Climate Change, All-Hazard Preparedness and Determination of Fungicides by LC/MS/MS

#### Climate Change, All-hazard Preparedness and Determination of Fungicides by LC/MS/MS



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# Outline

- Climate Change
- Soybean Rust
- Fungicides
- Method Development
- 💲 Iowa Tornado
- 😵 Fish Kills
- Summary



## Global climate change: What it means to Iowa

State outpaces U.S. in greenhouse gas emissions; challenges await

#### By PERRY BEEMAN

owa's greenhouse gas emissions are growing faster than the nation's as a whole, even as new state programs fight to limit the damage from global climate change, a new report shows.

The study conducted for Iowa's Climate Change Advisory Council found that the state faces a tough task in cutting greenhouse gases, said Jerald Schnoor, an environmental engineering professor at the University of Iowa who is leading the panel. The gases, which include water vapor, carbon dioxide and ozone, trap heat that otherwise would escape into the atmosphere. That warms the globe, threatening an increase in disease, heat-related deaths, severe weather and crop damage.

The study by the Harrisburg, Pabased Center for Climate Strategies found gross emissions of the gases in lowa rose approximately 20 percent from 1990 to 2005, while the country's emissions rose 16 percent. Iowa's emissions accounted for 1.7 percent of the U.S. total in 2005.

"We're increasing rapidly, more than a percent a year," said Schnoor, co-director of the U of I's Center for Global and Regional Environmental Research. "When can we begin to reduce? That's the challenge."

Experts say the new findings — and other recent research from across the globe — paint a clearer picture of what Iowa and the rest of the Midwest will be like by the end of the century. They also bring urgency to a number of policy decisions that could hurt or help the problem. "People are more worried," said Eugene

Takle, an atmospheric science professor at Iowa CLIMATE, PAGE 6A

#### Possible consequences for Iowa

The Des Moines Register's analysis of climate change research found that scientists are starting to get a clearer picture of what the warming might mean for lowa:

WEATHER: Hotter and wetter conditions with higher humidity overall, but fewer 100-degree days.

**HEALTH:** Added health threats from heat spells and a longer allergy season worsened by ozone.

EMISSIONS: Greenhouse gas emissions rising faster than the national average, but possibly offset by added wind power, biofuels energy efficiency and plantings that sweep carbon from the air.

AGRICULTURE: A mixed bag for agriculture, with longer growing seasons and higher yields tempered by new pests, more drought, floods and plant-damaging ozone.

**WILDLIFE:** A change in the mix of birds because of shifts in migration and nesting.



#### The series

lowa's role as an agricultural leader means it also is a major contributor to climate change. The state also is home to some of the nation's leading experts on the subject and innovative efforts to reduce greenhouse gas emissions dramatically. Today begins a yearlong series examining lowa's role in climate change and how the state's agriculture, weather, wildlife and public health are expected to change

http://www.desmoinesregister.com/apps/pbcs.d/ 0511/NEWS10/805110344/1011



#### **Des Moines Register** Sunday, May 11<sup>th</sup> 2008

#### By Perry Beeman



# **Iowa Climate Change**





Anticipate

- Milder Winters
- Hotter
   Summers



Union of Concerned Scientists – *Climate Change in the Hawkeye State* http://www.ucsusa.org/assets/documents/clean\_energy/lowa\_Impacts\_summary-Final\_2004.pdf

## **Emerging Concern-Soybean Rust**

- Foliar disease
- Identified in US soybean production fields in November of 2004.
- Fungicides are effective for managing disease
- Fungicides are not regulated



Early and late stages of soybean rust

Early and late stages of soybean rust. Photo by Glen L. Hartman.

http://ohioline.osu.edu/ac-fact/0048.html



# Soybean Rust



#### **Distribution of Soybean Rust in Iowa - 2007**



Soybean rust was found in a field in Dallas County, Iowa, on Tuesday, September 25, 2007.





# **Soybean Rust - Treatment**





Photo by Gregory E. Shaner, Purdue University.



Photo by Shawn P. Conley, Purdue University.

