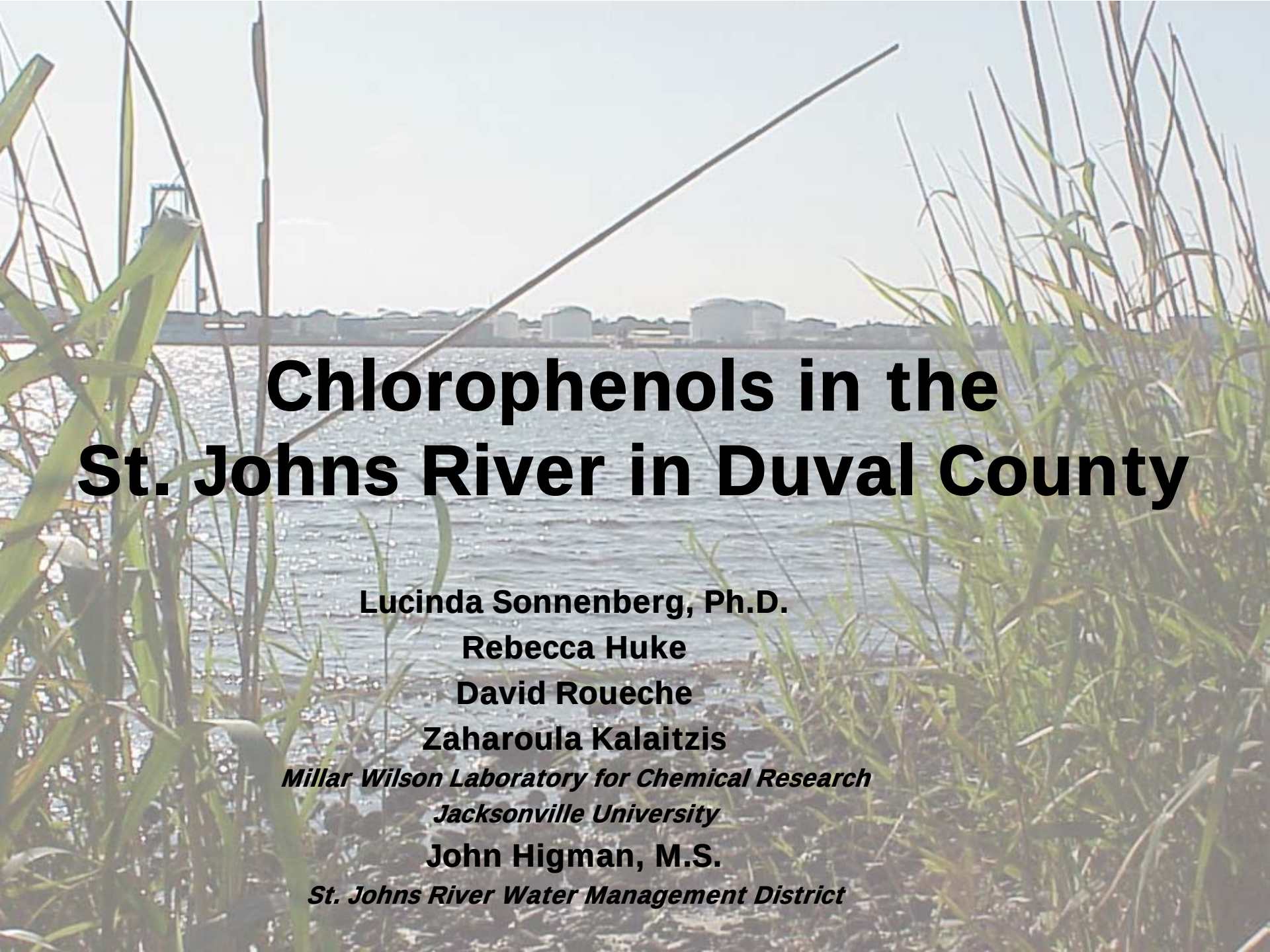


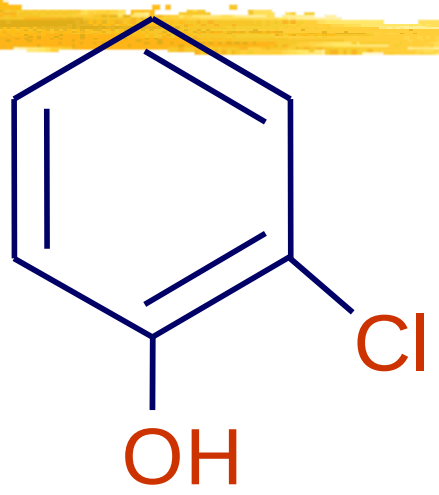
Chlorophenols in the St. Johns River in Duval County

Lucinda Sonnenberg, Ph.D.
Rebecca Huke
David Roueche
Zaharoula Kalaitzis
Millar Wilson Laboratory for Chemical Research
Jacksonville University
John Higman, M.S.
St. Johns River Water Management District

Background – Chlorophenols

- **Chlorophenols**

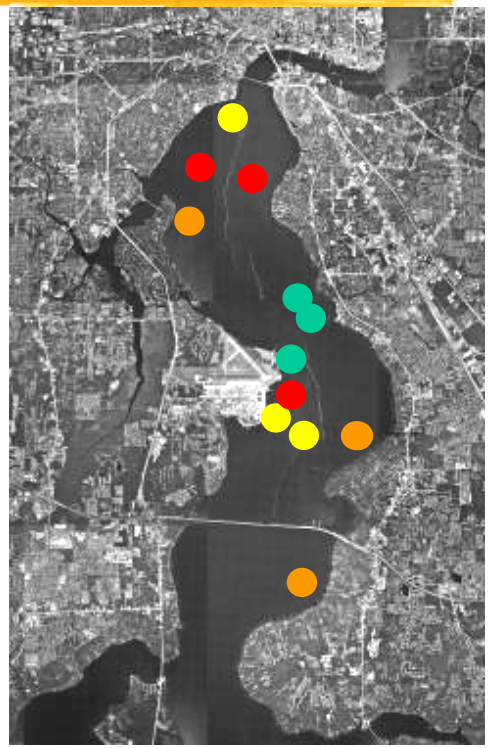
  Class of aromatic, hydroxylated, chlorinated organic compounds



- **Significance**
  - **Widespread**
  - **Uncouple oxidative phosphorylation**
  - **Human health**
  - **Persistent**
  - **Bioaccumulate**
- **Sources:**
  - **Chemical manufacturing intermediates**
  - **Pesticides**
  - **Disinfection byproducts**
  - **Incineration emissions**
  - **Bleached pulp production**

Background – Original Study

- **Screening study of CPs in LSJR sediments conducted in mid 1990s by SJRWMD and Battelle Ocean Sciences**
  - **Nonspecific, nonselective HPLC-UV method used**
- **Results indicated that CPs were ubiquitous at high concentration, especially 2-CP**
  - **Further investigation was warranted**



- 0 - 236 ppb dw 2-CP
- 237 - 489 ppb dw 2-CP
- 490 - 934 ppb dw 2-CP
- 935 – 3580 ppb dw 2-CP

