

# Vanadium Toxicity: A Potentially Unrecognized Hazard to Waterfowl ?

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# Fly Ash Pond

Winter and Spring 2003



Vanadium 467,000  $\mu\text{g/L}$



# **Necropsy Findings of Dead Geese**

- **no infectious agents**
- **no brain ChE inhibition**
- **no evidence of trauma**
- **birds in good flesh**
- **brain, lung, liver and kidney congested**
- **small intestine hemorrhagic enteritis**

# Delaware Department of Natural Resources & Environmental Control

**Goose liver V**                      **57.3  $\mu\text{g/g dw}$**

**Goose kidney V**                      **226  $\mu\text{g/g dw}$**

**As, Cd, Cr, Pb, Ni, Se, Tl < 0.5  $\mu\text{g/g dw}$**

**Hg  $\leq$  0.02  $\mu\text{g/g dw}$**

**V Confirmed by PACF and NWHC**

# Form of Vanadium

- $V_2O_5$  in fly ash enters pond
- Once in the pond converted to salts of  
metavanadate ( $VO_3^-$ )  
tetravanadate ( $V_4O_{12}^{-2 \text{ to } -4}$ )  
pyrovanadate ( $V_2O_7^{-4}$ )

# Cause of Die-off ?

- Intestinal lesions due to vanadium toxicity
- Dehydration
- Inhibition of enzyme systems (unspecified)
- Cold weather and limited fresh water sources may have been a contributing factor

# Vanadium Toxicity

- Occupational exposure - respiratory system
- Na,K-ATPase inhibitor and Oxidative Stress
- Rodent LD<sub>50</sub>

$V_2O_5$	10-86 mg/kg
$NaVO_3$	75-98 mg/kg
- Limited toxicity data in birds

# Objectives

- **Determine LD<sub>50</sub>, and signs of toxicity and pathology of V forms present in fly ash pond**
- **Estimate the diagnostic values for V in tissue associated with toxicity and mortality**

