Risk to Ozone and ozone-derived oxidation products on commercial aircraft

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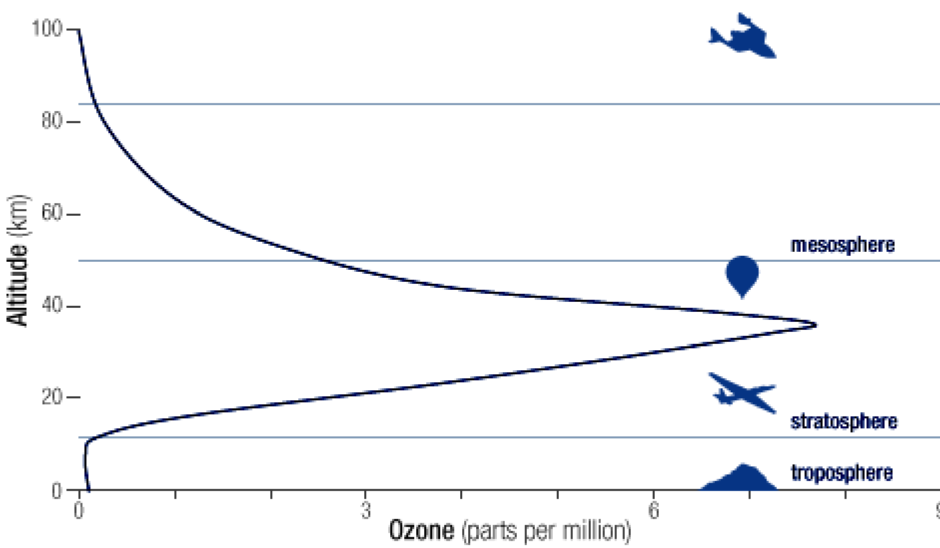
Background

- At cruise altitude (10000 to 11000 m), ozone levels outside an aircraft are high – typically 200 to 800 ppb
- Atmospheric conditions, such as folds in the tropopause, can result in an influx of stratospheric air into the lower atmosphere.



Thus even lower flying aircraft can encounter high ozone levels

Background

- **In the 1960s high ozone levels Dr. David Bates placed rubber bands (specially produced without antioxidants) in planes and observed that they cracked in an analogous fashion to a similar set exposed to ozone on the ground. At the same time toxicological symptom associated with ozone was observed occurring in flight attendants**
- **To reduce ozone on planes that cruise at high altitude most wide-body aircraft have ozone filters to remove ~85% of the ozone from the ventilation air**
- **However, only ~ 1/2 narrow-body aircraft remove ozone from the ventilation air**

Background

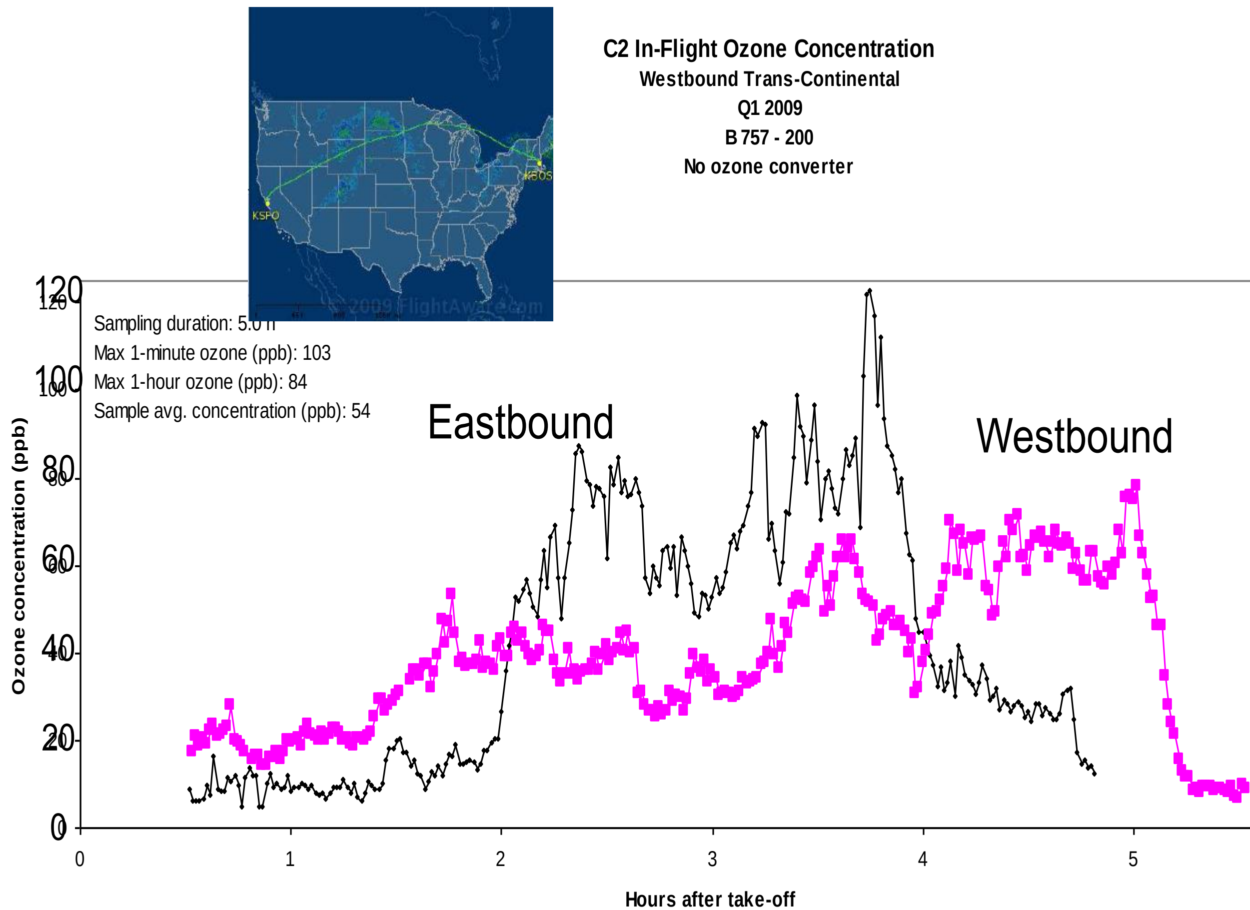
- **In 1980 FAA set an ozone standard in the airplane cabin of 100ppb average for flights exceeded 3 hours and 250ppb maximum – sea level equivalent. (Note ground level standard in 75ppb for 8 hours and 120ppm for 1hour)**
- **Ozone controlled by converters and route planning – but not all planes with converters**
- **Ground levels standards lowered several times since 1980**
- **Ground level ozone is also considers other photochemical oxidants and indoor air studies have found that ozone reacts to form additional compounds**
- **Simulated aircraft cabin studies have identified the formation of aldehydes by ozone**

Ozone levels on transcontinental aircraft

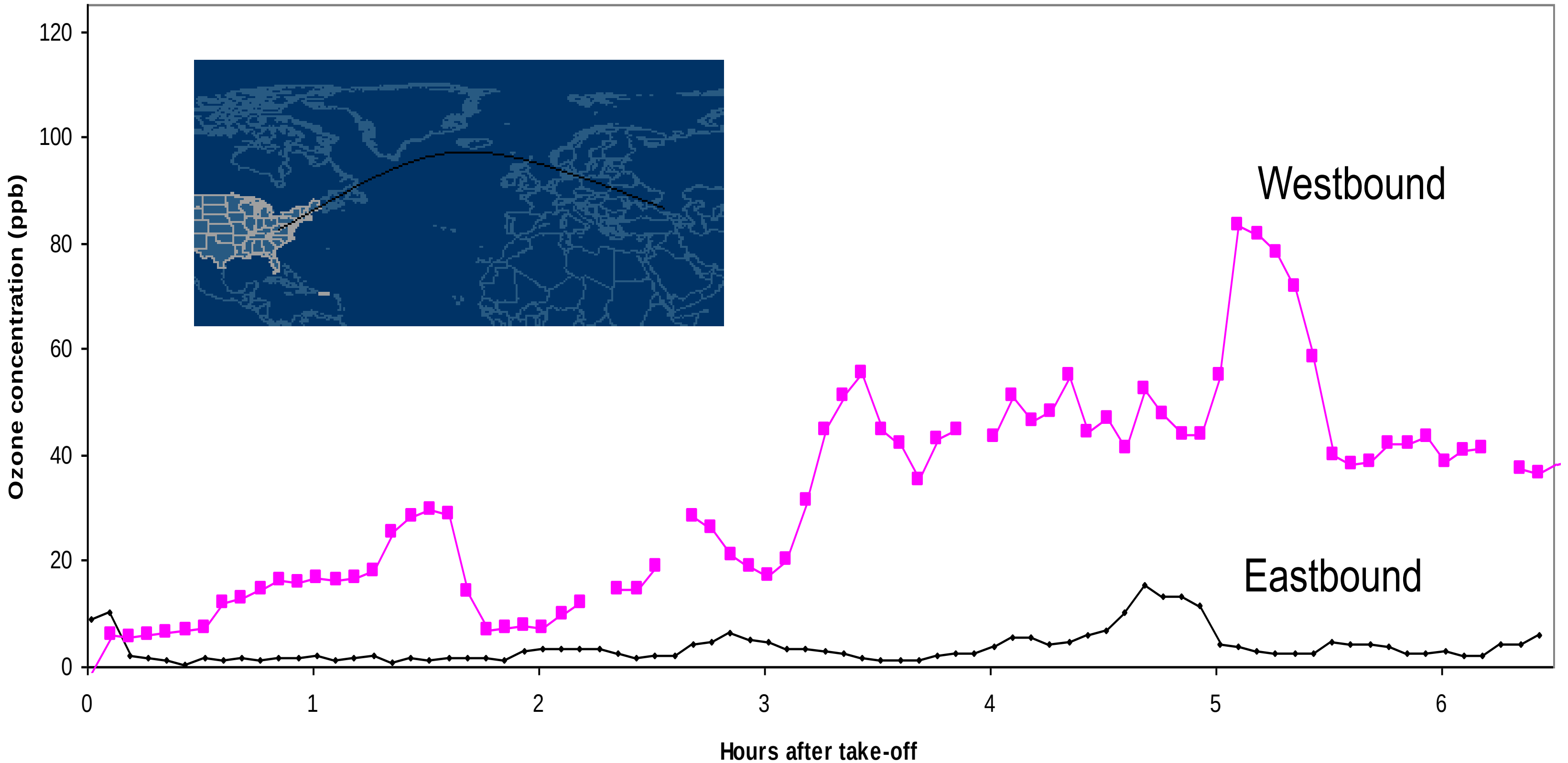
•At cruise altitude, ozone outside aircraft ~ 200 - 800 ppb

•Only about half the narrow-body aircraft remove ozone from ventilation air

•Ozone levels in commercial aircraft cabins are frequently > 50 ppb

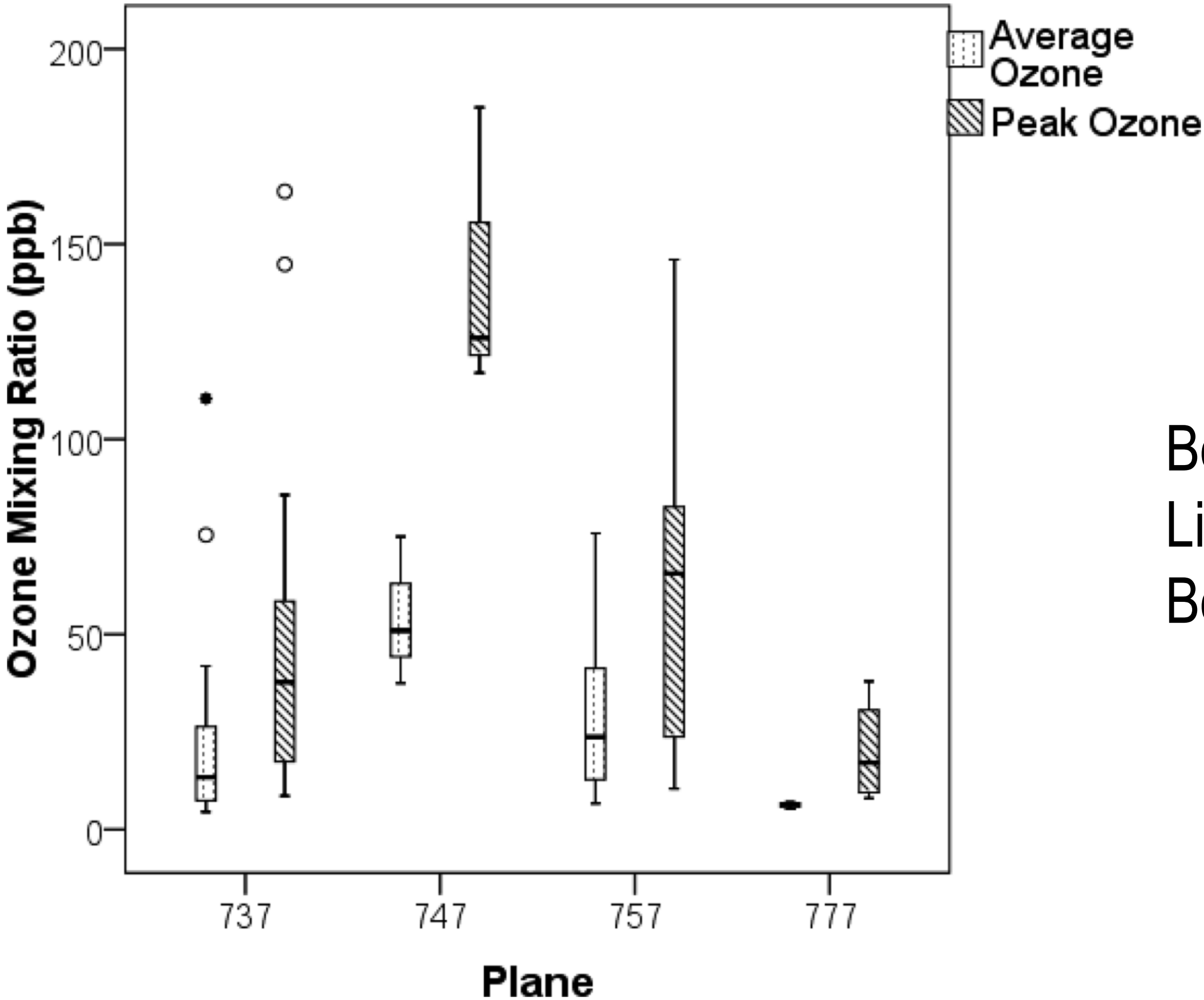


In-flight ozone data - transcontinental



Planes (747) had ozone converter. The condition were not known and the have a limited lifetime of effectiveness.

