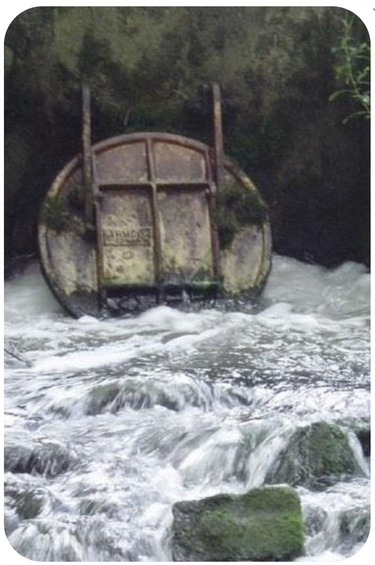
Insights from a Spatially and Temporally Resolved Nanoparticle Fate Model



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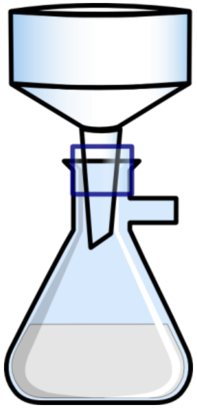
To assess the environmental risk of engineered NPs, we need models that capture NP transport and transformations in soil, water, & sediment

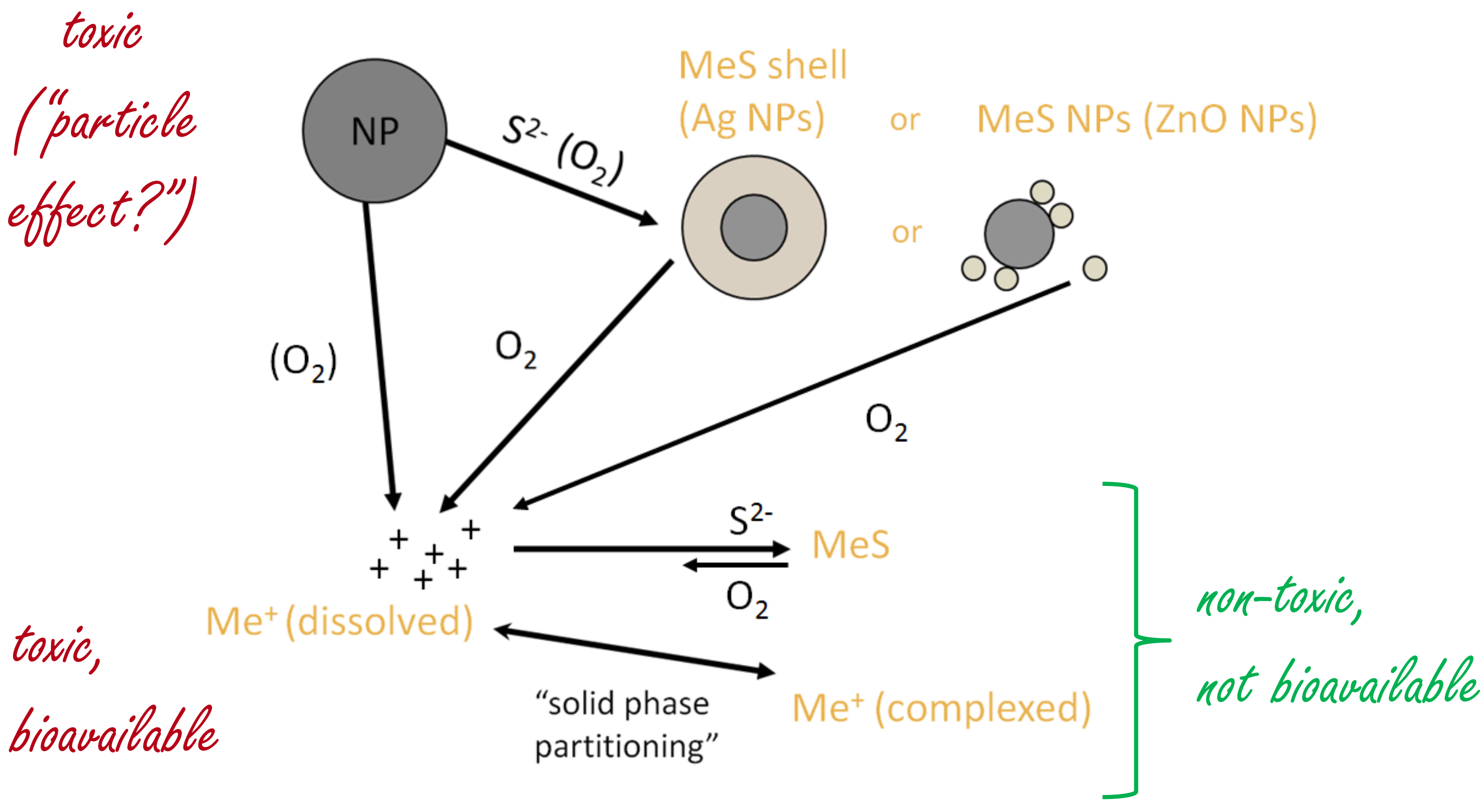


But what environmental processes and model features are essential?

1. Sediments determine NP transport

& hydrology determines sediment transport

