Deposition of Carcinogenic Atmospheric Anthraquinone on Tea Plantation

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Motivation

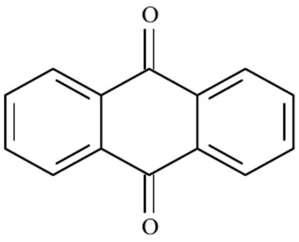
- The current **Maximum Residue Limit (MRL) in EU for anthraquinone (AQ)** on tea products is **0.02 mg/kg**
- According to the *2016 European Union report on pesticide residues in food* from the European Food Safety Authority, AQ residue exceeds the EU MRL in ~10% of tea samples, among which most are from East Asia
- The exceedance of AQ residue in tea products is affecting the tea trade in some key tea-exporting countries
- Possible sources of AQ: **Environmental contamination**, formation by microorganism on tea plants or in soil, contamination from fertilizers or pesticides, contamination during the tea production processes (Romanotto & Gassert, 2017)

Objective

Could the deposition of atmospheric AQ on tea plants be one of the possible sources of this AQ residue exceedance?

What is anthraquinone (AQ)?

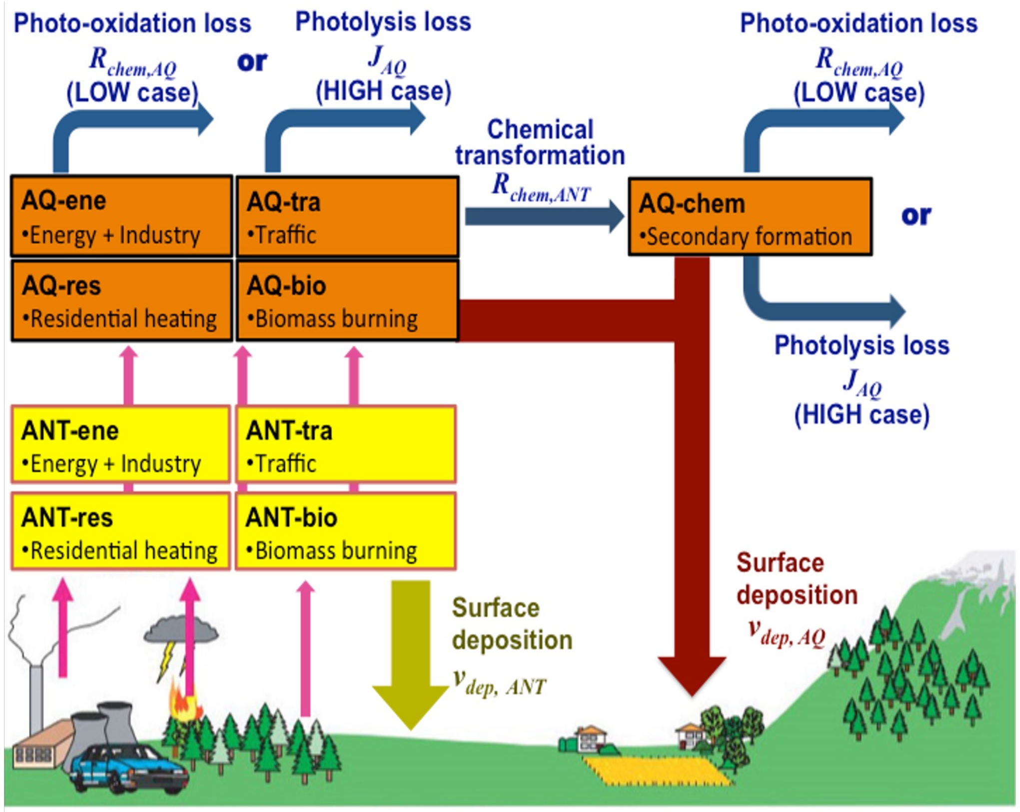
- Anthraquinone, 9,10-anthraquinone ($C_{14}H_8O_2$)
- Structural formula:



