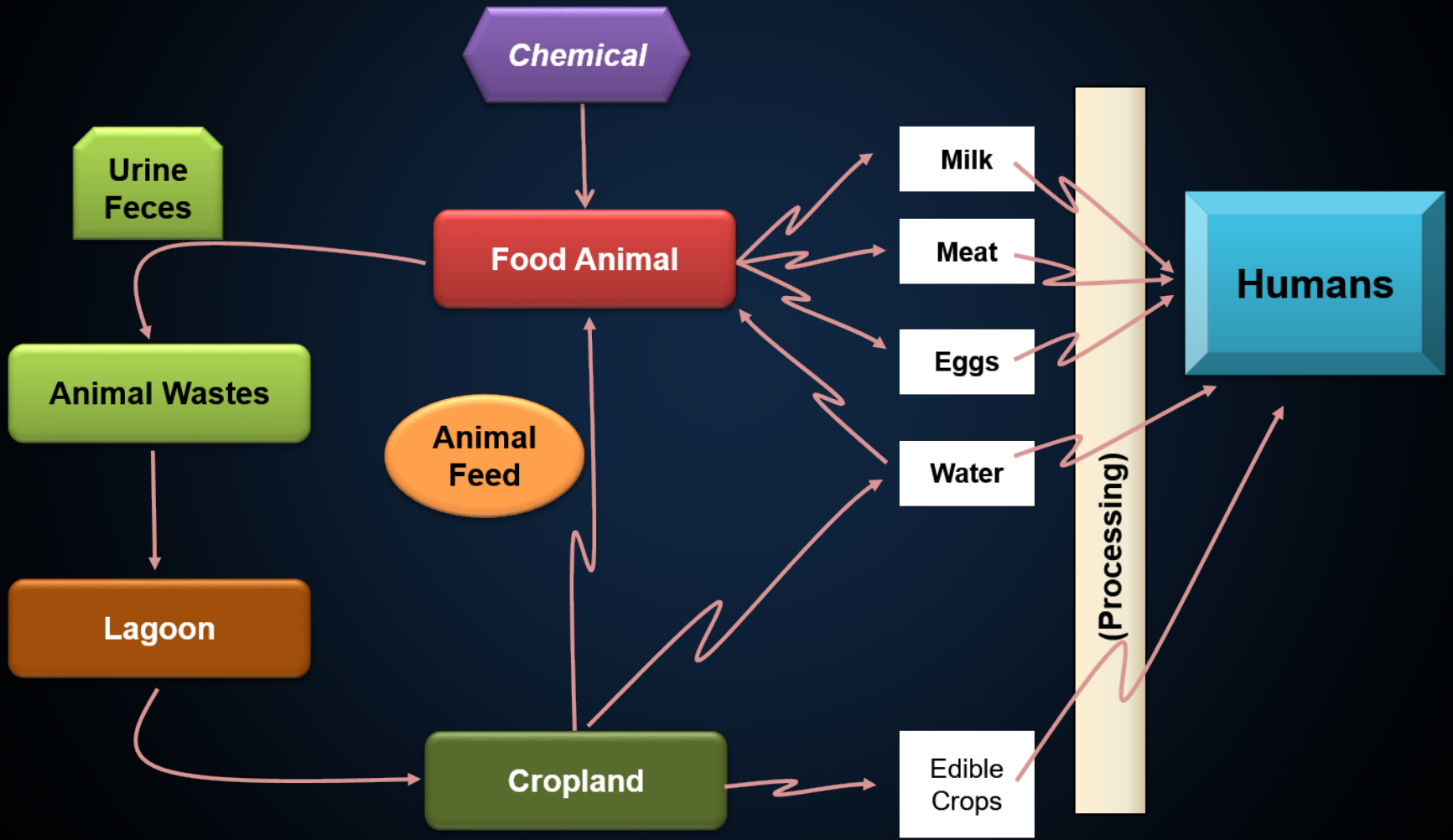
Detection and Fate of Chemical and Biological Residues in Food and Environmental Systems

David J. Smith (LS)
Nancy Shappell
Weilin Shelver
Animal Metabolism-Agricultural Chemicals Research
Fargo, ND

Premise


Chemical
Urine
Feces
Food Animal
Milk
Meat
Eggs
Water
Humans
(Processing)
Animal Wastes
Animal
Feed
Lagoon
Cropland
Edible
Crops

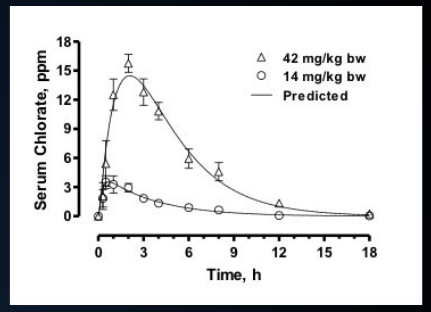
Objective 1

Develop and (or) validate sensitive and accurate analytical tools to rapidly detect and quantify chemicals in food animals, food animal products, or other foods.