2. Transformations affect fate



Objectives

- Model the fate of NPs and their transformation by-products in a freshwater watershed at high spatial and temporal resolution

- Investigate the effect of common simplifying assumptions on NP fate model predictions

Model Framework

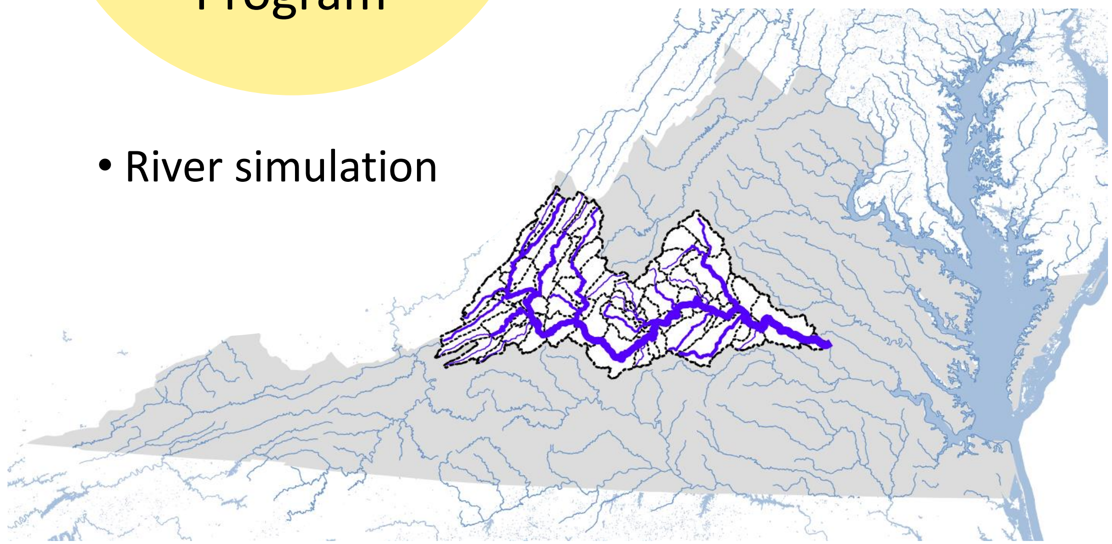
WSM:
Chesapeake Bay Watershed Model (HSPF)

→

WASP7:
Water Quality Analysis Simulation Program

- Meteorology
- Land simulation (crop runoff)
- Stream hydrology
- Point sources (WWTP effluent)

