Applications of radium isotopes to studies of submarine groundwater discharge

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Definition of SGD:

Submarine groundwater discharge (SGD) is the flow of water through continental margins from the seabed to the coastal ocean, *with scale lengths of meters to kilometers*, regardless of fluid composition or driving force.

This definition eliminates bedform-induced flow and shallow bioturbation and bioirrigation.

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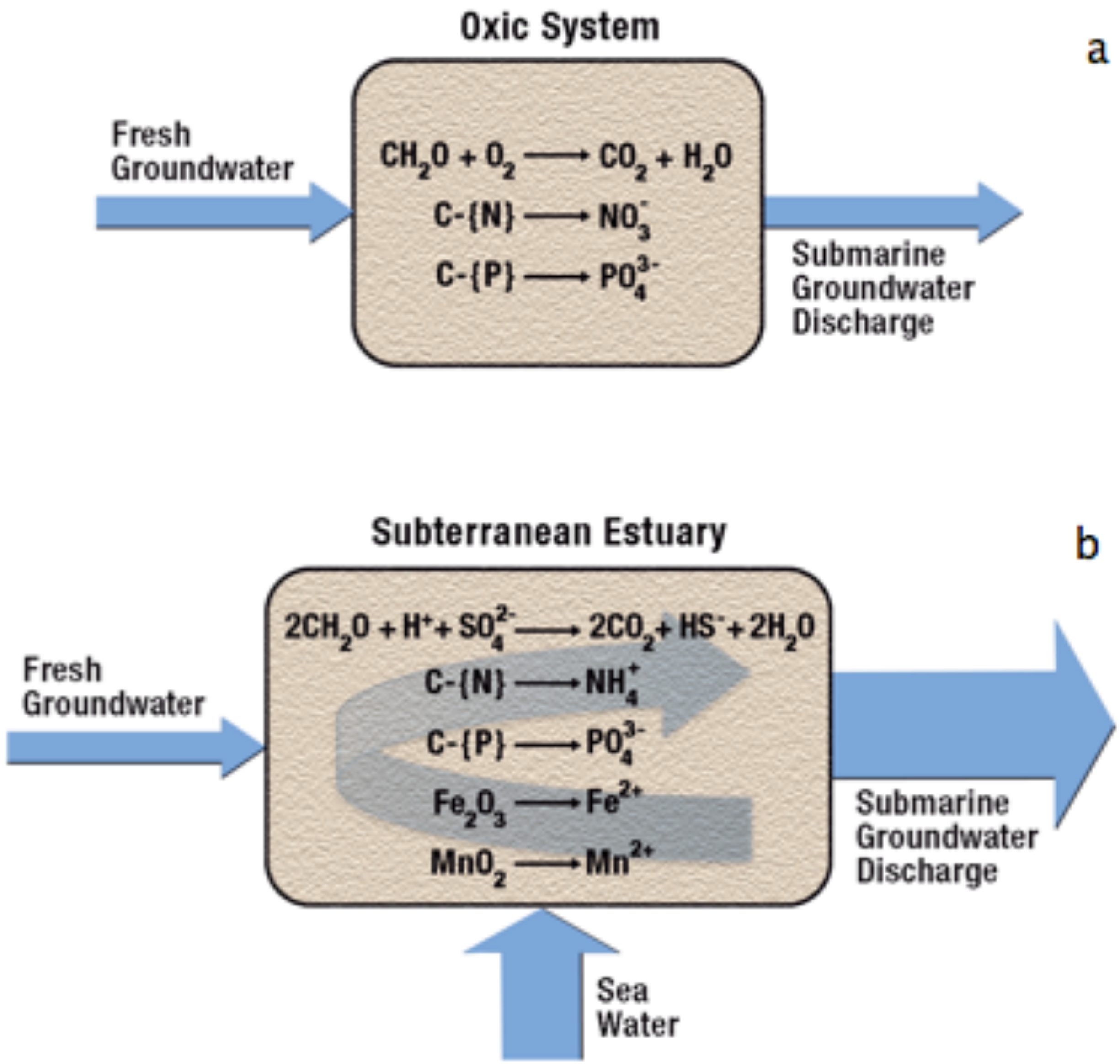
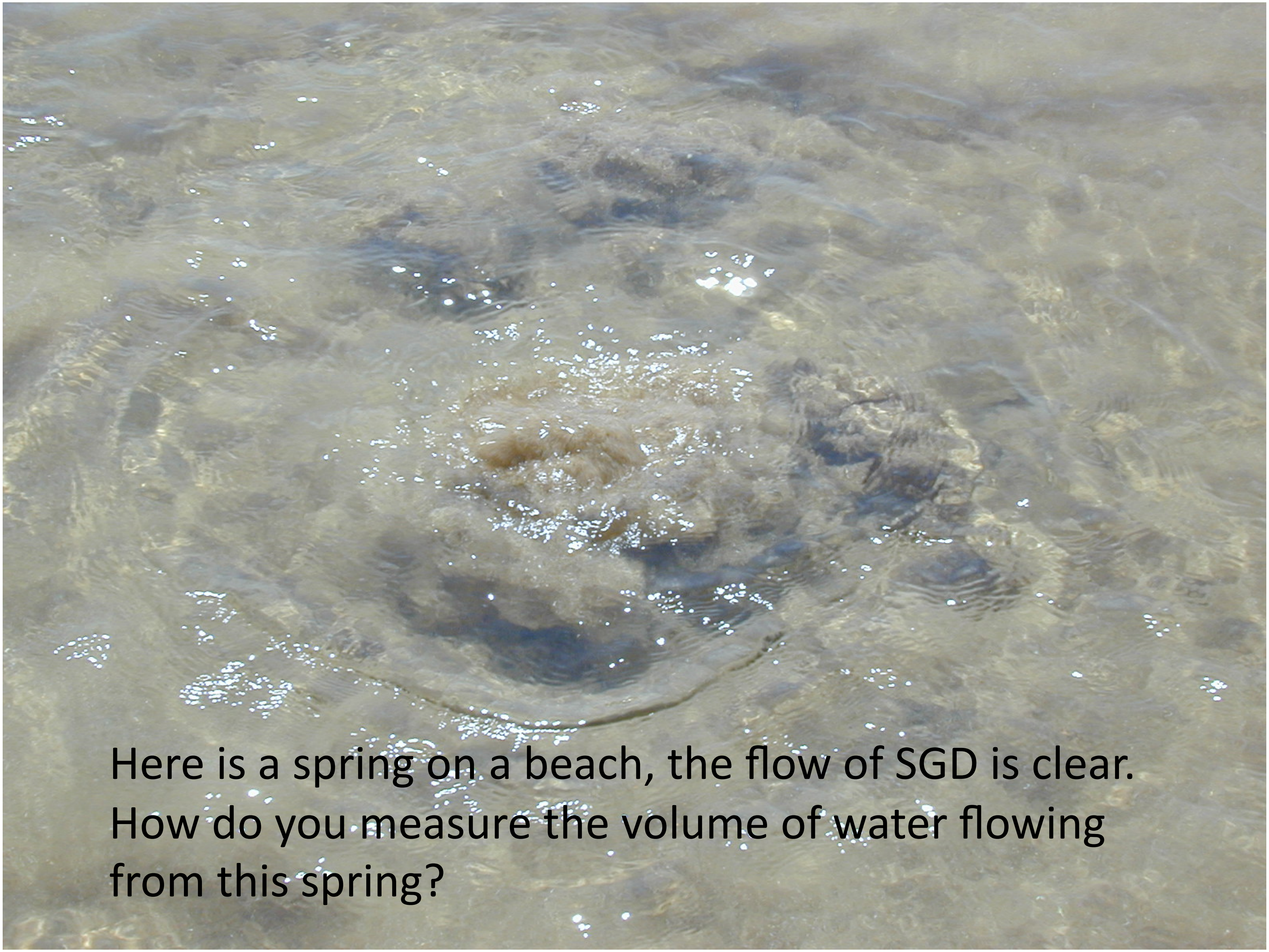
It is important to recognize that SGD can be fresh or salty water and that the composition is usually very different from the water that entered the aquifer. SGD is usually enriched in nutrients, metals, and carbon. The mixing zone of fresh and salty groundwater is called the ***subterranean estuary***.


Oxic System
a
Fresh Groundwater
CH2O + O2 → CO2 + H2O
C-{N} → NO3-
C-{P} → PO4 3-
Submarine Groundwater Discharge
Subterranean Estuary
b
2CH2O + H+ + SO4 2- → 2CO2 + HS- + 2H2O
C-{N} → NH4+
C-{P} → PO4 3-
Fe2O3 → Fe2+
MnO2 → Mn2+
Fresh Groundwater
Submarine Groundwater Discharge
Sea Water