- Validate using incurred animal matrices
- Develop/validate on-site detection methods of new and emerging residues

Objective 2

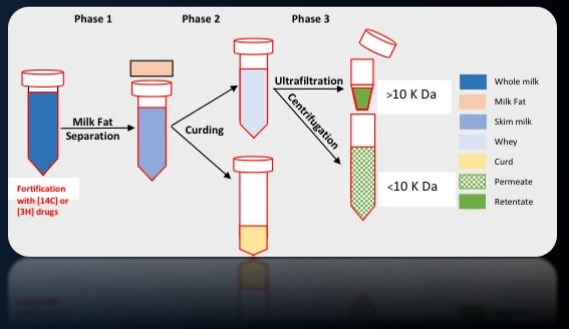
Investigate the kinetics of uptake, metabolism, distribution, and (or) the elimination of chemicals in and from food animals and (or) produce with the goal of reducing public exposure to chemical residues in foods



- Determine the effect of mediators of inflammation on clearance and violative residues in food animals
- Determine the fate and distribution of chlorine dioxide gas in foods treated for pathogen or rot-organism remediation

Objective 3

Determine the fate of endogenous reproductive hormones, antibiotics, and or other chemicals, including biologically-active metabolites or degradation products in wastes of food animals or in food processing systems



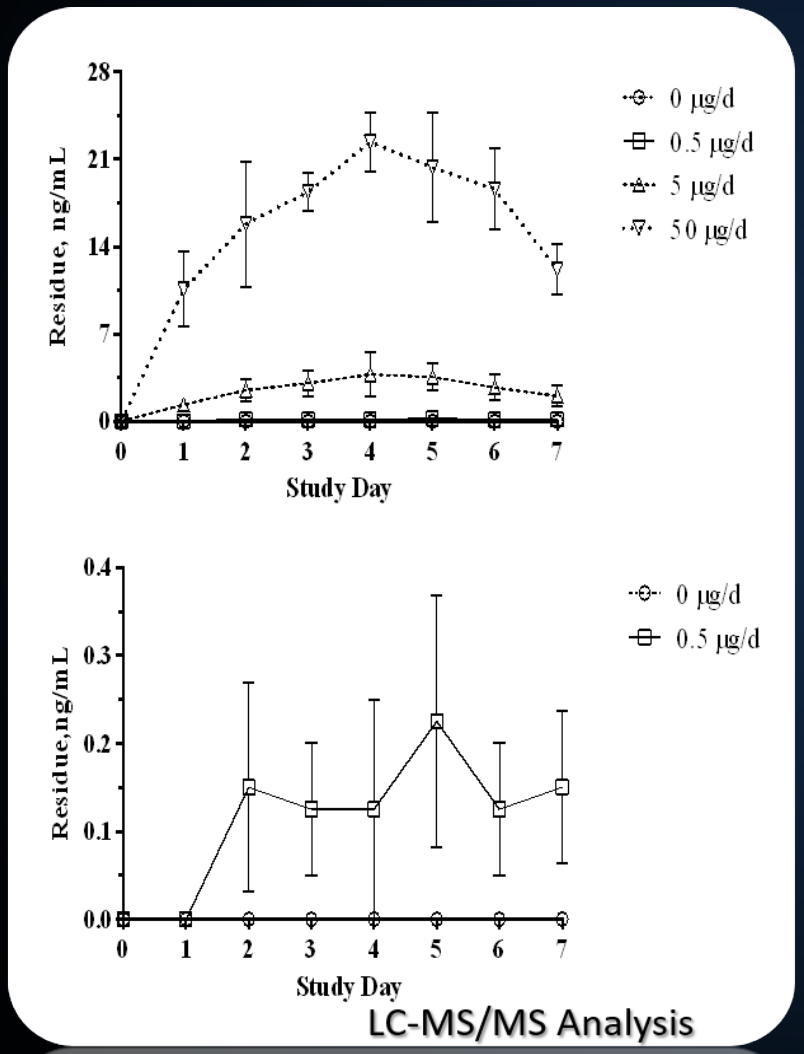
- Determine the partitioning of chemical residues into cream, curd, whey, and water fractions during milk processing
- Determine the fate of estrogens in animal wastewater systems

