## Fluxes of carbon from the land to the ocean

Elizabeth W. Boyer Pennsylvania State University

### Collaborators

Richard B. Alexander, US Geological Survey, Reston, VA Richard A. Smith, US Geological Survey, Reston, VA Gregory B. Schwarz, US Geological Survey, Reston, VA Jhih-Shyang Shih, Resources for the Future

## Outline

- Overview of SPARROW water quality modeling approach.
- SPARROW model of total organic carbon in conterminous USA
- Estimates of TOC and DOC loadings to regional-scale coastal watersheds
- Future Directions



#### <u>SPA</u>tially <u>Referenced Regression on Watershed Attributes</u> **SPARROW** water quality model



#### Regional interpretation of water-quality monitoring data

Richard A. Smith, Gregory E. Schwarz, and Richard B. Alexander

Abstract. We describe a method for using spatially referenced regressions of contaminant transport on watershed attributes (SPARROW) in regional water-quality assessment. The method is designed to reduce the problems of data interpretation caused

#### <u>SPA</u>tially <u>R</u>eferenced <u>R</u>egression <u>on</u> <u>W</u>atershed Attributes SPARROW water quality model

#### **Potential uses:**

- Predicts mean annual loads, yields, and concentrations
- (and uncertainties) in unmonitored stream reaches
- ..Apportions stream loads to major nutrient sources and upstream watersheds
- ...Assesses the effects of hydrological and biogeochemical processes on nutrient transport and fate in watersheds
- ...Simulates stream water-quality response to future changes in land use and climate
- ..Informs network monitoring and use of watershed management simulation models

#### **SPARROW model components**



#### **SPARROW model components**



Load = C \* Q

#### Long term streamflow observations are essential



#### **Example:**

- Nutrient data retrieved from U.S. databases (EPA, USGS, state agencies) for 21,500 stream sites in SE USA for regional nutrient modeling.
- Of these 21,500, only 3400 sites (15%) with "sufficient" waterquality record (i.e., minimum quarterly sampling over 2 years)
- Of the 3400 "sufficient" sites:



Source: Hoos et al. 2008







- Total organic carbon data retrieved from USGS NWIS & EPA STORET databases, for 1970-2008.
- 1125 sites (of about 5000 sites with TOC data ) met criteria and were used:



#### **SPARROW model components**



#### **SPARROW model components – example sources**

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#### Differences in Phosphorus and Nitrogen Delivery to The Gulf of Mexico from the Mississippi River Basin

RICHARD B. ALEXANDER,\*\*\* RICHARD A. SMITH,\* GREGORY E. SCHWARZ,\* ELIZABETH W. BOYER,\* JACQUELINE V. NOLAN,\* AND JOHN W. BRAKEBILL\* National Water Quality Assessment Program, U.S. Geological Survey, 413 National Center, Reston, Virginia 20192, Department of Environmental Science, Policy, and Management, University of California, Berkeley, California 94720, Maryland-Delaware State Science Center, and U.S. Geological Survey, Baltimore, Maryland 21228

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Alexander et al. 2008

## SPARROW: A Spatially-Explicit Mass-Balance Watershed Model

Quantifies nutrient sources and sinks for annual time periods



## SPARROW model components: example sources, diffuse & point

#### **Example SPARROW significant point & diffuse sources (N model)**

#### Atmospheric Deposition



#### Animal Waste



#### Fertilizer Application



#### **Point Sources**





# **Example SPARROW significant land-to-water delivery variables (N model)**

#### Soil Permeability



#### Mean Air Temperature



#### Artificial Drainage



#### Drainage Density





#### **Example SPARROW significant** aquatic transport factors (N model)

#### Stream Velocity



#### Reservoir Hydraulic Load



#### **SPARROW model components**



Alexander et al. 2002

### **SPARROW** mathematical form

reach-scale mass balance; relate watershed data to monitored loads



- mass balance form; nonlinear processes
- The optimal set of rate coefficients are estimated, balancing the nutrient mass of the source inputs, stream loads, and storage/loss on land and in water.
- All calibrated parameters are simultaneously determined to best fit the data.