# Acute Toxicity Trials



**Doses: 0, 10, 18, 34, 62, 113, 208, 382, 700 mg/kg**  
**4 drakes/dose, observe for 7 days**



**January -  $\text{NaVO}_3$**



**February -  $\text{V}_2\text{O}_5$**

<b>Doses</b>	<b>mg/kg</b>	0	18	38	76	151
<b>Geese</b>	<b>N</b>	3	1	2	6	2



**March  $\text{NaVO}_3$**

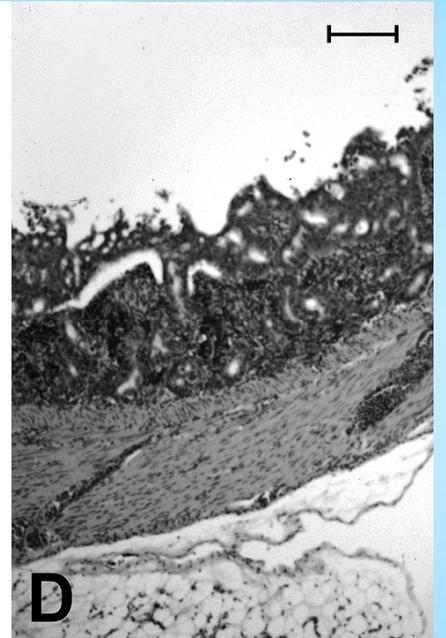
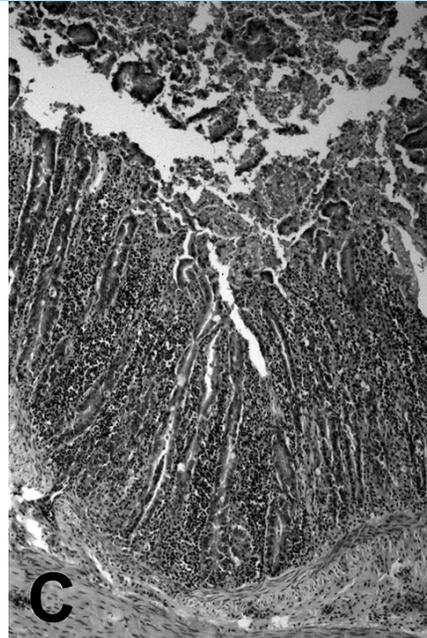
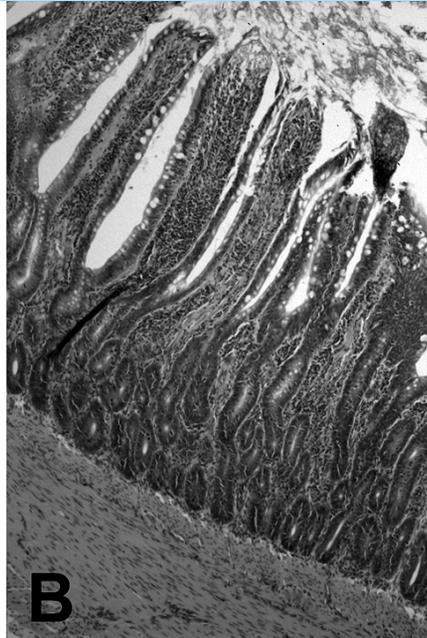
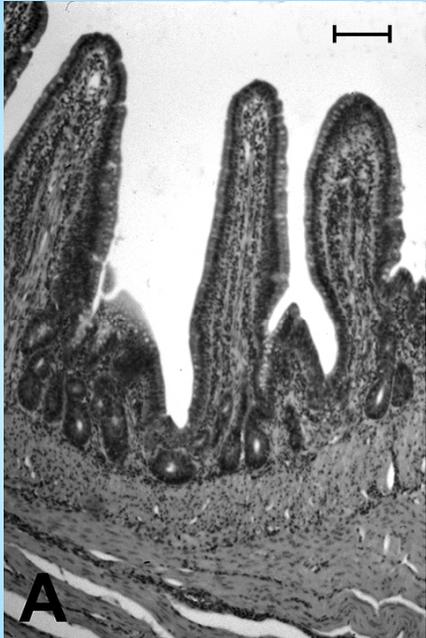
Species Form of V	Mallard $V_2O_5$	Mallard $NaVO_3$	Goose $NaVO_3$
$T_a$	-3 to 7 °C	-10 to 4 °C	5 to 17 °C
LD50	113.2 mg/kg	75.7 mg/kg	37.2 mg/kg
95%CI	84.2-157 mg/kg	44.8-125 mg/kg	12.1-72.2 mg/kg
Overt Signs	Some Head tremor Swallowing Abnormal Gait	Head & Tail Tremor	Un-groomed, Tremor Diarrhea Sloughing of Mucosa
Signs Death	2-24 h 1-2 d	2-48 h 1-2 d	2-48 h 2-3 d
Necropsy	Hemorrhagic Enteritis Sloughing of Mucosa Ventricular Hemorrhage	Ventricular Hemorrhage Liver Enlargement Enteritis	Hemorrhagic Enteritis Sloughing of Mucosa Ventricular Hemorrhage