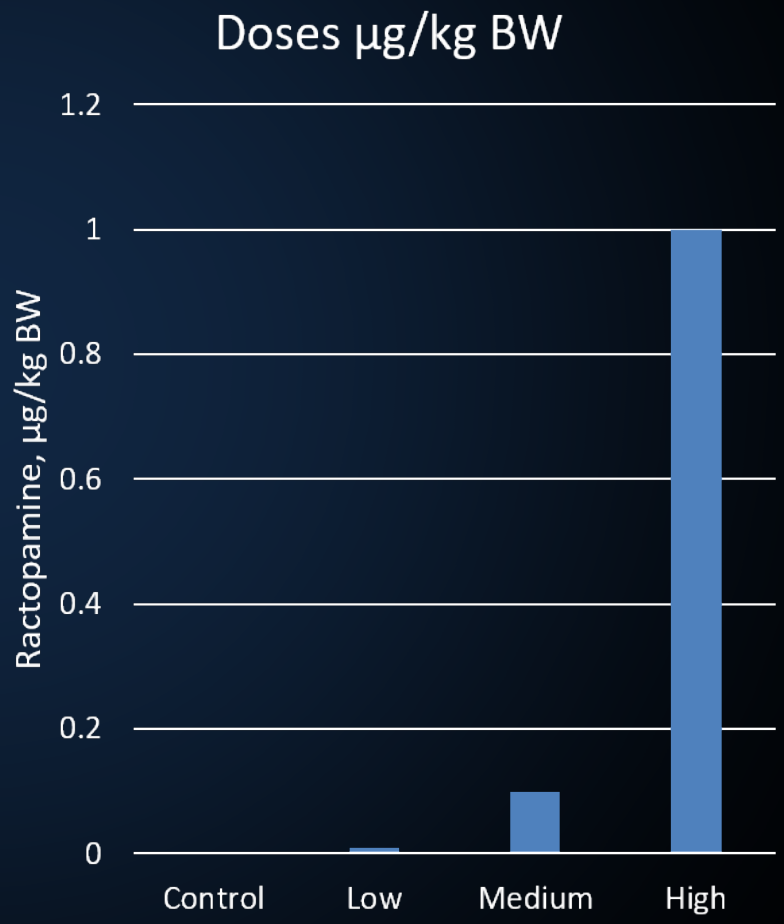
Validate Rapid Screening Using Incurred Residues

Advantages of Incurred Studies

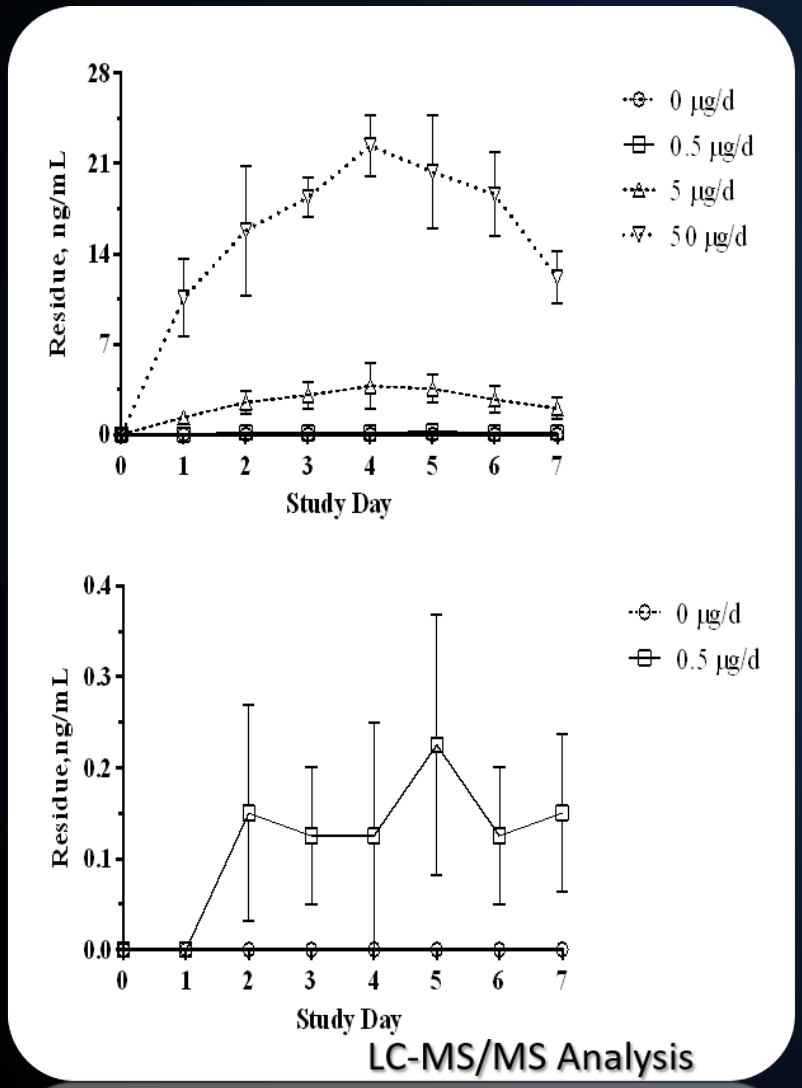
- Animal variation with respect to matrix effects on animal performance
- Influence of metabolites on assay performance
- Influence –if any– over time on assay performance
- Assess false positive or false negative rates
- Assess actual exposures which may cause screens to test positive