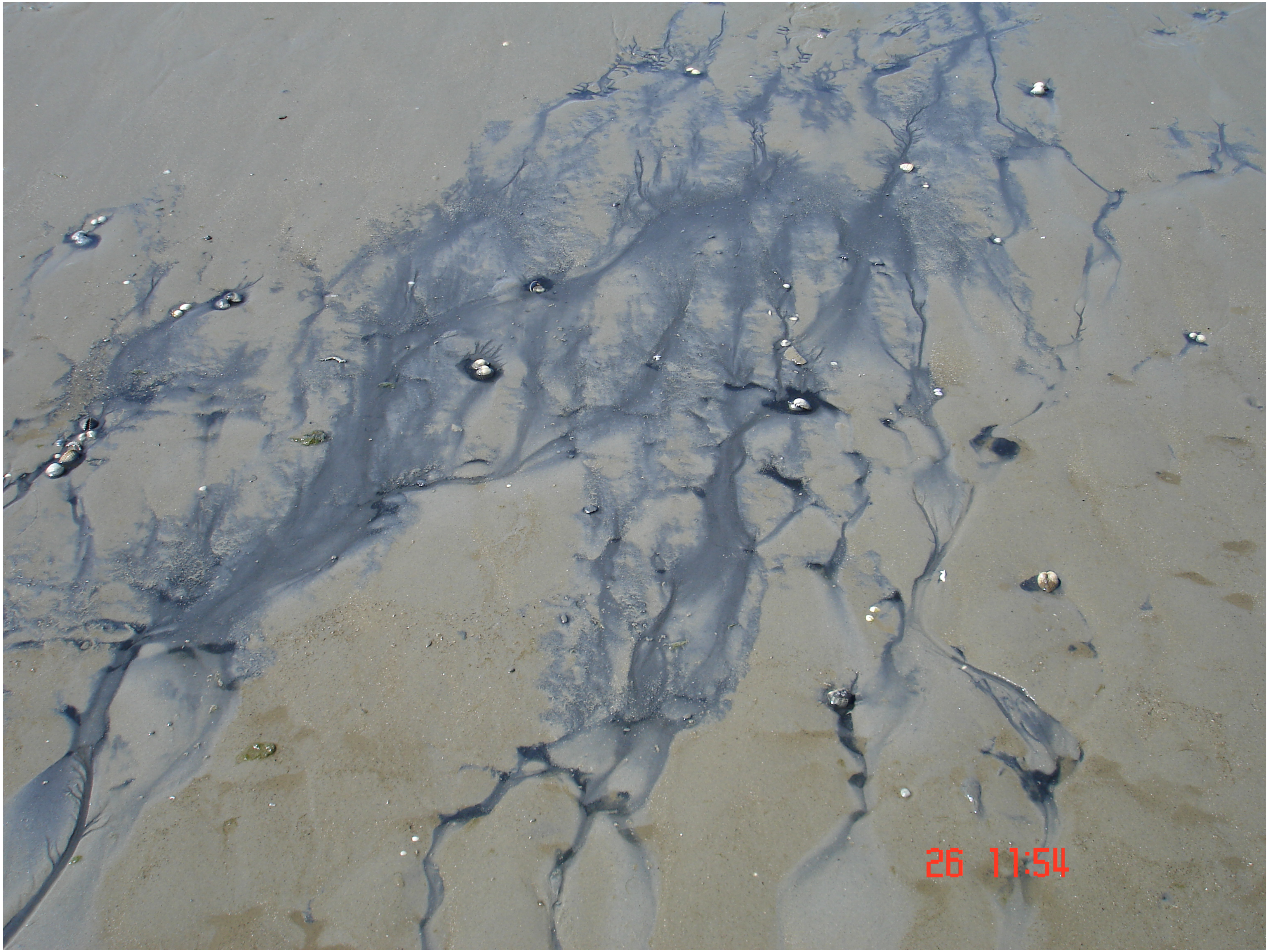


Here is a spring on a beach, the flow of SGD is clear. How do you measure the volume of water flowing from this spring?

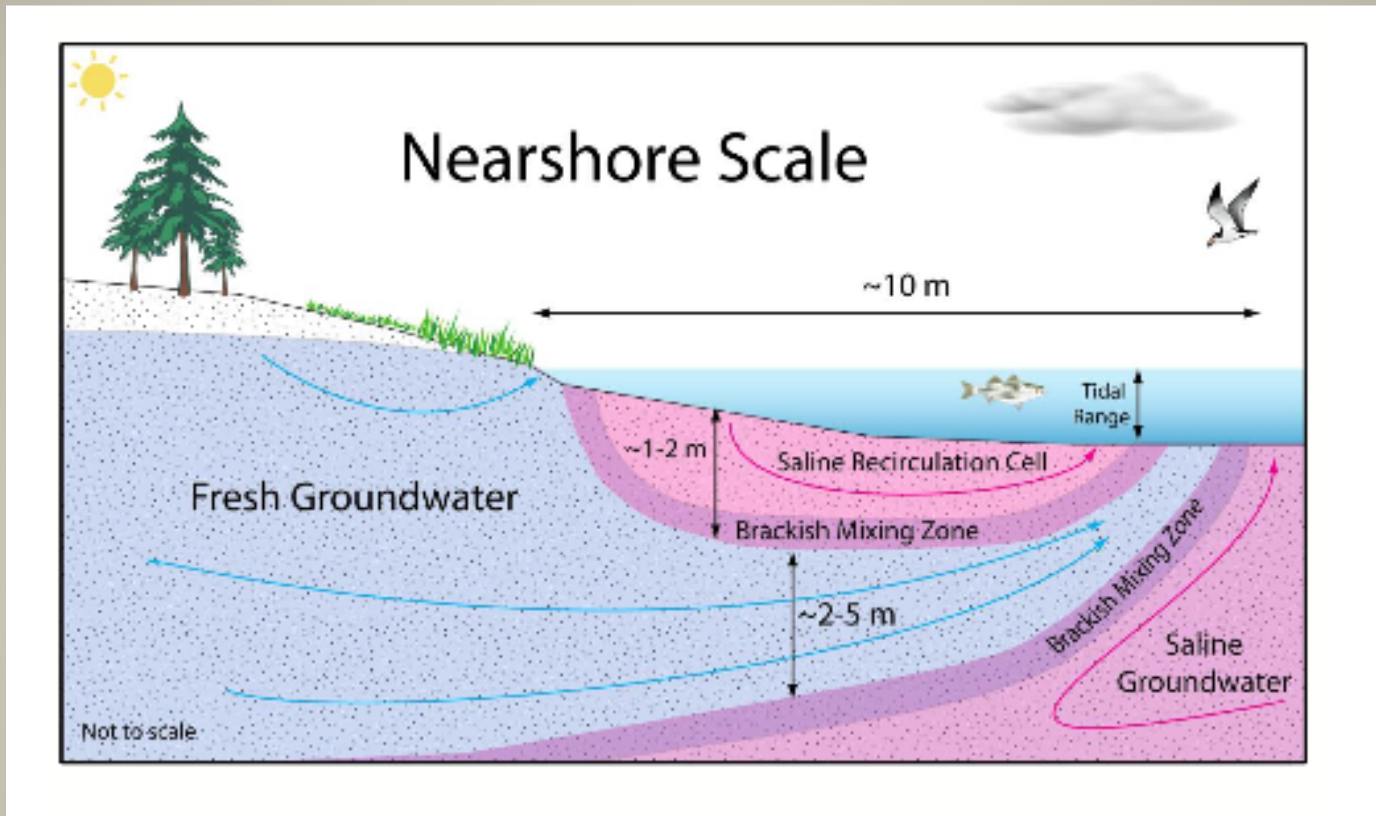
Crescent Beach spring, Florida east coast

How do you measure the volume of the water flowing from this spring, which is 40 meters deep?

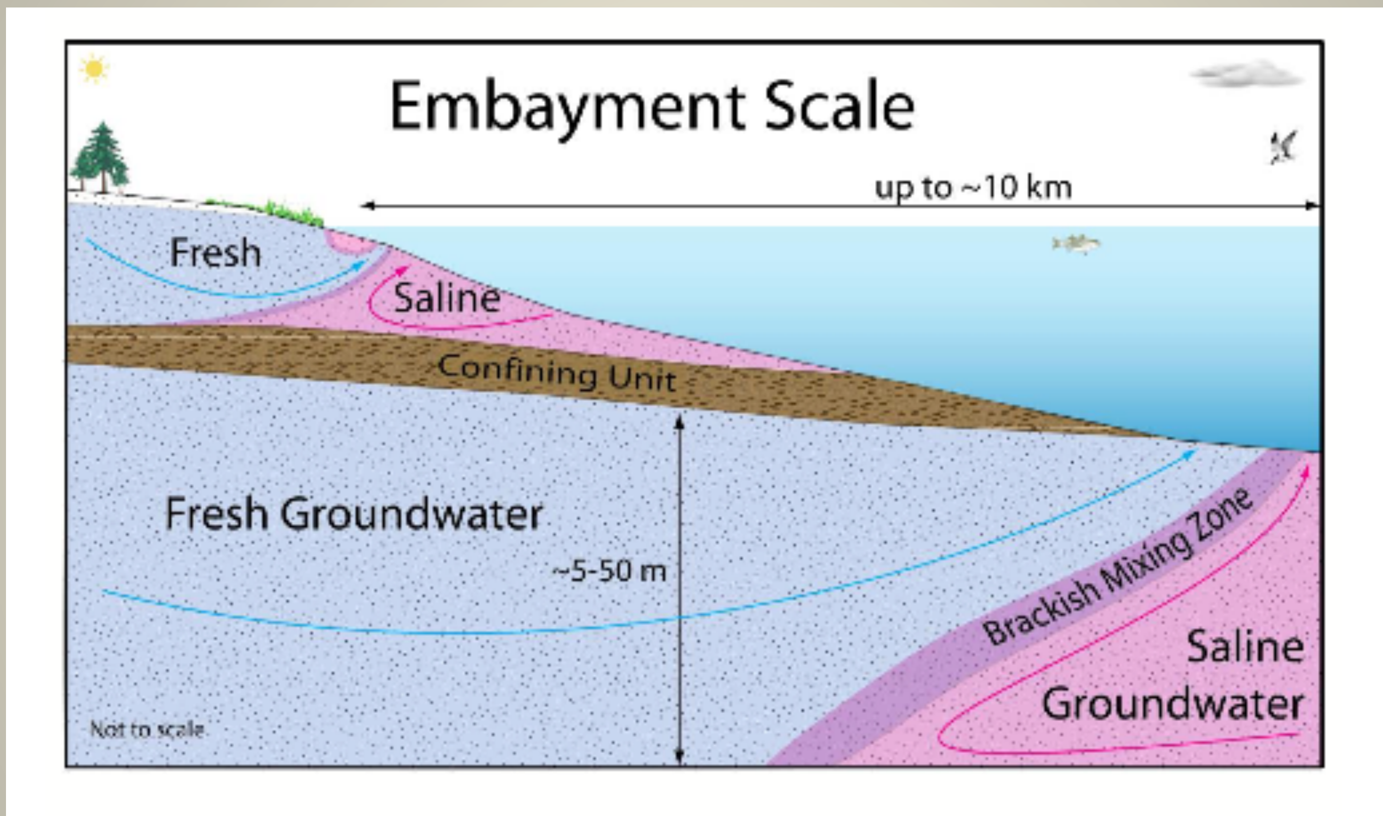
Even if you could measure the volume of SGD entering the ocean from obvious springs, you would miss the >95% of SGD that enters from unseen sources.