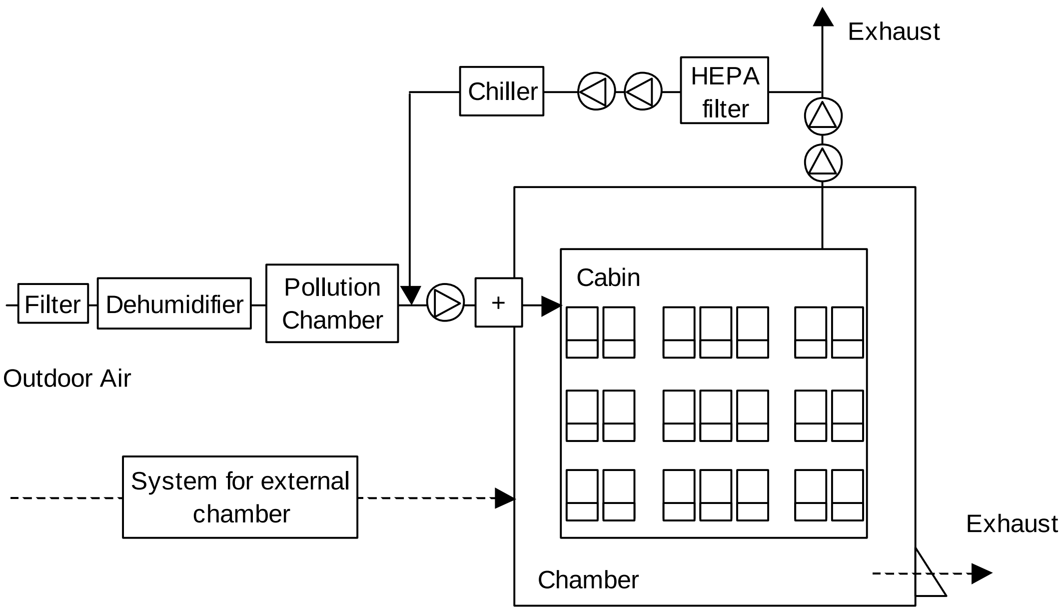
Measured O_3 levels (52 flights)



Box plot:
Line – median
Box – 25th & 75th

Weisel, CP, Weschler, CJ, Mohan, K, Vallarino, J, Spengler, JD "Ozone and Ozone By-Products in the Cabins of Commercial Aircraft" Environmental Science and Technology, 47 (9), 4711–4717, 2013

O_3 & humans in a simulated aircraft cabin



Simulated B-767; 3 rows, economy

- 16 passengers; 4-hour flights
- Outdoor airflow: 4.4 h^{-1} or 8.8 h^{-1} ; total airflow: 23 h^{-1}
- [O_3]: 60 to 80 ppb

Weschler et al., Environ Sci &Technol 41, 6177 (2007)

Chemical measurements

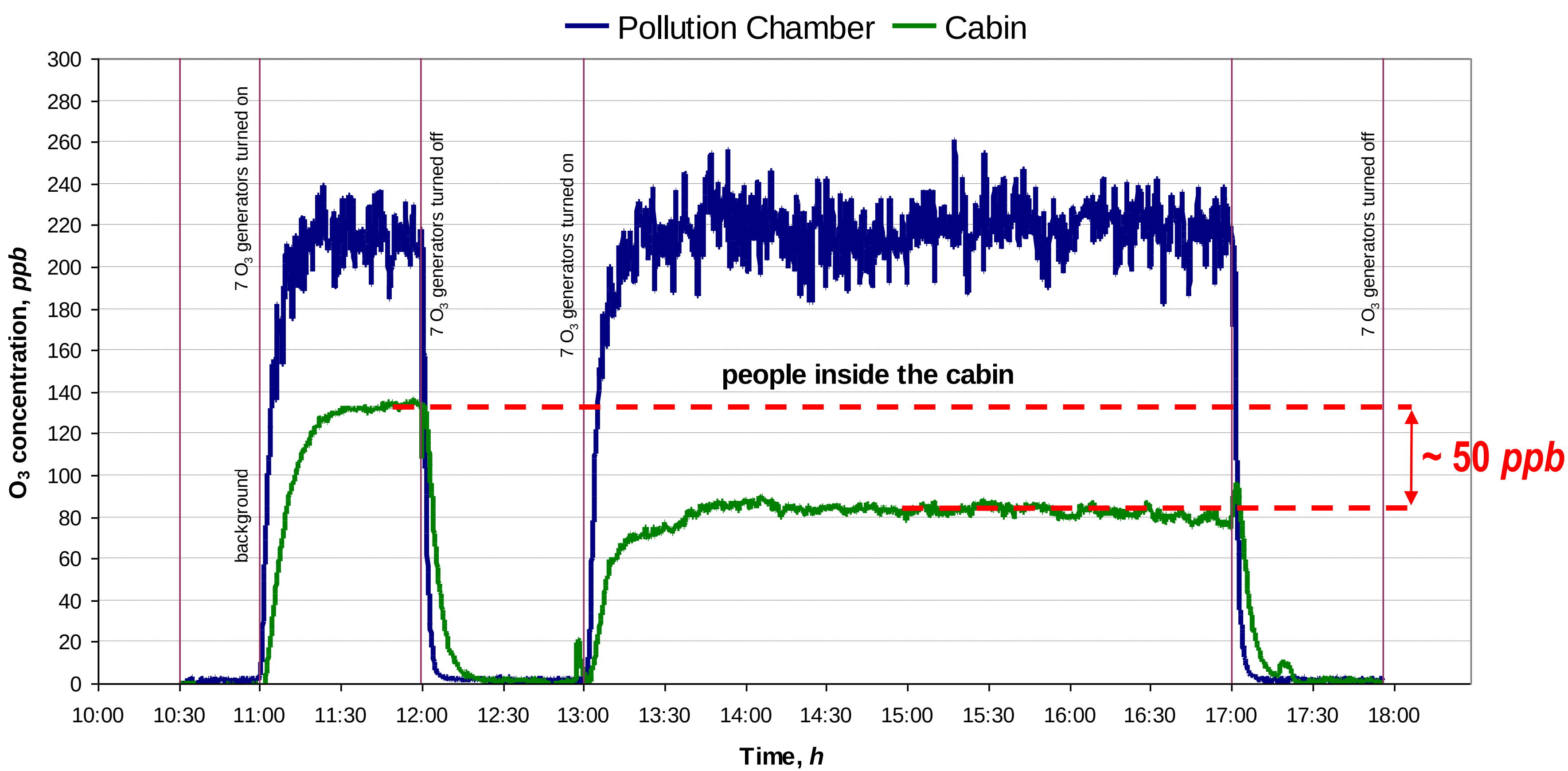
- Proton Transfer Reaction/Mass Spectrometry (PTR/MS) (Identify transient and unknown compounds)
- Multi-Sorbent tubes (Volatile Organic Compounds)
- DNPH cartridges (Formaldehyde & Acetaldehyde)
- DNSH cartridges (Acrolein)
- UV (Ozone)
- Nondispersive Infrared (Carbon Dioxide)

In-plane sources of O_3-reactive chemicals

Occupants	**Skin oil (i.e., squalene, oleic acid, unsaturated sterols)**, isoprene, nitric oxide (NO),
Carpet & backing	4-PCH, 4-VCH, unsaturated fatty acids
Seats	**Skin oil**, fabric
Soiled air filters	Unsaturated organics associated with captured particles

Humans are large O_3 sinks

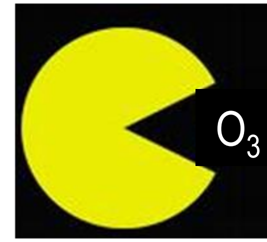
Simulated aircraft cabin



airflow: 75 L/s (8.8 h^{-1})

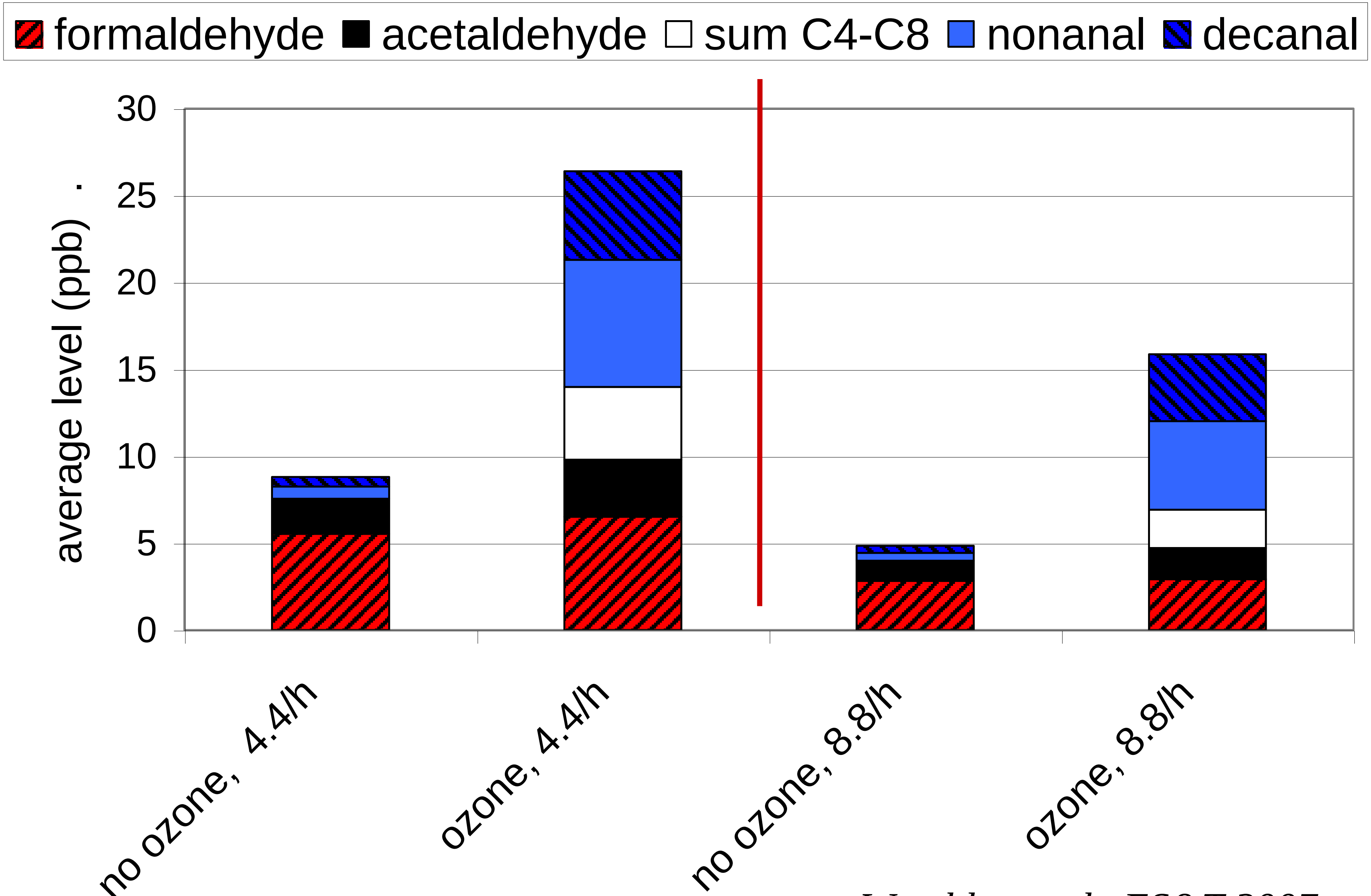
Weschler et al., Environ Sci &Technol 41, 6177 (2007)

Ozone reactive constituents of skin oil



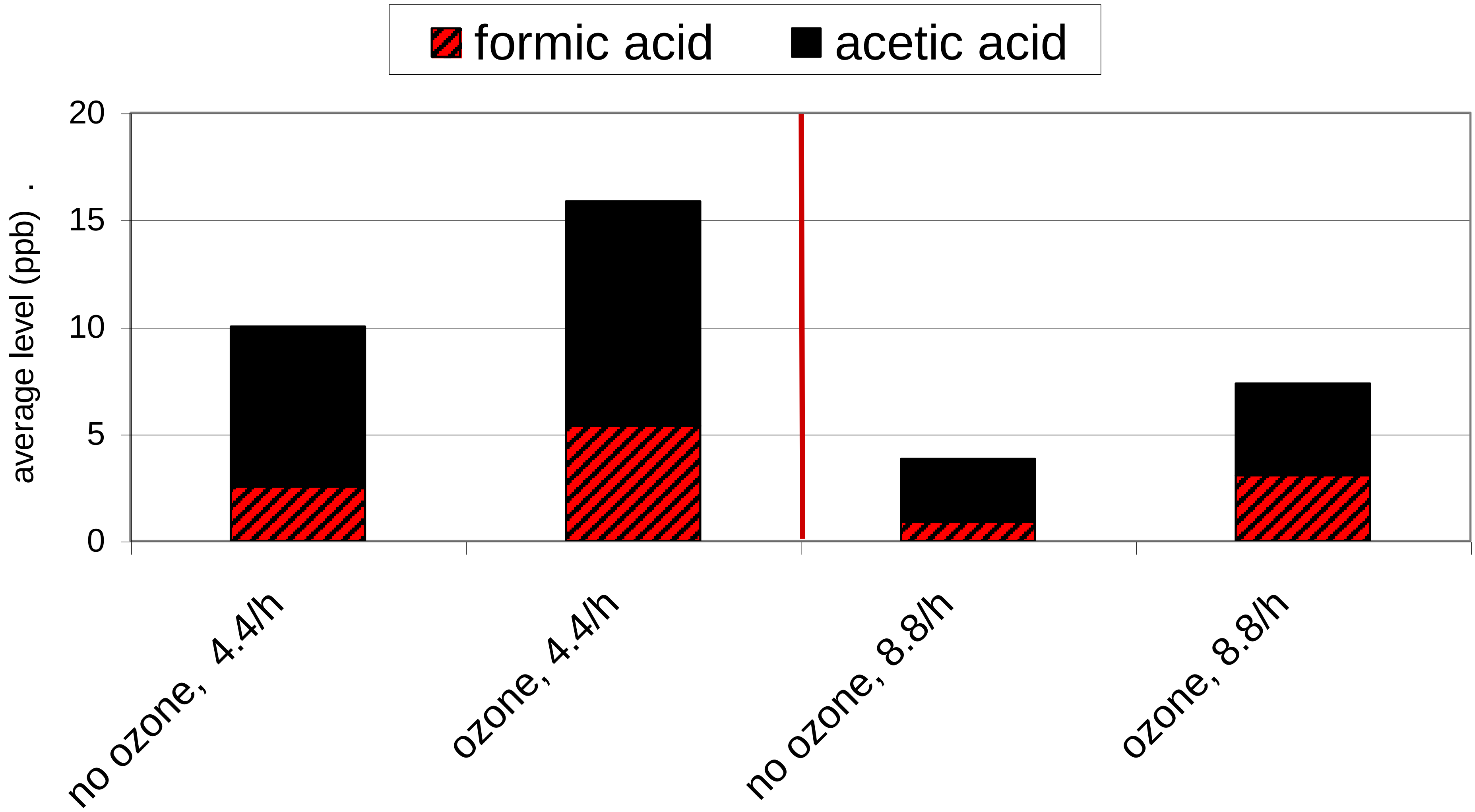
- Squalene (~ 10 – 15 μg/cm^2)
- Unsaturated fatty acids: (~ 11 – 17 μg/cm^2)
  - Some with Δ^6 unsaturation unique to humans
- Cholesterol (~ 3 – 4 μg/cm^2)
- Vitamin E (~ 0.013 – 0.020 μg/cm^2)
- Ubiquinone, aka CoQ_{10} (~ 0.012 – 0.018 μg/cm^2)
- Even smaller amounts: vitamin A, β-carotene, lycopene, ascorbic acid, glutathione, uric acid

