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Phase distribution, deposition, and precipitation scavenging of atmospheric semi-volatile organic compounds (SVOCs) under steady-state partitioning theory

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Phase distribution, deposition, and precipitation scavenging of atmospheric semi-volatile organic compounds under steady-state partitioning theory

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PART ONE : STEADY-STATE PARTITIONING THEORY

STEADY-STATE PARTITIONING

MODEL EVALUATION

ENVIRONMENTAL BEHAVIOR

CASE STUDIES

1 Environmental mediums and partitioning in the atmosphere under equilibrium

- Particle-gas partitioning：
  Harner-Bidleman model，Junge-Pankow model, etc. (Harner and Bidleman, 1998) (Pankow, 1994)
- Rain(Snow)-gas partitioning
  Lei-Wania model, etc. (Lei and Wania, 2004)

⇩

The a premise of the equilibrium partitioning assumption is:

× No external factors affect the partitioning *Or*

× The partitioning speed is fast enough to ignore the influence of external factors

⇩

There are deviations in the calculation of the partition ratios of SVOCs

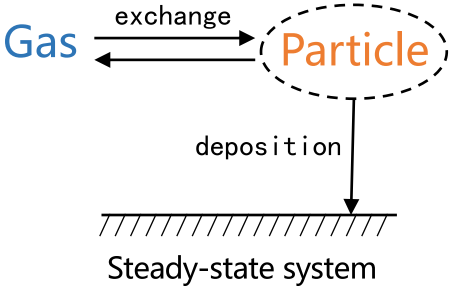
2 Particle-Gas steady-state partitioning

2015 (Li, 2015)

dozens of publication

ten years

Li et al. proposed the particle-gas steady-state partitioning model (Li-Ma-Yang model)

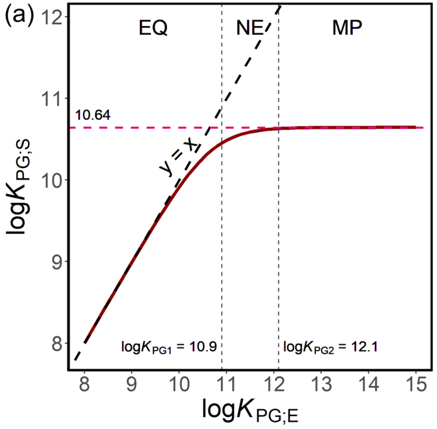


Li-Ma-Yang model

$$\log K_{PG;S} = \log K_{PG;E} + \log \alpha_P$$

Steady-state partition ratio | equilibrium partition ratio

Upper limit: 10.64



* The real partitioning deviates from equilibrium with the influence of particle deposition.

3 Rain (Snow)-Gas steady partitioning

2025 Rain (Snow)-Gas steady partitioning

Rain-gas steady-state partition model

$$\log K_{\mathrm{RG;S}} = \log K_{\mathrm{RG;E}} + \log \alpha_{\mathrm{R}}$$

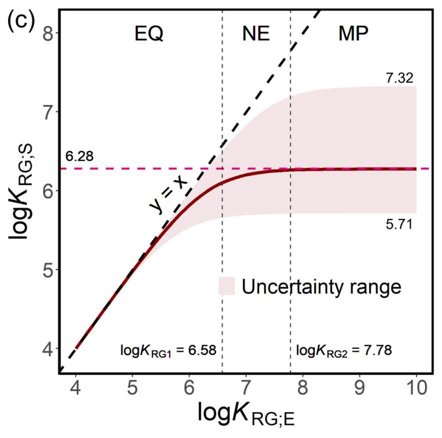
Steady-state partition ratio | equilibrium partition ratio