- River simulation

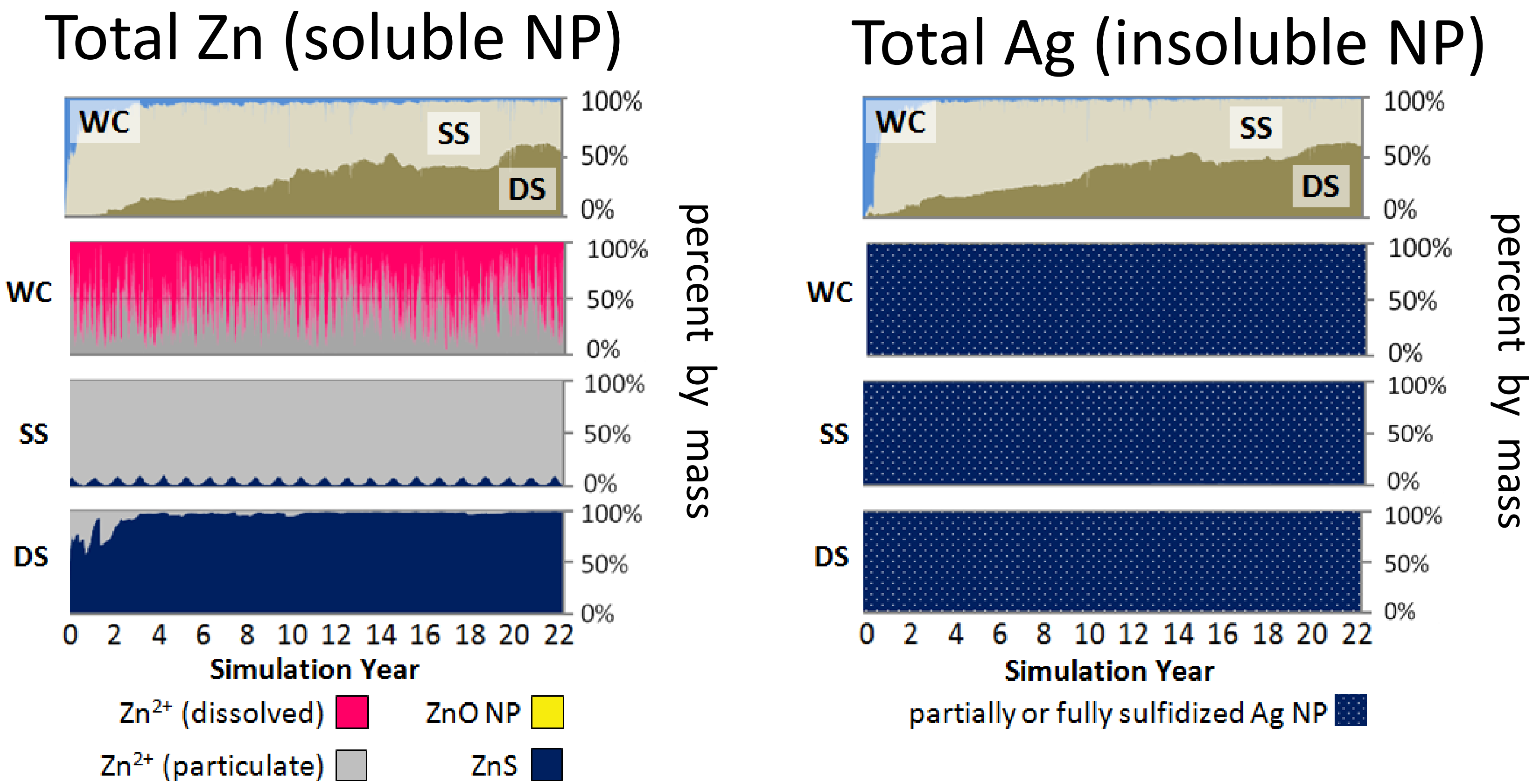


Key Model Features	Key Simplifying Assumptions
Hydrologic simulation: • WWTP locations & discharges • Stream velocity, volume, & depth • Daily time step	• All NPs are bound to larger particles • In the river, NPs transport with silts/fines*
Agricultural simulation: • historical land use, meteorology, and biosolids application data • models crop runoff to river	ZnO and Ag NP speciation in effluent and biosolids were assumed or modeled*
Dynamic sediment transport as a function of stream flow	Moderate spatial resolution: 30 km average stream segment length
Two sediment layers, oxic (surface) and anoxic (deep)	Constant loading scenario (Gottschalk et al., 2009)
Daily variation in temperature and oxygen	No spatial variation in temperature, oxygen
Temperature, oxygen, and sulfide-dependent transformations of NPs and their transformation by-products	Size-independent particle dissolution*