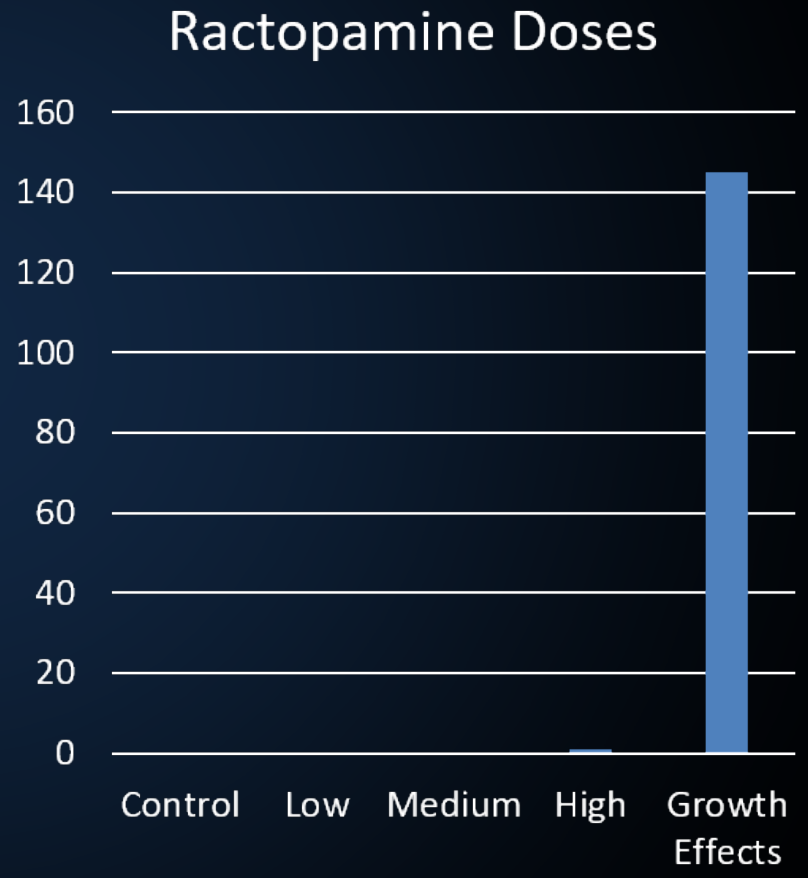
Total Ractopamine Residues (Urine)





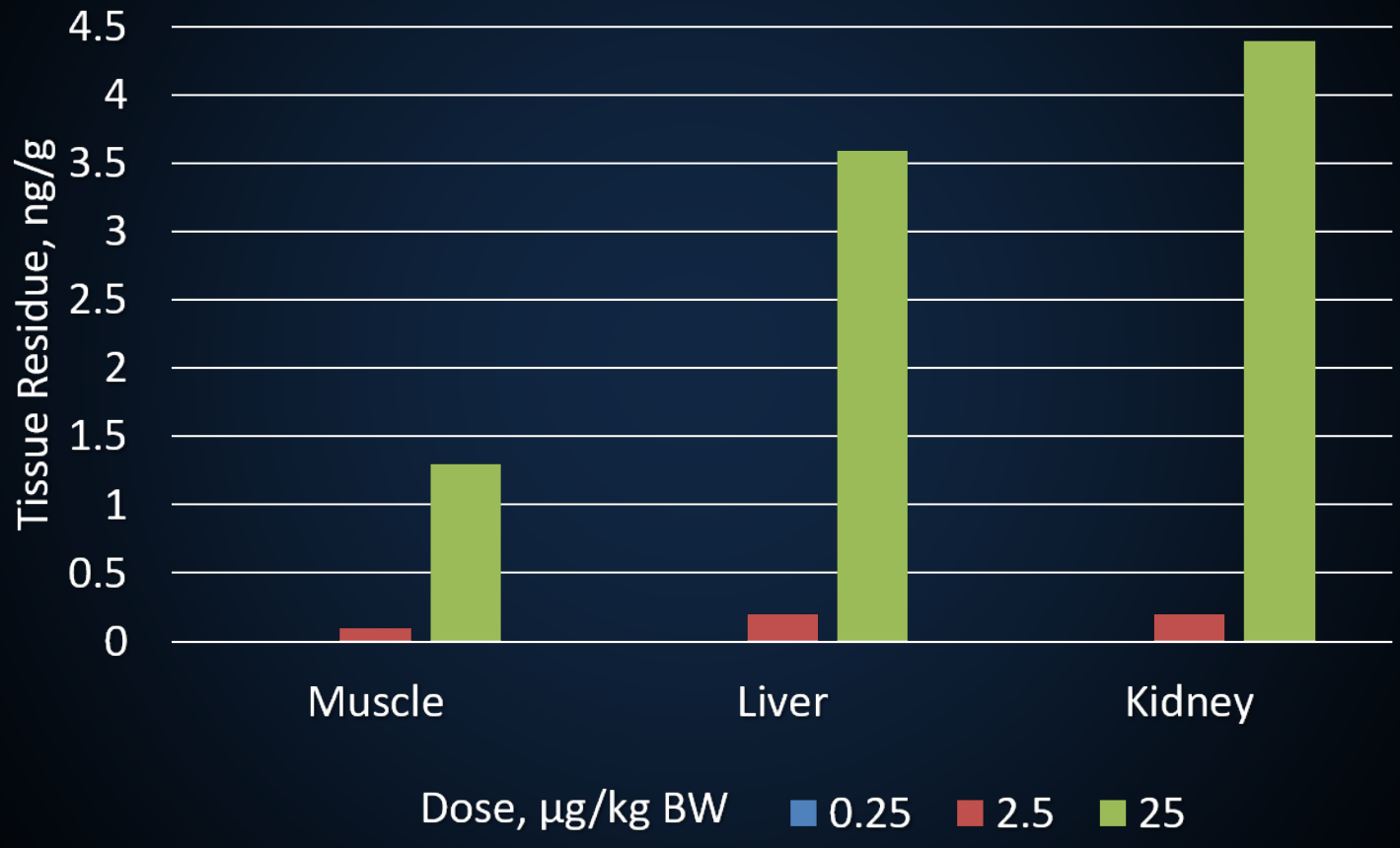
Total Ractopamine Residues (Urine) (2)