Saturated aldehydes produced by ozone and are irritatants



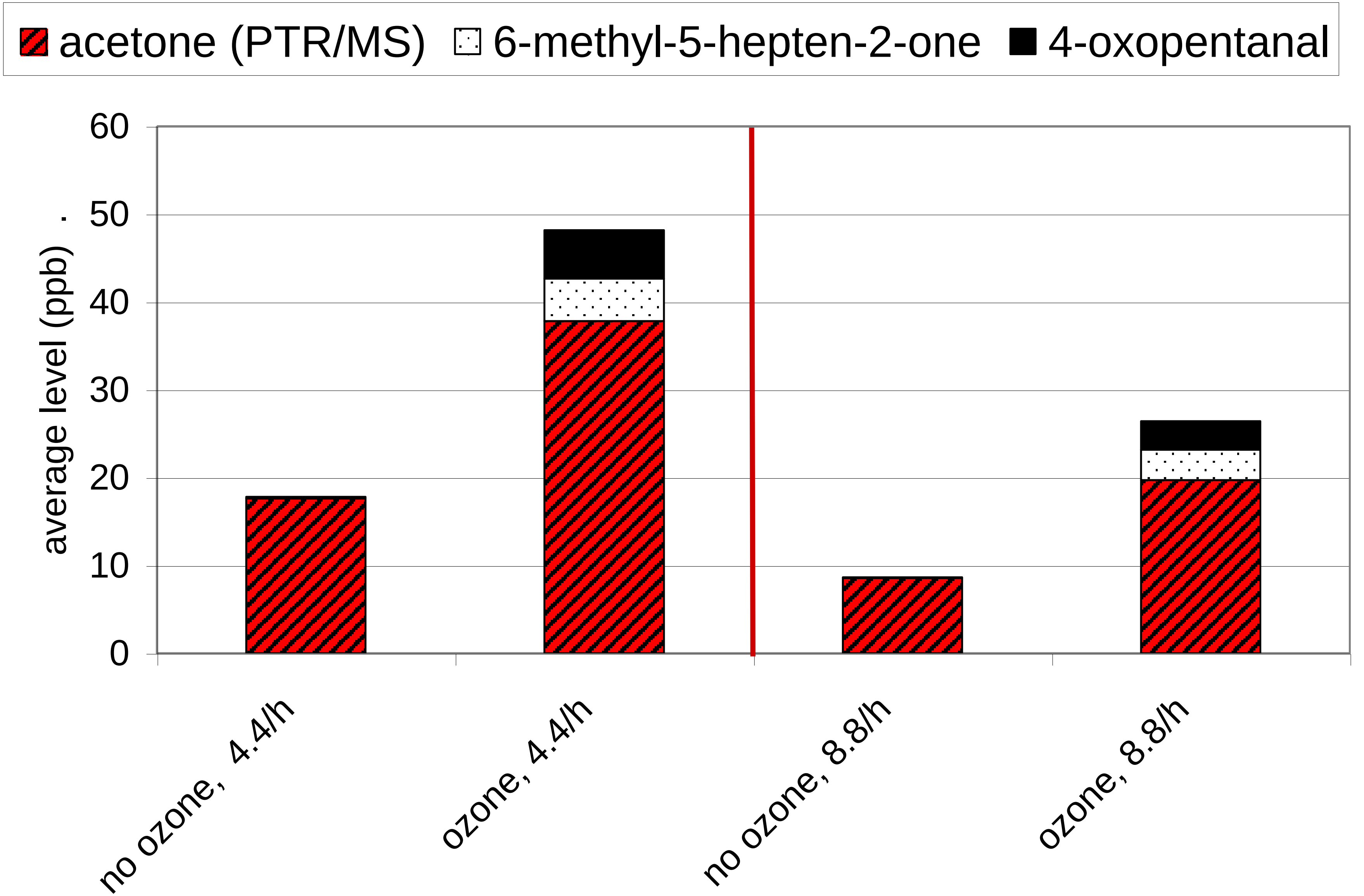
Weschler et al., ES&T 2007

Organic acids produced by ozone with one an irritatant



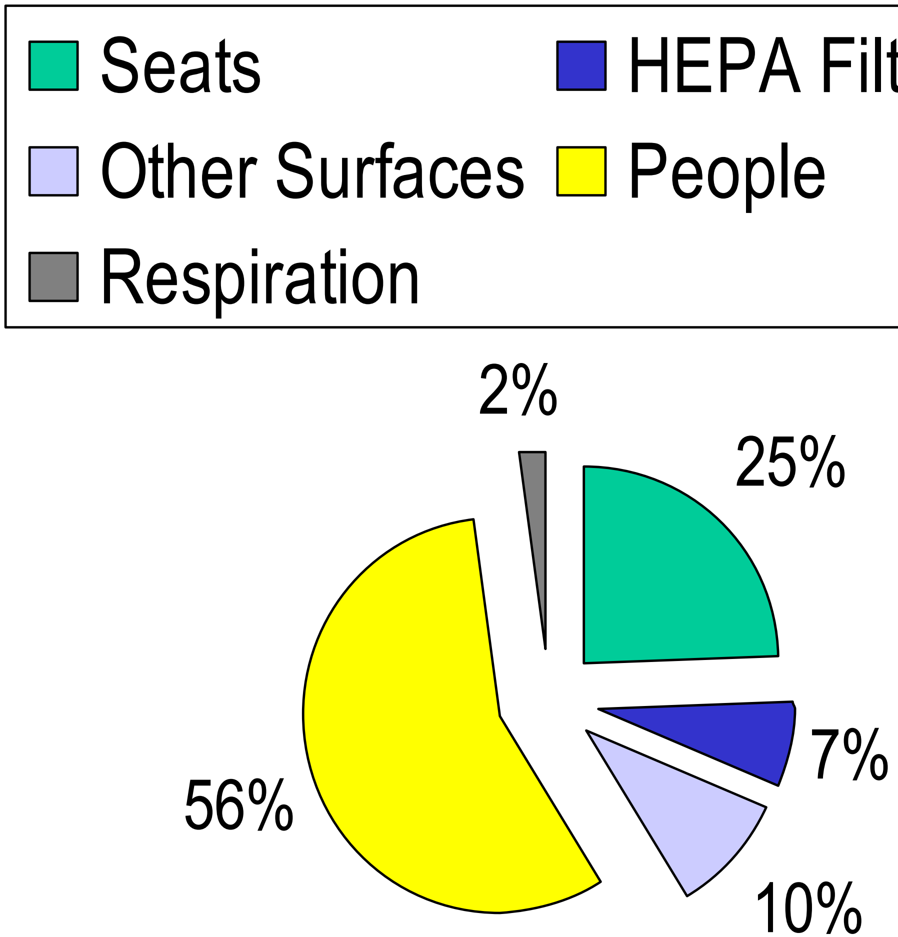
Weschler et al., ES&T 2007

Acetone, 6-MHO and 4-OPA



Weschler et al., ES&T 2007

Humans are large O_3 sinks



Contribution of different sinks to ozone removal in simulated Boeing 767

Symptom evaluations – DTU Chamber Study

Ozone in Cabin (ppb)	Flow of outdoor air (l/s/person)	Outdoor AER (h^{-1})	Flow of outdoor air (kg/m/person)
<2	2.4	4.4	0.17
61	2.4	4.4	0.17
<2	4.7	8.8	0.34
74	4.7	8.8	0.34

29 Female Subjects, 19-27 years
4 hour simulated flights 3row-21seat section
Completed questionnaires are various times during simulation
Statistical evaluation p<0.05 for significance

Stom-Tejsen, Weschler, Wargocki, Myssklo, Zarzycka The influence of ozone on self-evaluation of symptoms in a simulated aircraft cabin., JESEE, 18, 272-281, 2008

Symptom evaluations – DTU Chamber Study

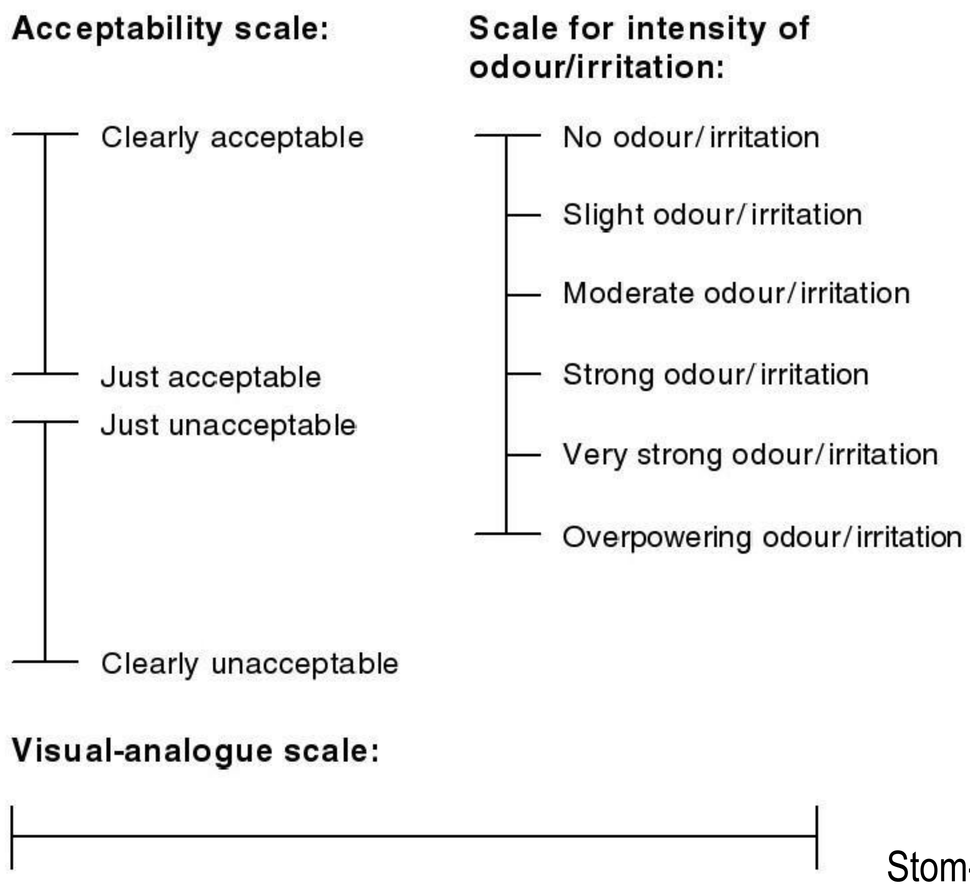


Figure 1. Scales for subjective assessments.

Stom-Tejsen, Weschler, Wargocki, Myssklo, Zarzycka The influence of ozone on self-evaluation of symptoms in a simulated aircraft cabin., JESEE, 18, 272-281, 2008

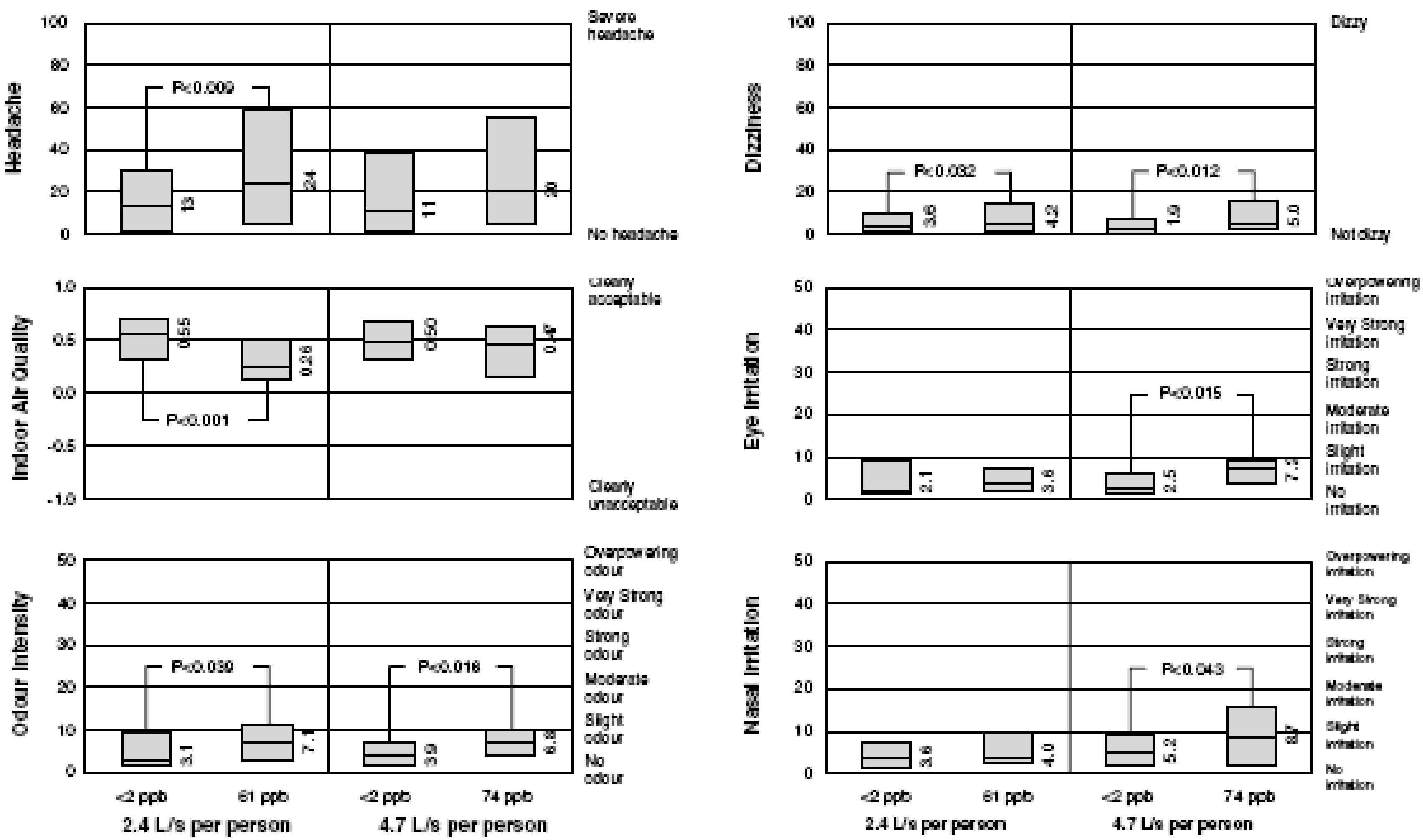
Air Quality and Symptoms Evaluated

Table 3. Variables probed in questionnaires.

Variable	Scale end points	
Air quality		
Indoor air quality[a,*]	Clearly unacceptable	Clearly acceptable
Odour intensity[b,*]	No odour	Overpowering odour
Eye irritation[b,*]	No irritation	Overpowering irritation
Nasal irritation[b,*]	No irritation	Overpowering irritation
Throat irritation[b,*]	No irritation	Overpowering irritation
Cabin environment		
Air humidity/dryness[c]	Too humid	Too dry
Freshness of air[c]	Air stuffy	Air fresh
Illumination[c]	Too dark	Too bright
Noise[c]	Too quiet	Too noisy
Thermal comfort and noise		
Thermal sensation[d]	Cold	Hot
Thermal environment[a]	Clearly unacceptable	Clearly acceptable
Air movement[a]	Clearly unacceptable	Clearly acceptable
Noise level[a]	Clearly unacceptable	Clearly acceptable
Symptoms		
Nasal occlusion[c]	Nose clear	Nose blocked
Nasal dryness[c]	Nose runny	Nose dry
Mouth dryness[c]	Mouth not dry	Mouth dry
Lip dryness[c]	Lips not dry	Lips dry
Skin dryness[c,*]	Skin not dry	Skin dry
Eye dryness[c,*]	Eyes not dry	Eyes dry
Eyes smarting[c,*]	Eyes not smarting	Eyes smarting
Eyes aching[c,*]	Eyes not aching	Eyes aching
Headache[c,*]	No headache	Severe headache
Thirst[c]	Not at all thirsty	Very thirsty
Dizziness[c]	Not dizzy	Dizzy
Fatigue[c]	Rested	Tired
Mental state[c]	Interested	Bored
Sleepiness[c]	Alert	Sleepy
Mental tension[c]	Relaxed, content	Uptight, frustrated
Claustrophobia[c]	Not a problem	Claustrophobic

[a]Acceptability scale.
[b]Intensity of odour/irritation scale.
[c]Visual-analogue scale.
[d]Thermal sensation scale.
*Variable included in the third questionnaire.

Results – box plot of selected outcomes



Results

- Based on self-reported symptoms at 3.75 hr point:

- Air quality & 12 symptoms (eye/nasal irritation, lip/skin dryness, headache, dizziness, tension, chlaustrophbia) were significantly worse for “ozone” condition compared to “no ozone” condition

Stom-Tejsen, Weschler, Wargocki, Myssklo, Zarzycka The influence of ozone on self-evaluation of symptoms in a simulated aircraft cabin., JESEE, 18, 272-281, 2008

In-flight evaluation of ozone by-products
Approach

- Sampling package – 2BTech Model 205 Dual Beam Ozone Monitor battery operated
- BGI Pump with Mixed bed adsorbent trap for C6-C10 aldehydes with KI trap (to remove ozone) and DNPH-Cartridge for Formaldehyde
- Sampling equipment place under seat with Teflon tubing inlet and sampling traps in breathing zone

Sample analysis

- Ozone monitor is a real time instrument based on UV absorption with 1ppb sensitivity and 1 minute averaging time
- Adsorbent traps analyzed by thermal desorption coupled to GC/MS
- DNPH extracted with actonitrile and analyzed by HPLC/UV

O_3 & humans in **real** aircraft cabins

- Ozone and carbonyls measured on 52 flights
- Mostly transcontinental U.S. flights; some transoceanic flights
- B-737, B-747, B-757 & B-777
- Ozone scrubber upstream of sorbent tube to avoid ozone reacting w. 6-MHO on sorbent

Weisel, CP, Weschler, CJ, Mohan, K, Vallarino, J, Spengler, JD “Ozone and Ozone By-Products in the Cabins of Commercial Aircraft” Environmental Science and Technology, 47 (9), 4711–4717, 2013

O_3 & humans in **real** aircraft cabins

Compound	Median (ppb)	Maximum (ppb)
Hexanal	2.8	8.4
Heptanal	0.77	4.0
6-MHO	0.73	13
Octanal	0.75	4.5
Nonanal	1.9	14
Decanal	1.6	12

- Statistically significant correlations between:
  - O_3 and 6-MHO
  - 6-MHO and % occupancy

Weisel et al, Environ Sci &Technol 2013

Other in-plane sources of O_3-reactive chemicals

Carpet & backing	4-PCH, 4-VCH, oleic acid, other unsaturated fatty acids
Seats	Skin oil, fabric
Soiled air filters	Unsaturated organics associated with captured particles

Summary

- Ozone is present on transcontinental US flight and when ozone converter not working optimally
- When O_3 present, concentrations of aldehydes, ketones & organic acids much larger
- People are major O_3 sinks – larger than carpet, seats and dirty HEPA filter combined
- Humans + $O_3 \longrightarrow$ acetone, nonanal, decanal, 6-MHO, geranyl acetone, 4-OPA
- Presence of O_3 and O_3-derived products adversely affected 12 of 29 self-reported symptoms