Objectives

- **Verify presence of CPs using GC/MS, a specific and selective method of detection**
  - **Compare identities and concentrations to screening study**
- **Evaluate environmental significance**
  - **Compare concentrations to aquatic and sediment quality guidelines and reported levels worldwide**
- **Elucidate important sources**
  - **Patterns of contamination**

Methods - Sampling

- **Sampling**
  - **“Judgmental” sampling design**
    - **Water and sediment samples collected at 13 sites:**
      - **Hot spots of 1990s (2)**

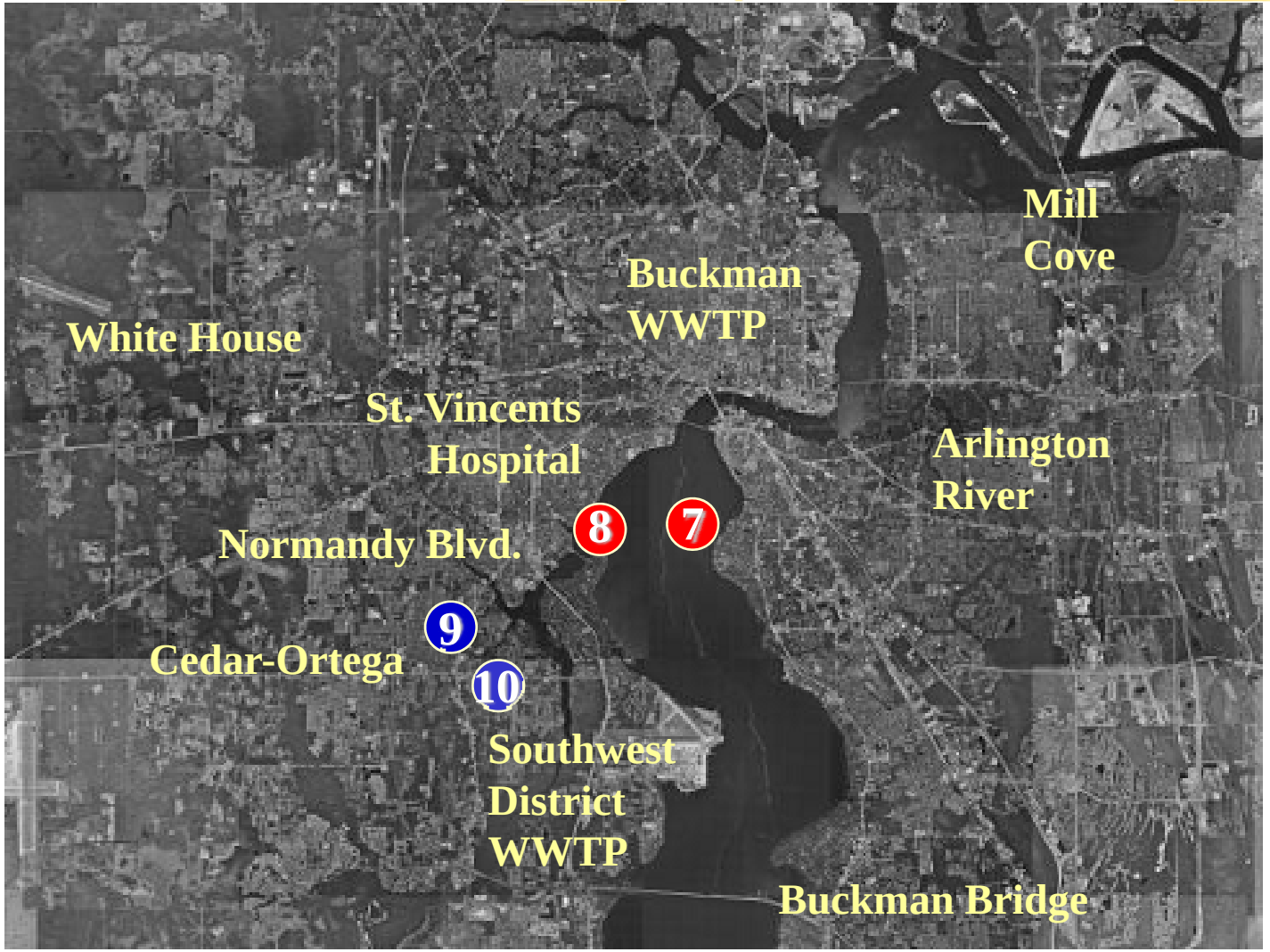
Study Sites


Mill
Cove
Buckman
WWTP
White House
St. Vincents
Hospital
Arlington
River
Normandy Blvd.
8
7
Cedar-Ortega
Southwest
District
WWTP
Buckman Bridge

Methods - Sampling

- **Sampling**
  - **“Judgmental” sampling design**
    - **Water and sediment samples collected at 13 sites**
      - **Hot spots of 1990s (2)**
      - **Aquatic weed herbicide spraying (2)**

Study Sites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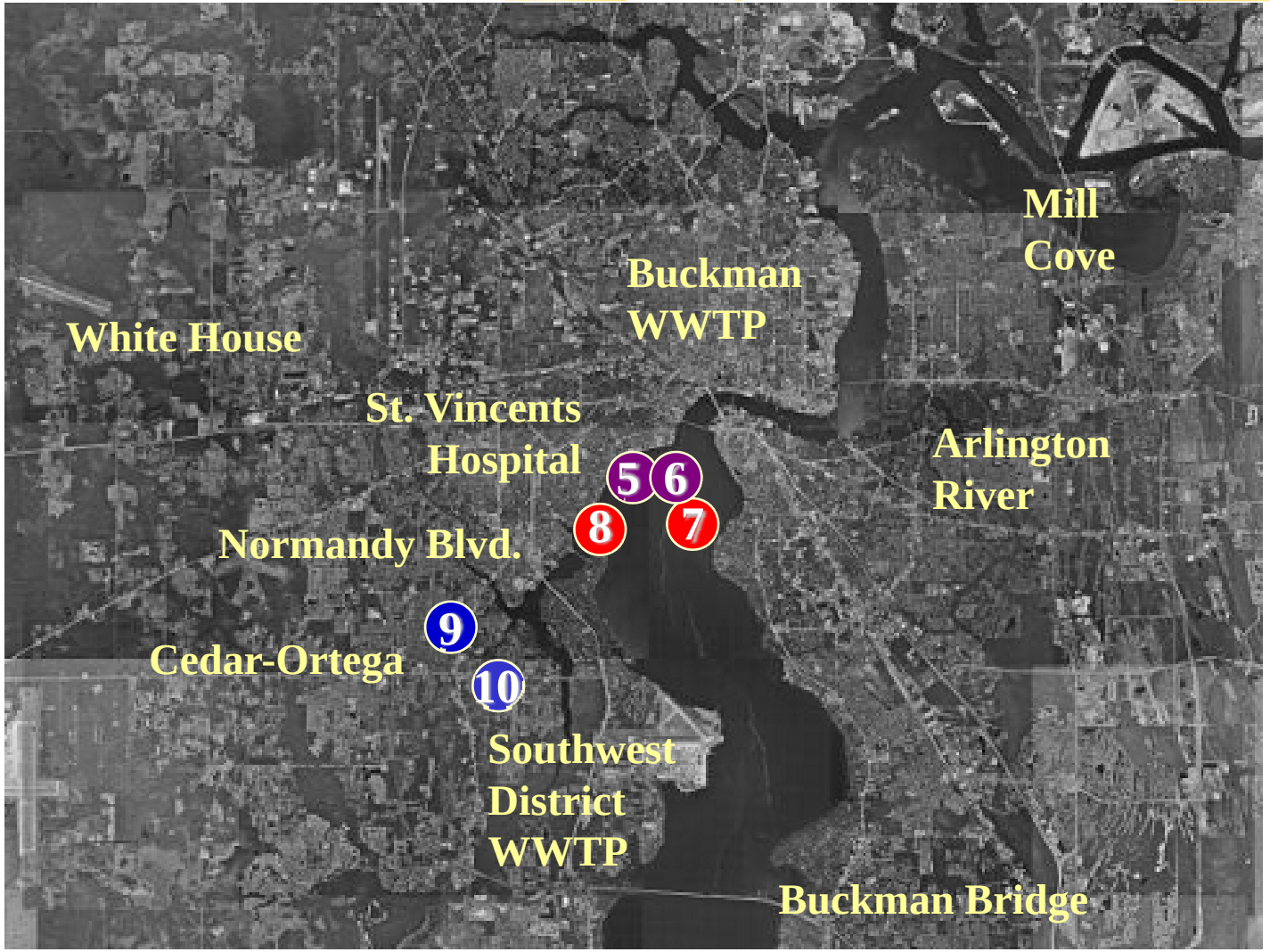
      - **Near former medical waste incineration (2)**