26 11:54

The objective of this lecture is not only to teach you about submarine groundwater discharge, but also to illustrate how very simple models based on radionuclides can make powerful statements about the environment.



from Bratton, Journal of Geology (2010) **118**, 565–575.



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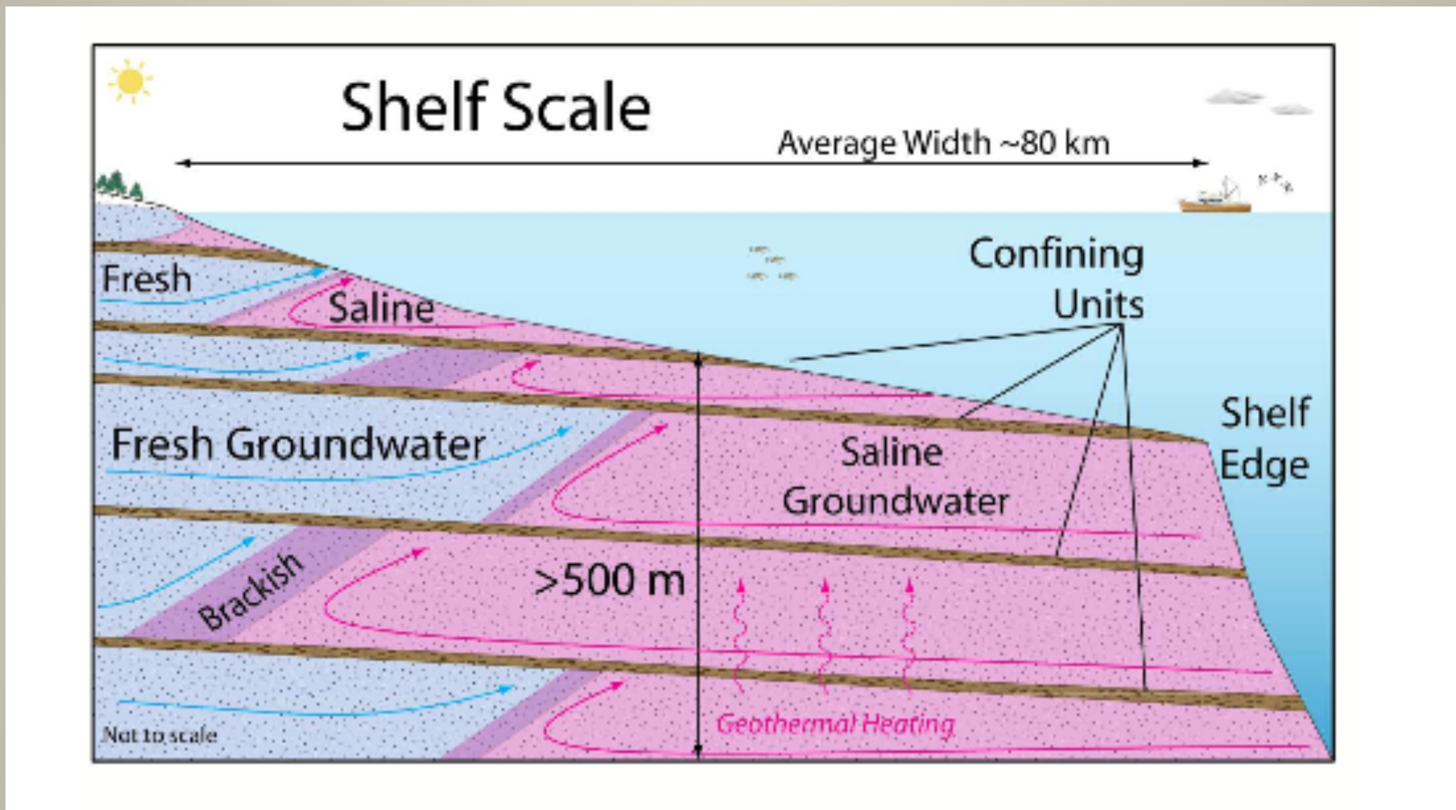

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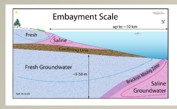
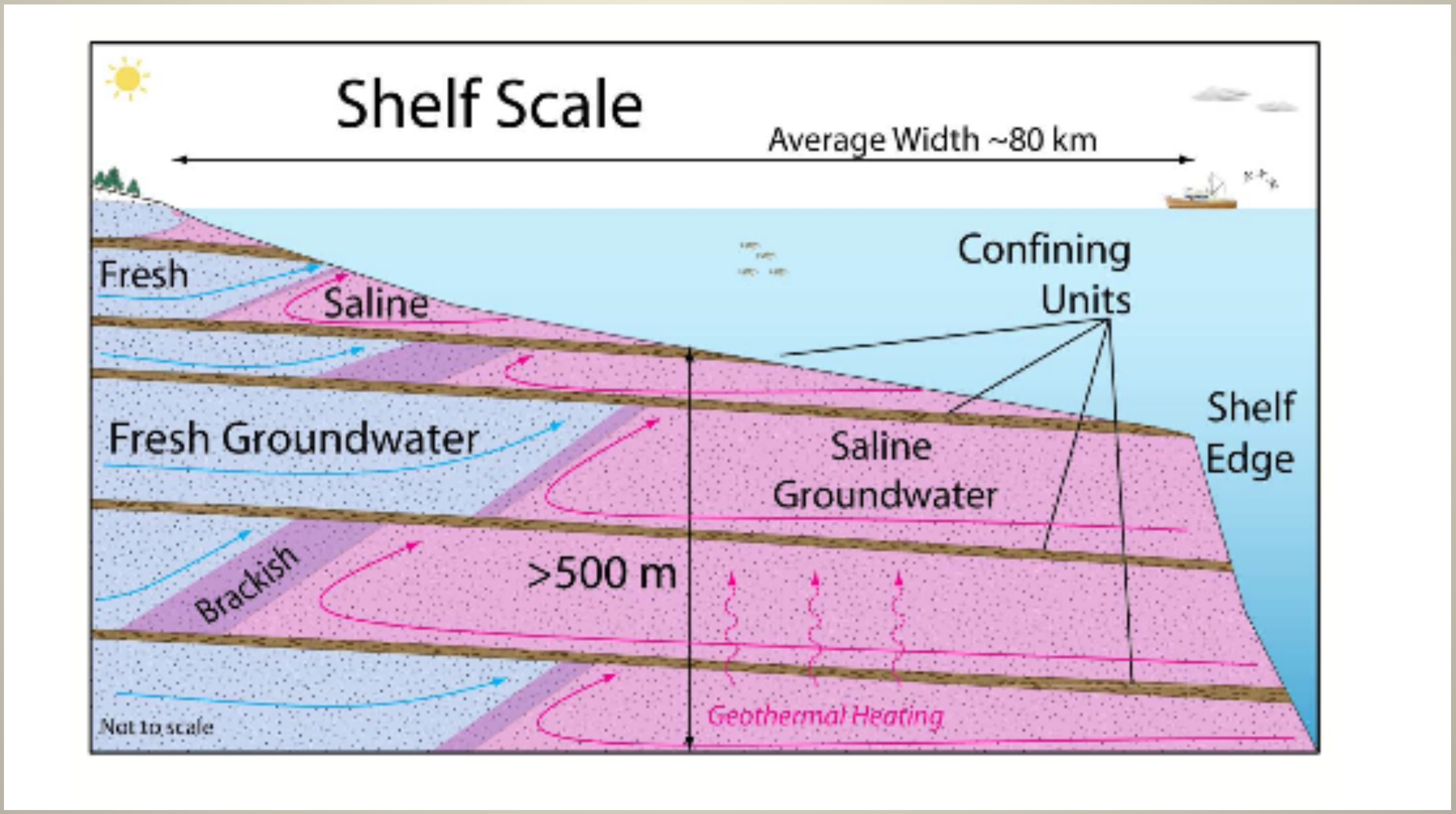
- Nearshore Scale x 100, where most SGD studies are conducted



Embayment Scale



To assess the volume of SGD on these different scales we must measure the volume flow of a great deal of water that we will never see.

Tracers provide a way to do this on these different scales and even on a global scale.