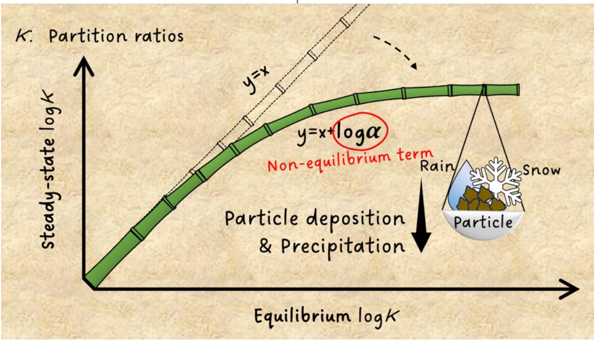
Snow-gas steady-state partition model

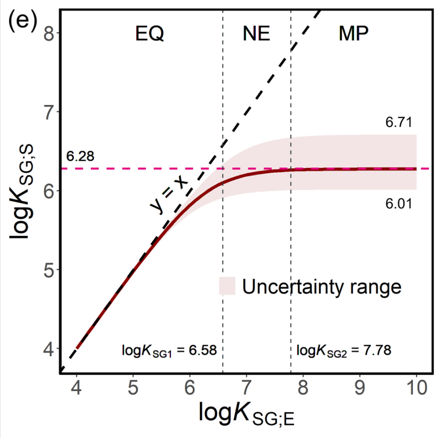
$$\log K_{\mathrm{SG;S}} = \log K_{\mathrm{SG;E}} + \log \alpha_{\mathrm{S}}$$

Steady-state partition ratio | equilibrium partition ratio

Upper limits： 6.28







PART TWO : MODEL EVALUATION

STEADY-STATE PARTITIONING

MODEL EVALUATION

ENVIRONMENTAL BEHAVIOR

CASE STUDIES

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1 Source of evaluation

- EBAS database (https://ebas.nilu.no)
- IADN database (https://iadnviz.iu.edu)
- SAMP II program (Yang, 2013)
- Other publications...

Chemicals	Sample number		
	$\log K_{PG}$	$\log K_{RG}$	$\log K_{SG}$
OCPs (12)			
α-HCH	10 (911)	10 (32)	10 (30)
β-HCH	10 (1024)	10 (16)	10 (18)
......Other 10 OCPs			
PCBs (7)			
CB-18	10 (428)	10 (13)	9 (9)
CB-28	10 (453)	10 (15)	9 (9)
......Other 5 PCBs			
PAHs (10)			
Pyr	10 (3644)	10 (33)	10 (30)
Phe	10 (4159)	10 (35)	10 (31)
......Other 8 PAHs			
PBDEs (7)			
BDE-28	10 (104)	4 (4)	0 (0)
BDE-47	10 (228)	6 (6)	0 (0)
......Other 5 PBDEs			
Sum (36)	360 (14189)	246 (455)	205 (379)

* The numbers in brackets are the number of records in the database, and the numbers outside are the random sampling number.

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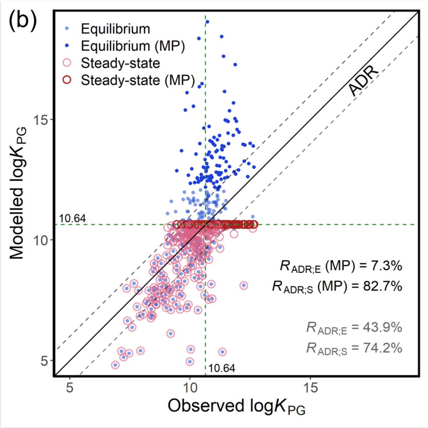
1 Source of evaluation

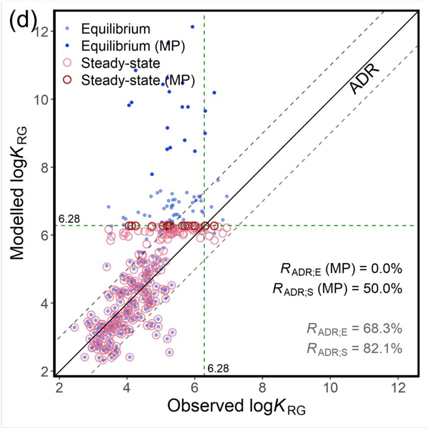
2 Evaluation results

2 Evaluation results

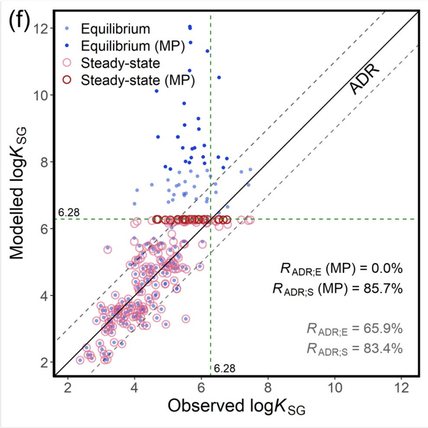
Particle-Gas (logK_{PG})