Study Sites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Method – Sampling

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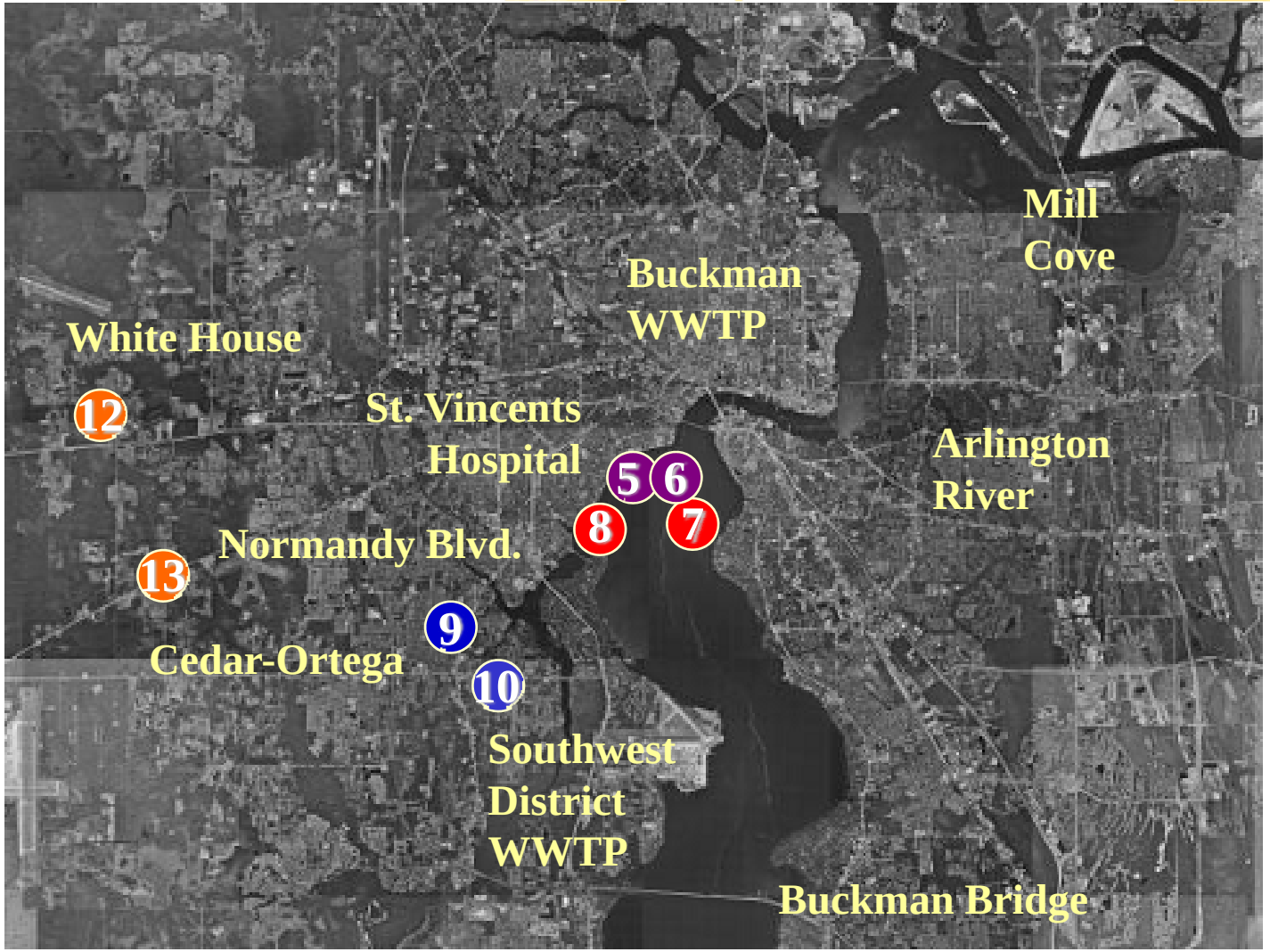
  - **"Judgmental" sampling design**
    - **Water and sediment samples collected at 13 sites**
      - **Hot spots of 1990s (2)**
      - **Aquatic weed herbicide spraying (2)**
      - **Near former medical waste incineration (2)**
      - **Superfund sites (2)**