Broader implications

- Ozone is present at levels exceeding 100ppb on aircraft without ozone convertors and if the converter is not functioning correctly, though not routinely exceeding current FARS
- EPA Ground Level Standards 75ppm over 8 hours, though USEPA-SAB recommended lower level
- Chemistry producing ozone by-products occurs **whenever** O_3 and humans simultaneously present in a room or aircraft
- Potential effects of by-products across current flying public still to be determined - O_3 can be filtered from ventilation air

Quantifying Exposure to Pesticides on Commercial Aircraft

Clifford Weisel

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Kris Mohan
Sagnik Mazumdar
Yong Zhang

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Congressional Mandate

- **MANDATE: Collect pesticide exposure data to determine exposures of passengers and crew**
- Approach:
  - Measure surface loadings on commercial aircraft
  - Measure urinary pesticide biomarker levels in flight attendants
  - Apply CFD model to Top of Descent Spray and evaluate model with measurements
  - Estimate the risk to flight crew from pesticides

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Research Objectives

- Wipe Samples
  - Evaluate what aircraft surfaces and flights routes have pesticides
- Biomarker of Pesticides in Flight Crew
  - Determine urinary pyrethroid metabolites for flight attendants
  - Evaluate permethrin PBPK model for flight attendants
- CFD Model from Top of Decent Disinsection
  - Computational Fluid Dynamic (CFD) modeling to predict air concentration and surface loading
  - Evaluate with data from KSU's mock 757 aircraft
- Risk Paradigm to Permethrin
  - Estimate risk based on exposures

Purpose of Aircraft Disinsection

To prevent or minimize the transport of insects which pose a health threat to humans, animals and plants

- Adopted by US in the 1930s; discontinued since 1979
- Required by many other countries currently, e.g., Australia, New Zealand, India, China and many islands
- Most countries reserve their right for this practice on flights from particular regions of endemic diseases

Disinsection Methods

- When passengers and flight crew are on board: Top of descent, blocks away and, pre-flight. (*phenothrin, permethrin,* or both)

- During scheduled maintenance (no passengers on board): Residual treatment:
    (permethrin)

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What Was Collected

- Examined surfaces on aircraft from
  - 15 US domestic flights,
  - 18 flights landing in Central or South America,
  - 8 flights landing in Australia or New Zealand,
  - 4 flights landing in Africa or Europe and
  - 15 flights landing in Asia during 2008 and 2009

- Collected from Seat Cushions, Seat Backs, Tray Tables, Arm Rests, Galley Area, Lavatory

- Problem with recovery – so only relative amounts are determinable

Mock Boeing–Simulated Disinsection Surface Loading (μg/cm^2)

	High Ventilation		Low Ventilation	
	50-CM [a]	100-CM [b]	50-CM	100-CM
25th percentile	0.13	0.08	0.53	0.48
median	0.13	0.11	0.69	0.64
75th percentile	0.14	0.13	0.83	0.90
max	0.19	0.16	1.07	0.98
N	10	17	15	22
% RSD	22	29	30	32

Destination Continent	Permethrin Mean * (max)	Phenothrin Mean*(max)	Total Flights	Permethrin Above Detection	Phenothrin Above Detection
Asia	0.034±.002 (0.035)	0.031±.026 (0.061)	3	2	3

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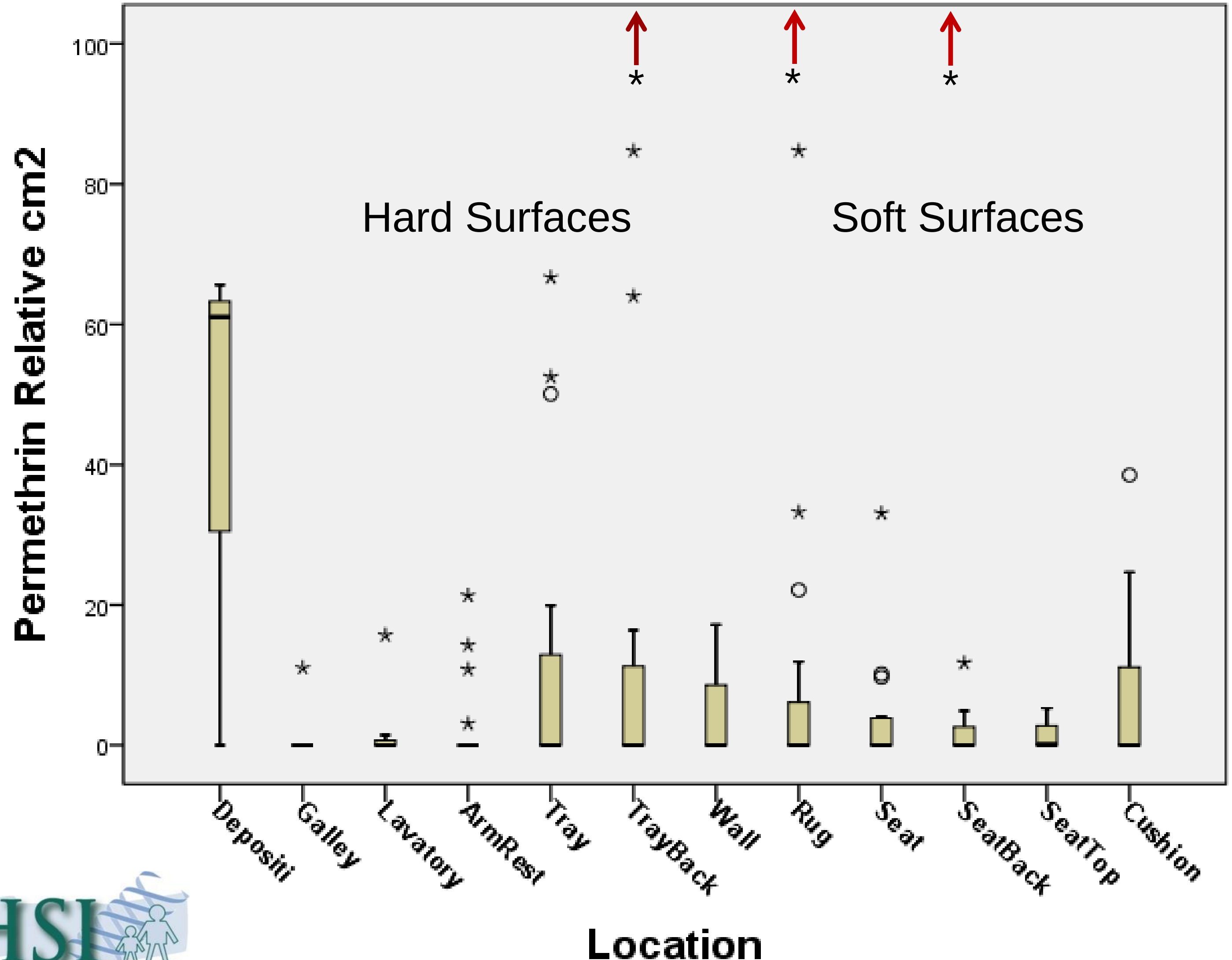
Surface Loading by Surface Type

(Relative amounts per cm^2)



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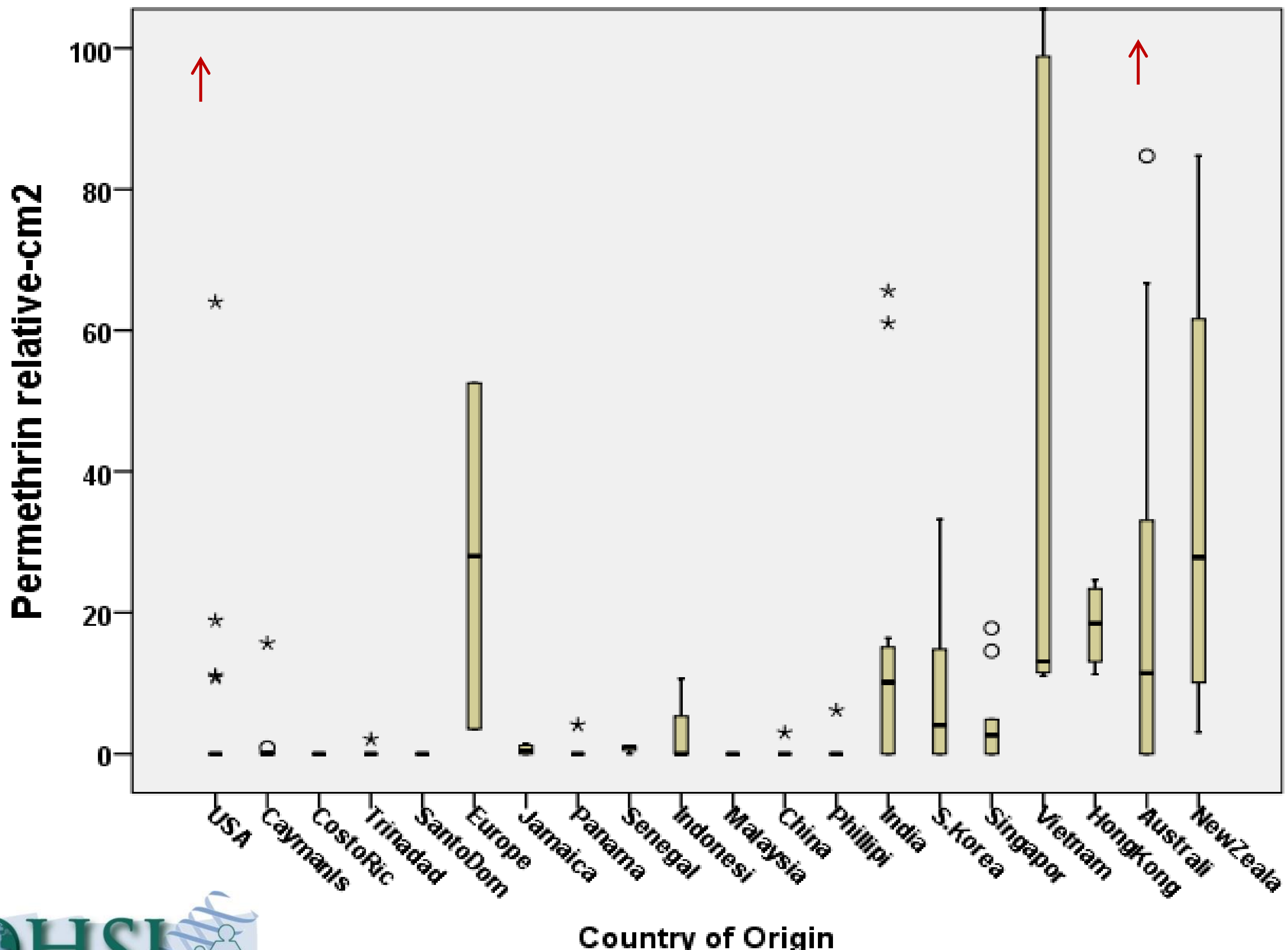
Surface Loading by Origin (Country)
(Relative amounts per cm^2)



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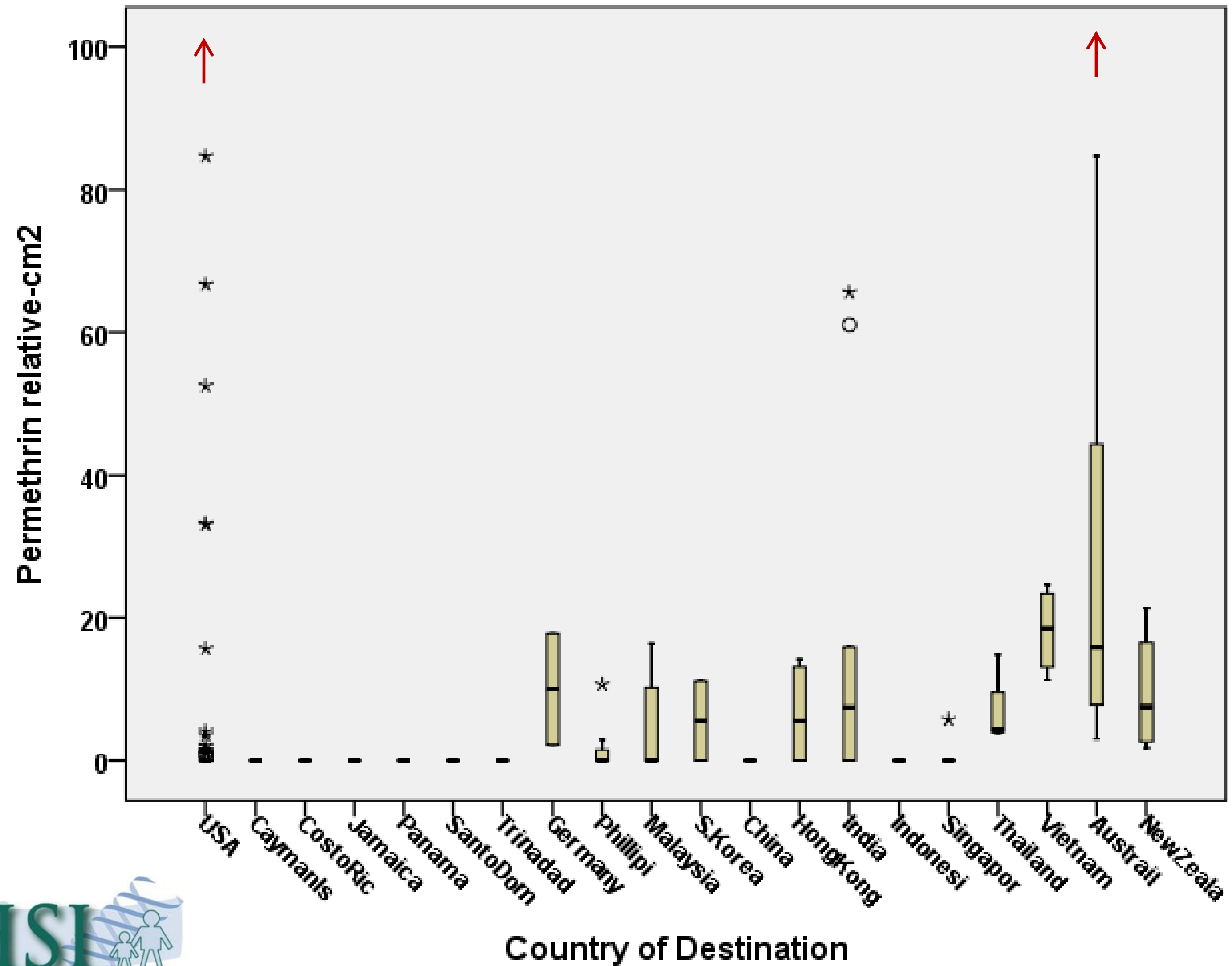
Surface Loading by Destination
(Relative amounts per cm^2)



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Conclusions

- Pyrethroids were not detected on US domestic flights
- Pyrethroids were routinely detected on international flights
  - To/from countries requiring disinsection, performed maintenance of aircraft or may use aircraft that service selected countries
  - Permethrin detected for residual
  - Permethrin & phenothrin in on board spraying
- Use of KSU's mock Boeing 767 aircraft cabin documented inhalation and dermal exposure during simulated disinection with passengers

Biomarker of Pesticides in Flight Crew

Urinary Metabolite Levels of Pyrethroid Insecticides in Flight Crew

References: Wei, B, Mohan, K, Weisel, CP “Exposure of Flight Attendants to Pyrethroid Insecticides on Commercial Flights: Urinary Metabolite Levels and Implications, Occupational and Environmental Medicine, 215(4) 465-473, 2012 and Wei, B, Isukapalli, SS, Weisel, CP “Physiologically Based Pharmacokinetic Modeling of Exposure Pyrethroids Insecticides in Flight Attendants”, Journal of Exposure Science and Environmental Epidemiology, 6 March 2013; 10.1038/jes.2013.12,

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Project Objectives

Do we see elevated levels of urinary pyrethroid metabolites in flight crew after they fly on aircraft that were disinsected?

How do those levels compare with other populations?

Can they be used to drive pharmacokinetic models and in population risk estimates?

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Urinary metabolites of pyrethroids

Pyrethroid metabolites measured:

- **3-phenoxybenzoic acid (3-PBA),**
- **cis- and trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane carboxylic acid (cis-, and trans-DCCA),**
- **cis-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropane-1-carboxylic acid (cis-DBCA)**
- **4-fluoro-3-phenoxybenzoic acid (4F-3-PBA)**

Table 1. Pyrethroids and their corresponding urinary metabolites.