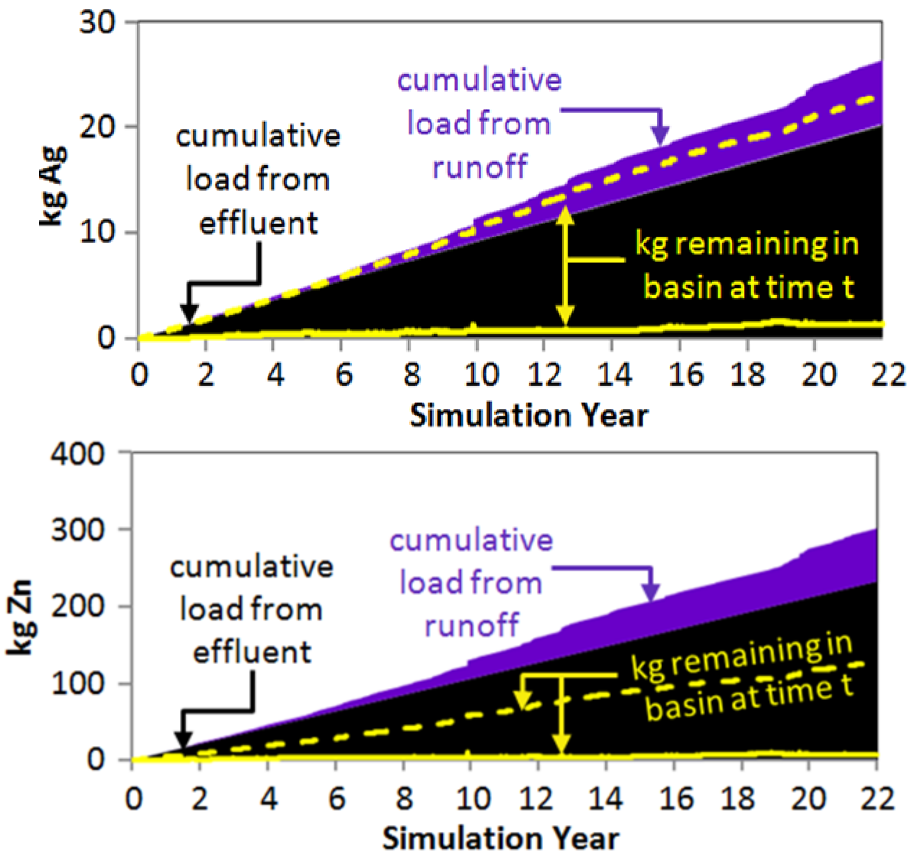
**model found to be insensitive to these assumptions*