The Radium Quartet

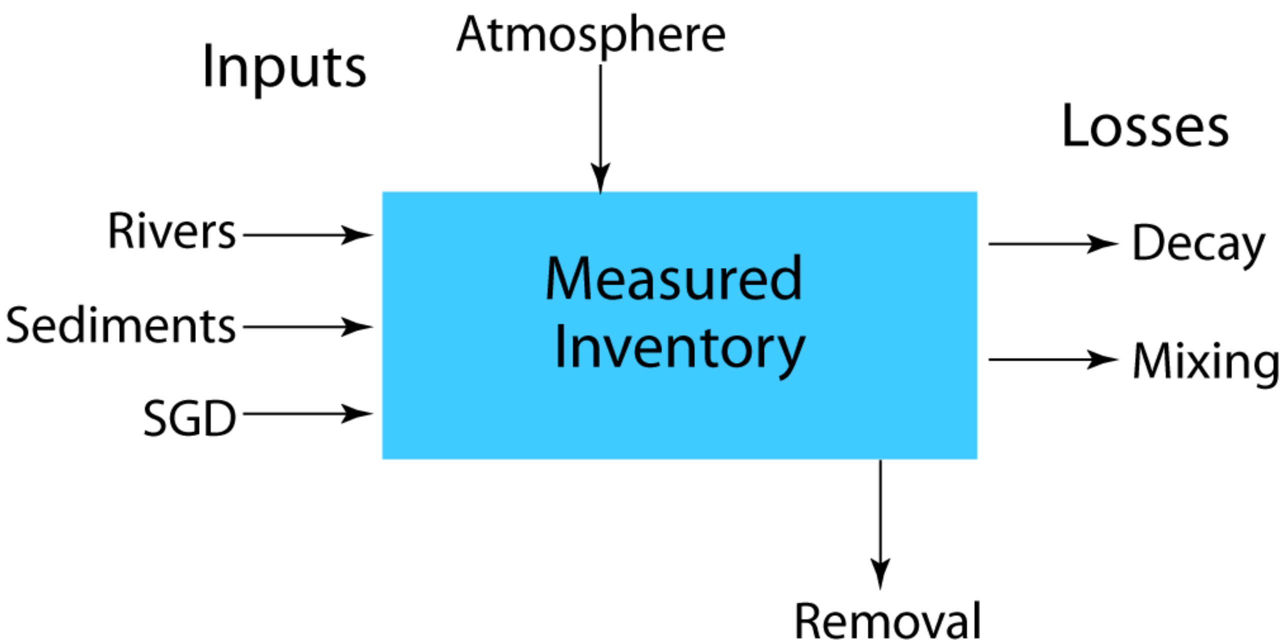
Each is derived from decay of a thorium isotope.

Ra adsorbs to particles in fresh water, but is mobile in salt water.

Ra is not reactive in coastal waters.

Ra concentrations are usually high in submarine groundwater and low in ocean water.

General Model for Quantifying SGD Using Radium Isotopes



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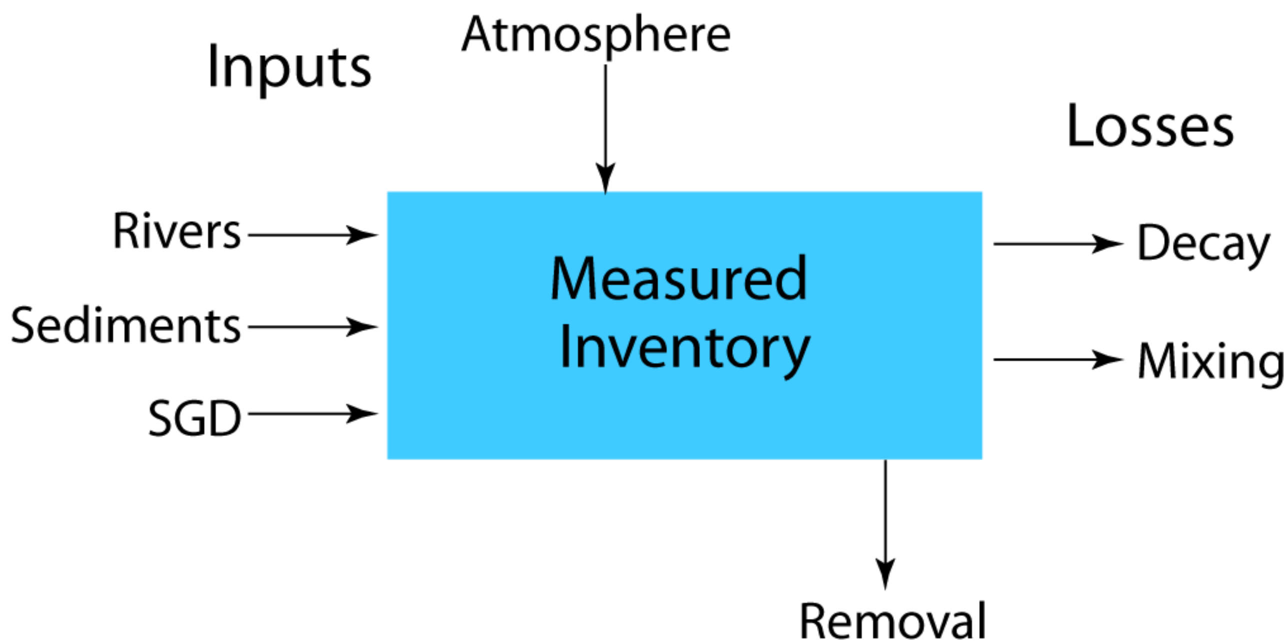

Using ^{226}Ra ($t_{1/2}$ = 1600 y) on a 600 km coastline

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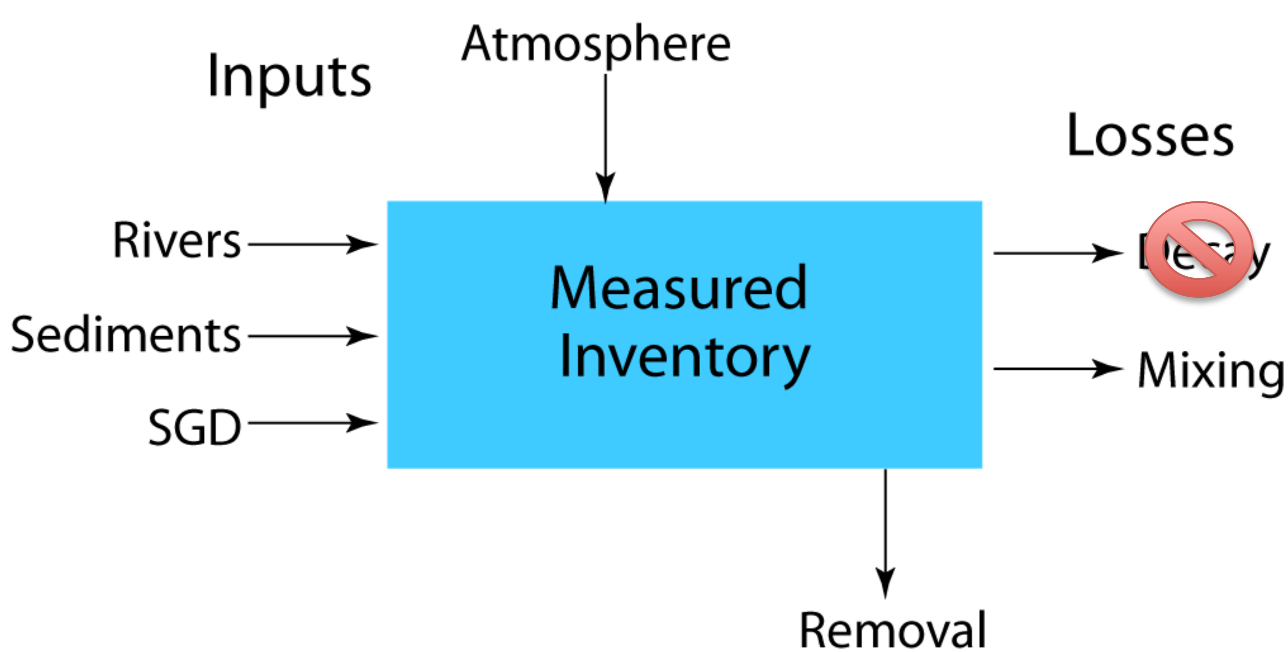

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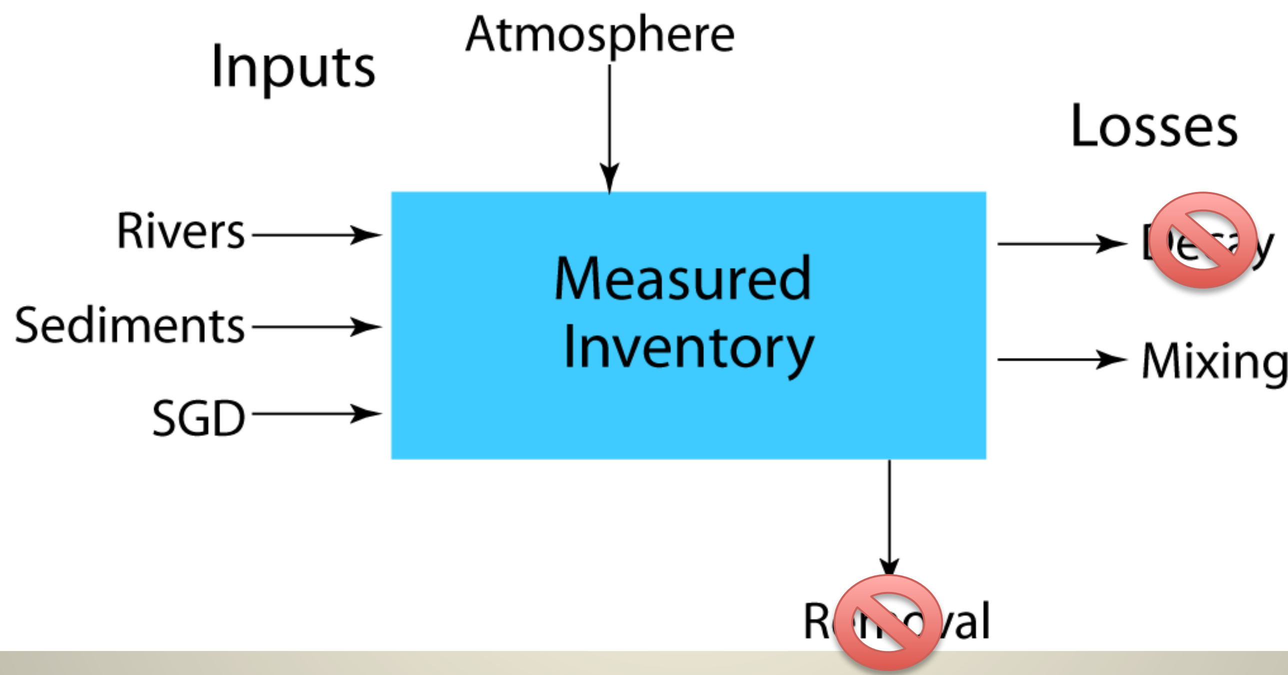