Rain-Gas (logK_{RG})



Snow-Gas (logK_{SG})



- In the low molecular weight (high volatility) stage (lower half of the figure), the results of the equilibrium model and the steady-state model are almost exactly the same, which is consistent with the measured data.
- In the high molecular weight (low volatility) stage (upper half), the equilibrium model significantly overestimates the partition ratio, while the steady-state model is consistent with the measured data.

PART THREE : HOW TO INFLUENCE ENVIRONMENTAL BEHAVIOR

STEADY-STATE PARTITIONING

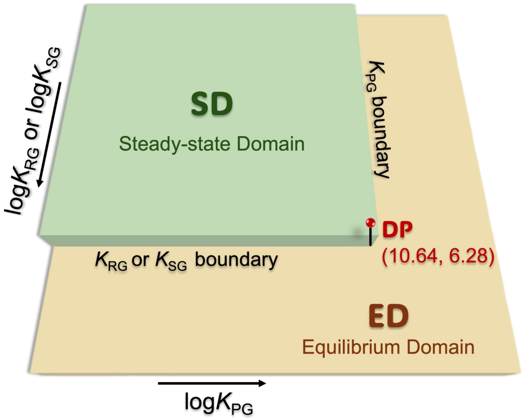
MODEL EVALUATION

ENVIRONMENTAL BEHAVIOR

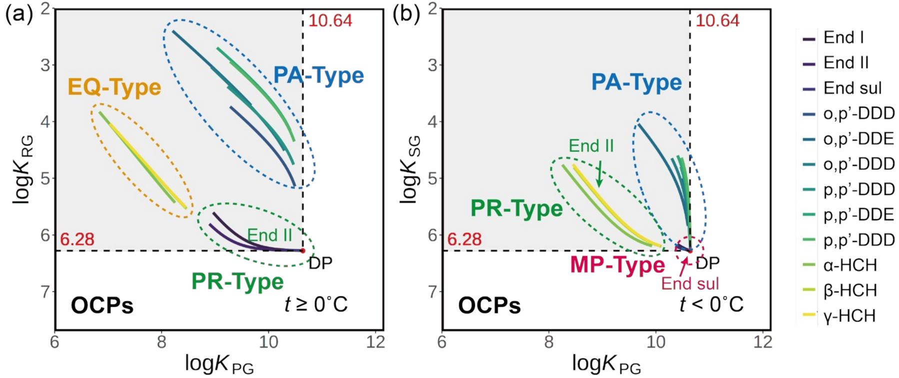
CASE STUDIES

1 Chemical space map
2 Distribution fraction
3 Deposition contribution
4 Scavenging ratio

1 Chemical Space Map（CSMs)



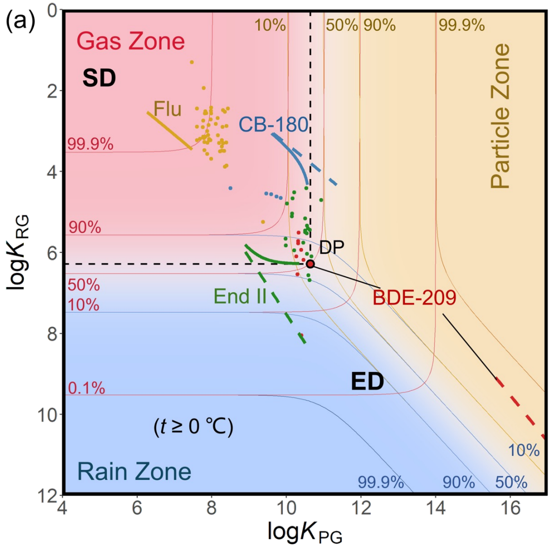
- The x-axis $\log K_{PG}$, the y-axis is $\log K_{RG}$ or $\log K_{SG}$；
- SVOCs change with temperature on a CSM to form segments.
- Since there are upper limits for $\log K_{PG}$, $\log K_{RG}$, and $\log K_{SG}$, SVOCs can only be distributed in SD under steady-state conditions, while there are no limits in equilibrium. The point formed by the intersection of the upper limits is called DP (10.64, 6.26).