- An oxygenated polycyclic aromatic hydrocarbon (OPAH)
- **Carcinogenic**
- **Precursor: Anthracene** ($C_{14}H_{10}$), a polycyclic aromatic hydrocarbon (PAH)
- Main source: incomplete combustion, secondary formation from anthracene
- Atmospheric behaviour rarely studied, no existing emission inventory
- From observations: Large seasonal variation, semivolatile but mostly in particulate phase

(IARC, 2012)

Methods: Model configuration



Model used: MOZART-4 (Emmons et al., 2010)

Resolution: 0.50° × 0.63°

Emissions: Self-compiled AQ emission inventory based on PKU-PAH-ANT in 2014 (Shen et al., 2013; 0.1° x 0.1°), emission factors of AQ, and temporal profiles of CAMS-GLOB-TEMPO (Guevara et al., 2020)

Meteorology: GEOS-5 meteorology datasets in 2013 & 2014 (Tilmes, 2016)

4-5 tagged AQ/ANT species:
ene: Energy + Industry
tra: Traffic
bio: Biomass burning
res: Residential combustion
chm: Secondary formation (only for AQ)

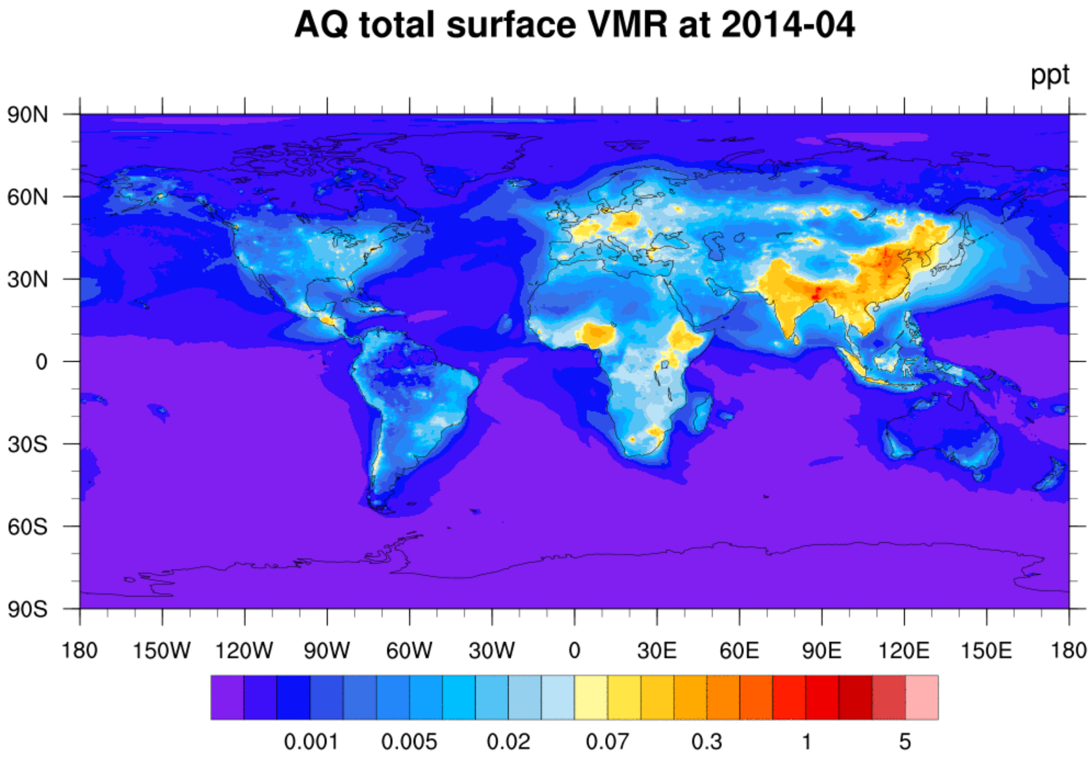
Several **sensitivity cases** to quantify the uncertainties resulting from the lack of information about **emission** and **photochemical processes**.