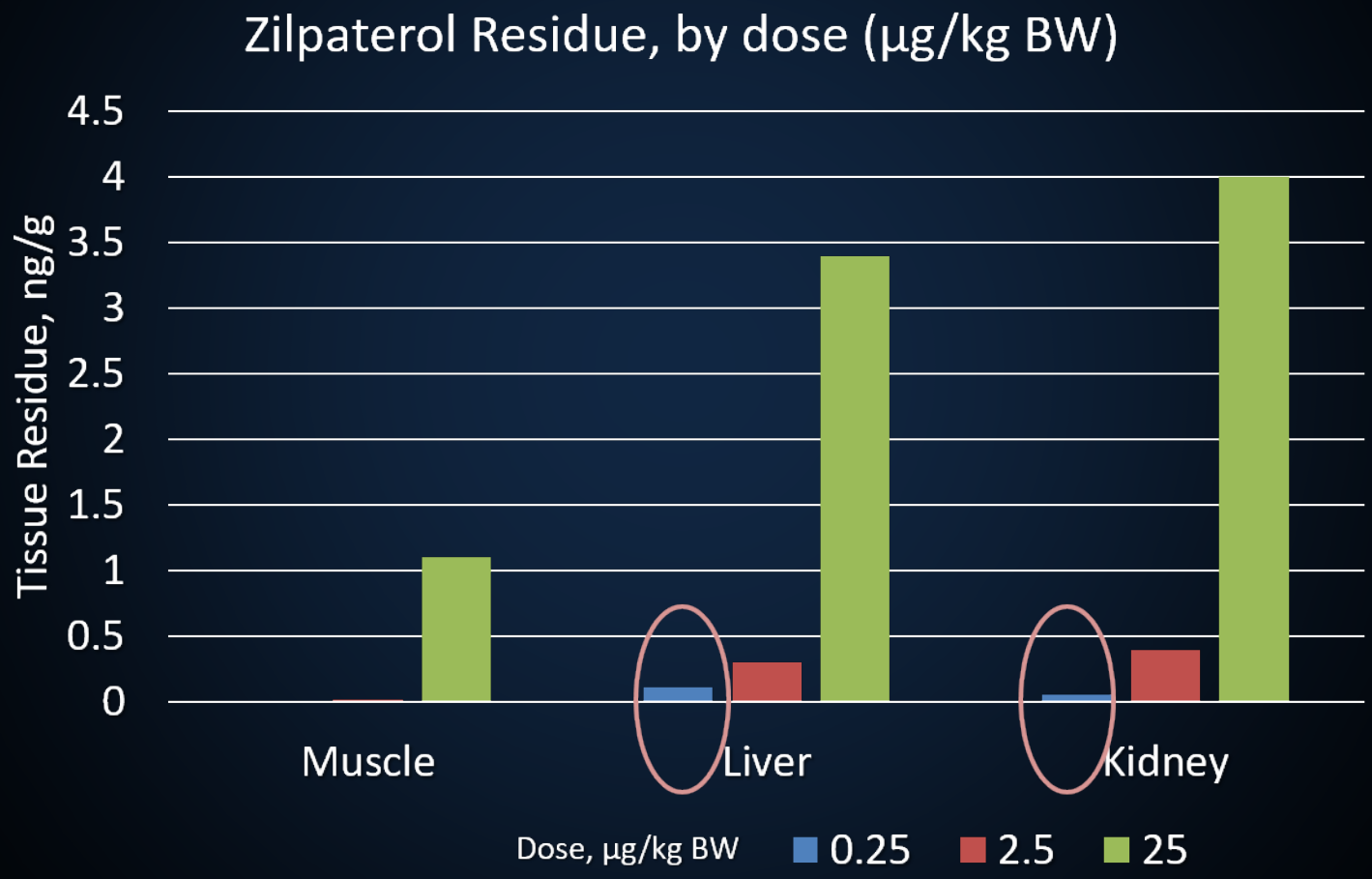
Zilpaterol Residues (Tissues)

UPLC MS/MS Analysis



Zilpaterol Residues (Tissues)