Based on the position of SVOCs on CSMs, we divided SVOCs into four types: EQ, PA, PR, and MP.

2 Distribution fraction

Distribution Fraction, Φ, %. Under medium precipitation scenario

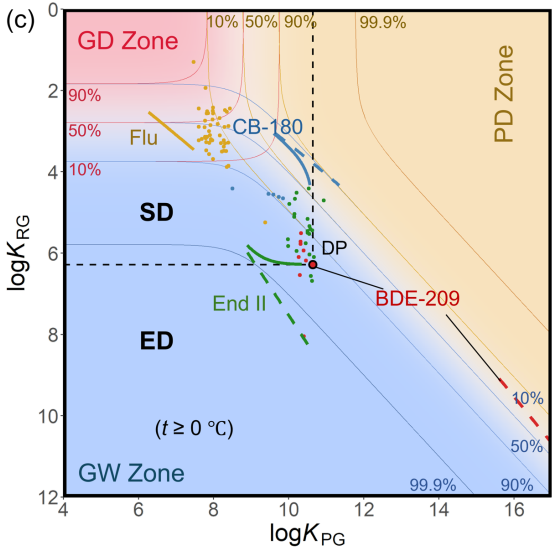


- ❖ **Fluorene (Flu, EQ)** The equilibrium and steady state segment coincide, and almost completely distributed in the gas phase (>99.9%);
- ❖ **Endosulfan II (End II, PR)** The equilibrium will exceed the $\log K_{RG}$ upper limit, and the distribution will be dominated by precipitation, but in the steady state, it is still >50% distributed in the gas phase;
- ❖ **CB-180 (PA)** The equilibrium will exceed the $\log K_{PG}$ upper limit, and part of it will be distributed in the particle phase, but in the steady state, >50% will be distributed in the gas phase;
- ❖ **BDE-209 (MP)** The equilibrium will exceed the two upper limits and move away from DP, but in the steady state, 50% will still be in the gas phase.

Fraction in gas, particle, and precipitation (ϕ_G, ϕ_P, and $\phi_{R/S}$) can be put on the CSMs as the background. The darker the corresponding color, the higher the distribution fraction (Gas Zone, Particle Zone, and Precipitation Zone).

3 Deposition contribution

Deposition Contribution, Ψ, %. Under medium precipitation scenario

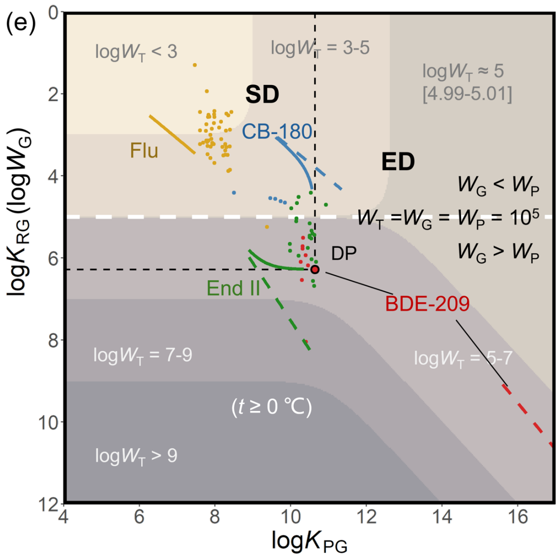


- **Fluorene (Flu, EQ)** has an overlap between equilibrium and steady state, with half being dry gas deposition and the other half being wet gas deposition;
- **Endosulfan II (End II, PR)** has a deposition dominated by wet gas deposition in both equilibrium and steady state, but the proportion in equilibrium (>99.9%) is higher than that in steady state (>90%);
- **CB-180 (PA)** has >50% being dominated by particle deposition in both equilibrium and steady state, but it is close to 90% in equilibrium;
- **BDE-209 (MP)** is dominated by particle deposition in equilibrium, but is dominated by wet gas deposition in steady state.