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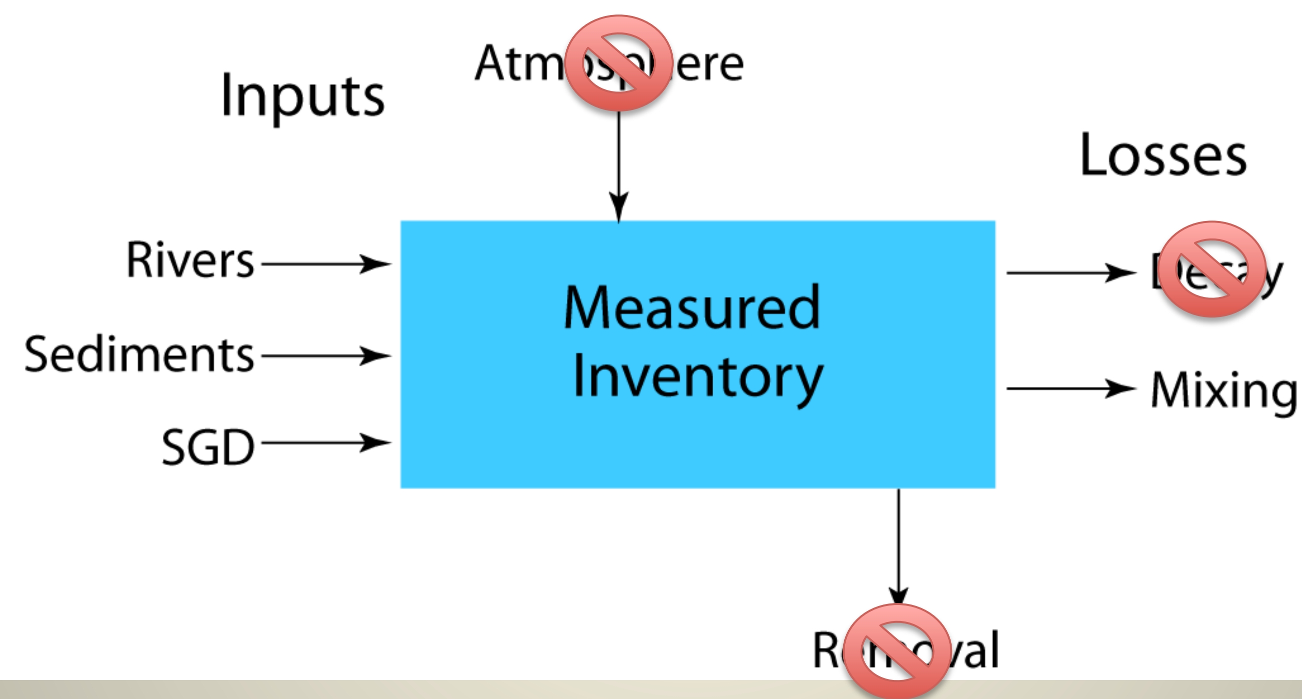

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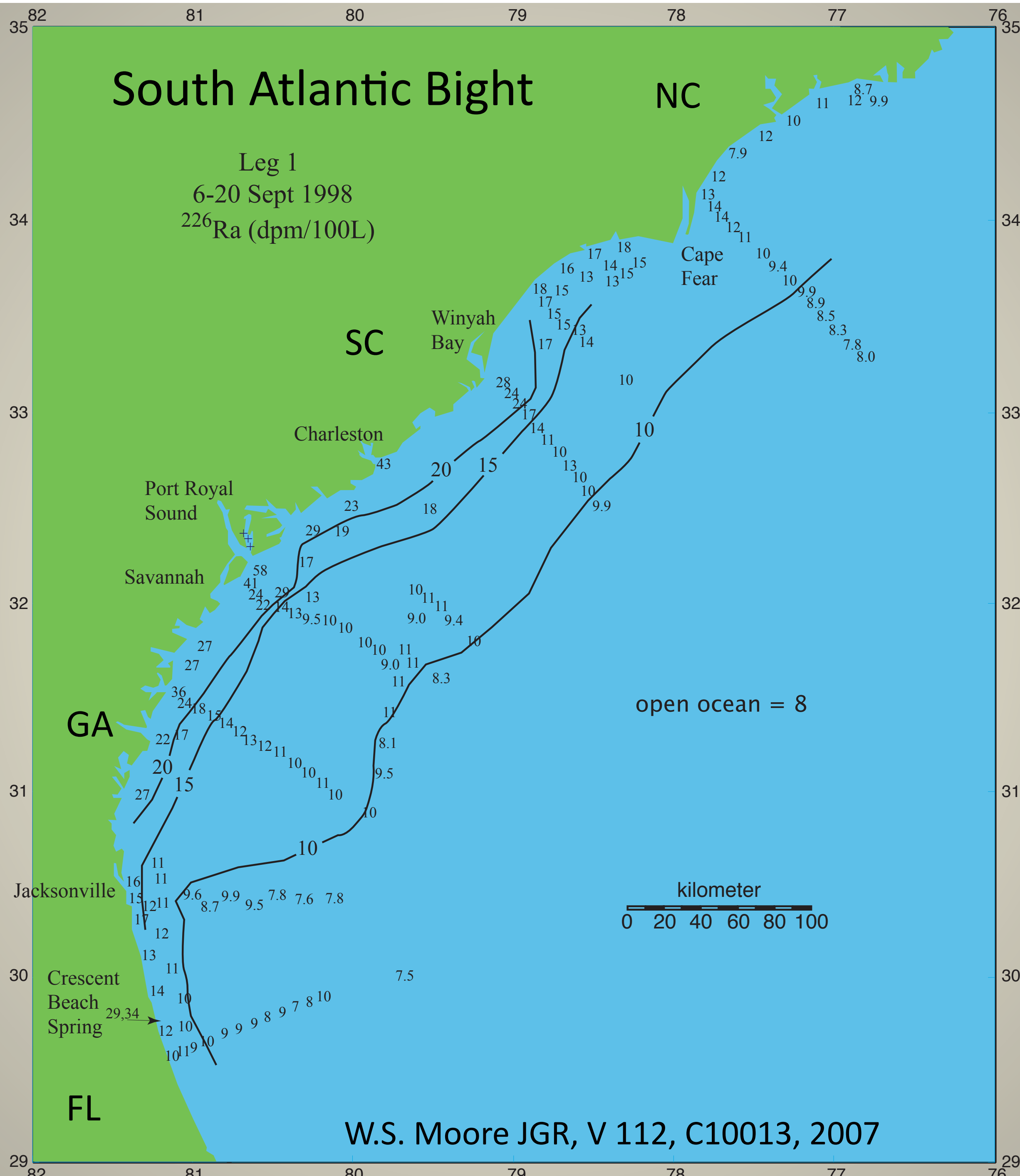
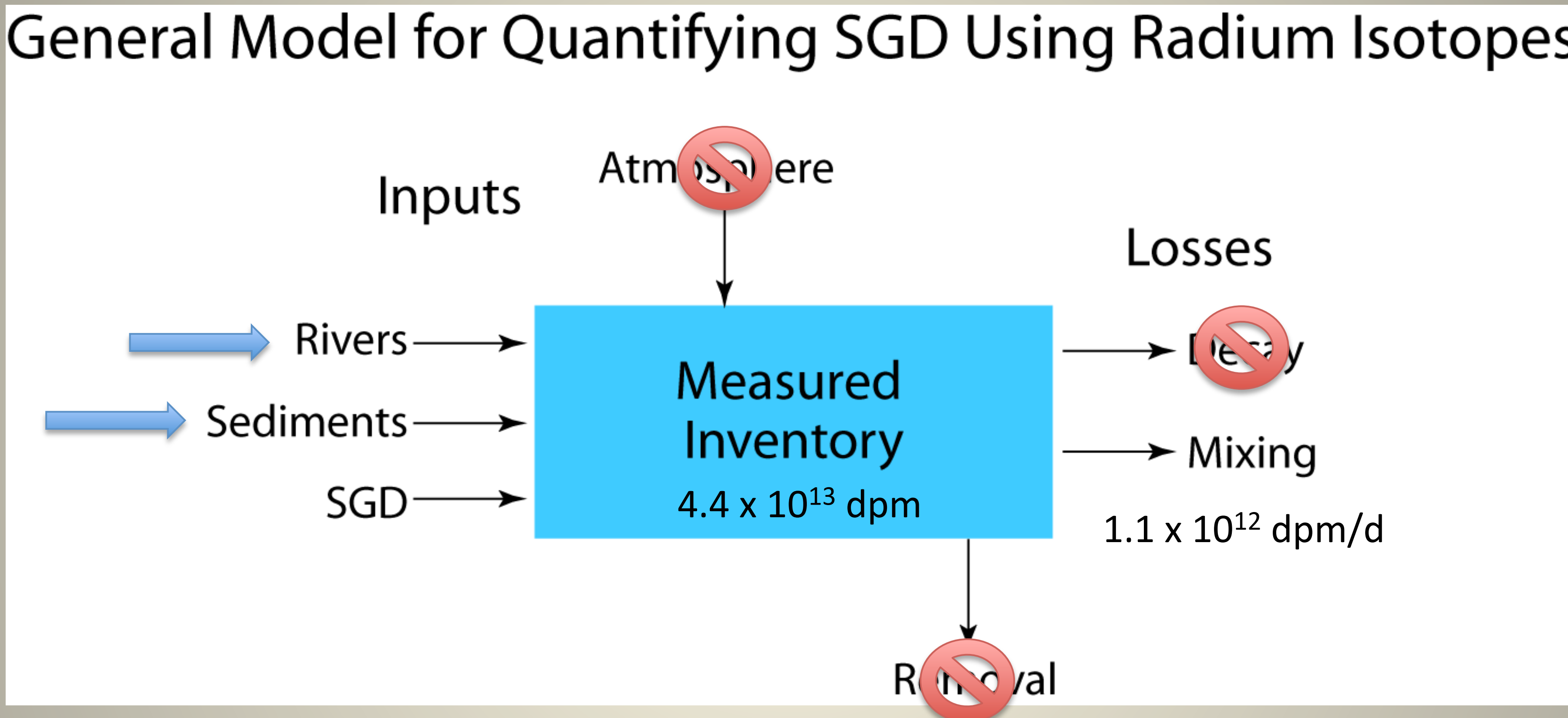