RESULTS

- Metals accumulate in sediments
- ZnO NPs dissolve, sulfidized Ag NPs persist

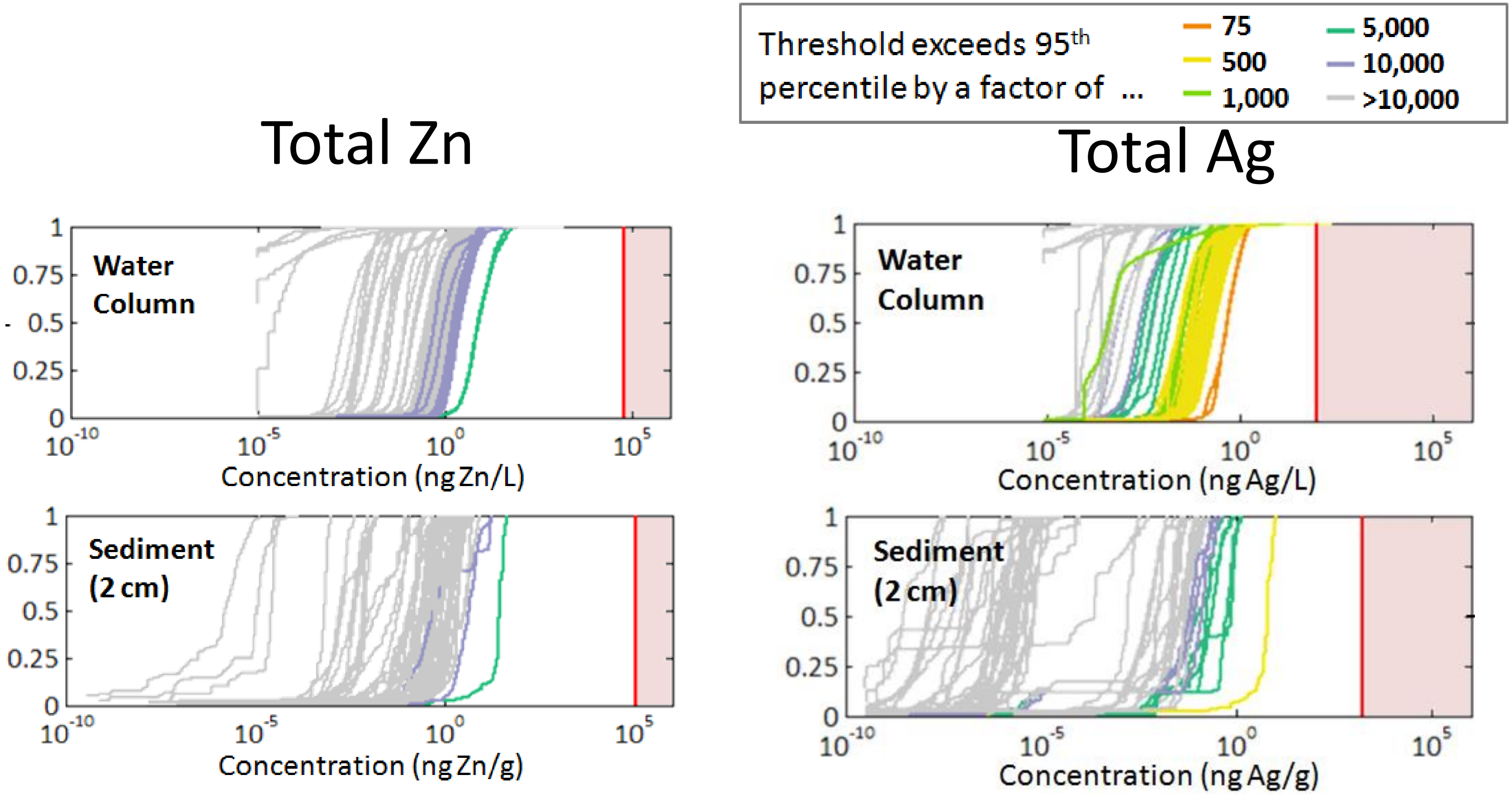


- Runoff is roughly a quarter of total stream loads
- Metal mobility is surprisingly high (<6% accumulation)
  - NP-derived Zn is twice as mobile as Ag

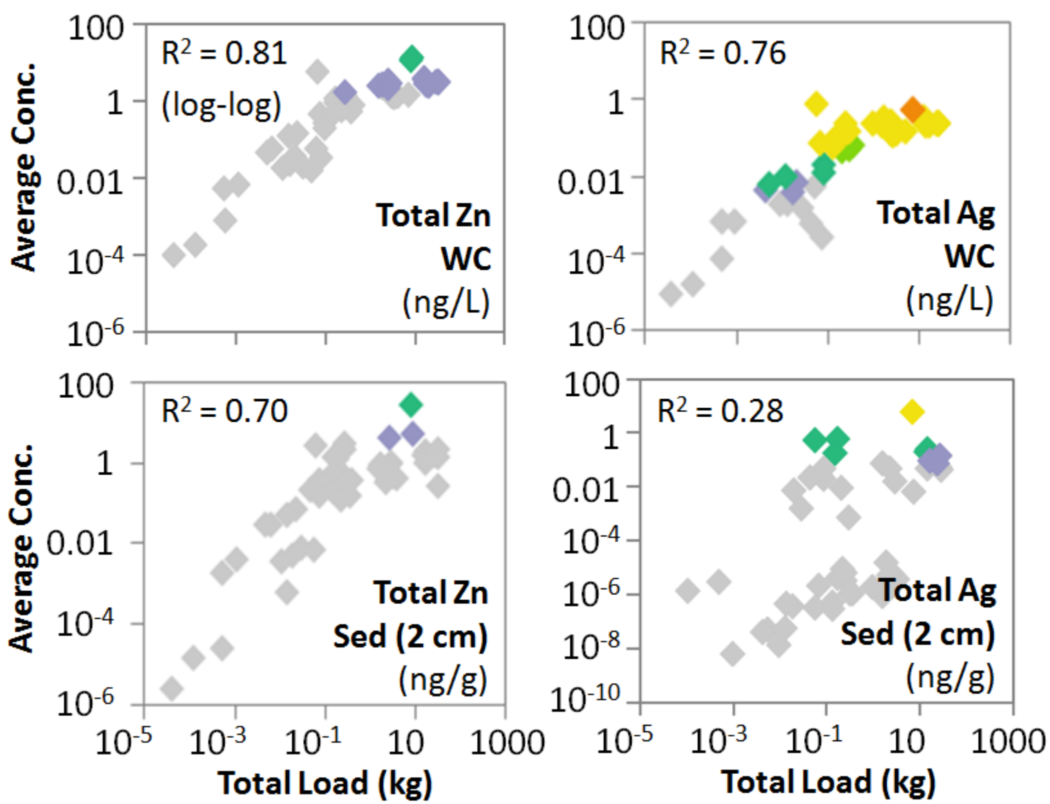


Setting deposition and resuspension rates to commonly used constant values dramatically overpredicted accumulation