Correlation between observed and modelled data

Simulation	Description of case	Background (n=49)		Non-background (n=100)	
		Slope	R^2	Slope	R^2
M1	High chemical production, low loss, highest seasonality in emissions, detailed deposition treatment	1.04	0.56	0.45	0.46
M2	High chemical production, highest loss, high seasonality in emissions, detailed deposition treatment	0.52	0.51	0.18	0.40
S6	High chemical production, low loss, high seasonality in emissions	0.80	0.46	0.83	0.36
S8	High chemical production, highest loss, highest seasonality in emissions	0.83	0.44	0.87	0.35

AQ global modelled concentration distribution

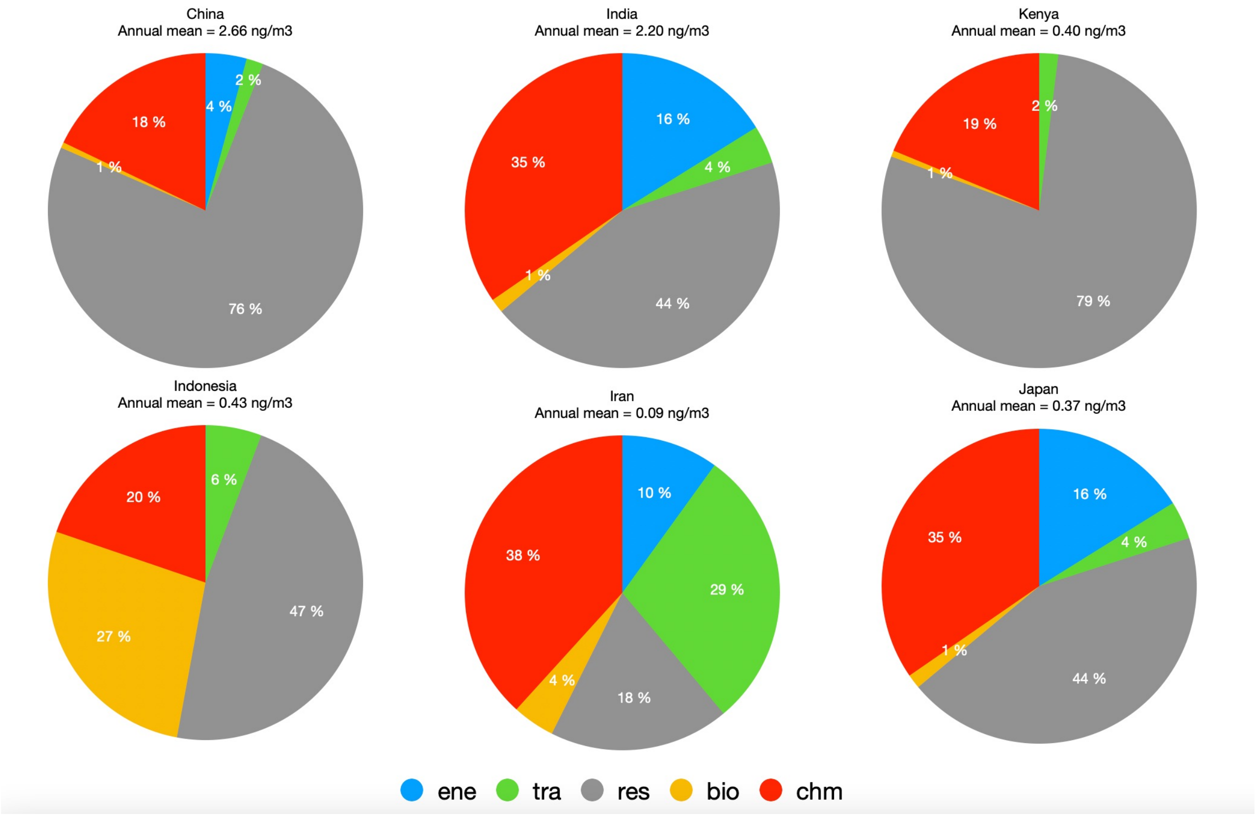
Case M1 High chemical production (Y1), low loss (D1), highest emission seasonality (E3)



Contamination hotspots:
NE China, North India, Eastern Europe
(Significantly higher level in wintertime)