South Atlantic Bight
Leg 1
6-20 Sept 1998
226Ra (dpm/100L)
NC
SC
GA
FL
Cape Fear
Winyah Bay
Charleston
Port Royal Sound
Savannah
Jacksonville
Crescent Beach Spring
open ocean = 8
kilometer
0 20 40 60 80 100
W.S. Moore JGR, V 112, C10013, 2007

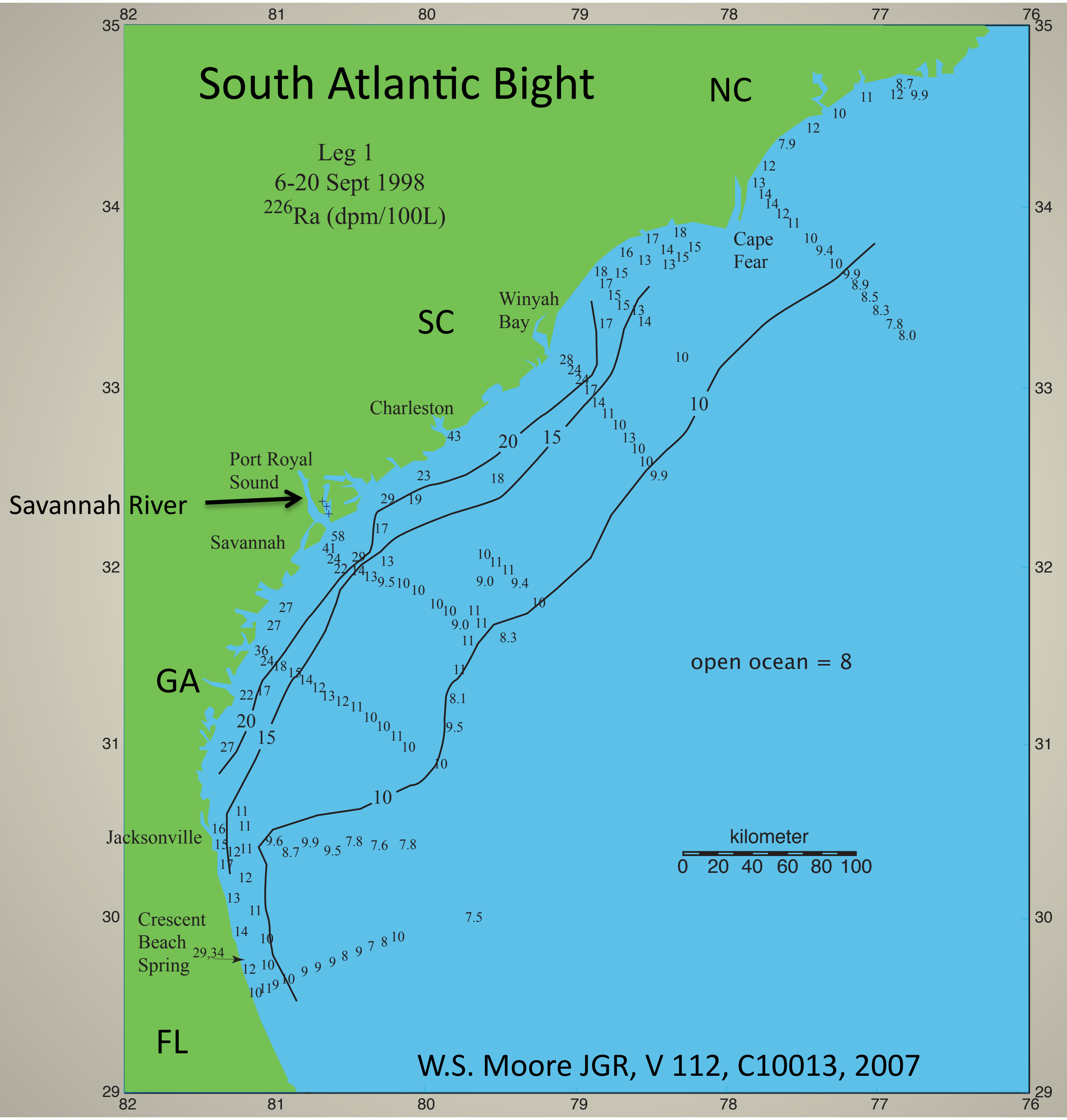
The water column was well-mixed inside of 20 km, but stratified further offshore. ~10 m surface layer.
^{226}Ra surface inventory August 1998 = 4.4×10^{13} dpm

Surface water residence time = 40 days based on ^{223}Ra and ^{224}Ra distributions and physical oceanography.

If the system is steady state on this 40 day time scale, the required ^{226}Ra flux = 1.1×10^{12} dpm/d from 0-20 km offshore.



Using ^{226}Ra on a 600 km coastline



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NC
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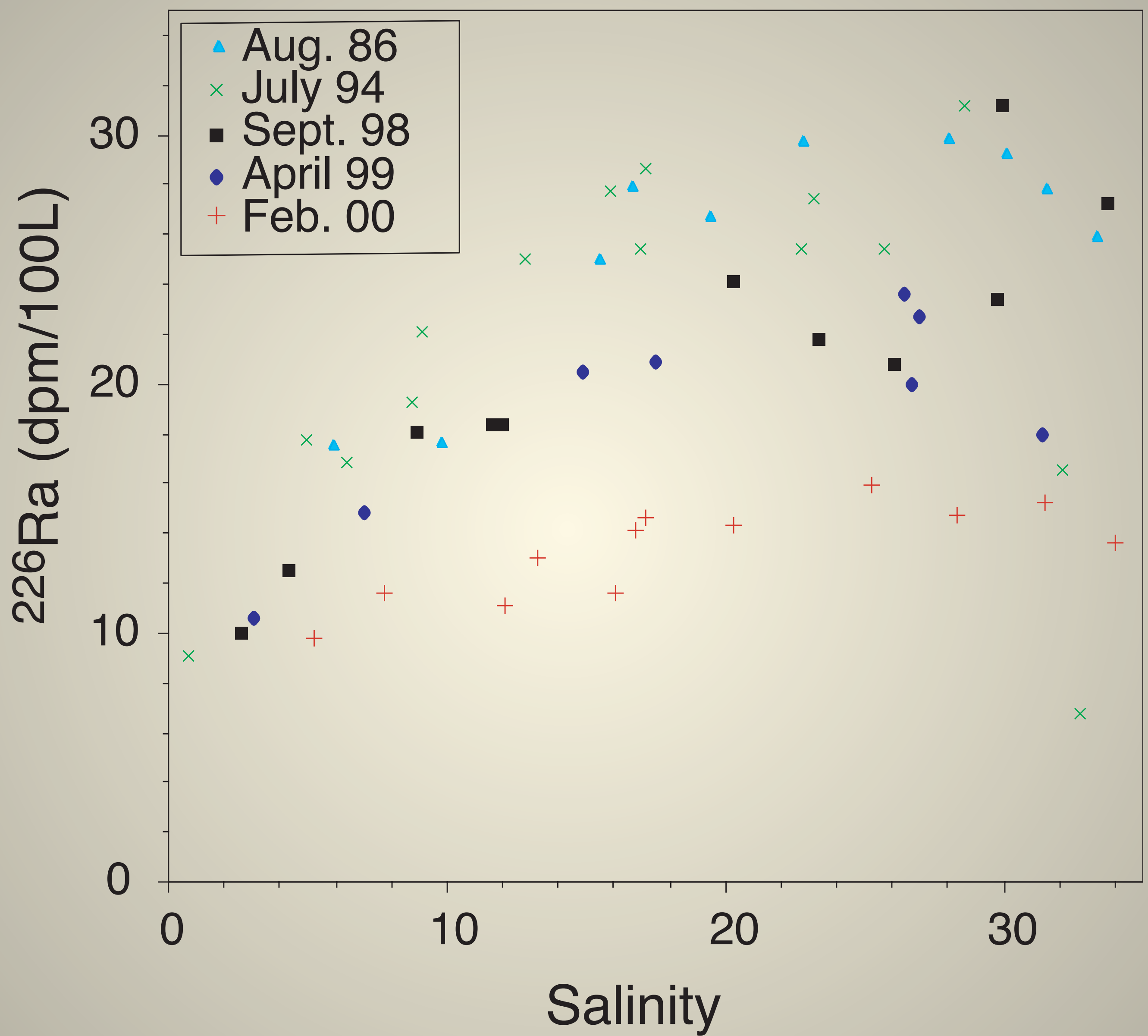
W.S. Moore JGR, V 112, C10013, 2007

Savannah River Estuary



W.S. Moore, T.J. Shaw, Marine Chemistry 108 (2008) 236–254

Calculate Savannah River flux ^{226}Ra:

Average river discharge (Aug 1988) = 236 m^3/s
= 2.0×10^7 m^3/d
^{226}Ra freshwater endmember = 60 dpm/m^3
Suspended sediment concentration = 10 g/m^3
Suspended sediment flux = 2×10^8 g/d
^{226}Ra release from SS (lab studies) = 2 dpm/g

Dissolved ^{226}Ra flux = 1.2×10^9 dpm/d
Desorbed ^{226}Ra flux = 4×10^9 dpm/d
Total Savannah ^{226}Ra flux = 5×10^9 dpm/d

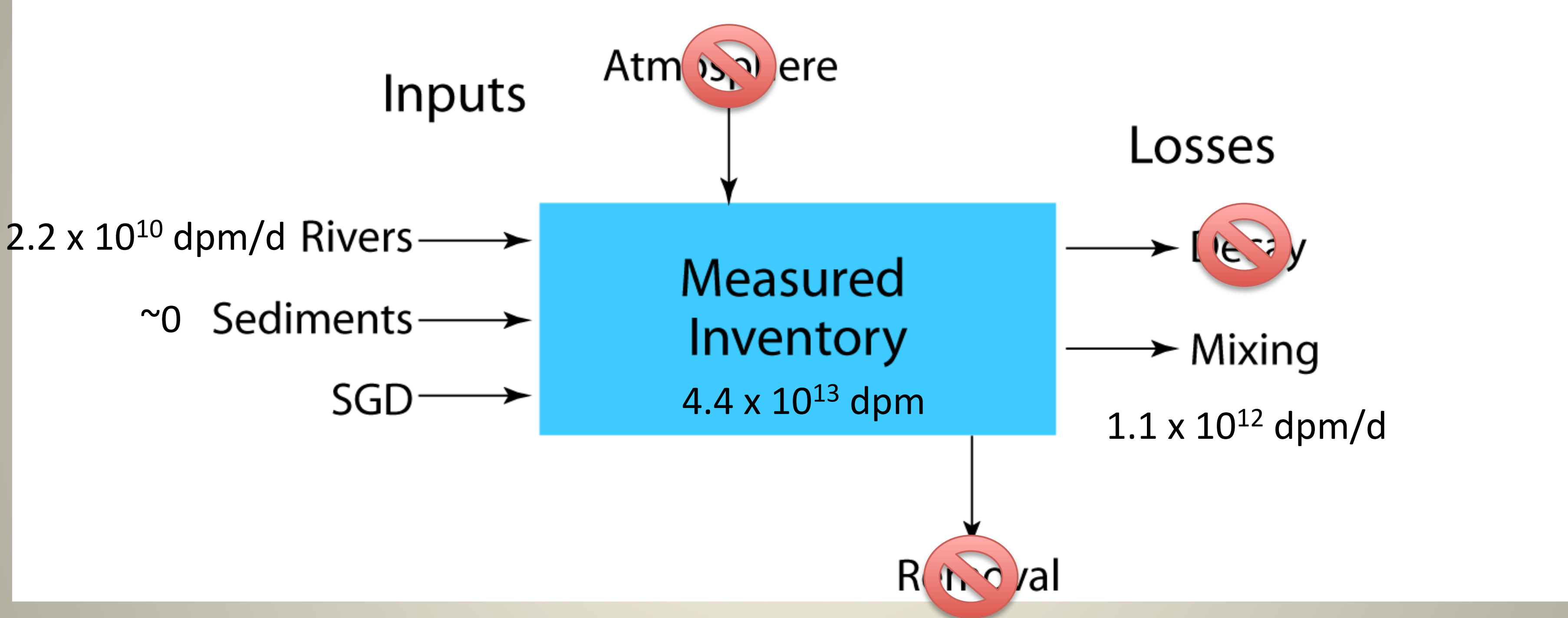
Total All river ^{226}Ra flux to SAB = 2.2×10^{10} dpm/d

Required ^{226}Ra flux = 1.1×10^{12} dpm/d
Total River ^{226}Ra flux = 2.2×10^{10} dpm/d
Rivers supply ~2% of the required flux

After desorbing Ra, sediments require 500 years to regenerate 20% of ^{226}Ra. So sediments supply negligible ^{226}Ra.

Conclusion: Almost all ^{226}Ra is supplied by SGD.

General Model for Quantifying SGD Using Radium Isotopes



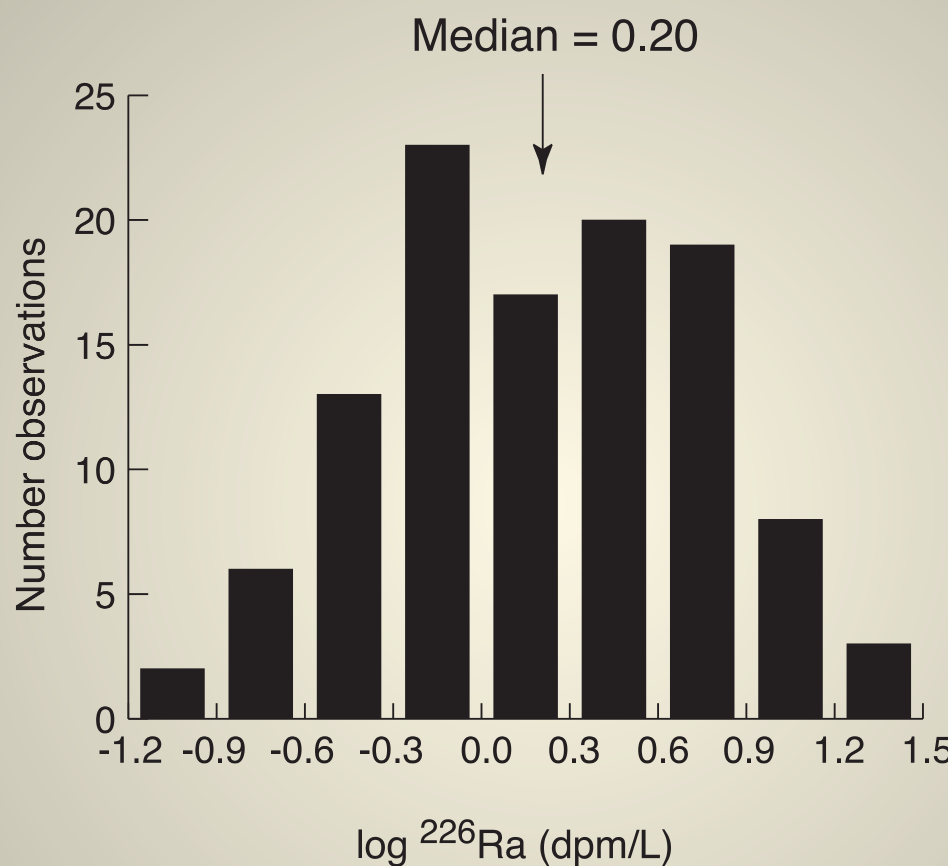
SGD ^{226}Ra = 1.1 x 10^{12} dpm/d – 2.2 x 10^{10} dpm/d = 1.1 x 10^{12} dpm/d

Using ^{226}Ra on a 600 km coastline

SGD ^{226}Ra flux (September) = 1.1×10^{12} dpm/d

To estimate the SGD water flux, we must know the concentration of ^{226}Ra in SGD.

What is the concentration of ^{226}Ra in SGD?



Median concentration of ^{226}Ra in SGD = 1.5 dpm/L

W.S. Moore, GLOBAL BIOGEOCHEMICAL CYCLES, VOL. 24, GB4005, 2010

SGD ^{226}Ra flux September = 1.1×10^{12} dpm/d

Concentration of ^{226}Ra in SGD = 1.5 dpm/L

$$\frac{1.1 \times 10^{12} \text{ dpm/d}}{1.5 \text{ dpm/L}} = 7.3 \times 10^{11} \text{ L/d}$$