- Spatial variation is very high! (hot spots!)
- PECs never exceed EPA regulatory thresholds for total metals

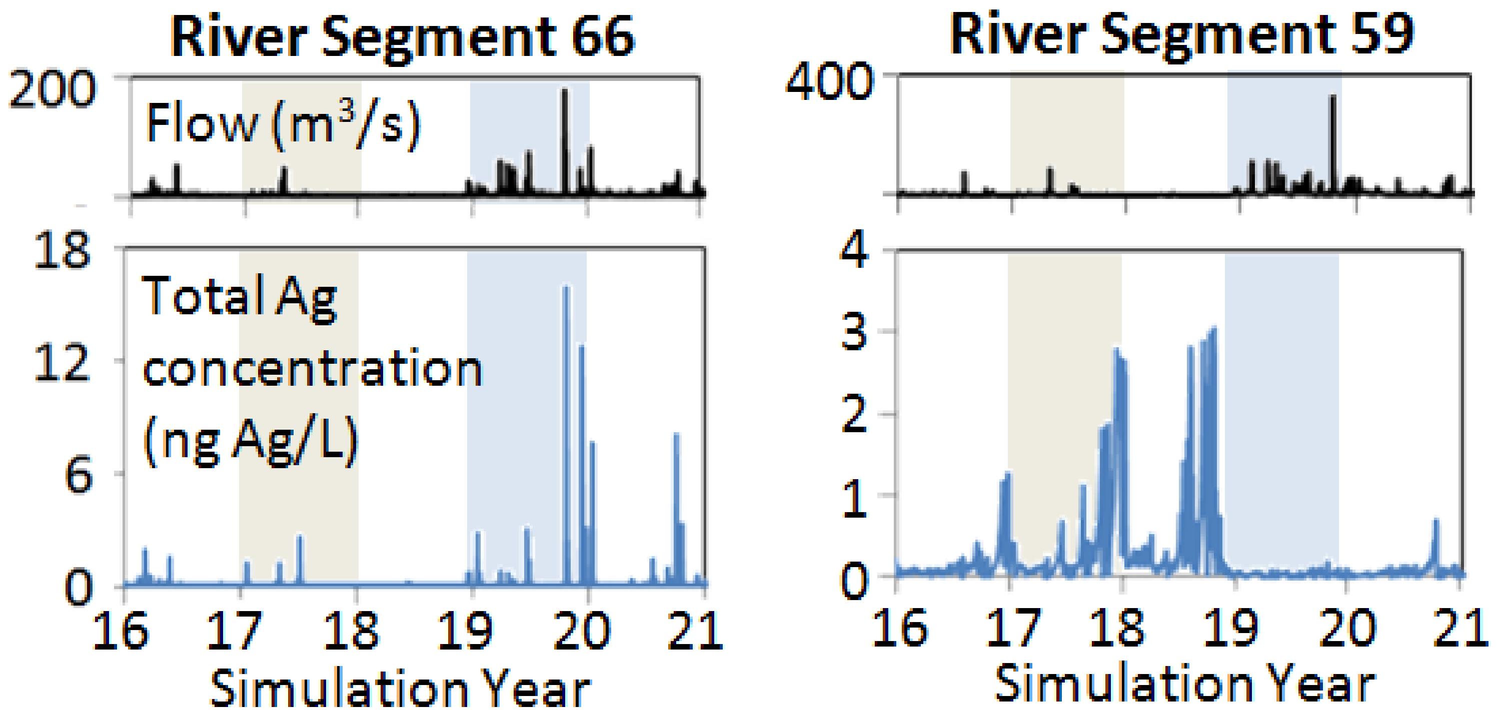


Load Imperfectly Predicts Concentration



The highest PECs occur in segments with high loads & *high sediment deposition*

Dilution during high flows does not alone predict concentrations



CONCLUSIONS

Hydrology, sediment transport dynamics, chemical transformations, and spatial variation in loads strongly impact Ag and ZnO NP fate in a watershed.

Spatial variability appears more significant than temporal variability

Models that exclude these features may be limited in their ability to characterize environmental risks from these emerging chemical pollutants.


Thank You

Common assumptions bias risk predictions for many NP fate models!