Control

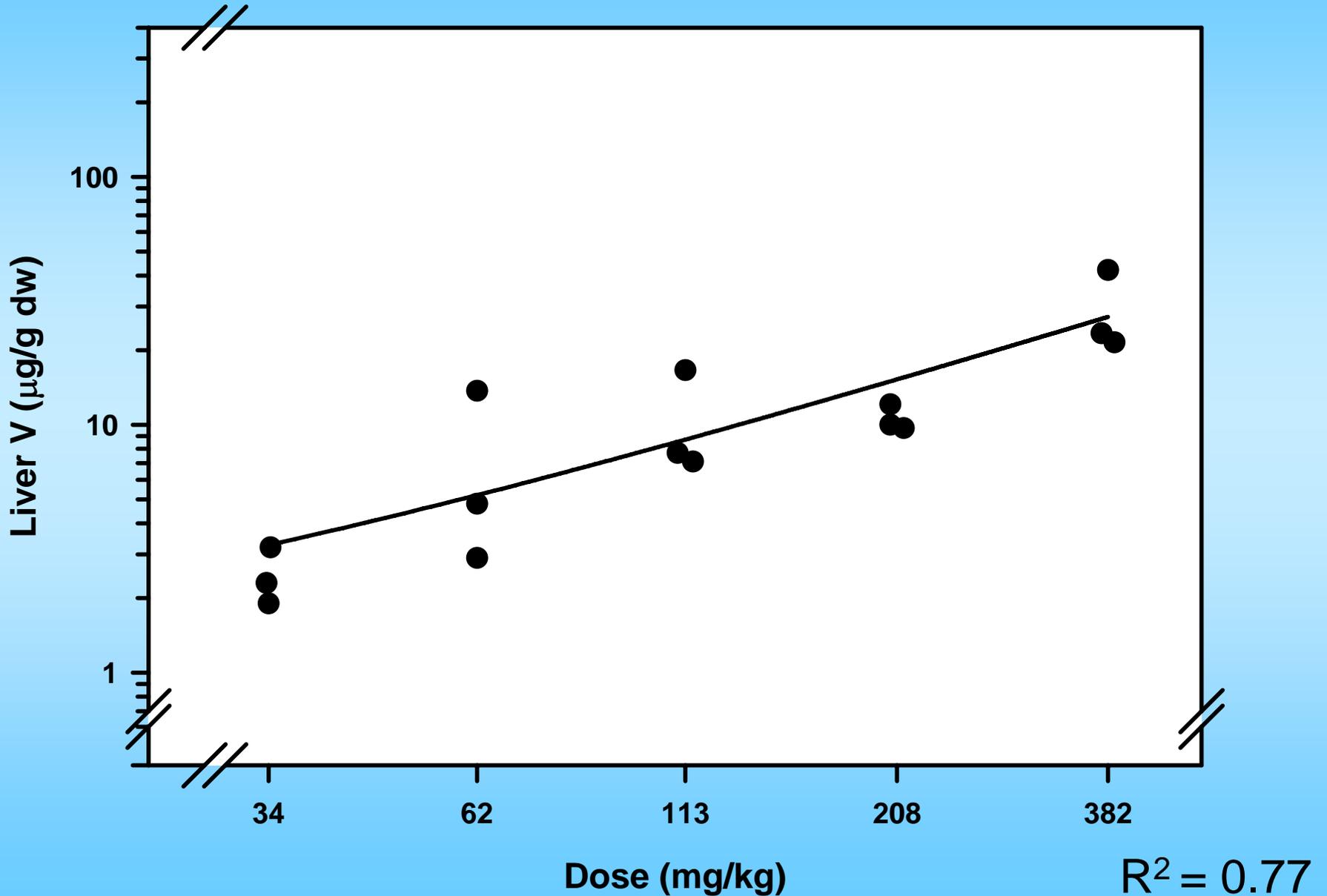
62 mg/kg

113 mg/kg

113 mg/kg



# Mallards - Sodium Metavanadate



# Extreme V Values ( $\mu\text{g/g dw}$ )

	<u>Liver</u>	<u>Kidney</u>
• Goose Die-off	57	226
• Mallard $\text{V}_2\text{O}_5$	28	118
• Mallard $\text{NaVO}_3$	42	295
• Goose $\text{NaVO}_3$	17	37

# Diagnostic Concentrations

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V Concentration ( $\mu\text{g/g dw}$ )		Birds Encountered Dead	
Liver	Kidney	Estimated Lethality of Exposure (%)	90% Confidence (Lower Bound)
1	0.5	6.3	0.3
2	2	26.9	3.2
5	10	70.7	28.1
10	25	90.1	58.5
15	50	96.3	77.0
20	100	98.7	88.0
30	200	99.6	94.5
40	300	99.8	96.7
57.3 <sup>a</sup>	226 <sup>a</sup>	99.8	96.4

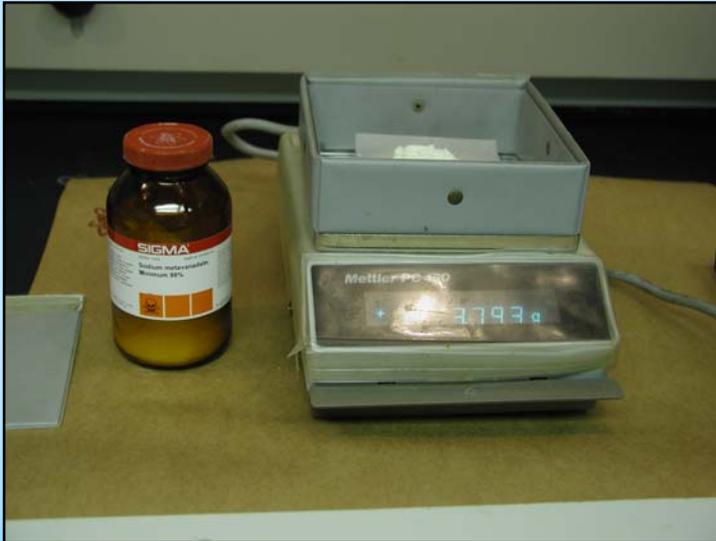
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Diagnostic thresholds of toxicity

