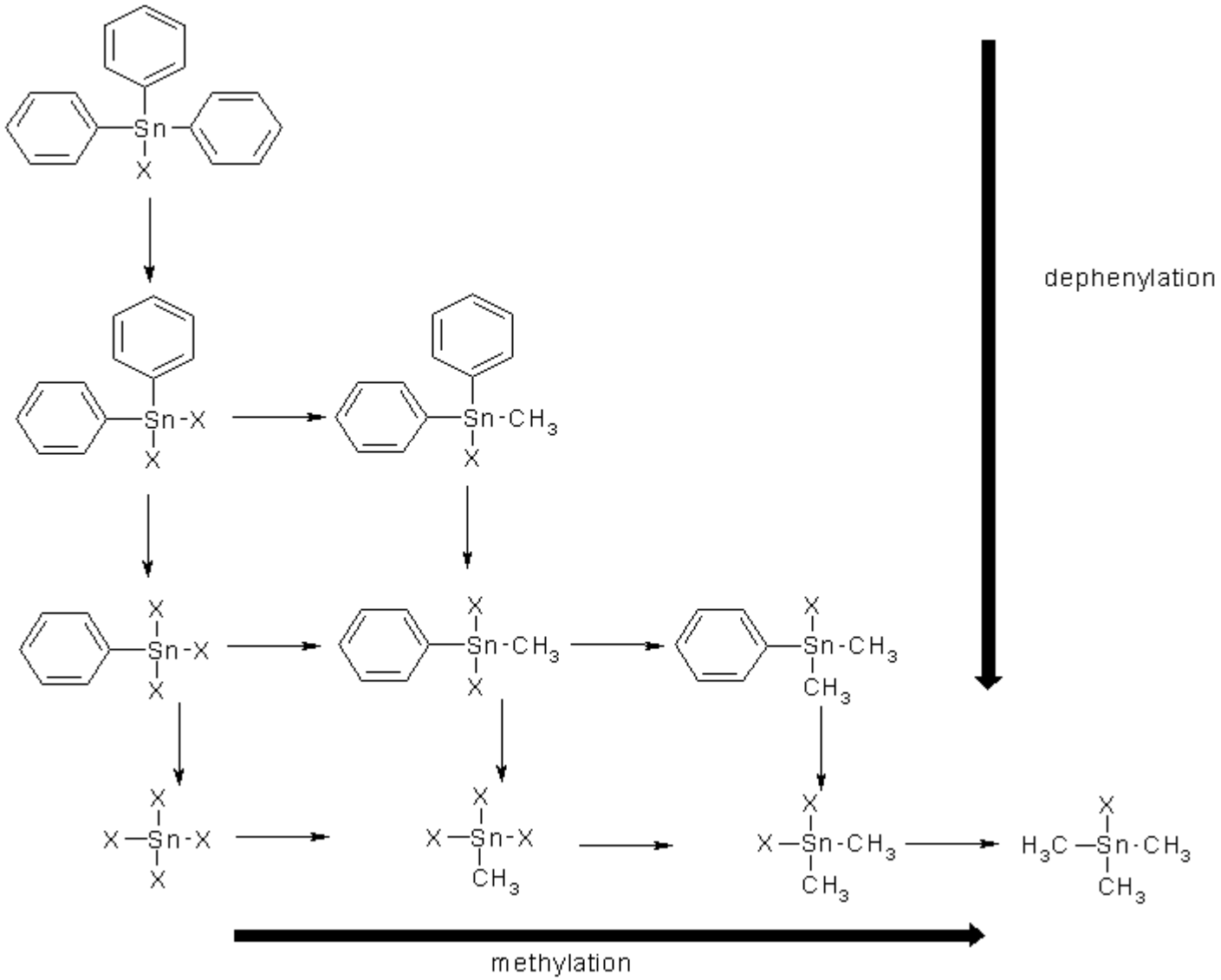

Figure S3: Degradation pattern of TPhT in the paddy soils, which undergoes stepwise dephenylation. Every phenyltin can however be methylated to give the mixed phenylmethyltin species. All except monomethyltin have been tentatively identified and quantified in the rice paddies and roots of the rice plants.

1. Ministério da Agricultura, http://extranet.agricultura.gov.br.

2. Mitra, S. K., Jiang, K. J., Haas, K., Feldmann, J., Municipal landfills exhale newly formed organotins. *J. Environ. Monit.* **2005**, *7*, 1066-1068; DOI: 10.1039/b511767d.