#### Application of fungicides



Photo by Shawn P. Conley, Purdue University.

http://www.ces.purdue.edu/extmedia/ID/ID-324.pdf

### **Current – Soybean Rust**



http://sbr.ipmpipe.org/cgi-bin/sbr/public.cgi



## **Fungicides Applied in Iowa**

Active Ingredient	Product (Trade Name)
pyraclostrobin (57%)	Headline, Stamina, Cabrio, Insignia
propiconazole (20%)	<u>Tilt,</u> Bumper, <u>Propimax</u>
azoxystrobin (13%)	<u>Quadris</u>
tetraconazole (8%)	Domark
propiconazole + trifloxystrobin (3%)	<u>Stratego</u>
azoxystrobin + propiconazole	<u>Quilt</u>
chlorothalonil	Bravo, Echo, Equus
myclobutanil	Laredo EC
azoxystrobin + cyproconazole	Quadris Xtra
cyproconazole	Alto
flusilazole	Punch
flutriafol	Topguard
metconazole	Caramba

### **Determinative Method Needed**

- Ideal method
  - Relatively rapid
  - Limited sample preparation
  - Reliable
  - Sufficient selectivity
  - Sufficient sensitivity
- LC/MS/MS



#### Instrumentation



- Agilent 1100 Liquid Chromatography System with binary pump, cooled autosampler, heated column compartment and vacuum degassing module (or equivalent)
- Applied Biosystems API 4000 Tandem Quadrupole Mass Spectrometer (or equivalent)



### **Sample Collection/Preparation**

- 1L or 250 mL amber glass bottle
- Cooled to 4 ± 2 °C
- Stored at 4 ± 2 °C upon receipt
- Aliquot filtered through 0.45 µm syringe filter
- 10 mL sample
- Internal standard added Colchicine
- 10 µL direct injection



### **Analytical Operating Parameters**



**Chromatographic Conditions:** 

Column: 2.1 mm x 150 mm x 5  $\mu$ m, C<sub>18</sub> column held at 30 °C Solvents: A1: 90% H<sub>2</sub>O + 10 mM NH<sub>4</sub>O<sub>2</sub>CH<sub>3</sub>/10% MeOH B1: ACN

Gradient:

Time (min)	Flow (µL/min)	%A1	%B1
0	300	75	25
0.5	300	75	25
7	300	10	90
12	300	10	90
12.1	400	75	25
16	400	75	25
16.1	300	75	25



### **Mass Spectrometer Conditions**



Analyte	Q1 mass	Q3 mass	T <sub>Dwell</sub>	V <sub>DP</sub>	V <sub>EP</sub>	V <sub>CE</sub>	V <sub>CXP</sub>
TFS quant	409.1	186.2	50	51	10	23	10
TFS <sub>qual</sub>	409.1	145.2	50	51	10	65	6
AZS quant	404.03	372.1	40	46	10	21	22
AZS <sub>qual</sub>	404.03	344.1	40	46	10	35	20
PCS quant	388.03	194.1	50	51	10	19	10
PCS qual	388.03	163.2	50	51	10	33	8
TTZ <sub>quant</sub>	371.9	344.2	100	96	10	29	18
TTZ <sub>qual</sub>	371.9	329.2	100	96	10	37	20
PPZ quant	341.99	159.2	120	86	10	41	8
PPZ <sub>qual</sub>	341.99	41.1	120	86	10	65	6
TBZ <sub>quant</sub>	308.1	70.1	100	81	10	53	12
TBZ <sub>qual</sub>	308.1	125.1	100	81	10	57	6
CPZ <sub>quant</sub>	292	70.1	100	76	10	43	12
CPZ <sub>qual</sub>	292	125.1	100	76	10	41	6
MBN quant	289.04	70.1	100	66	10	39	12
MBN qual	289.04	125.1	100	66	10	47	6
Colchicine ISTD	400.159	310.3	100	51	10	35	22

### Chromatography



#### **Calibration**





### **Stability Study**

- Surface water samples collected by SHL Limnologists
- Serve as "real" matrices to spike
- Samples spiked with study compounds at 1 and 20  $\mu g/L$
- Samples held at typical EPA-recommended 4 °C storage conditions
- Analyzed at day 1, day 2, day 7, day 14 and day 28 to assess analyte stability or holding time