Study Sites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Buckman Bridge

Methods - Sampling

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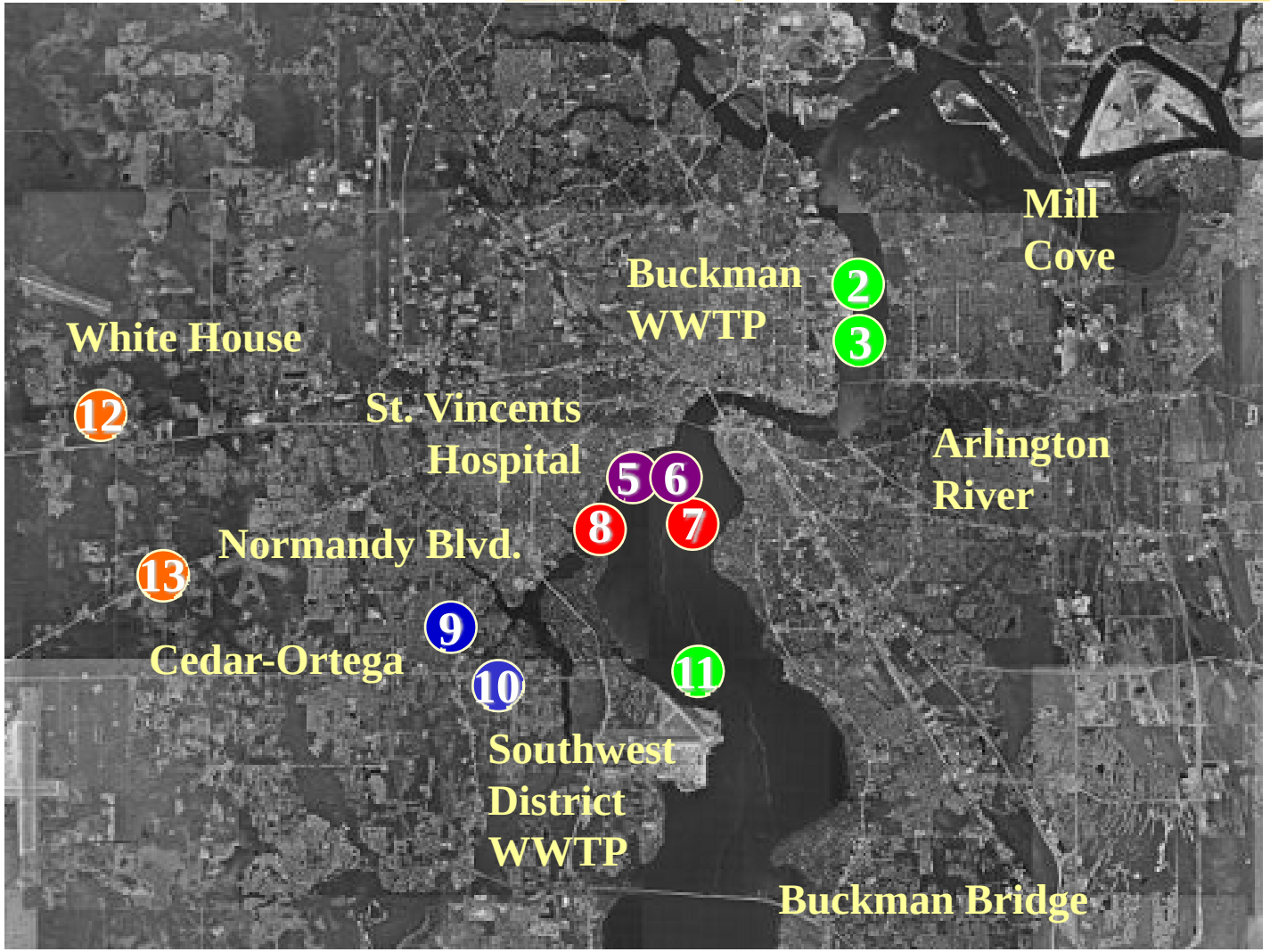
  - **“Judgemental” sampling design**
    - **Water and sediment samples collected at 13 sites**
      - **Hot spots of 1990s (2)**
      - **Aquatic weed herbicide spraying (2)**
      - **Near former medical waste incineration (2)**
      - **Superfund sites (2)**
      - **Municipal wastewater discharges (3)**

Study Sites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Methods - Sampling

- **Sampling**
  - **“Judgemental” sampling design**
    - **Water and sediment samples collected at 13 sites**
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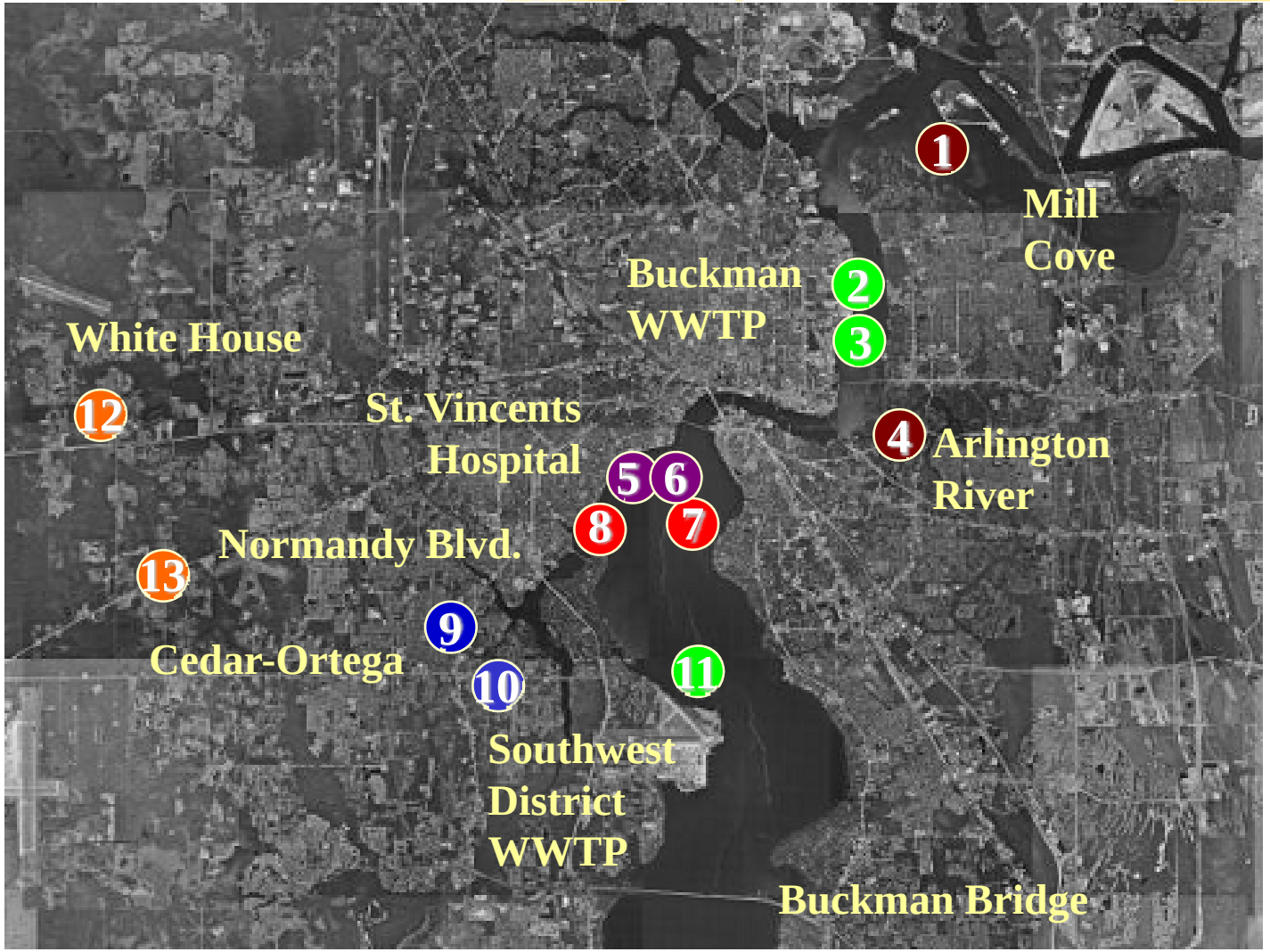
      - **Near former medical waste incineration (2)**
      - **Superfund sites (2)**
      - **Municipal wastewater discharges (3)**
      - **Reference (2)**