#### SPARROW model components aggregated reach-by-reach

+

Load leaving the reach

=

Load generated within upstream reaches and transported along the reach via the stream network Load originating within the reach's incremental watershed and delivered to the end of reach segment



#### **SPARROW model components**



**Diffuse & Point Sources** 

**Terrestrial Landscape** 

**Aquatic Landscape** 

Spatial referencing is accomplished by linking all data to a geographically defined stream-reach data set. Model Predictions 62,000 Stream Reaches

#### SPARROW nutrient model calibration observed versus predicted riverine yields of N & P



#### Alexander et al. 2008

#### **Development of SPARROW-Carbon models**

- What changes are occurring, and why? Trends in C concentrations (& fluxes) in rivers suggest changes in terrestrial C reserves.
- How much C is stored in aquatic systems anyway, and how much is delivered to coastal waters?
- How will changes in basic terrestrial ecosystem processes affect riverine C transport?

#### organic carbon delivered to upland streams

#### Dissolved organic matter (DOM) in streamwater is a fundamental water quality characteristic that:



- Affects ecosystem status -- important in the energy budget, food chains, primary productivity, & redox status.
- Affects the acid-base status of many low-alkalinity freshwater streams.
- Affects fate & transport of other solutes (e.g. trace metals, nutrients)

#### organic carbon delivered to coastal zone

More relevant to OCB group, developed initial, national-scale SPARROW model to explore how much organic carbon (total and dissolved) is transported in rivers and streams and ultimately delivered to the coastal margins of the conterminous US.



*Figure by T. Brown, taken from https://www.llnl.gov/ str/March06/Brown.html* 

#### organic carbon delivered to coastal zone

Results from our *initial* SPARROW carbon *model formulation* will be available in early 2011 in a USGS OFR.

Refinements of predictions of TOC, as well as DOC & DIC are underway.

Making estimates of C delivery to coastal reaches available to OCB synthesis groups.



An initial SPARROW Model of Land Use and In-stream

Controls on Total Organic Carbon in Streams of the

**Conterminous United States** 

By Jhih-Shyang Shih, Richard B. Alexander, Richard A. Smith, Elizabeth W. Boyer, Gregory E. Schwarz, and Susie Chung

Open-File Report 20XX-XXXX

U.S. Department of the Interior U.S. Geological Survey SCCooper Review 05 November 2010

#### **Calibration sites currently included in TOC model**

- Total organic carbon data retrieved from USGS NWIS & EPA STORET databases, for 1970-2008.
- 1125 sites (of about 5000 sites with TOC data ) met criteria and were used:



#### **Terrestrial C sources: proxies by land area**

Carbon source	Definition
Agricultural land	Area of row crops; small grains; fallow;
0	pasture; and orchards-vineyards-other.
Forest land	Area of deciduous, evergreen, mixed forest.
Range and grass lands	Area of shrub lands and herbaceous grass
	lands.
Urban land	Area of low-intensity residential, high-intensity
	residential, and commercial-industrial-
	transportation land; urban-residential grasses.
Wetlands	Area of woody wetlands; emergent herbaceous
	wetlands.
Photosynthesis in	Based on total phosphorus concentration, solar
streams	irradiance, and channel dimensions.
Photosynthesis in	Estimated surface area. <sup>2</sup>
reservoirs	32

### Aquatic C sources: in-stream C production

- 1<sup>st</sup> approximation of C production via photosynthesis accounts for:
  - Reach-level variation in total P (from SPARROW) and chlorophyll
  - Geographical variation in incident light
  - Light attenuation by chlorophyll and non-algal material over river depth
  - Rate of light energy trapping by chlorophyll
  - Rate of carbon fixation per unit of light energy trapped
- Adapted from Smith (1980, *Ecological Modeling*, a mechanistic model of primary production in natural waters), linked to Van Nieuwenhuyse & Jones (1997, Can J. Fish. Aquat. Sci, an empirical model of stream chlorophyll)

#### **Aquatic C sources: in-stream C losses**



SPARROW estimates of instream, net removal rate for TOC compared w/ other sparrow models. The net rates of TOC removal in streams decrease with increases in water depth.

B contrast, the net removal rate for reservoirs was estimated to be zero and was not statistically significant. This suggests that production and loss processed may be approximately balanced on average. The estimated TOC mass-transfer coefficient for streams was 0.034 m  $day^{-1}$  (12.4 m yr<sup>-1</sup>), which corresponds to the series of reaction rate coefficients (units of per day) as shown for a range of water depths in streams in the river network.

#### **TOC model calibration, to 1125 sites**



(kilogram per year)

Model accuracy plots for total organic carbon loadings from SPARROW model.