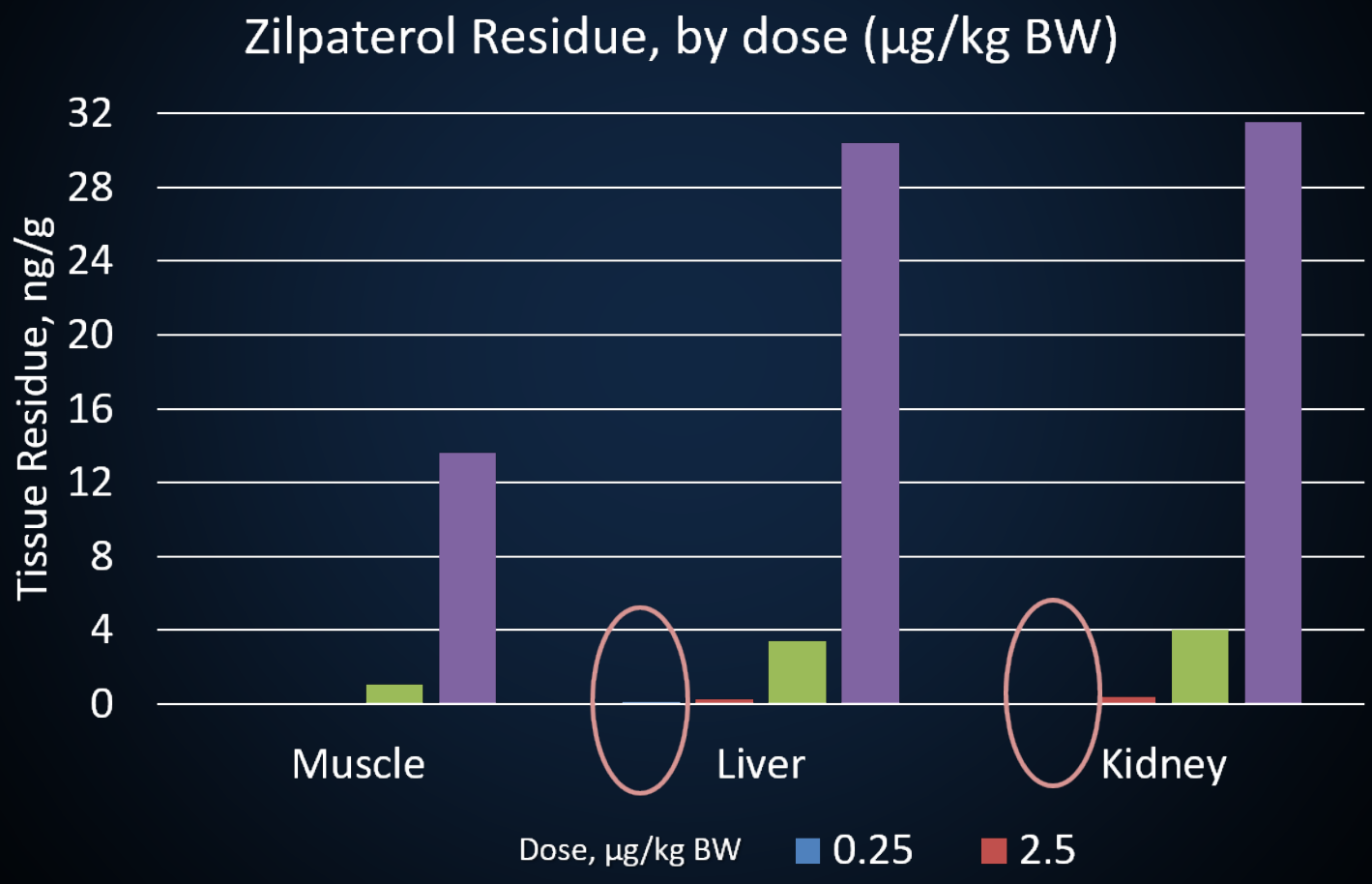
ESII MS/MS Analysis*



*Electrospray ionization inlet

Zilpaterol Residues (Tissues)

ESII MS/MS Analysis



Zilpaterol, Rapid Screen LODs

Banned = No Tolerance ≠ Illicit Intent

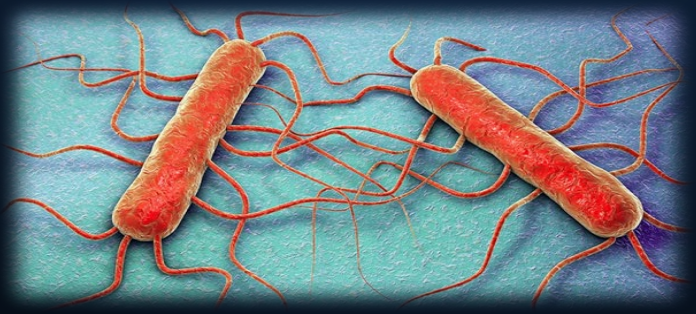
No ClO_2, 9 days, 10° C

5 ppmV ClO_2, 9 days, 10° C

Bai et al.,
Food Control 95 (2019) 18–26

Implications of Extending the Shelf-life of Produce for 1 Week?

Implications on Disease Outbreaks of Killing 1-3 log Units of Pathogens on Produce?