Seasonal hotspots:
Indonesia, Siberia, Central Canada
(Associated with forest fires)

AQ sectoral distribution in key tea-producing countries

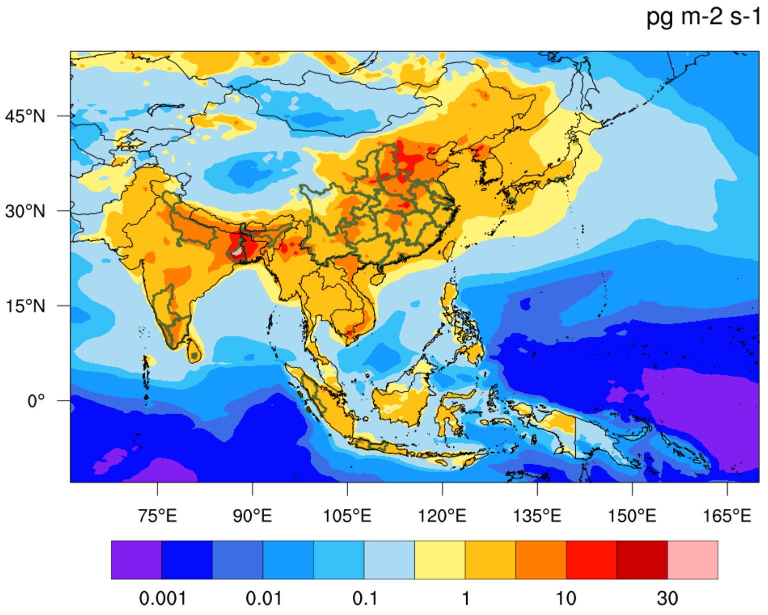


Most AQ contributions are from the **residential combustion**, followed by **secondary formation from ANT**.

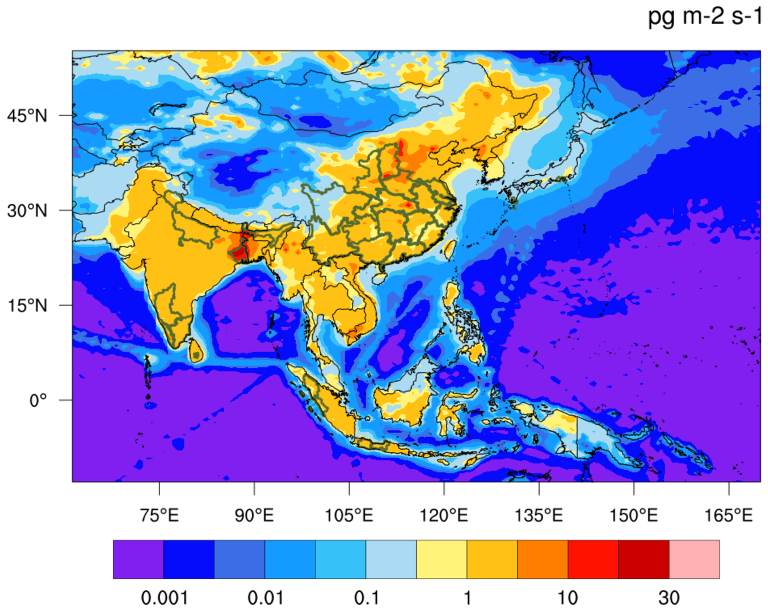
This distribution can vary largely between countries.

AQ deposition rate in East Asia in April (Harvest period)

Case M1 (high AQ content)



Case M2 (low AQ content)