Pyrethroid	Urinary metabolites
Permethrin	3-PBA, *cis*- and *trans*-Cl2CA
Cypermethrin	3-PBA, *cis*- and *trans*-Cl2CA
Deltamethrin	*cis*-Br2CA, 3-PBA
Cyfluthrin	4F-3-PBA, *cis*- and *trans*-Cl2CA
Phenothrin	3-PBA, *trans*-*CDCA*

Wei et al 2011

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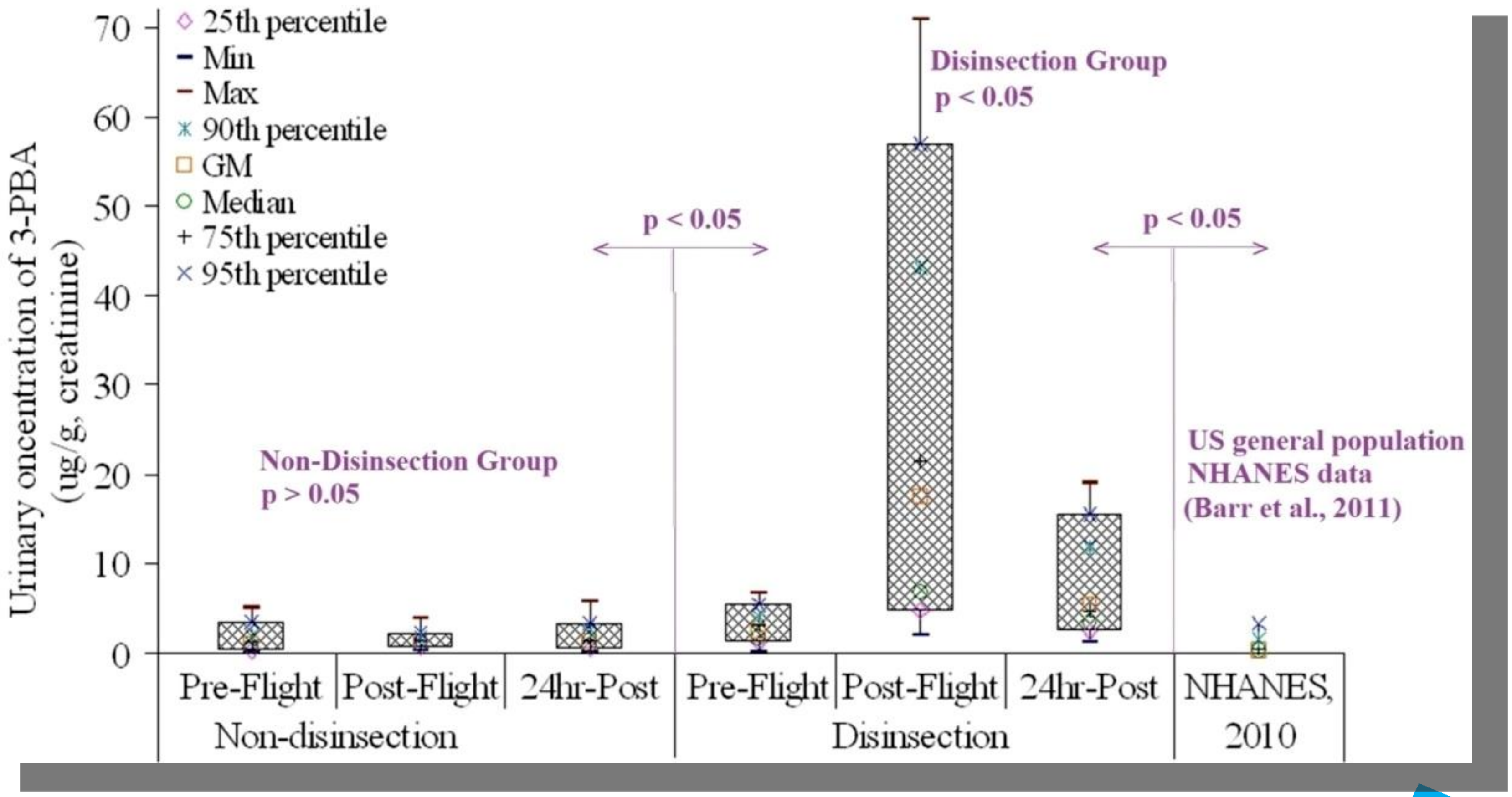
Urinary metabolite levels of 3-PBA
creatinine corrected



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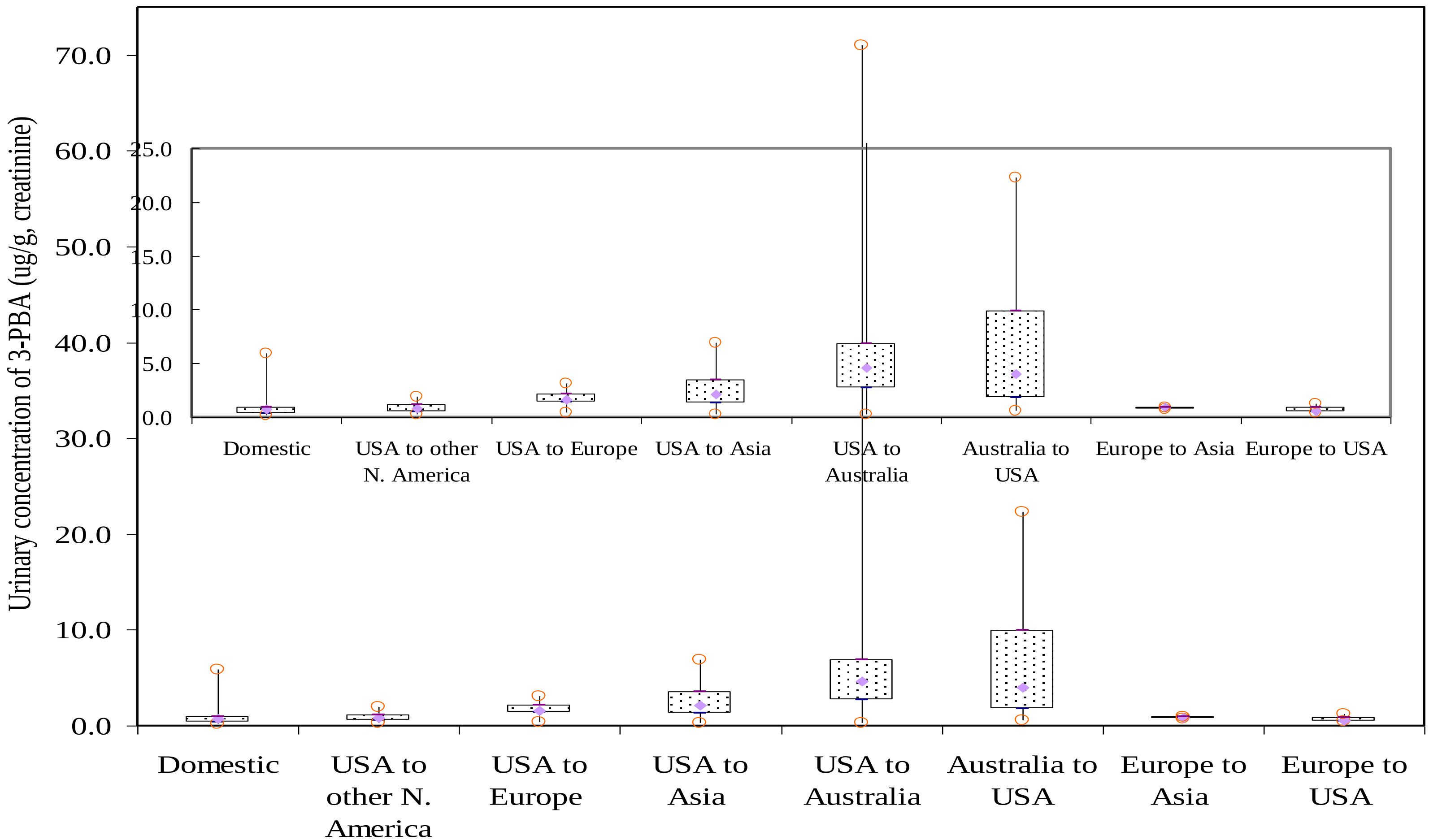
Urinary metabolite 3-PBA
Sorted by Domestic & International Flights



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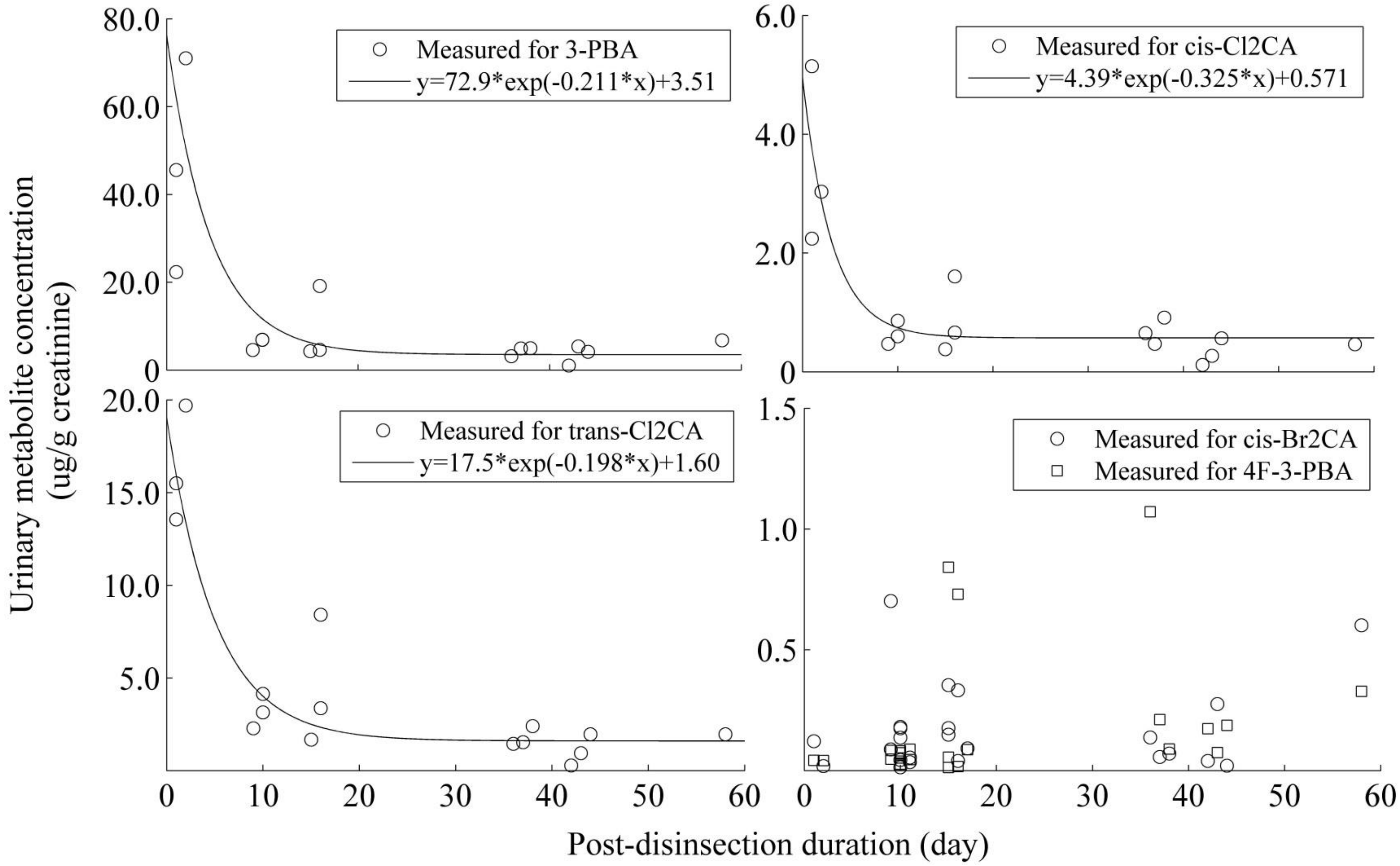
Urinary metabolite levels with time since disinsection



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Comparison with Other Studies

Type	Conc. of 3-PBA (ug/L)	Reference
US general population	0.324 (GM) 0.29 (50^{th}) – 3.35 (95^{th})	Barr et al., (2010)
Greenhouse workers	2-52	Tuomainen et al., 1996
Pest control workers	0.5- 277	Leng et al., 1997
Forestry worker	260	Kolmodln-Hedman et al.,1982
Flight attendants	0.8 – 81.5 (min - max) 5.2 – 51.0 (50^{th} – 95^{th})	This study

Exposure of flight attendant to permethrin is similar to those pesticide applicators

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Rationale for Model and Approach

- **PBPK models provide estimate of target tissue dose associated with an exposure**
- **Provide input for risk paradigm**

- **Develop and validate PBPK model for permethrin**
- **Assess potential variability in model**
- **Evaluate it with animal & human data**
- **Simulate exposure to flight attendants**

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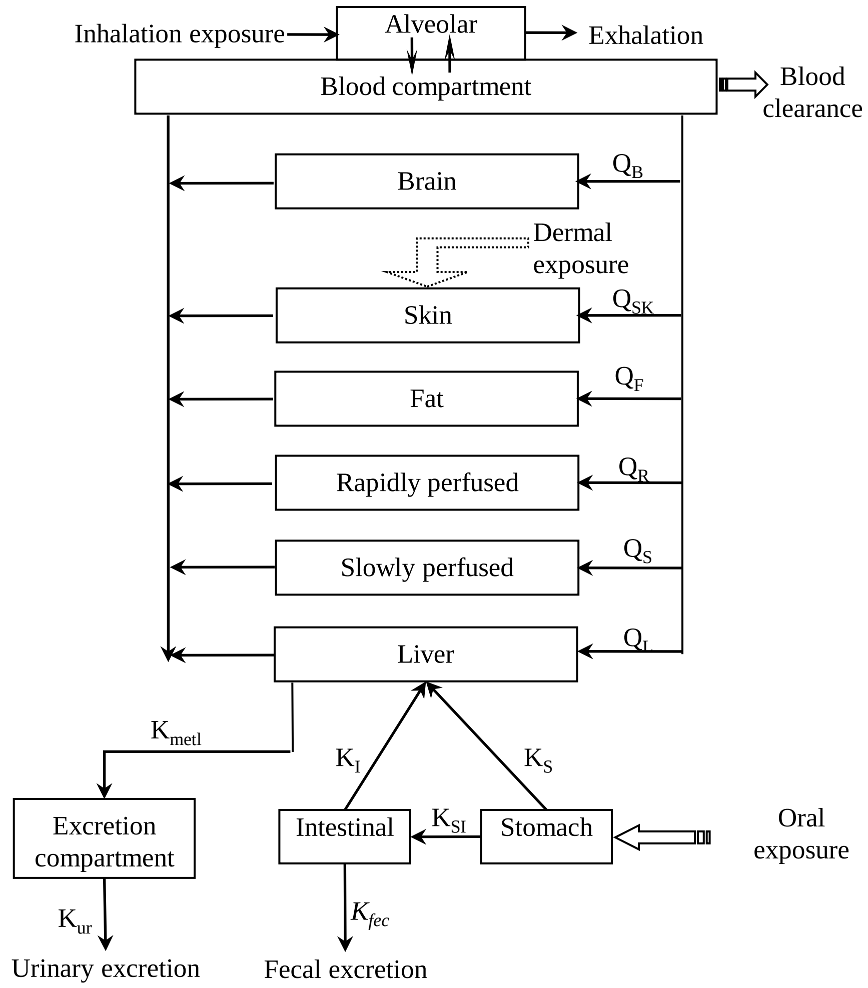
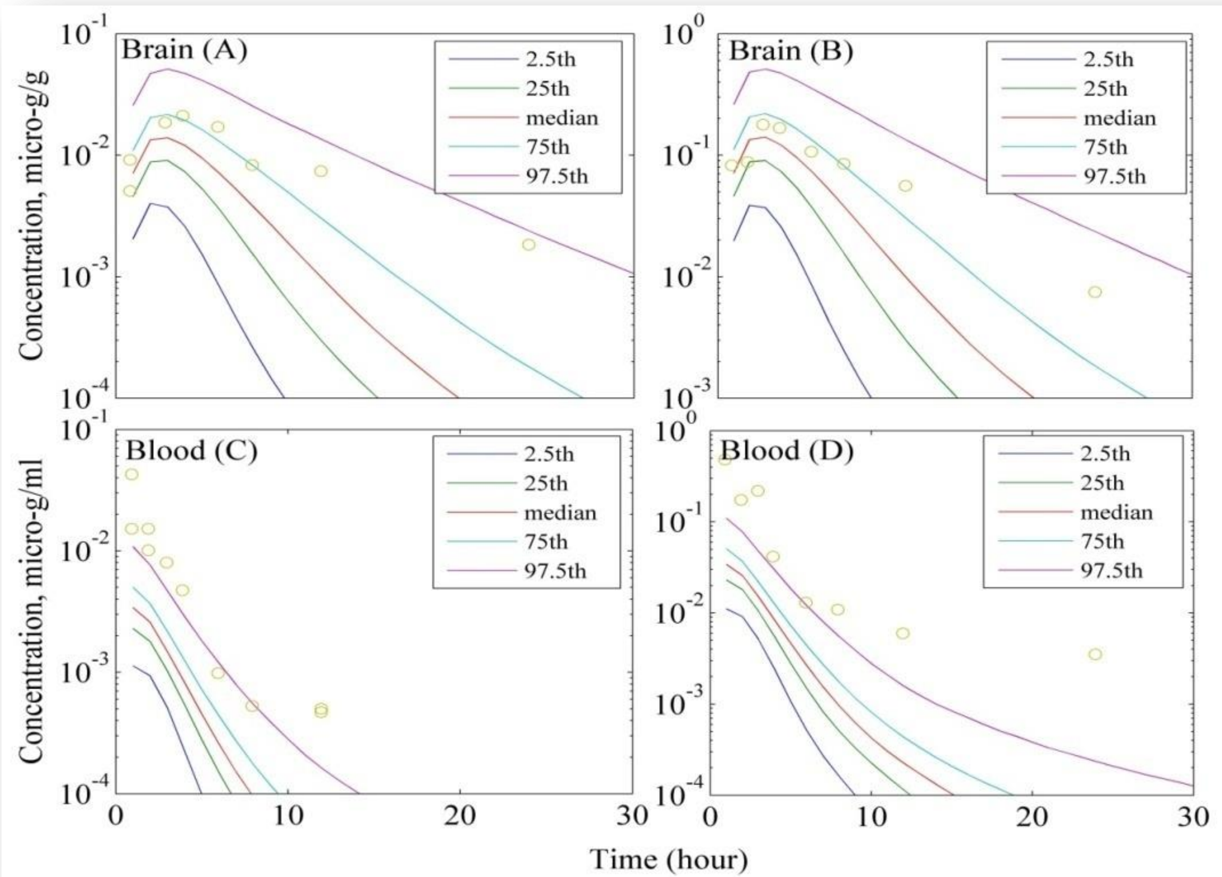
Model Structure