Similarly, Ψ_{GDD}, Ψ_{GWD}, and $\Psi_{(PWD+PDD)}$, can be drawn on the CSMs as the background, and the darker the corresponding color, the higher the deposition contribution (GD: Gaseous dry deposition, GD: Gaseous wet deposition, and PD: Particulate deposition).

4 Scavenging ratio

Scavenging ratio, W_T. Under medium precipitation scenario



$$W_T = \frac{W_G \Phi_G + W_P \Phi_P}{\Phi_G + \Phi_P}$$

W_G is the gaseous scavenging ratio K_{RG} (K_{SG})

W_P is the particulate scavenging ratio=10^5

- **Fluorene (Flu, EQ)** has a total scavenging ratio ($\log W_T$) between 2.5 and 3.5;
- **Endosulfan II (End II, PR)** has a total scavenging ratio between 5.8 and 6.1 at steady state, but can reach 8 at equilibrium;
- **CB-180 (PA)** has a total scavenging ratio between 3.7 and 4.6 at steady state, and the scavenging ratio will be slightly higher at equilibrium;
- **BDE-209 (MP)** has a total scavenging ratio of 6.1 at steady state, but close to 5 at equilibrium.

PART FOUR : CASE STUDIES

STEADY-STATE PARTITIONING

MODEL EVALUATION

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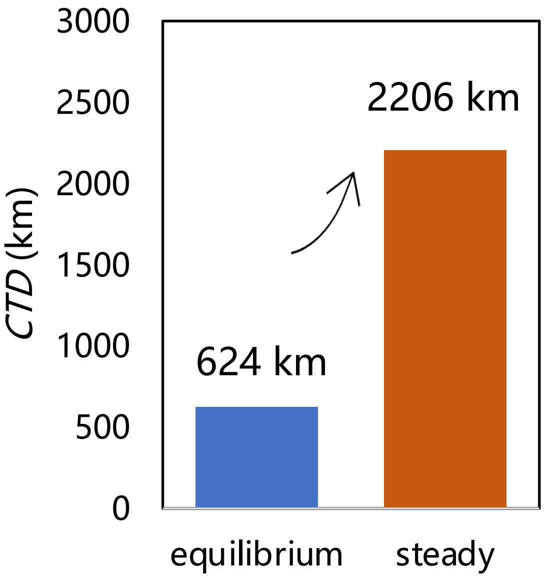
CASE STUDIES

1 Case study 1 β-HCH atmospheric transport in the Arctic

The characteristic transfer distance (CTD) is used to measure the transport potential of β-HCH in the Arctic.

The CTD is defined as the distance from the release point to where the concentration of a chemical drops to 1/e (about 37%) of its initial value.