10000

(kilogram per square kilometer per year)

A) observed and predicted load (mass/time);  $R^2 = 0.93$ 

B) observed and predicted yield (mass/area/time);  $R^2 = 0.77$ 

	Forest,
	deciduous
	Forest,
Model includes	Forest mixed
WIGHEI IIICIUUES	Urban
statistically	Wetlands
statistically-	Tra estencem
• • • •	n-stream photosynthesi
significant	photosynthesi
	Soil
Sources, Land-	permeability
	Precipitation
to_water	A
	Artificial
d alter a ser	Drainage
aenvery	density
	Land slope
factors, and In-	-
	In-stream
stroom factors	carbon remov
su cam factors	Log root mean
	square error

Parameter	Coefficien t units¹	Estimate	Standard Error	t value	Level of Statistic Significance, p
Agriculture	kg km <sup>-2</sup> yr <sup>-1</sup>	1454	167	8.65	0.000
Forest, deciduous	kg km <sup>-2</sup> yr <sup>-1</sup>	1061	191	5.54	0.002
Forest, evergreen	kg km <sup>-2</sup> yr <sup>-1</sup>	1378	167	8.21	0.000
Forest, mixed	kg km <sup>-2</sup> yr <sup>-1</sup>	2568	627	4.09	0.001
Urban	kg km <sup>-2</sup> yr <sup>-1</sup>	4777	778	6.14	0.000
Wetlands	kg km <sup>-2</sup> yr <sup>-1</sup>	25,008	2529	9.89	0.000
In-stream photosynthesis	dimensionles	1.10	0.13	8.67	0.000
Soil permeability	s log (cm hr <sup>-1</sup> )	-0.1407	0.0368	-3.82	0.000
Precipitation	cm	0.0047	0.0006	7.51	0.000
Artificial	percent area	0.0116	0.0031	3.82	0.001
Drainage	log (km <sup>-1</sup> )	0.4407	0.0545	8.08	0.000
Land slope	log (percent)	-0.0023	0.0040	-0.58	0.5620
In-stream carbon removal	per day	0.0338	0.0036	9.31	0.000
Log root mean	per any	0.540			
Number of observations		1125			
Adjusted R- squared		0.928			
Yield R- squared		0.77			

#### generates hypotheses about importance of various land-uses

Parameter	Parameter Coefficien t units <sup>1</sup>	
Agriculture	kg km <sup>-2</sup> yr <sup>-1</sup>	1454
Forest, deciduous	kg km <sup>-2</sup> yr <sup>-1</sup>	1061
Forest,	kg km <sup>-2</sup> yr <sup>-1</sup>	1378
Forest, mixed	$kg km^{-2} yr^{-1}$	2568
Urban	$kg km^{-2} yr^{-1}$	4777
Wetlands	kg km <sup>-2</sup> yr <sup>-1</sup>	25,008

Among these sources with comparable units, we find that wetlands make the largest mass contribution per unit area (or yield) to the stream organic carbon load, followed in declining order by urban lands, mixed forests, agricultural lands, evergreen forests, and deciduous forests .

#### generates hypotheses about importance of various land-uses

Watershed	Percentiles of total organic carbon yield exported from SPARROW watersheds <sup>1</sup> (kg ha <sup>-1</sup> yr <sup>-1</sup> )						Literature Yields <sup>2</sup> (kg ha <sup>-1</sup> yr <sup>-1</sup> ) <sup>3</sup>	
land-cover type	No. of watersheds	10 <sup>th</sup>	25 <sup>th</sup>	50 <sup>th</sup>	75 <sup>th</sup>	90 <sup>th</sup>	Range of values	
Agriculture	1,841	15.1	19.1	24.5	34.7	59.9	14.1-19.5 <sup>2</sup>	
Forest Deciduous	70	12.1	14.0	16.2	21.4	34.0	4-80 <sup>4</sup>	
Forest Evergreen	248	13.6	16.1	20.3	28.6	56.0	14-500 <sup>4</sup>	
Range	3,203	0.1	0.3	0.8	2.3	8.2	4-13 <sup>4</sup>	
Urban	143	36.3	48.3	73.3	108.6	329.3	19–146 <sup>4</sup>	
Wetlands	191	160.3	276.4	476.3	801.6	2180.0	50–220⁵	

Results are generally consistent with the magnitude and relative ordering of organic carbon exports for small catchments in these land use types.