## **Storage Stability**

Analyte	% Recovery ± Std. Deviation		
	(1 µg/L)	(20 µg/L)	
Pyraclostrobin	112.1 ± 9.4	106.0 ± 6.5	
Propiconazole	116.7 ± 12.6	109.2 ± 3.9	
Azoxystrobin	117.6 ± 7.5	111.5 ± 7.5	
Trifloxystrobin	95.5 ± 18.3	89.2 ±16.6	
Tetraconazole	106.8 ±5.5	102.1 ±4.9	
Tebuconazole	118.4 ±15.1	109.5 ± 6.7	
Cyproconazole	116.1 ± 13.1	109.1 ± 5.8	
Myclobutanil	113.1 ± 8.8	107.7 ± 2.5	

28-day sample spike holding time study at 1 & 20 µg/L



#### Iowa – Parkersburg Tornado





#### Sunday May 25, 2008





### Iowa – Parkersburg Tornado



#### Weather

Categories

0.5. news	
World news	D
Politics	D
Business	D
Sports	D
Entertainment	D
Health	D
Travel	D
Tech & science	D
Weather	D
Local Weather	D
Weather Maps	D
Local news	D
Browse	
Video	D
Photos	D
Community	D
Disable Fly-out <sup>▶</sup> [	

#### Iowa town torn apart by deadly twister

National Weather Service reports it was the strongest to hit in 32 years



Steve Pope / Getty Images

Most of Parkersburg, Iowa, was wiped out Sunday by a tornado that killed seven.

#### Ap Associated Press

updated 2:25 p.m. CT, Tues., May. 27, 2008

DES MOINES, Iowa - A tornado that leveled half a town in northeast Iowa and killed seven people was the strongest to hit the state in 32 years, the National Weather Service said



C Uptick in deadly twisters? May 27: Expert Greg Carbin talks with TODAY's AI Roker about the recent deadly





http://www.msnbc.msn.com/id/24840152/

Slide show

Launch

Devastated Residents pick through the wreckage after tornadoes ripped through the country's midsection over Memorial Day weekend.

### **All-Hazards Preparedness**



- Agricultural warehouse in Parkersburg destroyed
- Fungicide's released into environment and nearby stream
- SHL chemical threat preparedness staff and instrumentation available
- Fungicide method utilized to assess contamination plume





#### **Corn & Soybean Production in Iowa**

- Corn production up
- Acres in crop production up



## **Mystery of Summer Fish Kills**

- Jeff Vansteenburg
- Supervisor, Mason City Field Office
- Environmental Services Division



 Presented to Iowa Environmental Protection Commission



## **Strange Patterns**



- A rash of late summer fish kills in past two years
- Typically late July, August and September
- On site
  - Normal dissolved Oxygen, pH and temperature
  - Low ammonia levels
  - Clear water

# Investigations



- Aerial spraying prevalent in area
- Soybeans forming canopy
- Corn tasseling
- Possible link to two chemicals
  - Pyraclostrobin
    fungicide
  - Chlorpyrifos
    - insecticide



### **Pyraclostrobin**

- Sprayed near corn tasseling to control foliar diseases
- Profitable only on hybrids susceptible to gray leaf spot
- Highly toxic to daphnids, rainbow trout, blue gills, sunfish
- Low toxicity to birds and mammals
- No water quality standard in Iowa



## Chlorpyrifos

- Organophosphate insecticide (Similar to OP Nerve Gas)
- Inhibits acetylcholinesterase
- A suspected endocrine disrupter
- EPA cancelled approval for most household uses
- Agricultural use against soybean aphids



#### Specimen Label



#### Granular Insecticide

\*Trademark of Dow AgroSciences LLC

For control of various insects infesting certain field and vegetable crops.

Group	1B	INSECTICIDE		
Active ingredient: chlorpyrites: Q.( 2-pyridinyl) Other ingredients Total.	-diethyl O-(3,5, 64richloro- phosphorothiozia		15% 85% 100%	

IEPA Reg. No. 627 19-34

#### Keep Out of Reach of Children CAUTION

#### Precautionary Statements

Hazard to Humans and Domestic Animals

Harmful If Swallowed - Causes Moderate Eye Inflation

Avoid contact with eyes or clothing. Wash thoroughly with scap and water after handling.