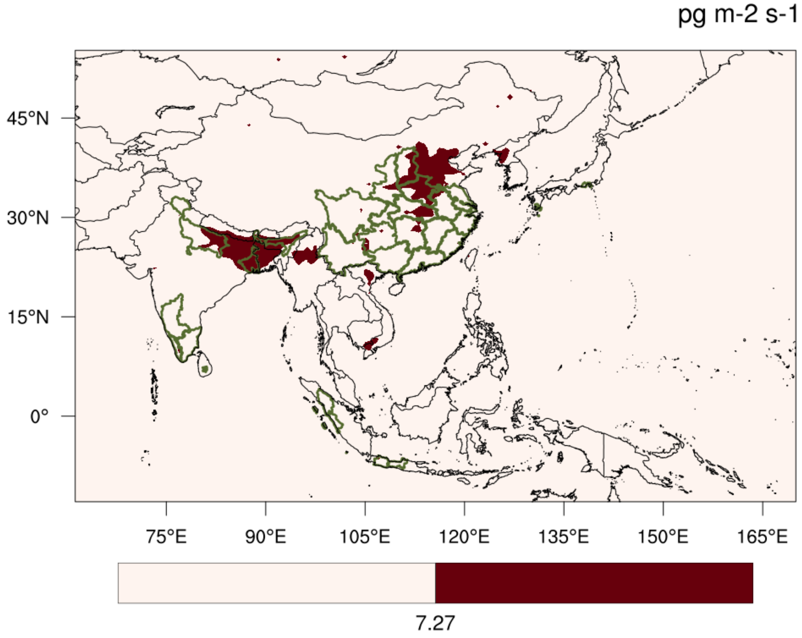


Green border: tea producing regions

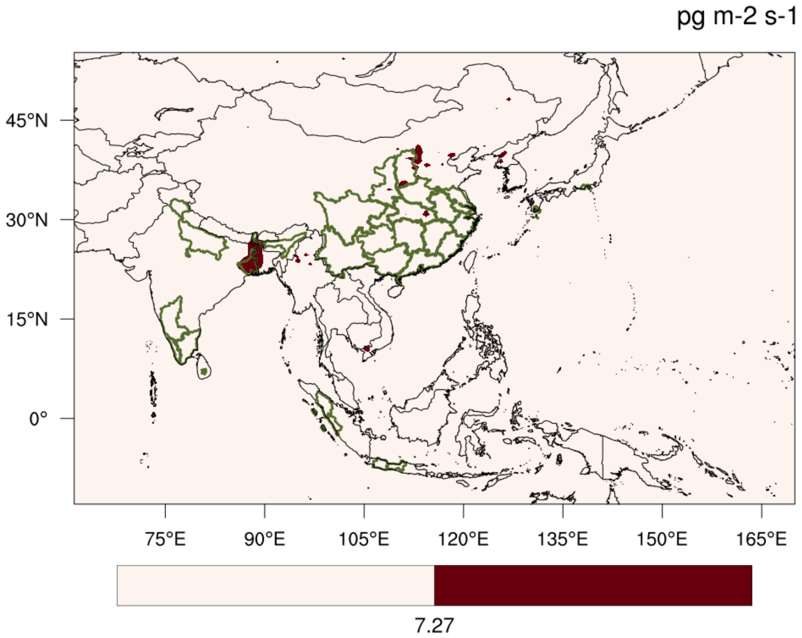
- Highest deposition rate occurs in the northern parts of China and India (in particular in the province of **Hubei** in China and the province of **West Bengal** in India for key tea-producing regions)

Regions in Asia in April with high risk exceeding MRL

Case M1 (high AQ content)



Case M2 (low AQ content)



Green border: tea producing regions

- AQ residue in processed tea can possibly be over 0.02 mg/kg (EU MRL) if the AQ deposited on fresh tea shoots exceeded **0.024 mg/kg of fresh tea leaves** (Wang et al., 2018)
- **0.024 mg AQ per kg of fresh leaves** is equivalent to **a deposition rate of 7.27 pg m^{-2} s^{-1} (highlighted in dark red in below maps)**

Conclusions

- Anthraquinone (AQ) is a carcinogenic oxygenated PAH that is found on some tea products.
- Atmospheric contamination is a possible source of AQ residues on tea plants
- The major source of AQ is residential combustion, followed by secondary formation from anthracene.
- Highest deposition rate occurs in the northern parts of China and India among the key tea producing regions
- Further studies including laboratory experiments and observations are required to constrain model uncertainties arisen from the lack of the pre-existing knowledge of AQ.

Thanks for listening!

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