Study Sites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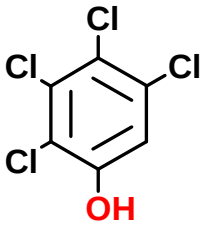
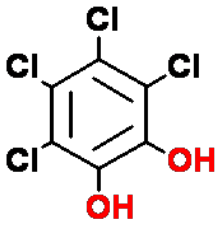
Methods

- **30 Chlorophenolic Compounds Studied**
  - **4 structure classes**
    - **Monohydroxylated**



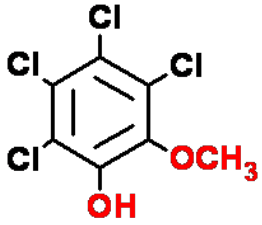
2,3,4,5-TeCP

    - **Chlorocatechols**



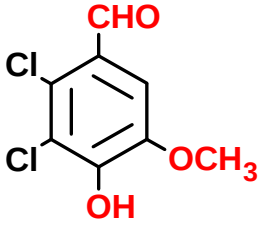
TeCC

    - **Chloroguaiacols**



TeCG

    - **Chlorovanillins**



5,6-DCV

Methods

- **Modified EPA Method 1653**
- **Identification**
  - **Match retention times and mass spectra of sample peaks to user-defined library**

Chromatogram of CPs w/RT

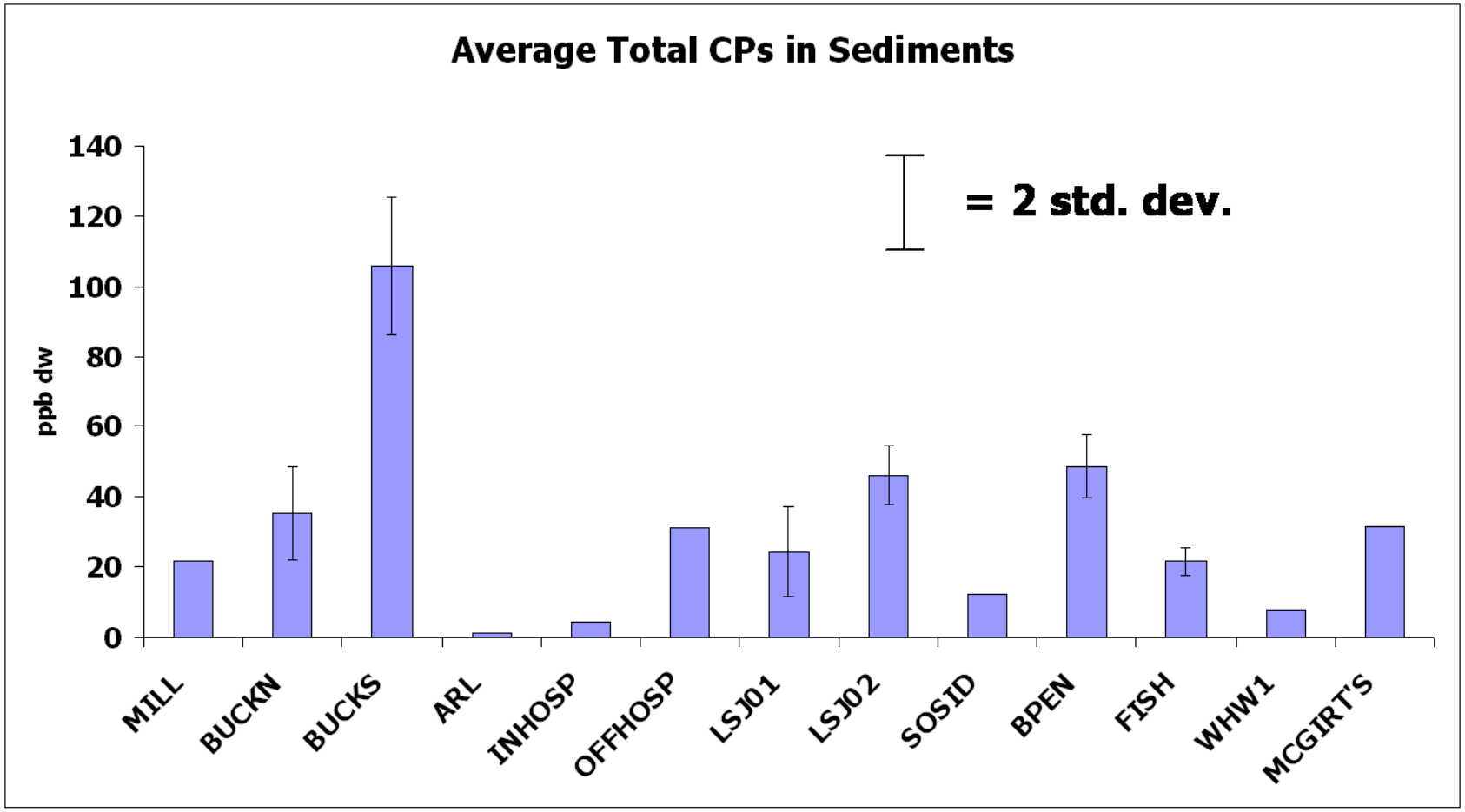
Selected ion mass spectrum

- **Quantitation**
  - **Recovery-corrected values determined from internal standard techniques using EI, PI, SIM mass spectrometric techniques**