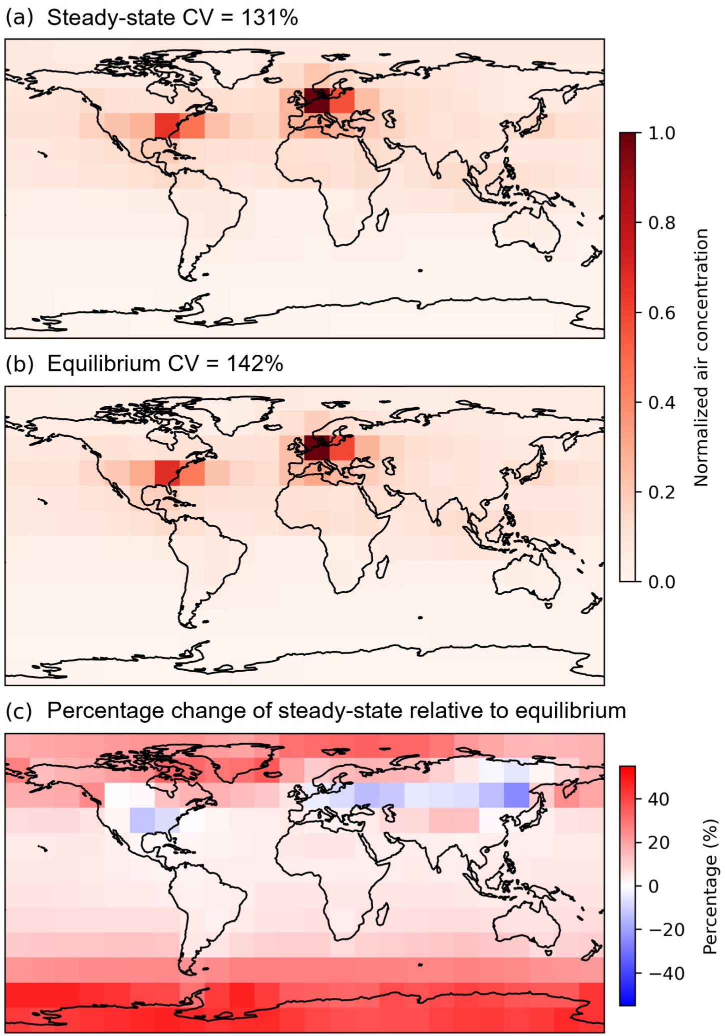


- At low temperatures, β-HCH is a PR-Type SVOCs, meaning that its rain-snow scavenging are overestimated by the equilibrium state.
- Under steady state, the atmospheric transport potential of β-HCH is much higher than that of equilibrium.

2 Case study 2 CB-180's global distribution

The BETR Global model is used to simulate the distribution of CB-180 in the global atmosphere.

- CB-180 is a typical PA-Type SVOCs, which means that its distribution in the particle phase and the proportion of particle deposition are overestimated.
- On a global scale, the global distribution simulated by the steady-state model is more uniform than that simulated by the equilibrium model.



3 Case study 3 BDE-209's annual deposition in Chinese cities

Based on the monitored BDE-209 gaseous concentration, its annual deposition flux in 10 Chinese cities was calculated.

Deposition flux	Gaseous dry deposition	Particlulate deposition (dry and wet)		Gaseous wet deposition		Sum	
($\mu g \cdot m^{-2}$)	E/S	E	S	E	S	E	S
Beijing	0.9 (0%/2.3%)	2.6×10^{8} (99.9%)	6.8 (18.2%)	1.6×10^{5} (0.1%)	29.5 (79.5%)	2.6×10^{8}	37.2
Chengdu	0.8 (0%/1.1%)	3.9×10^{7} (100%)	20.4 (29.2%)	746.2 (0%)	48.7 (69.6%)	3.9×10^{7}	69.9
Dalian	0.8 (0%/1.6%)	5.4×10^{7} (100%)	9.5 (19.1%)	329.0 (0%)	39.4 (79.3%)	5.4×10^{7}	49.7
Harbin	0.8 (0%/2.0%)	2.3×10^{9} (100%)	4.8 (11.9%)	38755.9 (0%)	34.3 (86.0%)	2.3×10^{9}	39.9
Kunming	0.4 (0%/0.8%)	9.8×10^{6} (100%)	7.5 (15.8%)	3170.7 (0%)	39.5 (83.3%)	9.8×10^{6}	47.4
Lhasa	0.4 (0%/2.7%)	2.3×10^{7} (99.8%)	1.9 (12.6%)	39631.0 (0.2%)	12.8 (84.7%)	2.3×10^{7}	15.1
Nanchang	0.2 (0%/0.6%)	2.0×10^{7} (100%)	3.7 (10.9%)	1954.2 (0%)	30.0 (88.4%)	2.0×10^{7}	33.9
Shanghai	0.2 (0%/1.4%)	2.4×10^{7} (100%)	1.9 (15.3%)	571.8 (0%)	10.0 (83.3%)	2.4×10^{7}	12.1
Shihezi	0.2 (0%/0.6%)	2.7×10^{9} (99.9%)	4.2 (11.4%)	3.3×10^{6} (0.1%)	32.1 (88.0%)	2.7×10^{9}	36.5
Xi'an	0.6 (0%/2.3%)	9.7×10^{7} (100%)	10.8 (15.8%)	1407.5 (0%)	57.2 (83.4%)	9.7×10^{7}	68.6

BDE-209 is a MP-Type SVOCs, and its distribution in both the rain and snow phase and the particle phase are overestimated by the equilibrium model. In the equilibrium state, almost 100% of the deposition is particulate deposition, and the deposition fluxes are extremely large. The steady-state results are more reasonable.

Thank you for listening!