Comparison to Animal Data

1.0 mg/kg oral dose

10. mg/kg oral dose



- 97.5th percentile
- 75.0th percentile
- 50.0th percentile
- 25.0th percentile
- 2.50th percentile

Lines are modeled time-conc profiles
Yellow circle are experimental data (USEPA 2007)

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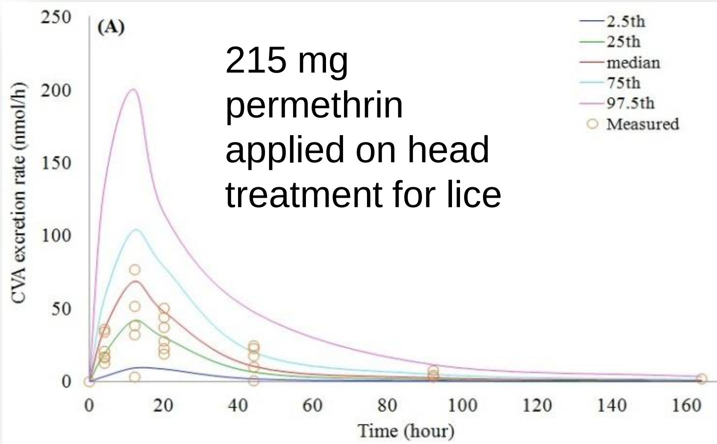
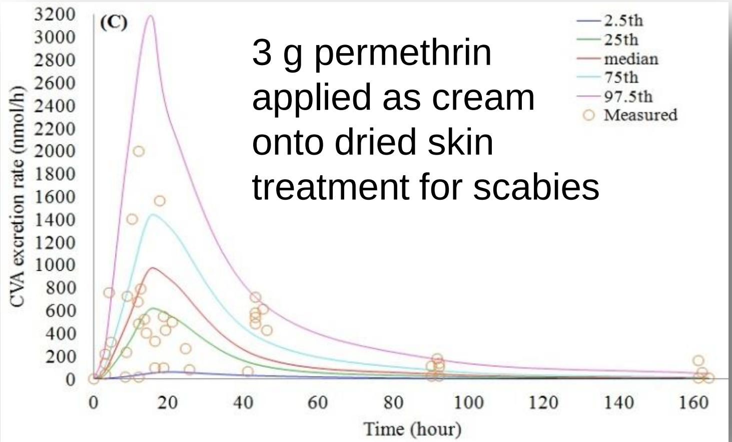
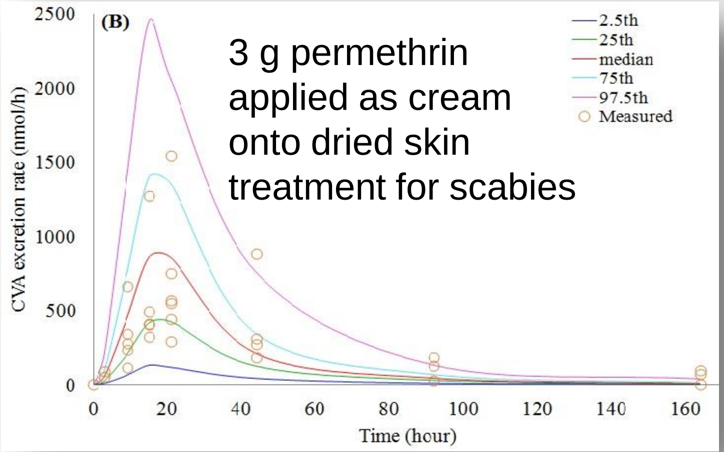
Comparison to Human Data







Modeling total urinary excretion rate of permethrin metabolites, *cis/trans*-3-(2,2-Dichlorovinyl)-2,2-dimethylcyclopropane carboxylic acid (CAV) (data from Tomalik-Scharte et al., 2005).

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Permethrin Exposure Scenarios

Aircraft Disinsection

- Residual Treatment
  - Done on the ground, with no crews and passengers on the plane
    - Surface loading (entire flight)
      log-normal distribution
      median: 35; STD: 35;
      range: 0.5 – 140;
      unit: µg/cm2
    - Air concentration (entire flight)
      log-normal distribution
      median: 0.5, STD: 0.5;
      range: 0.0 – 1.0
      Unit: µg/m3
- Pre-flight Spray
  - Can be done by crewmembers just prior to a plane's departure
    - Surface loading (entire flight)
      log-normal distribution
      median: 0.58; STD: 0.58;
      range: 0 – 2.32;
      unit: µg/cm2
    - Air concentration (stage I)
      log-normal distribution
      median: 65; STD: 65;
      range: 1.0 – 260;
      unit: µg/m3
      - Air concentration (stage 2)
        log-normal distribution
        median: 0.5, STD: 0.5;
        range: 0.0 – 1.0
        Unit: µg/m3

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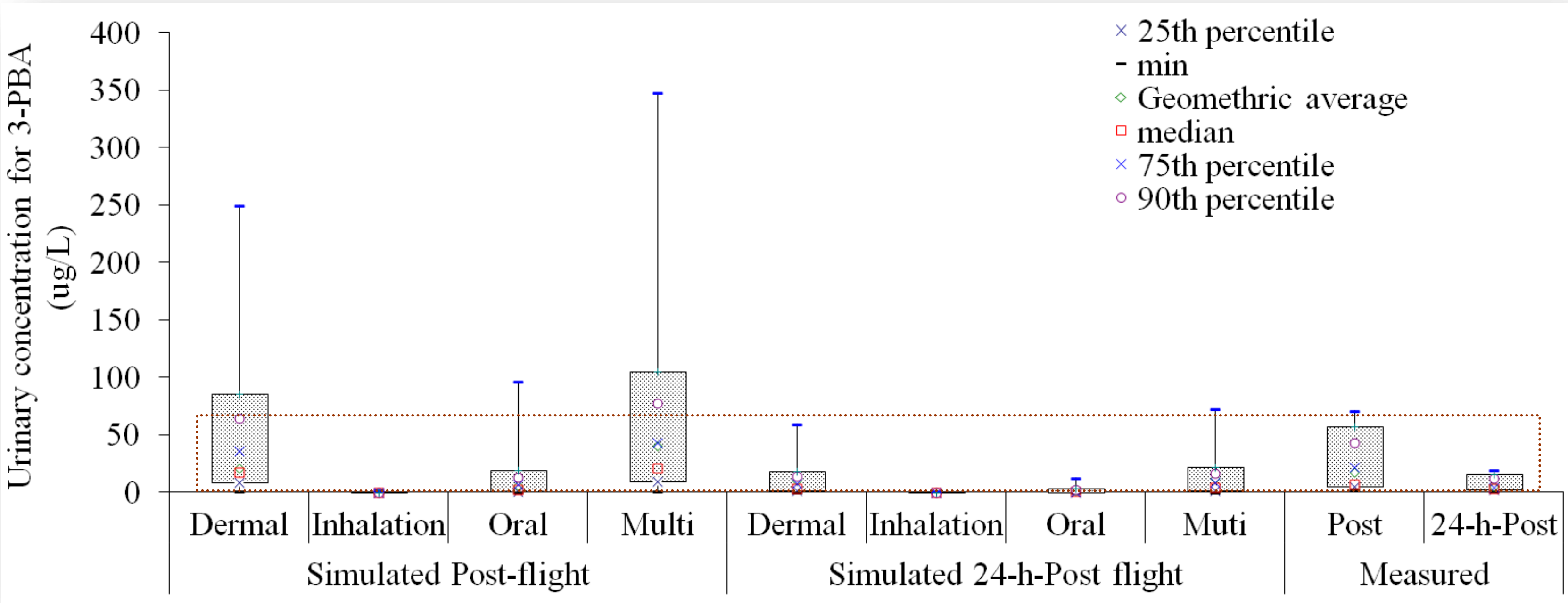
Predicted Urinary 3-PBA Conc for residual treatment scenario



Red box – measured levels for flight attendants

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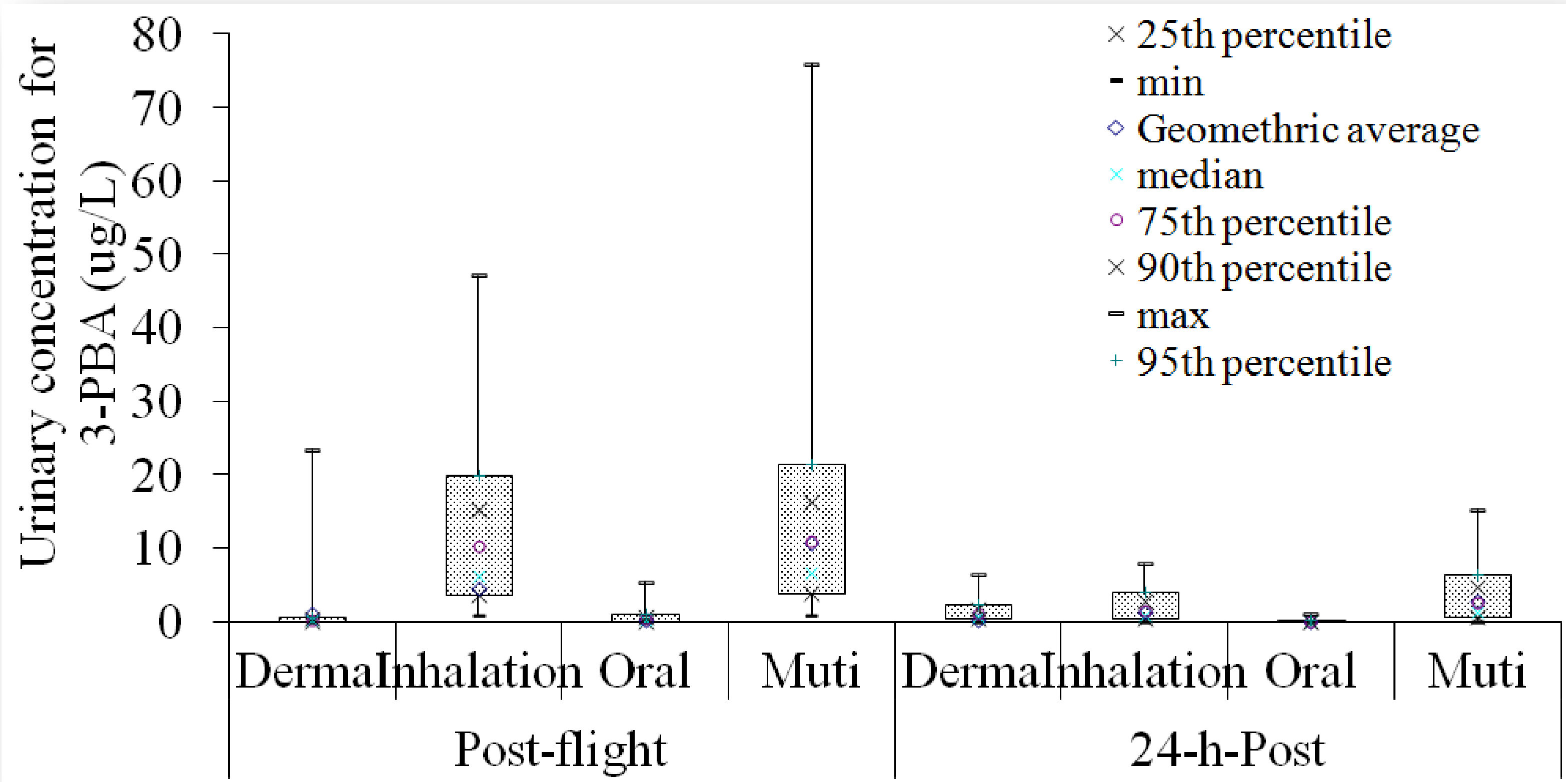
Predicted Urinary 3-PBA Conc for pre-flight spray scenario



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Conclusions

- Simulated 3-PBA concentrations in post- and 24-h-post urine were comparable to previously measured results.
- For residual disinsection mean (90^{th}%) predicted 3-PBA levels were 50 (350) µg/L with dermal providing ~84%, oral ~16 %, inhalation ~1 %
- For Pre-spray disinsection mean (90^{th}%) predicted 3-PBA levels were 10 (75) µg/L with inhalation providing ~90%, dermal ~5 %, oral ~3 %

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RISK ASSEMENT PARADIGM

Component 1: Determine air concentrations and surface loading over time
Initial conditions CFD Modeling for Spraying or Suggested Loading for Residual
Removal with time through contact, cleaning, volatilization

Component 2: Human activity that leads to contact
Frequency and duration of flight
Breathing rate
Inadvertent ingestion
Touching Rate

Component 3: PBPK modeling to determine uptake and distribution in the body
Estimate of risk by comparison to literature hazar

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CFD Pesticide Modeling

- Computational Fluid Dynamic (CFD) models provide an effective methodology for characterizing concentration distributions and exposures at a high spatial and temporal resolution

- CFD program FLUENT was used with a Re-Normalization Group (RNG) k-ε turbulence model

- Current model for a twin-aisle 11 row cabin mockup of a Boeing 767 cabin

- Evaluated the model with air concentration and surface loading measurements following simulated top of descent disinsection application

•Reference: Isukapalli, SS; Mazumdar, S; George, P; Wei, B; Jones, B; Weisel, C P, Computational fluid dynamics modeling of transport and deposition of pesticides in an aircraft cabin. Atmospheric Environment, 68, 198-207, 2013.