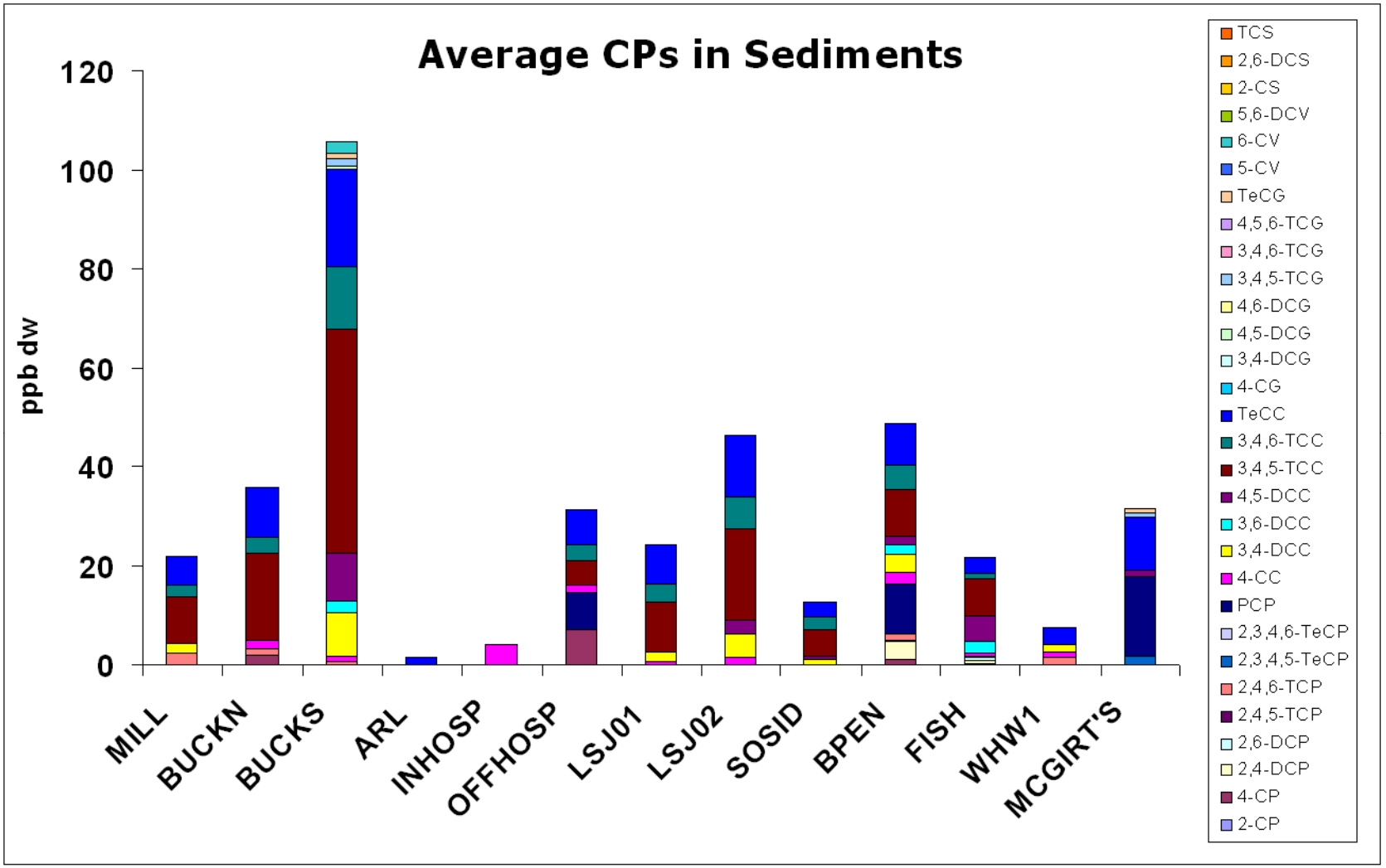
Results

- **No 2-CP found at any site**
- **The water quality is good with respect to CPs**
  - **only trace levels at one site**
- **Sediments contain CPs at ppb levels**
  - **12 out of 13 sites had CPs (92%)**
  - **19 out of 30 CP compounds (63%) detected**

Results


Average Total CPs in Sediments
ppb dw
140
120
100
80
60
40
20
0
= 2 std. dev.
MILL
BUCKN
BUCKS
ARL
INHOSP
OFFHOSP
LSJ01
LSJ02
SOSID
BPEN
FISH
WHW1
MCGIRT'S

Results


Average CPs in Sediments
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SOSID
BPEN
FISH
WHW1
MCGIRT'S
TCS
2,6-DCS
2-CS
5,6-DCV
6-CV
5-CV
TeCG
4,5,6-TCG
3,4,6-TCG
3,4,5-TCG
4,6-DCG
4,5-DCG
3,4-DCG
4-CG
TeCC
3,4,6-TCC
3,4,5-TCC
4,5-DCC
3,6-DCC
3,4-DCC
4-CC
PCP
2,3,4,6-TeCP
2,3,4,5-TeCP
2,4,6-TCP
2,4,5-TCP
2,6-DCP
2,4-DCP
4-CP
2-CP

Toxicity

- **Sediment Quality Guidelines [1]**
  - **Apparent Effects Threshold for Marine Sediments**

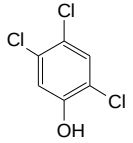
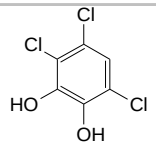
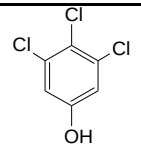
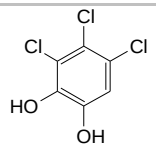
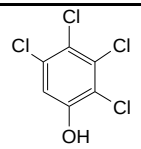
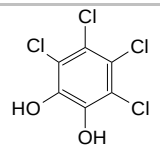
Analyte	Apparent Effects Threshold ppb dw	Duval County Max. 2006 ppb dw	LSJR Max. 1999 ppb dw
2-CP [2]	8	ND	3852
2,4-DCP [2]	5	4	496
2,4,5-TCP [3]	3	1	390
2,4,6-TCP [3]	6	3	908
PCP [4]	17	20	5895

1 NOAA 1999
2 Lowest AET for amphipods
3 Lowest AET for bivalves
4 Lowest AET for infaunal community impacts

Toxicity

- **No gross violations of current 5 SQGs**
  - **Slight PCP exceedance in McGirt's Creek**
- **However, CPs probably affect benthic health**
  - **Cumulative effect of all CPs and other stressors is important**
  - **Chlorocatechols, most prevalent type of CP, may be more toxic than the MHCPS that are assessed**

Toxicity

Compound	Structure	Organism	Test Conditions	Response, ug/L	Reference
2,4,5-TCP		Bluegill	24 hr LC50	3100	44
3,4,6-TCC		Brown Trout	96 hr LC50	900	46
3,4,5-TCP		Guppy	14 day LC50	5800	44
3.4.5-TCC		Rainbow Trout	96 hr LC50	1000	46
2,3,4,5-TeCP		Goldfish	24 hr LC50	750	78
TeCC		Rainbow Trout	96 hr LC50	400	46

Occurrence

- **Major LSJR CPs in worldwide sediments**

Compound	Concentration ppb dw	Sites
PCP	8.4	Rhine River
	0.01 - 2.4	Maine coast
	0.4 - 13	Downstream from pulp mill, NZ
	9.5	Downstream from pulp mill, Finland
	ND - 20.2	SJR & Tribs, Duval County 2006
4,5-DCC	0.6	Downstream from pulp mill, NZ
	ND - 11.1	SJR & Tribs, Duval County 2006
3,4,5-TCC	0.2 - 920	Downstream from pulp mill, Gulf of Bothnia
	ND - 58.1	SJR & Tribs, Duval County 2006
3,4,6-TCC	0.4 - 460	Downstream from pulp mill, Gulf of Bothnia
	ND - 16.3	SJR & Tribs, Duval County 2006
TeCC	0.1 - 770	Downstream from pulp mill, Gulf of Bothnia
	348	Downstream pulp mill, Finland
	ND - 22	SJR & Tribs, Duval County 2006

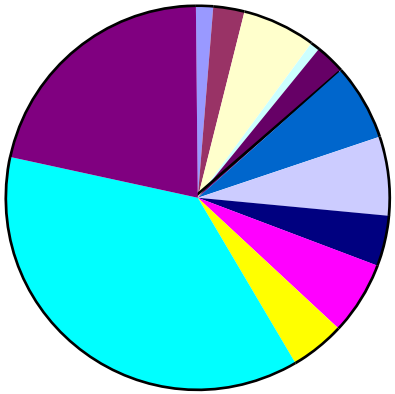
Important Sources

- **Pulp and paper mill "fingerprint" in most sediments**
  - **Present in most downstream site (Mill Cove)**
  - **In two tributaries (Butcher Pen, Fishing Creek)**
- **McGirt's sediments have PCP and metabolites**
  - **Coleman-Evans likely source**
- **Other sources minor**