LD50 ~ 10  $\mu\text{g V/g liver}$  + 25  $\mu\text{g V/g kidney}$

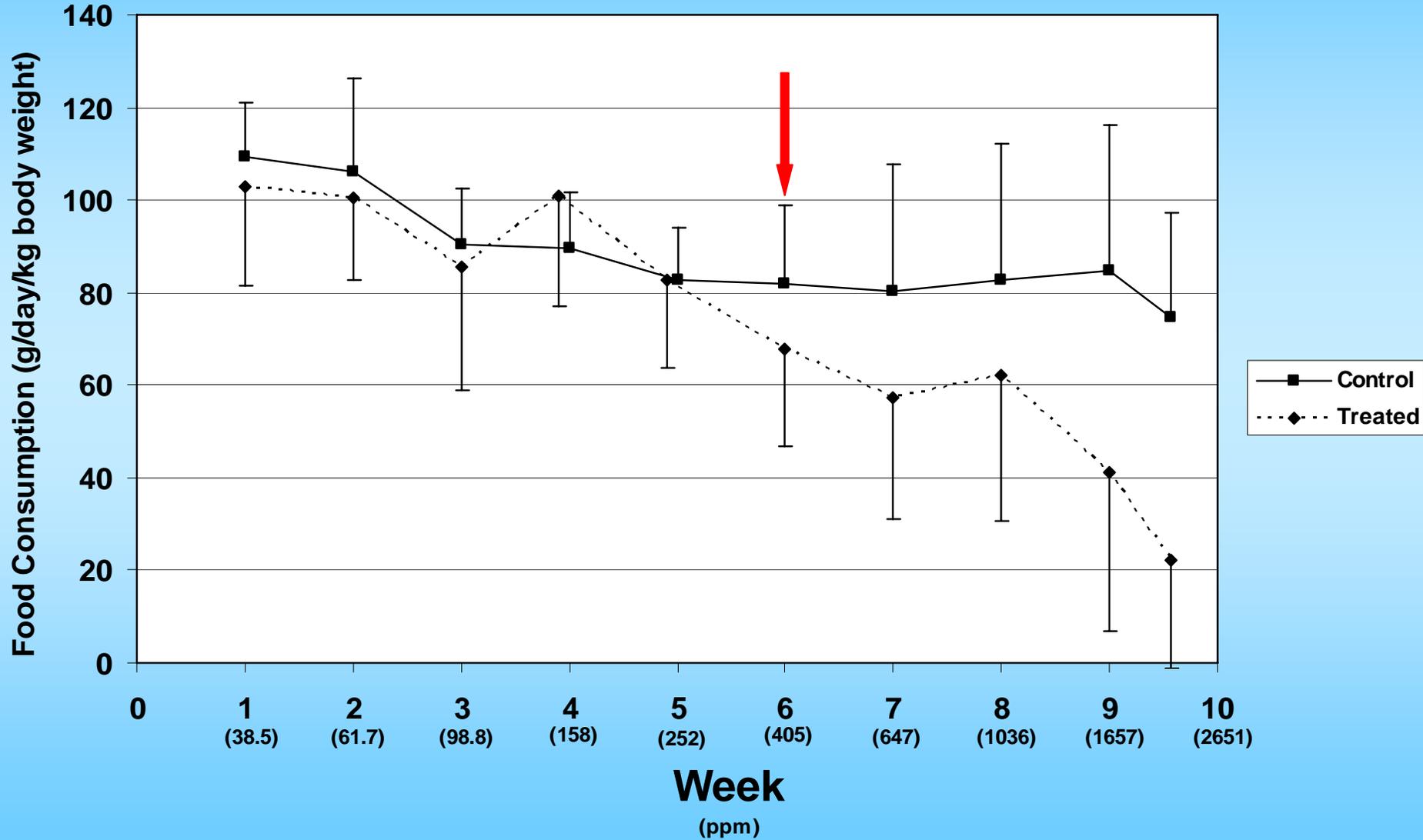
# Attempt to determine diagnostic V concentrations associated with toxicity and mortality