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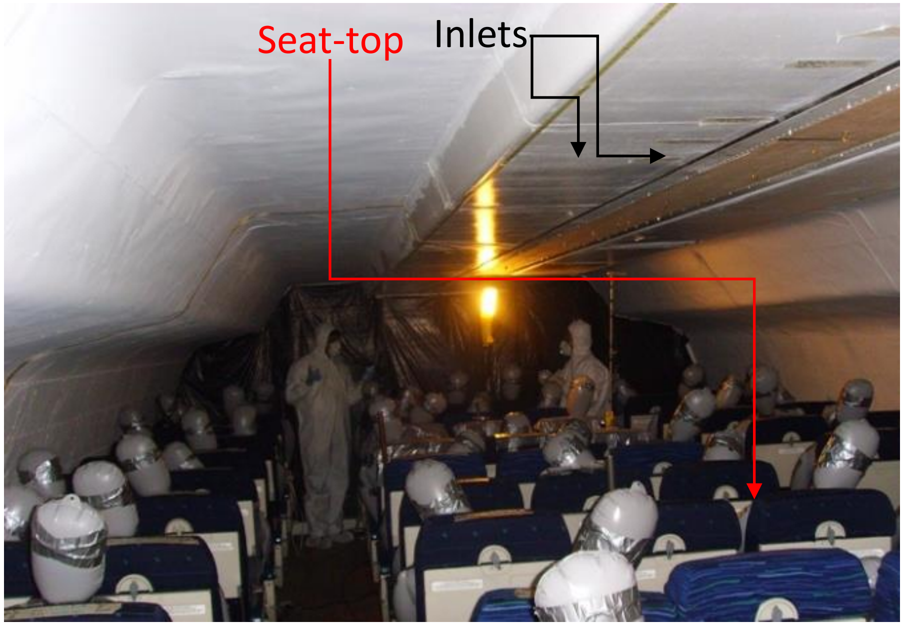
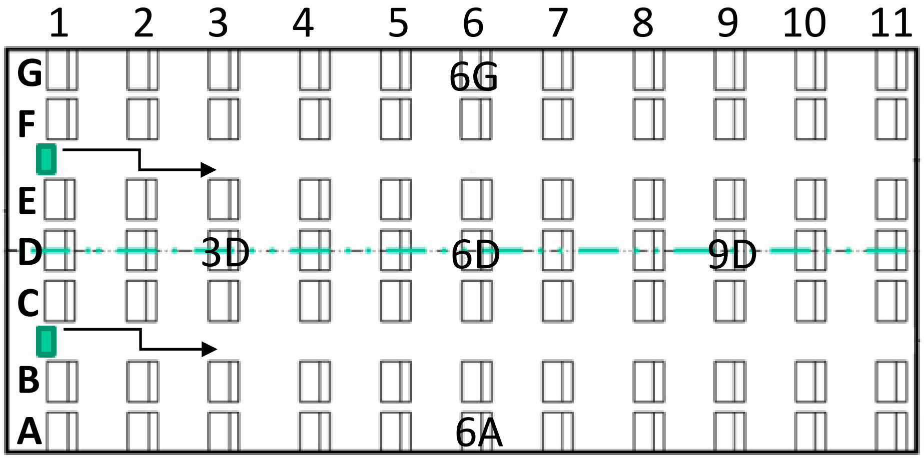
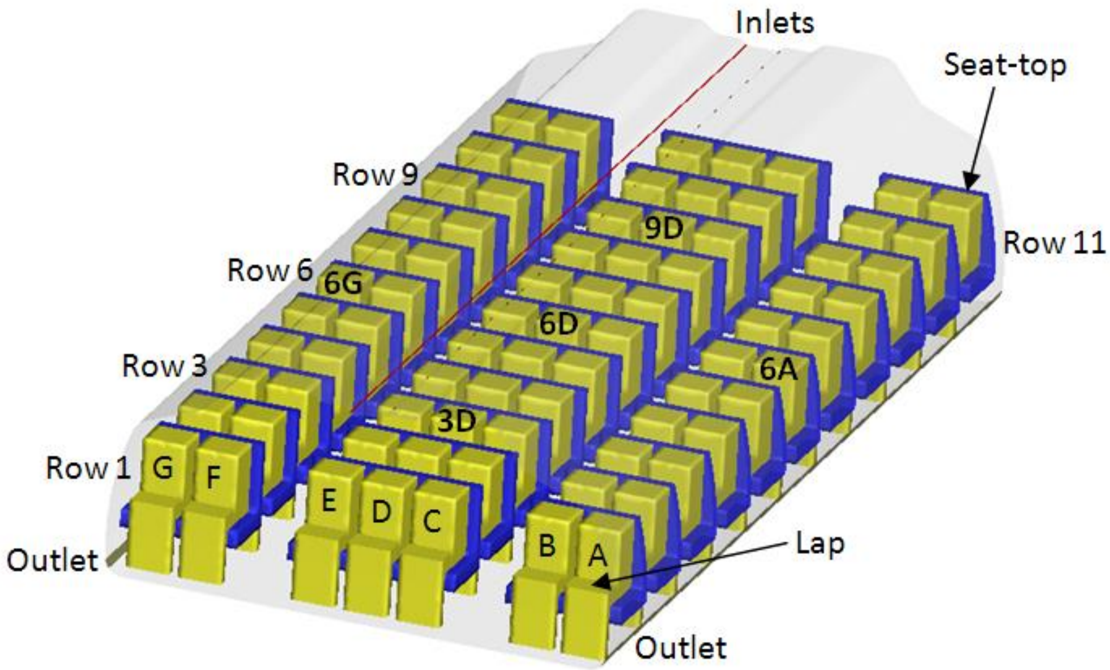
Data for model evaluation done at KSU Mock Boeing 767

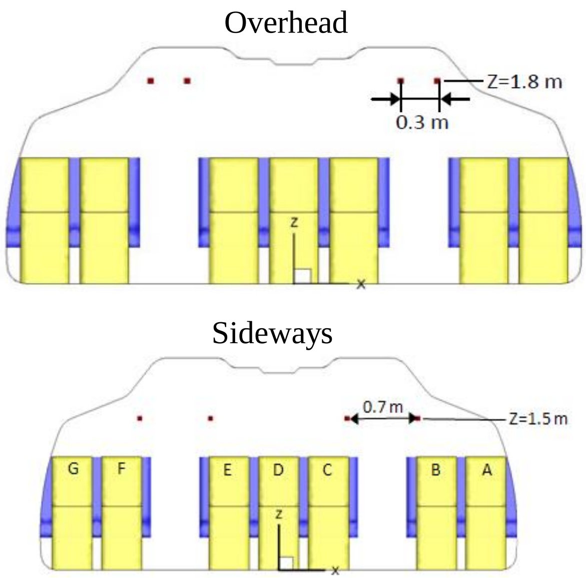
Schematic of the Sampling Locations



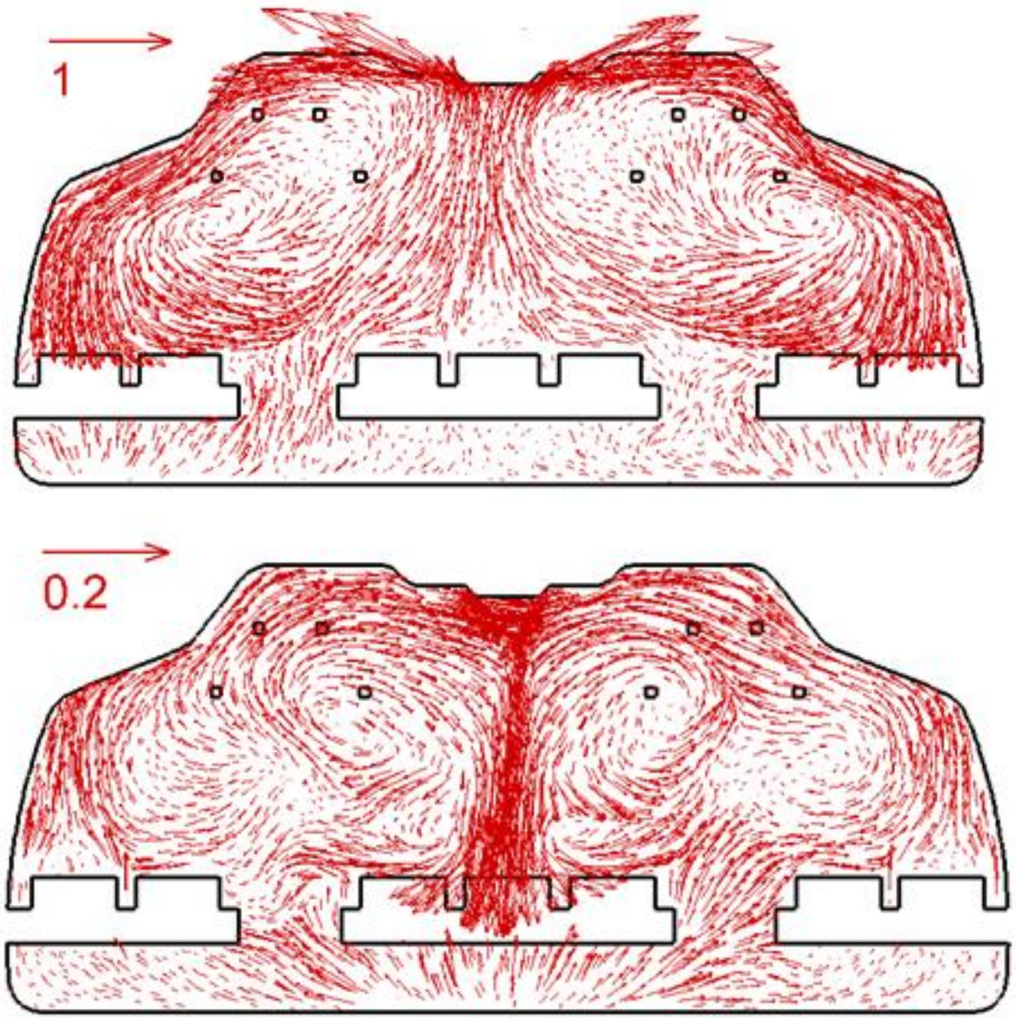


The CFD model and case setup for sideways and overhead spraying of pesticide in the 11-row cabin mock-up





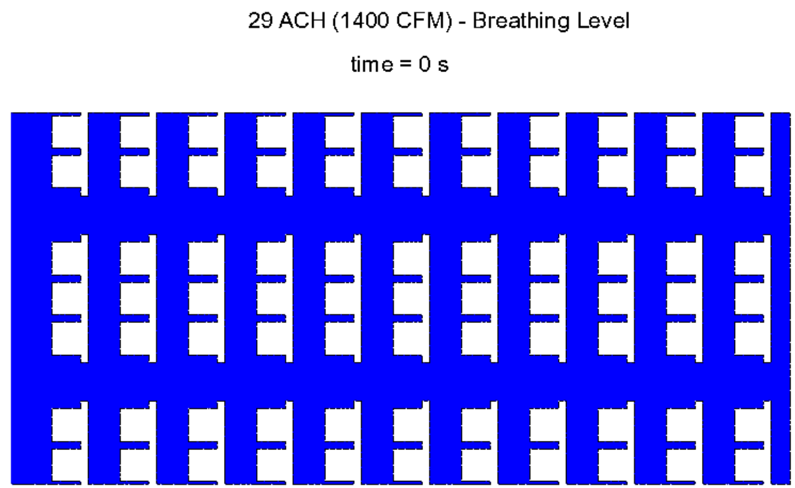
Comparison of airflow across the cabin cross-section



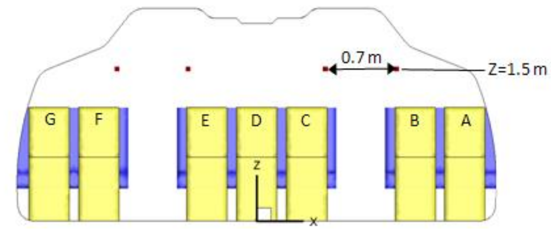
1400 CFM (29 ACH)

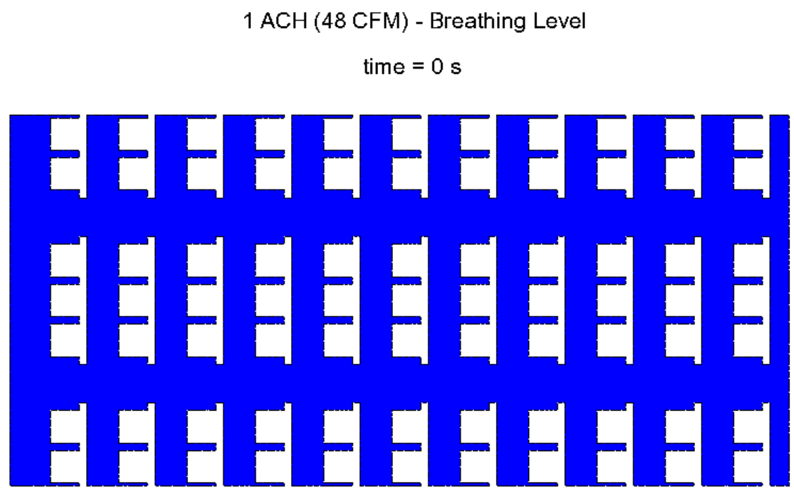
48 CFM (1 ACH)

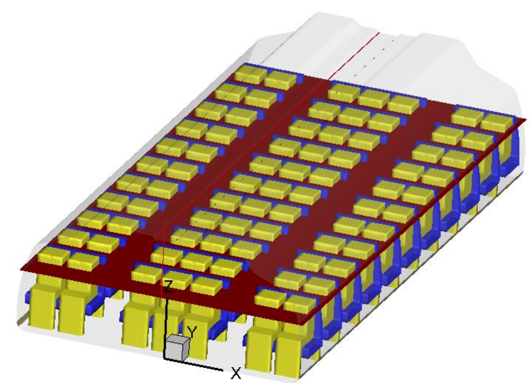
Breathing Zone Concentration ($\mu g/m^3$) at 1400cfm (29ACH) and 48cfm (1ACH)