ClO_2 Effective at Sanitizing Foods

- 1994 –
  - Roberts and Reymond, ARS Wenatchee
  - 14 to 18 ppm ClO_2 foam formulation
  - Reduced *rot fungi* on pears and distribution equipment
- >225 papers describe the efficacy of ClO_2 against a variety of microorganisms on foods
  - *Salmonella*
  - Hemorrhagic *E. coli*
  - *Lysteria monocytogenes*
  - *Cronobacter sakazakii*
  - Campylobacter
  - Viral pathogens
  - Numerous rot organisms including fungi

ClO_2 Efficacy Trials . . .

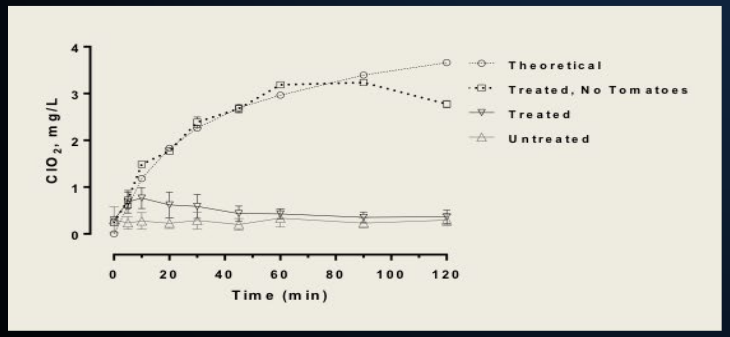
- Alfalfa Seeds, Alfalfa Sprouts, Apples, Blueberries, Cabbage, Cantaloupe , Carrot, Cucumber, Grapefruit, Green Peppers, Lettuce, Mungbean Sprouts, Onions, Oranges, Paprika, Peaches, Potatoes, Radish Seed, Raspberries, Red Chili Peppers, Spinach, Strawberries, Tomatoes . . .

Why Isn't ClO_2 Used to Sanitize Produce?

- *Aqueous* rinses (3 ppm) for some vegetables and poultry carcasses are approved by the US FDA
- No applications for treating foods with ClO_2 *gas* have been approved
- EPA's jurisdiction
  - *No residue data*
  - *No intellectual property = no sponsor ($$$$$)*

Project Objectives

1) Generate residue data supporting or refuting the safe use of chlorine dioxide for sanitation of human foods
   - Cantaloupes and tomatoes
2) Submit data to the US EPA for regulatory consideration (ICA Tri-Nova)



Data Packages Submitted to US EPA

- Total radioactive residue studies $^{36}ClO_2$
  - Cantaloupe & tomatoes
  - Disposition and fate
  - Residue characterization
- Fate of ^{36}Cl-chlorite in tomatoes
- Method of ClO_2 generation and exposure to light on residue formation
- Residue study (non-labeled) using commercial media
  - Cantaloupe and tomatoes
- 120-Day chlorate stability study
  - Cantaloupe and tomatoes
- Analytical method validation data
- All raw data
- Data Submitted, 2014 to 2017

Major Conclusions

- The major residue of on produce treated with ClO_2 (g) is chloride ion (Cl^-), a nutrient
- Residues that may form, depending upon conditions are chlorate and perchlorate
- The marker for ClO_2 (g) exposure is chlorate ClO_3^-
- Chlorite ion is not stable in tomatoes or cantaloupe
- Sanitation under light enhances chlorate formation
- Chlorate residue can be minimized or eliminated by protection from light

Chlorine Dioxide Use on Tomatoes and Cantaloupe is Now Approved by the US EPA

ENVIRONMENTAL PROTECTION AGENCY

40 CFR Part 180

[EPA–HQ–OPP–2017–0063; FRL–9986–85]

Chlorate; Pesticide Exemptions From Tolerance

AGENCY: Environmental Protection Agency (EPA).

ACTION: Final rule.

SUMMARY: This regulation establishes an exemption from the requirement of a tolerance for residues of chlorate in or on cantaloupe and tomato under the Federal Food, Drug, and Cosmetic Act (FFDCA).

C. Revisions to Petitioned-For Tolerances

The residue data indicate that following use of the pesticide, there were detectable chlorate residues on the cantaloupe rind, although none were detected in the edible portions of the cantaloupe, and that chlorate residues on tomato were indistinguishable from background levels of chlorate on tomato. Because EPA does not anticipate use on either commodity to contribute to dietary exposure, EPA is issuing an exemption from the requirement of tolerance residues on cantaloupe and tomato. This tolerance exemption covers potential residues in or on these commodities as a result of direct application and allows for the shipment of these commodities in interstate commerce.

Federal Register
Dec. 26, 2018

V. Conclusion

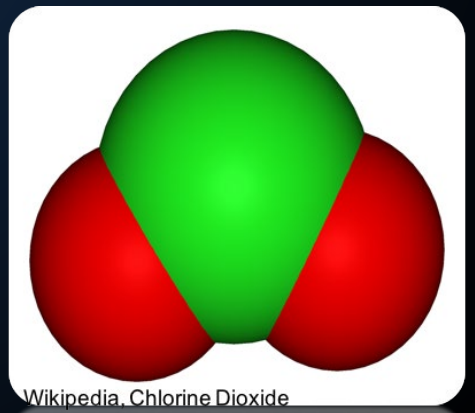
An exemption from the requirement of a tolerance is established for residues of chlorate in or on tomato and cantaloupe.