Assumption	Effect(s)
Spatially- and temporally invariant sediment transport	• Overpredicts accumulation in sediments • Mis-identifies "hot spots"
Ignoring chemical transformations (Ag and ZnO NPs)	• Predicts PECs for irrelevant species • Underpredicts NP mobility for soluble species
Regional & national spatial averaging	• Cannot identify regions of high local accumulation or their PECs
Long simulation time steps (monthly, yearly) or steady state	• Overpredicts accumulation in sediments by reducing variability in flow and sediment transport • Cannot capture acute peaks in PECs
No agricultural runoff (or spatially & temporal unresolved runoff models)	• Underpredicts PECs by underpredicting loads • Acute peaks in PECs during rainfall events will not be observed

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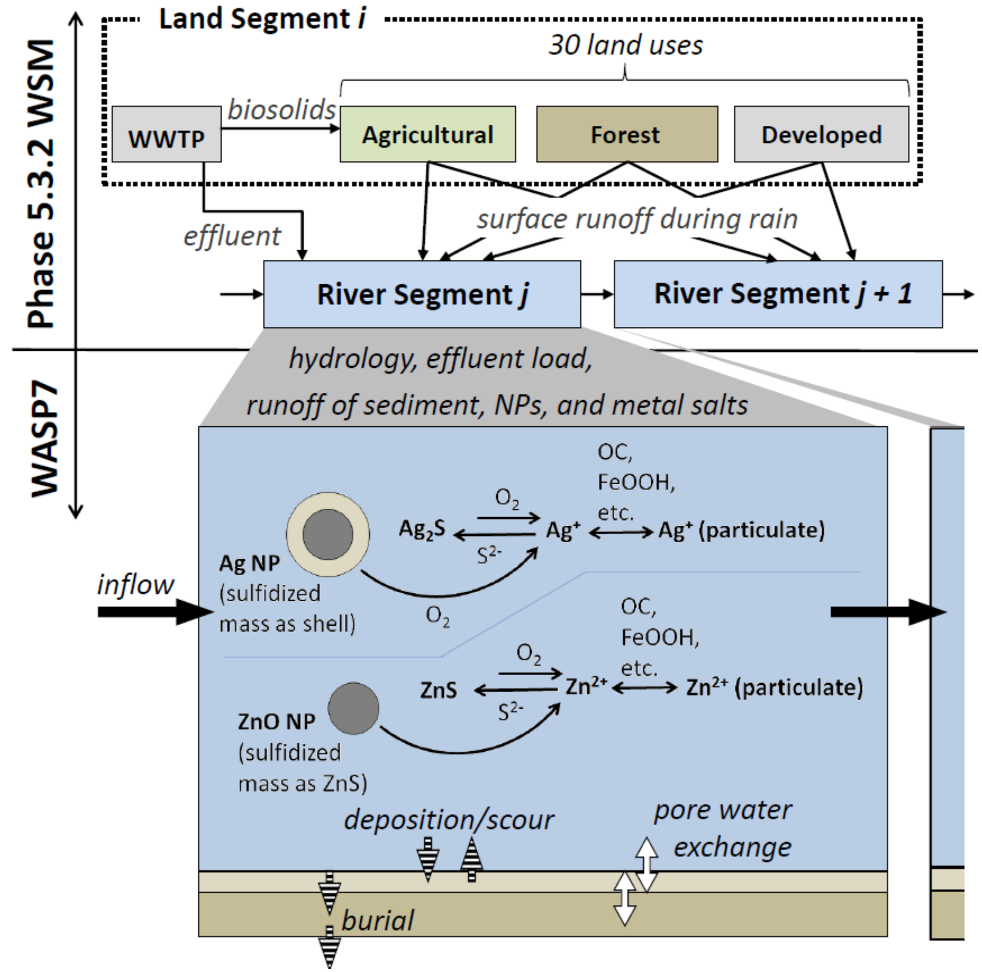
Land Segment i
30 land uses
WWTP
biosolids
Agricultural
Forest
Developed
effluent
surface runoff during rain
River Segment j
River Segment j + 1
Phase 5.3.2 WSM
WASP7
hydrology, effluent load,
runoff of sediment, NPs, and metal salts
inflow
Ag NP
(sulfidized
mass as shell)
O2
Ag2S
S2-
Ag+
OC,
FeOOH,
etc.
Ag+ (particulate)
ZnO NP
(sulfidized
mass as ZnS)
ZnS
Zn2+
Zn2+ (particulate)
deposition/scour
pore water
exchange
burial