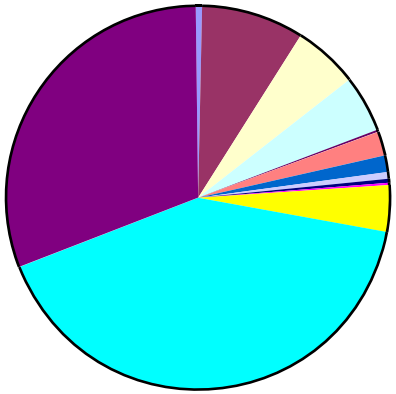
Important Sources

- **Pulp and paper signature**
  - **Chlorocatechols dominate, including 3,4-DCC, 3,4,5-TCC and TeCC**

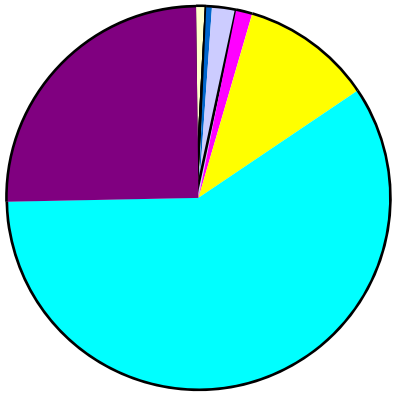
Bleached Kraft Mill WW Paasivirta 1985



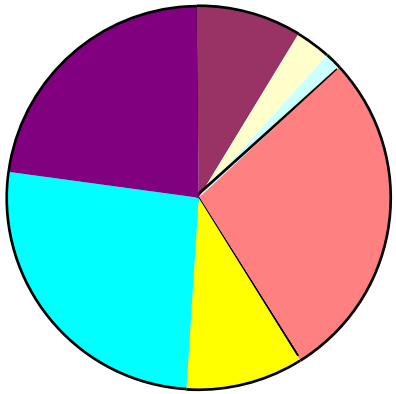
Rice Creek Sediments 2003



South Buckman Sediment



Butcher Pen Sediment



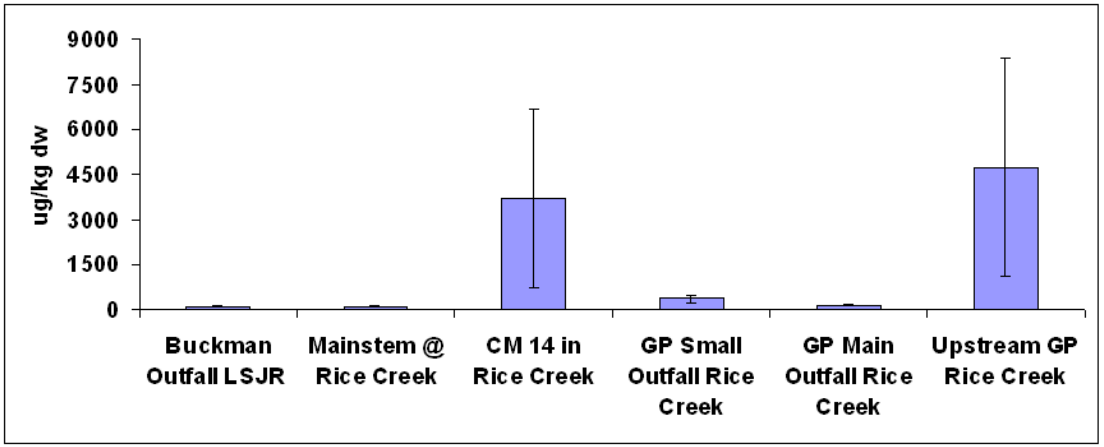
- **Long history of pulp and paper mill discharges**
- **Pulp and paper mill sources are declining**

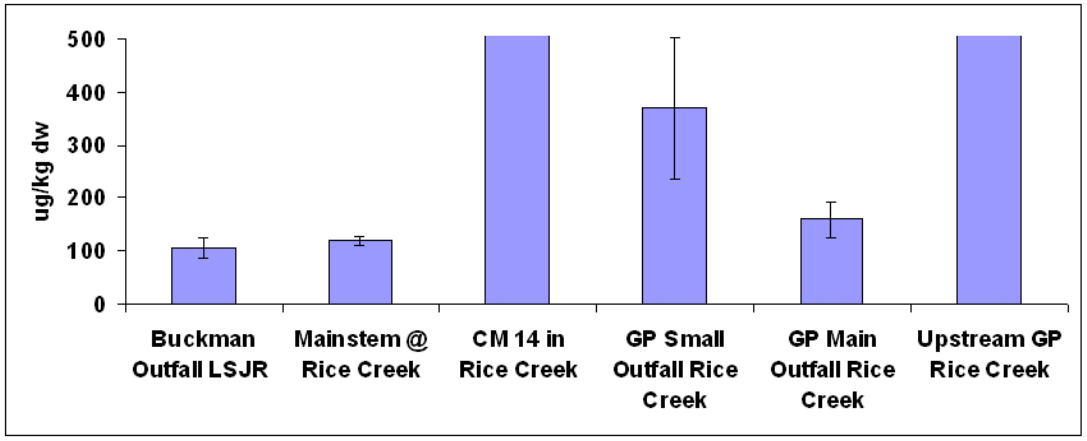
Summary

- **2-CP is not a contaminant of concern in the SJR in Duval County**
- **Water quality is not impaired by CPs**
- **CPs pervasive in SJR sediments at levels typical of industrially impacted rivers**
- **Primary source of CPs is likely historic pulp and paper mill discharges**
- **Overall, total load in the river is declining**

Update

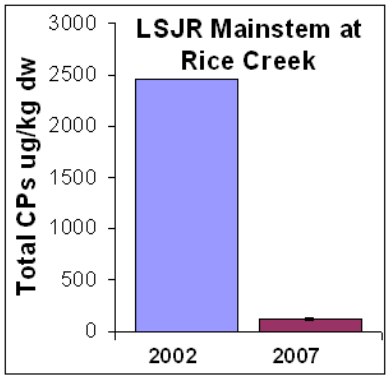
- **Total CPs in LSJR and Rice Creek 2006-2007**