- NaVO<sub>3</sub> Feeding Study (March-May 2004)

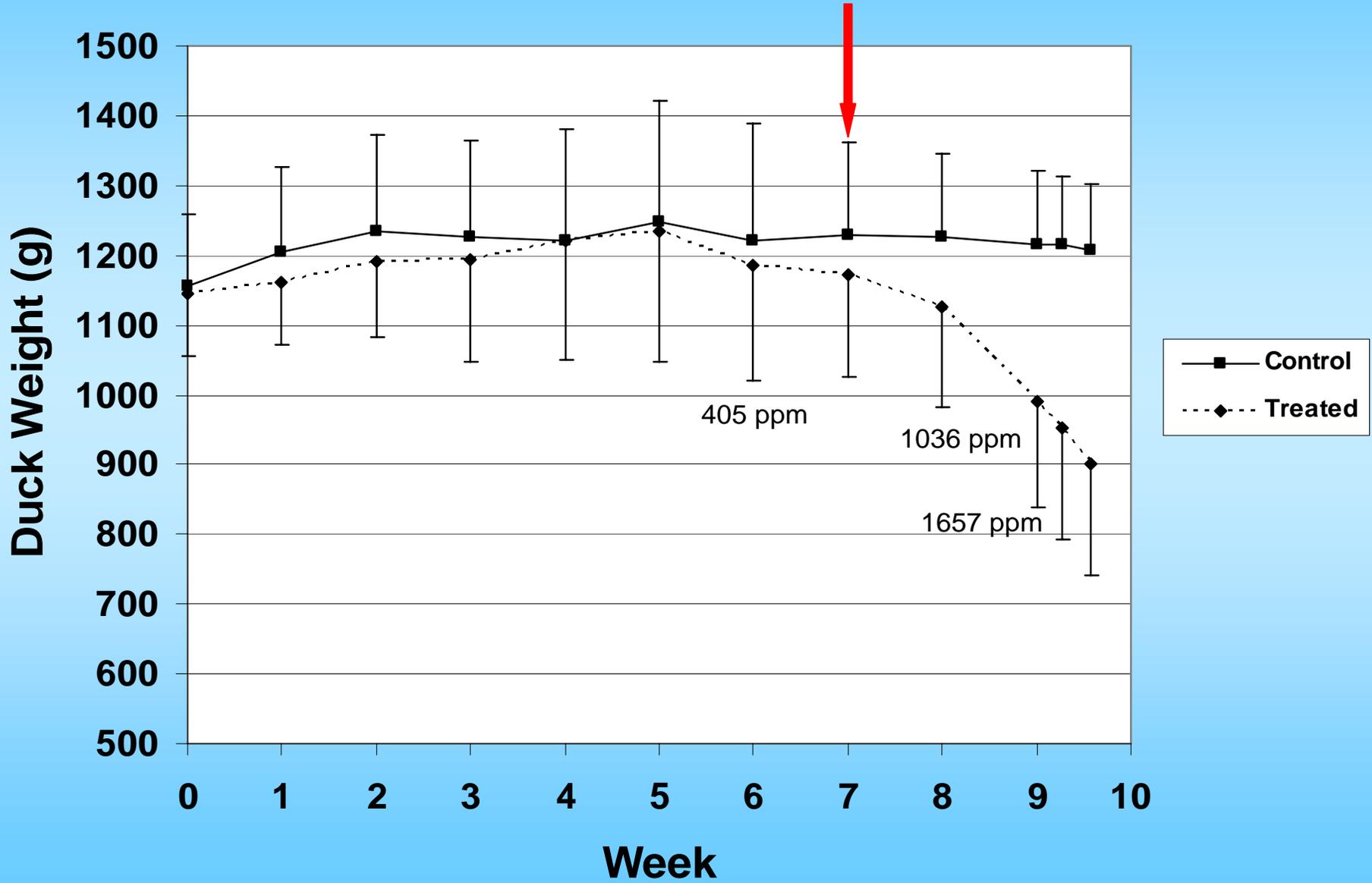


- Increase weekly (1.6X)  
**38, 62, 99, 158, 252, 405, 647, 1035, 1657, 2651 ppm**