Personal Protective Equipment (PPE) Some materials that are chemical-resistant to the product are barter laminate or viton. For more information, follow instructions in Supplement Three of PR Notice 93-7. If you want more options, follow the instructions for category H on an EPA chemical resistance category selections chart.

Loaders, applications and all other handlers must wear:

- Coveralls over long-sleeved shirt and long pants
- Chemical-resistant gloves
- Chemical-resistant footwar plus socks
   A NICSH-approved dust mist filtering respirator with MSHA/NIOSH approval number prefix TC-21C or a NIOSH-approved respirator with any N, R, p. or HE filter

Follow manufacturer's instructions for cleaning/maintaining PPE. If no such instructions for washables exist, use detargent and hot water. Keep and wash PPE separately from other laundry.

Engineering Controls Piotsmust use an enclosed cockpit in a manner that meets the requirements listed in the Worker Protection Standard (WPS) for agricultural peeticides (40 CFR 170.240(d)(6)).

When applicators use closed cab equipment in a manner that meets the requirements listed in the WPS for agricultural pedicides [40 CFR 170.240(d)(4-6)], the handler PPE requirements may be reduced or motified as specified in the WPS.

#### User Safety Recommendations

- Users should: • Wash hands before eating, clrinking, chewing gum, using tobacco or using the tollet.
- Remove clothing/PPE immediately if pesticide gets inside. Then wash theroughly and put on clean clothing.
- Remove PIPE immediately after handling this product. Wash the outside of gloves before removing. As soon as possible, wash
- theroughly and change into clean clothing.

#### First Ald Organophosphate

E evallowed: Call a poison control center or doctor immediately for treatment advice. Have a person sip a glass of water if able to swallow. Do not induce vomiting unless told to do so by a poison control center or doctor. Do not give anything by mouth to an unconsclous person. If in eyee: Hold eye open and rinse slowly and genity with water for 15-20 minutes. Remove contact lenses, if present, after the first 5 minutes, then continue incling eye. Call a poison control center or doctor for treatment advice.

Hote to Physicians: Chlorpyrifos is a cholinestenase inhibitor. Treat symptometically if exponent, plasma and set Nunni rail cholinestenase tasts may indicate significance of exposure (baseline data are useful). Attopine, only by hijection, is the preferable antidicte. Oximes, such as 2-PAM/protopern, may be therapeutic if used early, however, use only in conjunction with attopine. In case of severe acute poisoring, use antidole immediately after establishing an open allway and respiration.

Have the product container or label with you when calling a poison control center or doctor, or going for treatment. You may contact 1-800-992-5994 for emergency medical treatment information.

#### Environmental Hazards

This pacticities is toxic to frish, arguetic invertebrated, small many mails and brish. Do not apply directly to water, or to areas where surface water is present or to intertidal areas, below the mean high water mails. Diff and sunoff many be hazatobic to acquate organisms in water adjacent to treated areas. Do not contaminate water when interaing equipment or dispositing of equipment waterwaters or interate. This product is highly to to been exposed to dreat instament or readiuse or biogram groups or weeds. Do not apply this product or allow it to othit to biogram groups or weeds. Do not apply this product or allow it to othit to biogram groups or weeds. Do not apply the treatment area

Notice: Read the entire label. Use only according to label directions. Before using this product, read Warranty Disclaimer and Limitation or Hermadias essentiare on the label. If ferms are unacceptatice, refurn at once unopened.

#### Environmental Hazards

This pesticide is toxic to fish, aquatic invertebrates, small mammals and birds. Do not apply directly to water, or to areas where surface water is present or... Drift and runoff may be hazardous to aquatic organisms in water adjacent to treated areas.

## Chlorpyrifos



- Highly toxic to fish and invertebrates; can be toxic to birds
- Persistent in water 35 to 78 days
- Water quality Standards IAC 567-61.3(3) Table 1
  - Chronic 0.041 µg/L
  - Acute 0.083 µg/L
- Same standard for Class B cold and warm water Streams
- SHL utilizes GC/MS or GC/NP to determine in surface water





- Association between climate change and soybean rust appearance in Iowa
- Fungicides applied in Iowa on both soybeans and corn
- LC/MS/MS method developed to determine fungicide compounds in surface water
- Fungicide detects associated with fish kills in Iowa