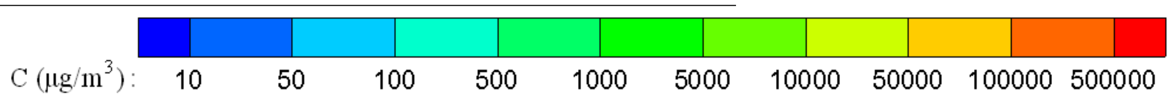


Sideways



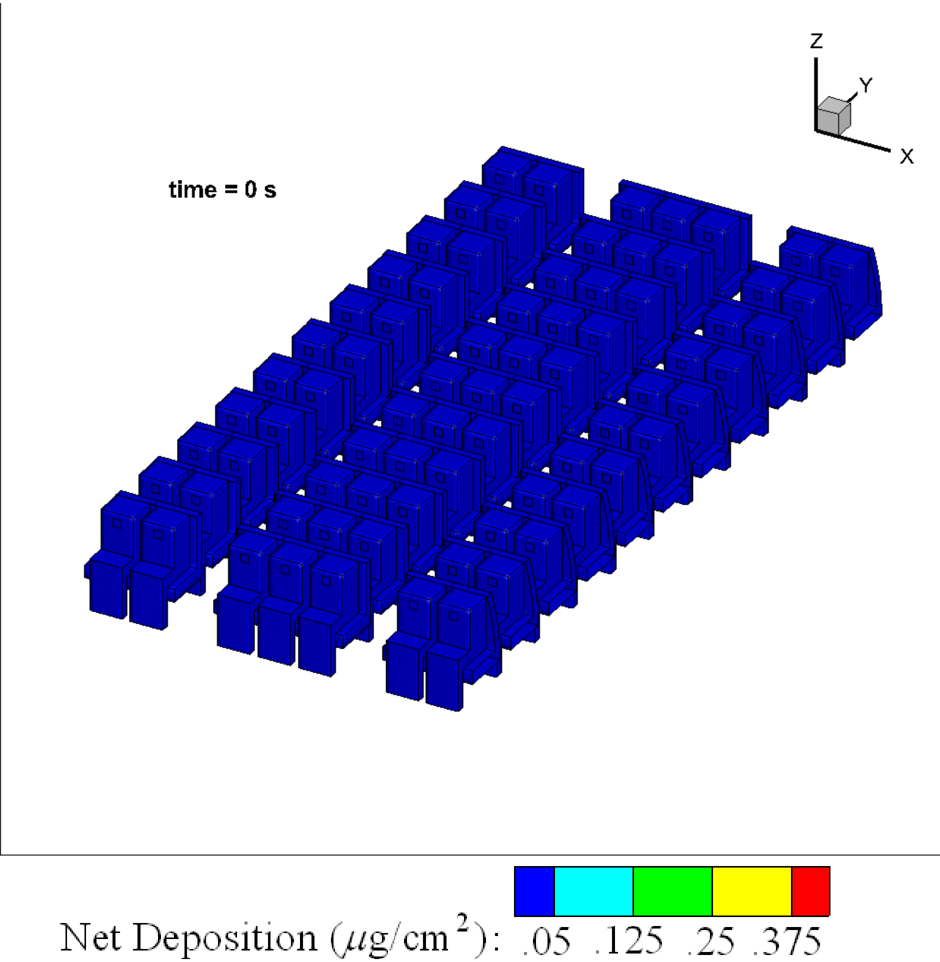




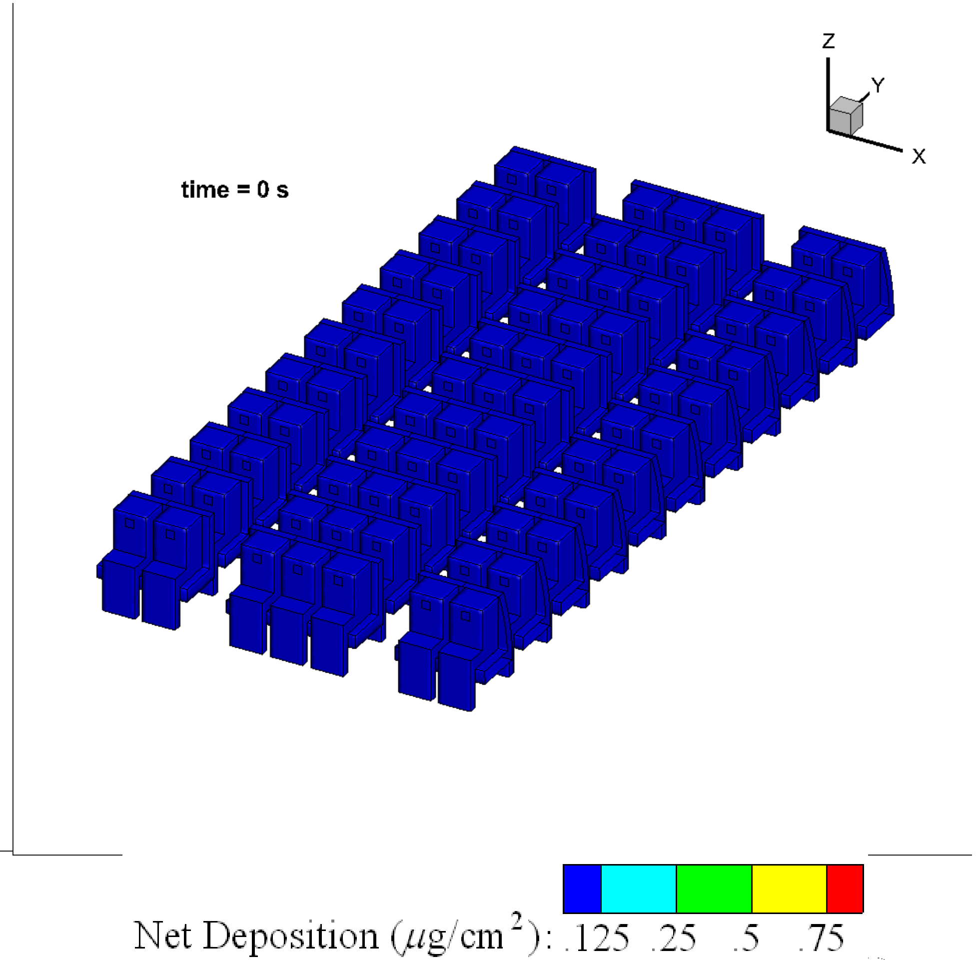


Net Deposition (μg/cm²) 1400cfm (29ACH) and 48cfm (1ACH)

29 ACH



1 ACH



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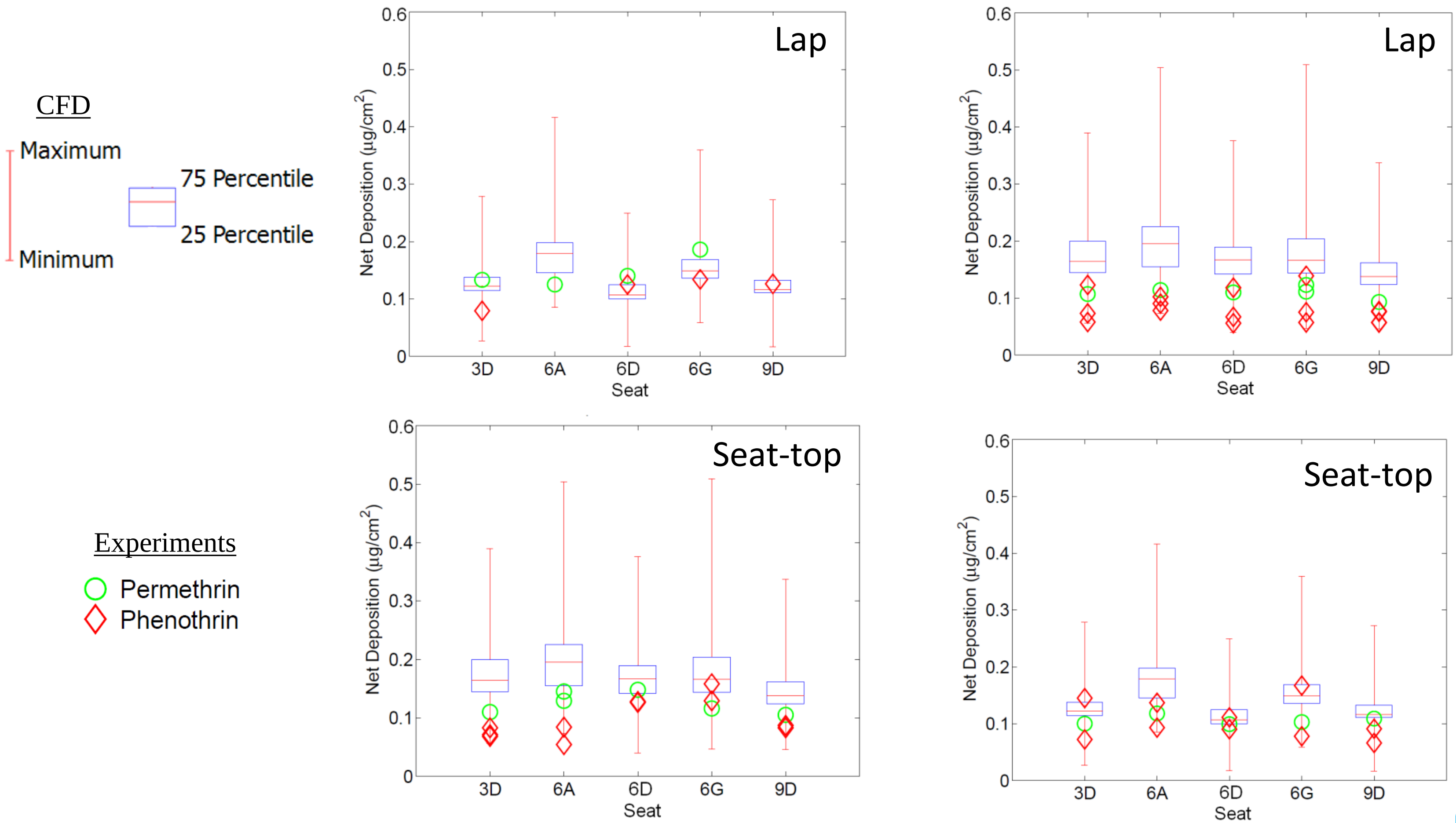
Comparison of Model and Experimental Deposition (μg/cm^2) at High Ventilation



Sideway Spray

Overhead Spray

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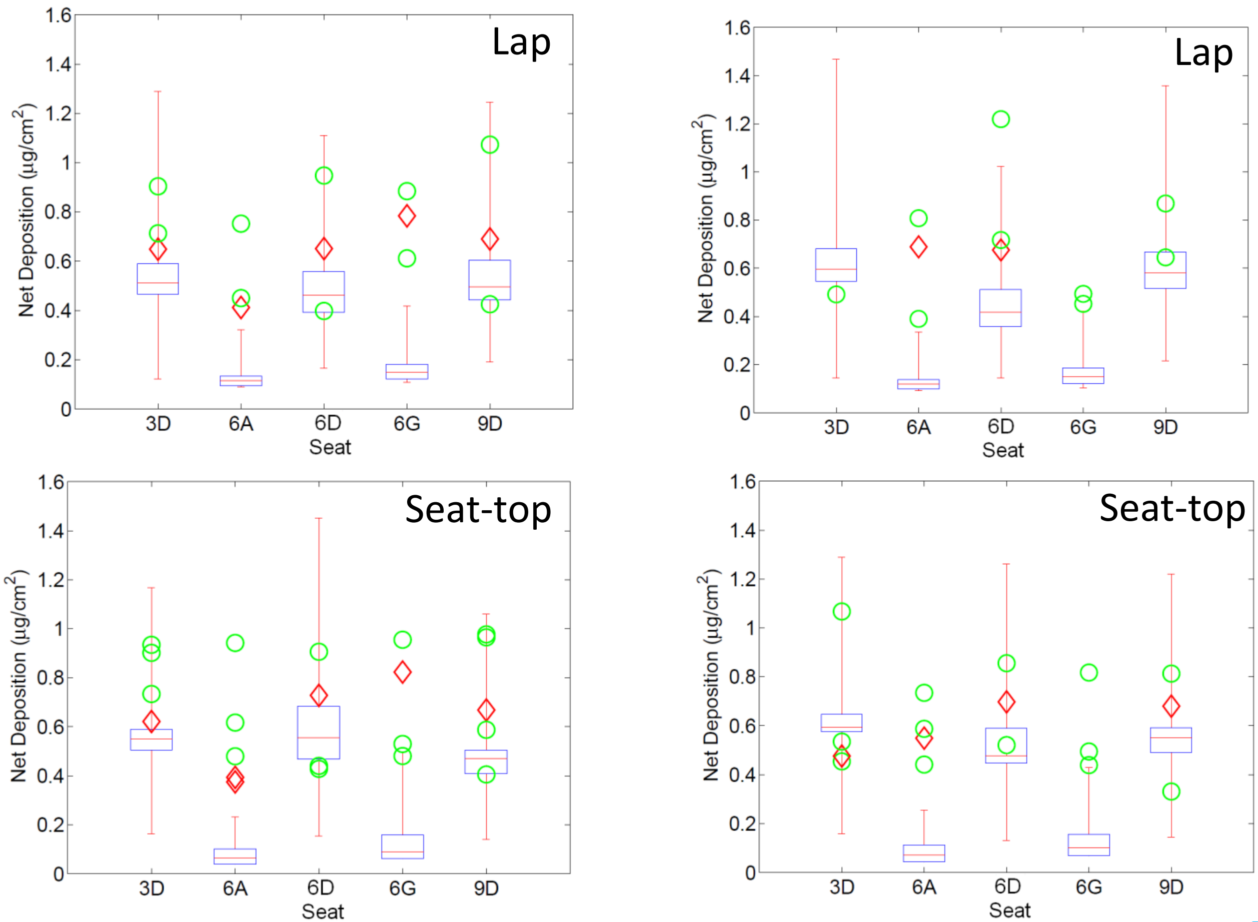
Comparison of Model and Experimental Deposition (μg/cm²) at Low Ventilation

CFD
Maximum
75 Percentile
25 Percentile
Minimum

Experiments
Permethrin
Phenothrin



Sideway Spray

Overhead Spray

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Conclusions

- CFD model was effective for studying the spatial and temporal variation of pesticide deposition and concentration
- Contrasting flow features were observed for the high-29 ACH and the low-1 ACH
- Surface deposition levels at measured locations varied from 0.33-1.22 μg/cm^2 to 0.05-0.20 μg/cm^2 for the low and high ventilation, respectively and the air concentration decline much more rapidly (8 min vs 20 min) at high ventilation
- CFD Model results at high ventilation matched experiment results well, but at low ventilation differences near the window seat were observed

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RISK PARADIGM

- Pesticide exposures to crew and passengers can occur
  - Inhalation while there is active spraying (Top of Descent)
  - Inhalation from volatilization or resuspension of dust
  - Dermal from direct contact with ski
  - Unintentional ingestion from transfer to hands or food
- Top of descent, residual and preflight spray treatments were all considered
- A methodological approach was developed that can be used for other agents in an aircraft cabin

•Reference:Zhang, Y, Isukapalli, S, Georgopoulos, PG, Weisel, CP. "Modeling Flight Attendants's Exposures to Pesticides in Disinsected Aircraft Cabins", Environmental Science and Technology: 47(24):14275-14281, 2013. doi: 10.1021/es403613h. Epub

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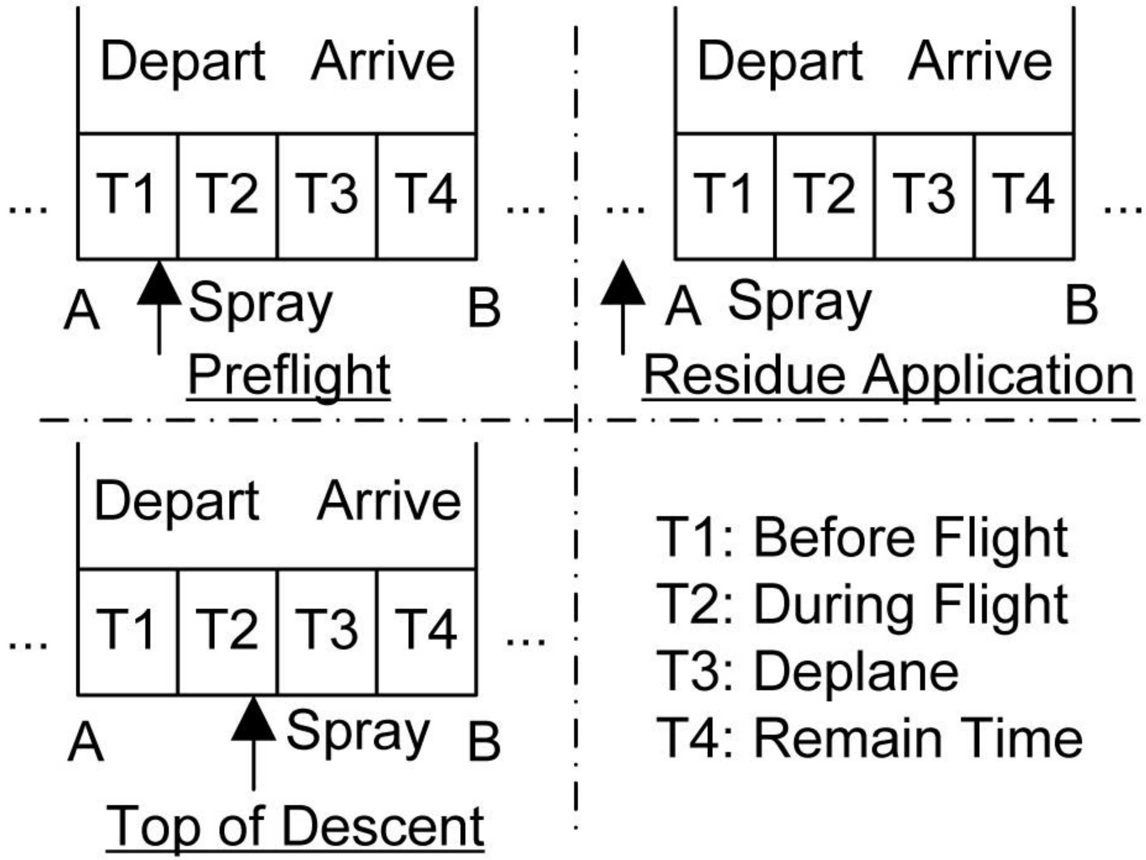
EXPOSURE CONSIDERATIONS

- Each crew member was assigned four different time periods during which the exposure was calculated for. (Remain time = 24 hours –T1-T2-T3)



SURFACE LOADINGS AND AIR CONCENTRATIONS

- Input from CFD model for spraying.

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Overall Summary and Recommendation

- Flight attendants and passengers are being exposed to pyrethroid pesticides on aircraft that were disinsected
- The urinary metabolite levels of permethrin for flight attendants after working on disinsected aircraft is similar to pesticide applicators
- The risk associated with disinsection should be reevaluated based on these exposure data exposure and new toxicological studies of the adverse health effects of pyrethroids

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Conclusions

- Flight attendants working on the pyrethroids disinsected aircrafts had significantly higher levels of 3-PBA, *cis*- and *trans*-Cl2CA in the post- and 24-h-post flight urine samples than those working on non-disinsected aircrafts and the general U.S. population
- The urinary levels of 3-PBA, *cis*- and *trans*-Cl2CA exponentially decay with post disinsection duration
- Permethrin exposure of flight attendants flying on disinsected aircrafts is similar to pesticides applicators.