Additional Studies

- Completed residue studies for
  - Ready-to-eat meat (total residues study, $^{36}ClO_2$)
  - Alfalfa sprouts (cold residue study)
- In progress or planned, residue studies for
  - Eggs ($^{36}ClO_2$)
  - Avocados ($^{36}ClO_2$)
  - Onions ($^{36}ClO_2$)
  - Sweet potatoes ($^{36}ClO_2$)

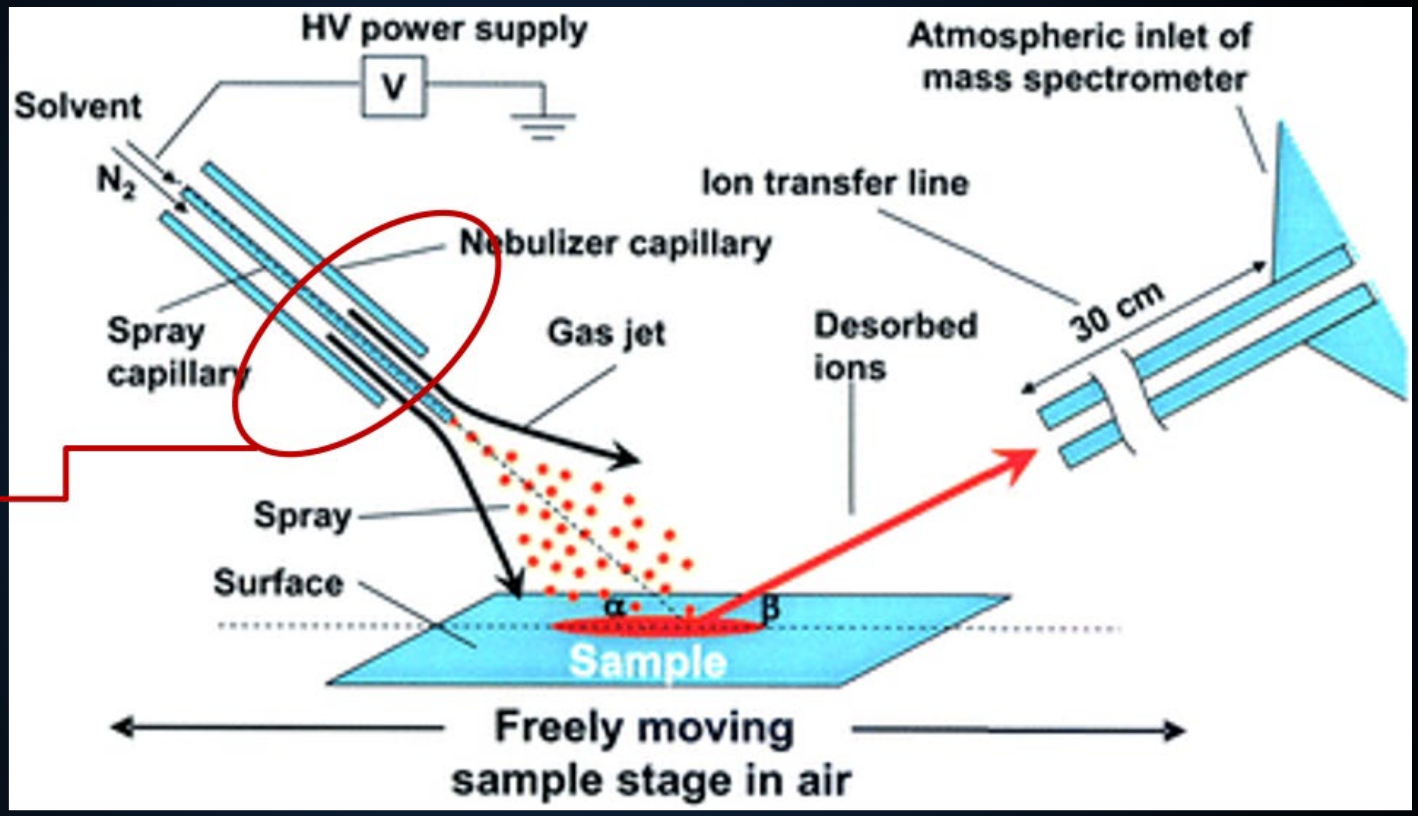
Acknowledgements

- ICA-TriNova
  - Joel Tenney
  - William Ernst
- Purdue University – Mark Morgan
- USDA ARS
  - Mike Giddings, Grant Herges, Abigail Skapanski
  - Jason Holthusen
  - Insects RU
    - Osama Mahdi



Modified DESI-MS/MS

350 °C
25 µL/min



Ingram et al., Chem. Sci. 2016, 7:39-55.

Urine Analysis: ASAP-MS/MS

Urine Analysis: ASAP-MS/MS