<sup>a</sup> The land-cover types represent the following percentages of the land area in SPARROW watersheds: agricultural land (>90%), forest (>95%), urban (>90%), wetlands (>95%), and range (95%). <sup>b</sup>Dalzell et al. 2007. <sup>c</sup>Hope et al. 1994; North America, New Zealand, Russia (total organic carbon). <sup>d</sup>Mulholland 2003 (dissolved organic carbon).

#### **Residuals to consider bias in predictions**



- -2.0 -1.0
- -1.0 0.0
- 0.0 1.0
- 1.0 2.0
- > 2.0

Studentized residuals for sites. Negative residuals indicate over-prediction and positive values indicate under-prediction of the mean annual total organic carbon stream load. Evidence of prediction biases in selected regional watersheds,

Overpredication at sites in areas of the Pacific Northwest, western Texas, Ohio basin, and the Southeast.

- Underprediction in southern California, central United States, and the extreme Northeast.
  - Related to temporal differences in the environmental conditions reflected by the period of record covered by the various monitoring stations.

#### **TOC simulations**



#### TOC incremental yield

Percentage 0 to 20 20 to 40 40 to 60 60 to 80 80 to 100

#### **TOC Source Shares for Selected Parameters**



Expressed as a mean of the reach-level source share percentages: The stream photosynthesis source is the largest overall source (22.4%), followed by (in order) wetlands (19.9%), agriculture (19.9), evergreen forest (19.7), mixed forest (6.4), deciduous forest (7.5), and urban land (4.3).

#### **TOC Yields and Source Shares Delivered to Coastal Areas** from seven major regional drainages



#### **Relation between TOC and DOC in water regions**



			Mean Concentration (mg/L)				
HUC2	Name	Number of Sites	DOC	тос	Ratio		
1	Northeast	34	13.65	14.24	0.90		
2	Mid-Atlantic	131	4.58	5.63	0.83		
3	Southeast	142	9.86	11.15	0.86		
4	Great Lakes	66	8.62	9.75	0.89		
5	Ohio	64	3.49	4.59	0.79		
6	Tennessee	27	3.24	4.29	0.80		
7	Upper Miss.	52	6.60	8.80	0.76		
8	Lower Miss.	30	6.70	8.71	0.78		
9	Souris-Red-Rainy	23	13.41	14.51	0.92		
10	Missouri	100	7.88	10.52	0.79		
11	Red-White	44	5.53	7.48	0.80		
12	Texas Gulf	34	6.70	8.34	0.83		
13	Rio Grande	8	5.33	9.52	0.74		
14	Upper Colorado	14	5.33	8.60	0.77		
15	Lower Colorado	16	6.84	17.31	0.73		
16	Great Basin	16	5.56	6.35	0.85		
17	Pacific Northwest	37	2.89	3.41	0.85		
18	California	22	5.87	7.08	0.85		

### Conclusions

- TOC loadings have been estimated across USA using the SPARROW model. Refinements are underway. Other carbon models (DOC, DIC) underway.
- Results available to OCB synthesis efforts
- SPARROW models allow us to:
  - Quantify carbon fluxes and sources over space & time, with estimates of uncertainty
  - Explore impacts of land use change and climatic variability
  - Consider scenarios of energy policy & land management

#### **Current efforts to improve predictability**

- More calibration sites
- More headwater sites
- Improved load estimates

#### **Current efforts to improve predictability**

# OC <u>sources</u>: net primary productivity, Soil C:N ratio, soil nitrogen, other soil elements



Boyer et al., in prep.

#### **Current efforts to improve predictability**

# **<u>Aquatic Transport</u>:** Attenuation of sediments in reservoirs, geochemical reactions in streambed



Relationships to streambed geochemical environment control water column DOC concentrations

McKnight et al. 2002

#### At the end of the day



- Transfers of C via land-to-water are orders of magnitude lower than transfers from land-toatmosphere.
- Small shifts in the C balance of the terrestrial landscape will result in disproportionately-large changes in aquatic C export.
- Important implications for water quality & ecosystems.



#### Beth Boyer ewb100@psu.edu

#### **SPARROW MODEL**



Home page: http://water.usgs.gov/nawqa/sparrow Documentation (theory, application, user manual): http://pubs.usgs.gov/tm/2006/tm6b3/ Software: http://water.usgs.gov/nawqa/sparrow/sparrow-mod.html