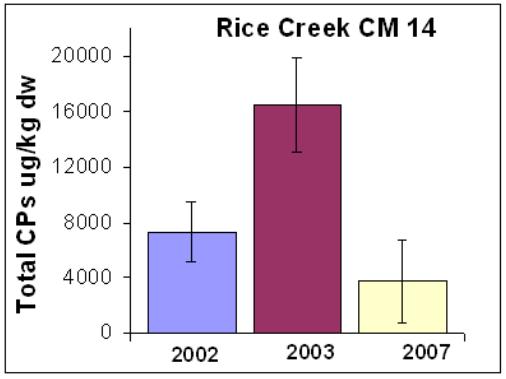


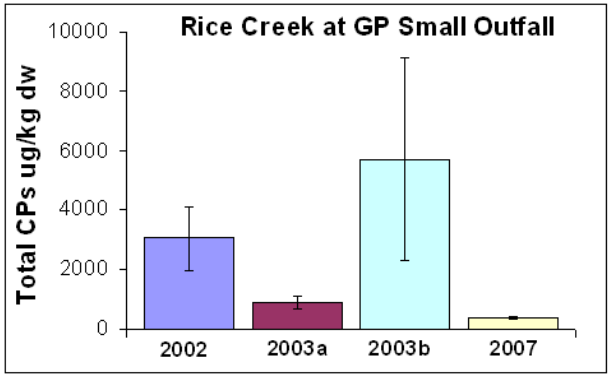


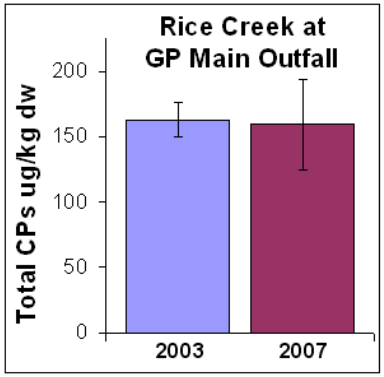
Update

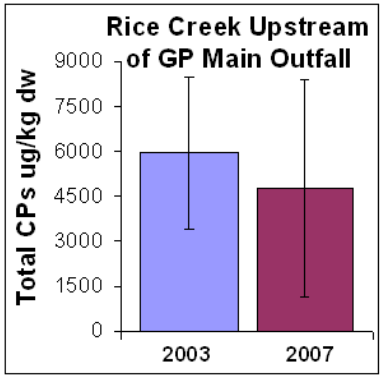
- **Total CPs in Rice Creek 2002-2007**





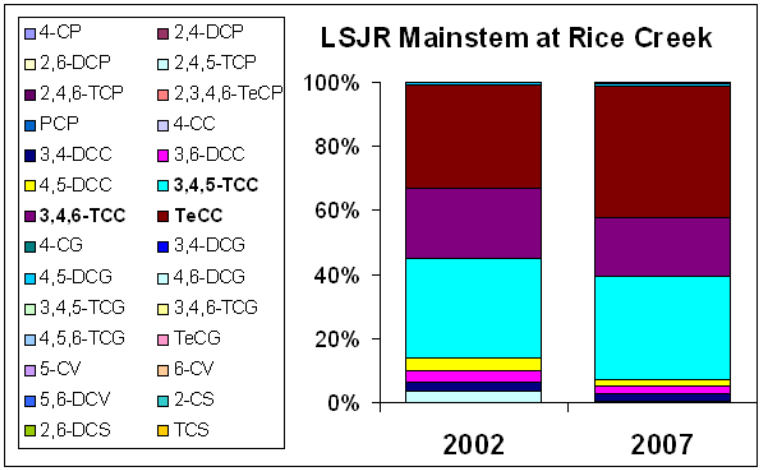


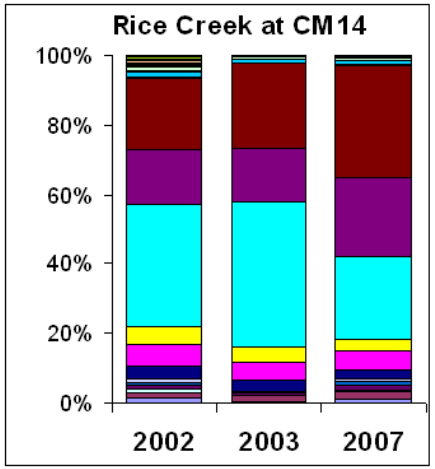


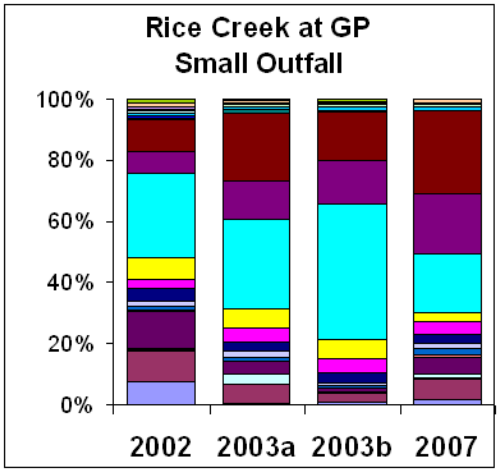


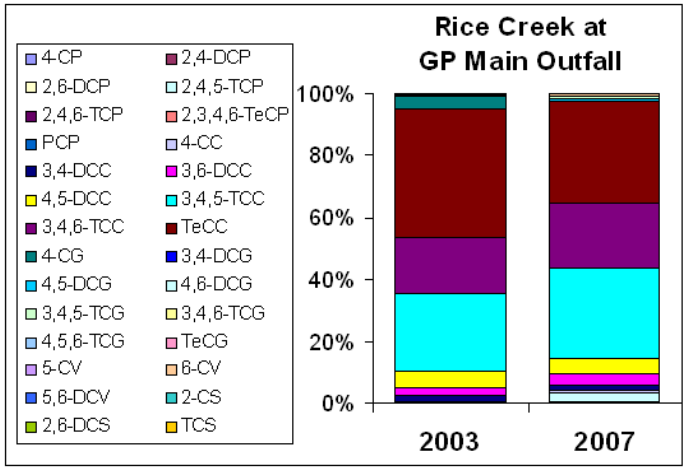
Update

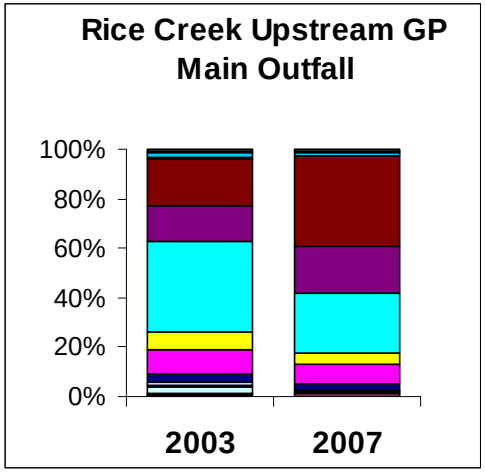
➢ Distribution of CPs





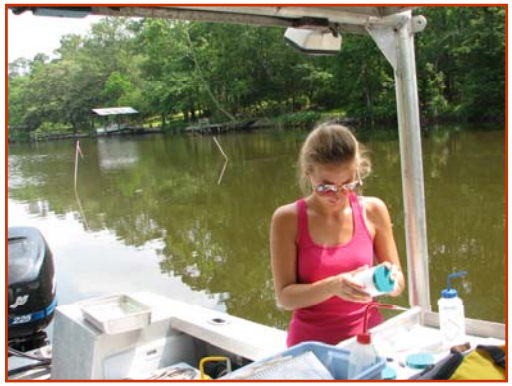






Acknowledgments

- **Environmental Protection Board**
- **City of Jacksonville**
- **SJRWMD**
- **MWL student researchers, including Rebecca Huke, David Roueche, Joy Kalaitzis**



Project Benefits

- **Complements clam study**
  - **Clams not present in worst areas**
  - **Clam burden did not mirror sediment**

- **Instrument benefits undergraduate education/environmental research**
  - **Research assistants in MWL**
  - **Environmental Chemistry**
  - **Instrumental Chemistry**
  - **Organic Chemistry**