# Food Consumption



# Body Weight



# Dietary $\text{NaVO}_3$ Exposure

(38-2651 ppm)

- Weight loss ~ 25%
- Mild hemorrhagic enteritis 7 of 12
- Liver Lesions 5 of 12
- Hematocrit, serum AST, P ↑
- Serum Na and Cl ↓
- Oxidative stress ↑
- Lipid peroxidation ↑
- Liver V 25.2  $\mu\text{g/g dw}$
- Kidney V 13.6  $\mu\text{g/g dw}$

# Conclusions

- In acute trials, pathological lesions and liver and kidney [V] were similar to dead geese from the fly ash pond
- At V concentrations exceeding  $5 \mu\text{g/g dw}$ , histopathological lesions in intestine, liver kidney and heart become apparent

# Conclusions

- **In chronic trials, toxicity and V accumulation were less pronounced**
- **V seems to pose a greater threat to wild birds in an acute exposure scenario**

# Guess What?

Another Die-Off at Site

60 Canada Geese - December 2004

# Perspective

USEPA

55<sup>th</sup> Report of TSCA ITC

USEPA Toxic Release Inventory

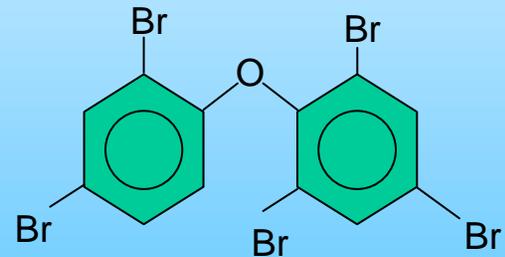
**18,000,000 lbs V surface impoundments**

**172 Facilities – Power Plants, Mines,  
Chemical Manufacturers**

**Impoundments in 33 States – AR, MS, NV**

# Polybrominated Diphenyl Ethers

- Brominated flame retardants
  - Foam, plastic TV and computer casings
- Similar structure to PCBs (209 congeners)
- Migrate out of product into environment
  - ubiquitous
  - Sediment, sewage sludge
  - Biota
    - breast milk, fish, bird eggs



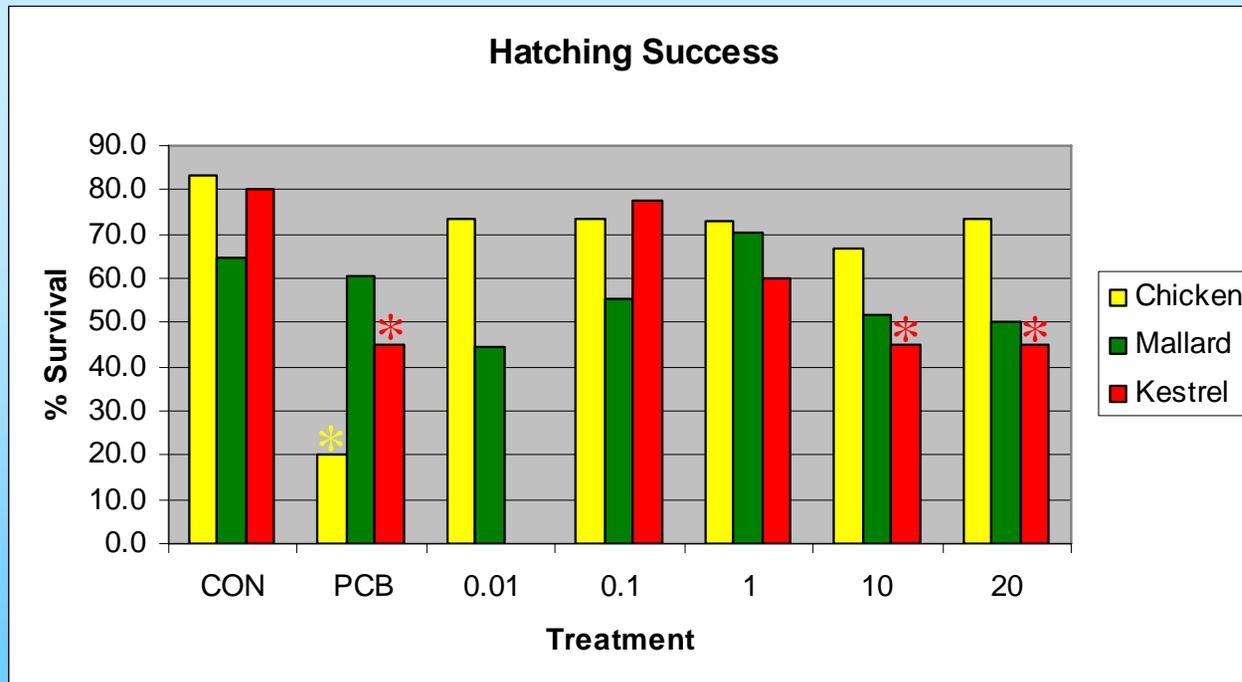
# Species and Endpoints

- Series of avian egg injections
  - Chicken
  - Mallard
  - American Kestrel
- Inject early in embryo development
  - Survival through incubation
  - Hatching success
  - Organ weights
  - EROD activity
  - Thyroid hormones



# Embryotoxicity

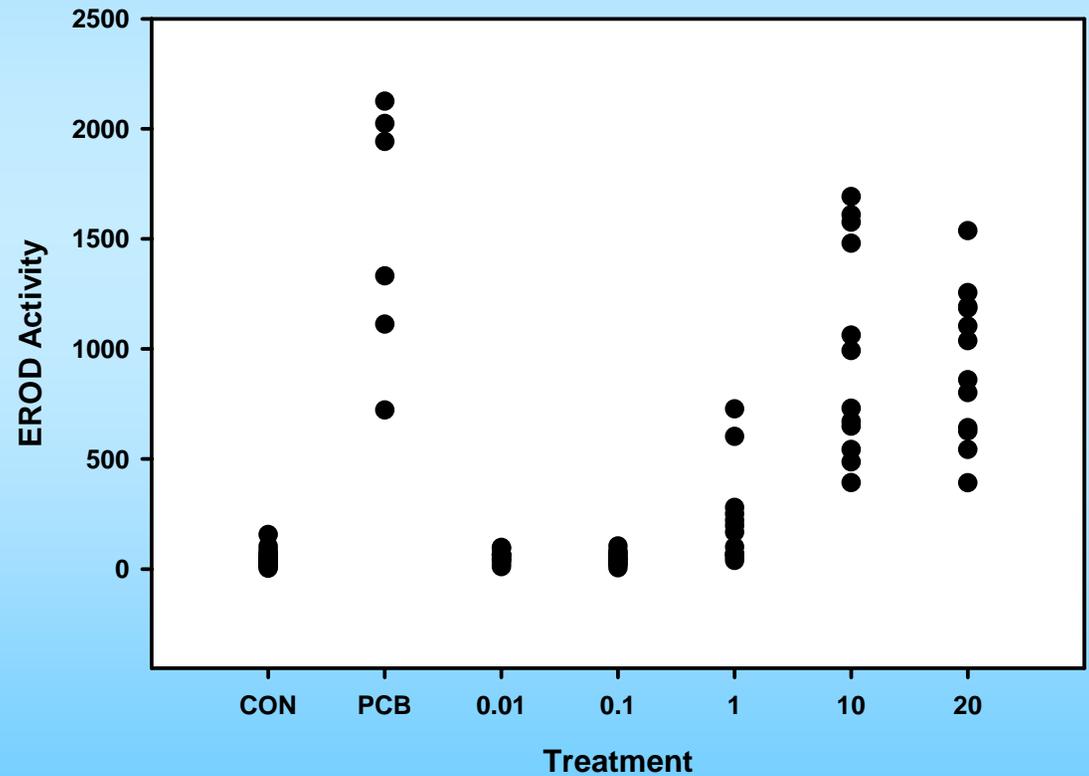
- Survival, Hatching Success
  - Chickens and mallards tolerant of high doses
  - American kestrels sensitive



# Cytochrome P450

- EROD activity
  - Chickens induced
  - Mallards, no induction
  - Kestrel data pending

## Chicken Hepatic EROD Activity



# Diclofenac Toxicity Study in New World Vultures

- NSAID – Treatment of arthritis in cattle
- Carcasses consumed by *Gyps* vultures
- Vultures succumb from Diclofenac Toxicity
  - Alters  $\text{PGE}_2$  &  $\text{PGI}_2$  synthesis
  - Impairs renal blood flow
  - Visceral gout (urates)
- Decimated OWBVs population
- Sensitivity of New World Vultures???