= 8500 m^3/s

~3x river flux

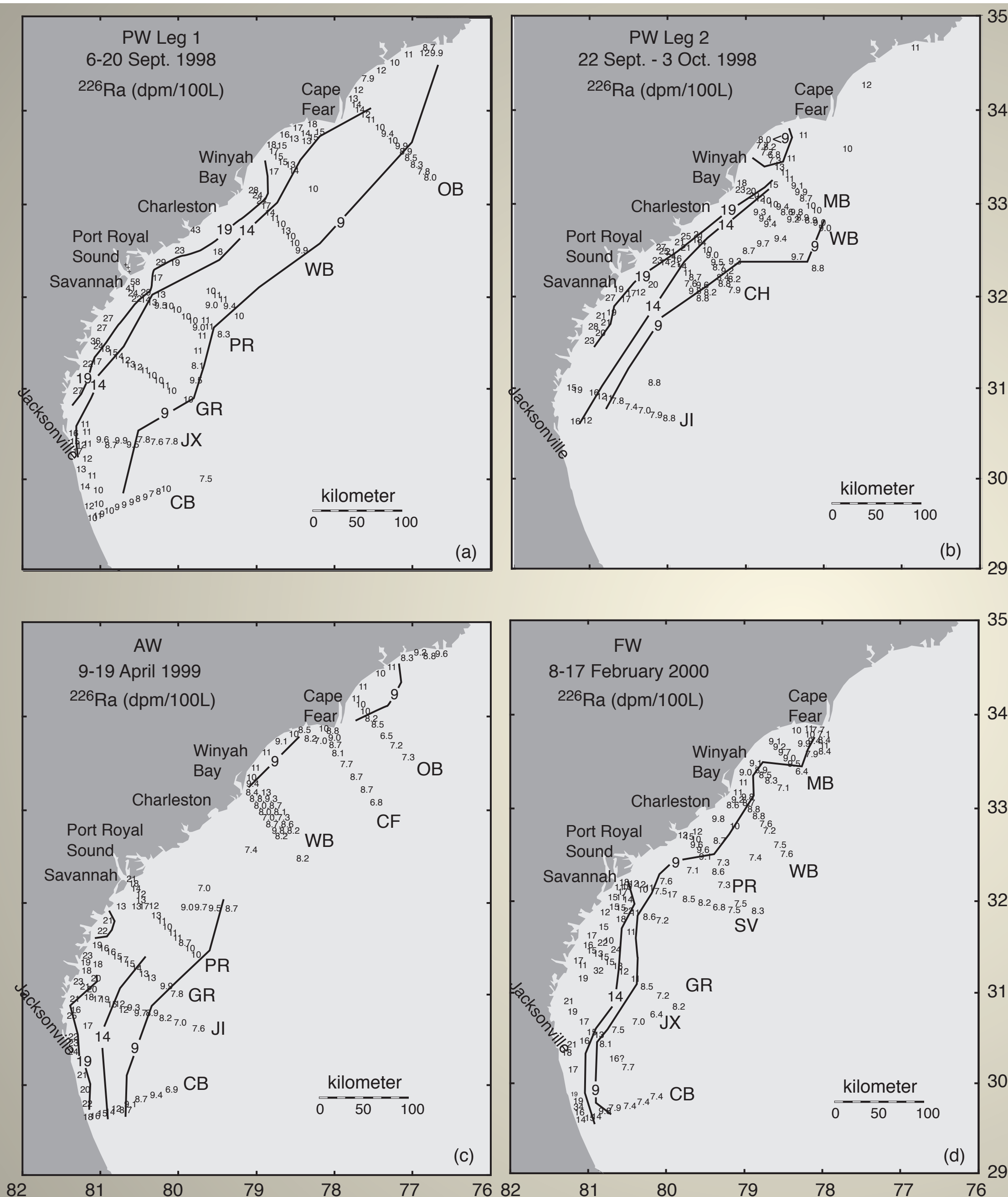


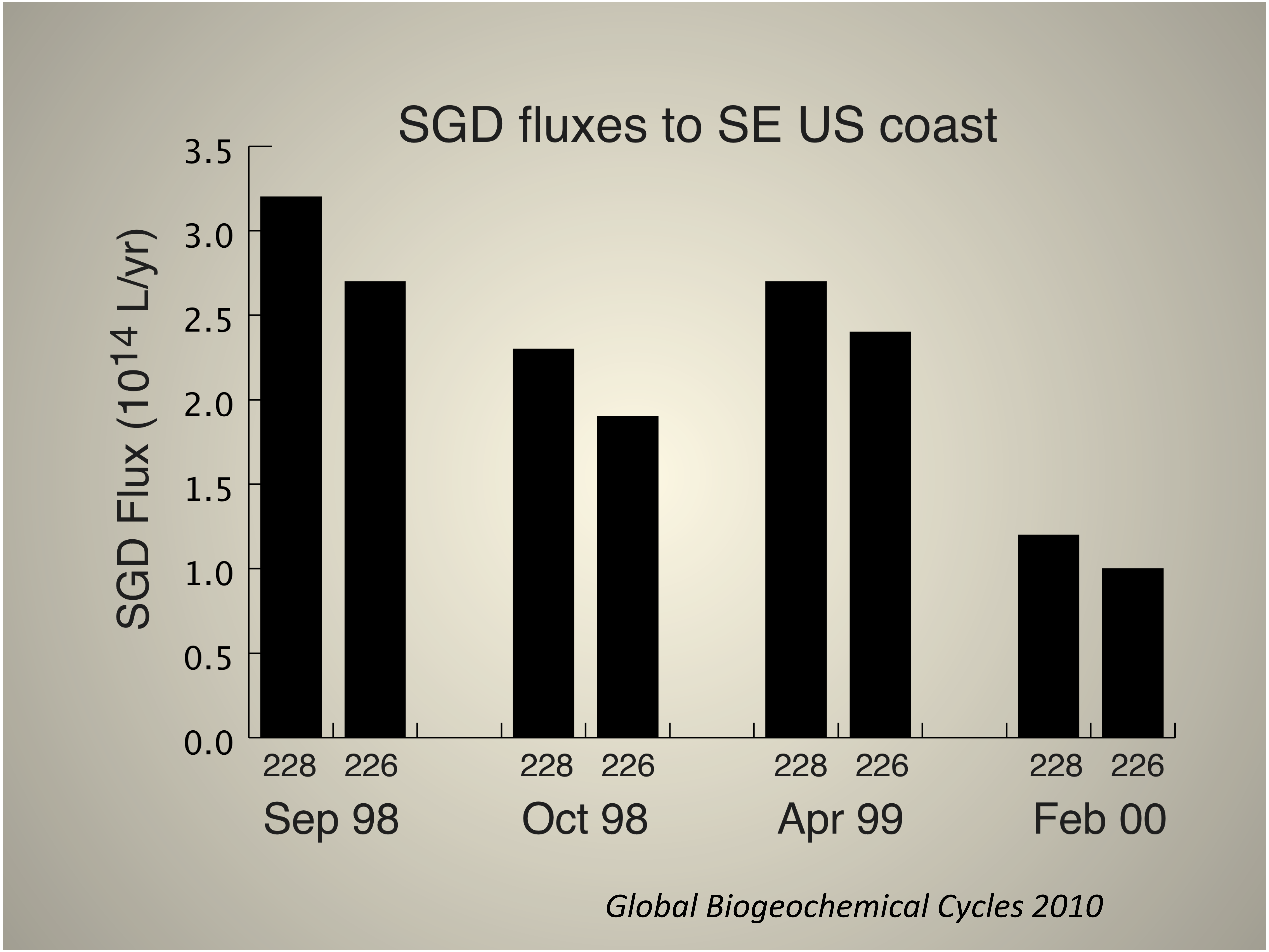
Figure 1

W.S. Moore JGR, V 112, C10013, 2007

There are considerable seasonal changes in inventory.

The concentration of ^{226}Ra in ground water changes much less.

Flux of SGD must change seasonally.


SGD fluxes to SE US coast
SGD Flux (10^14 L/yr)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
228
226
228
226
228
226
228
226
Sep 98
Oct 98
Apr 99
Feb 00
Global Biogeochemical Cycles 2010

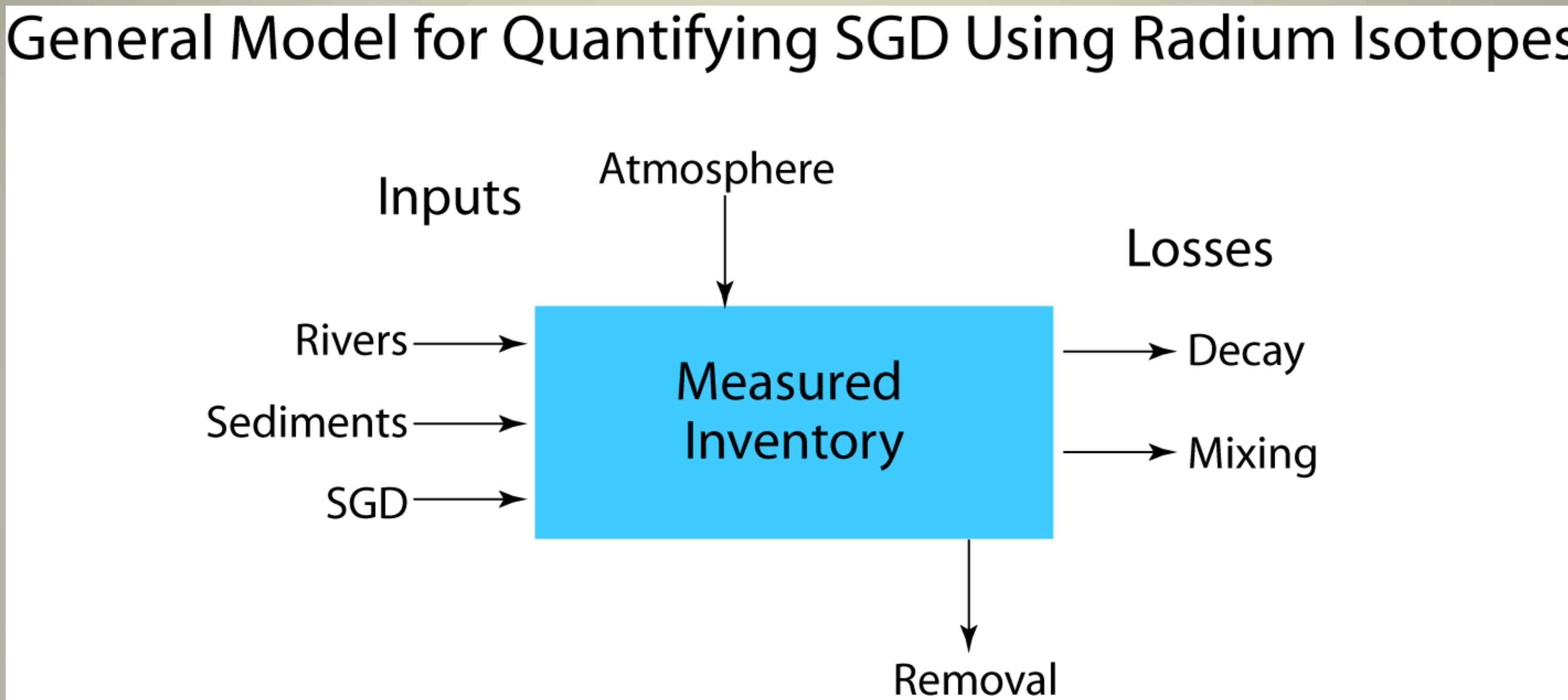
Average SGD ^{226}Ra flux = 8.3×10^{11} dpm/d

Concentration of ^{226}Ra in SGD = 1.5 dpm/L

$$\frac{8.3 \times 10^{11}\ \text{dpm/d}}{1.5\ \text{dpm/L}} = 5.5 \times 10^{11}\ \text{L/d}$$

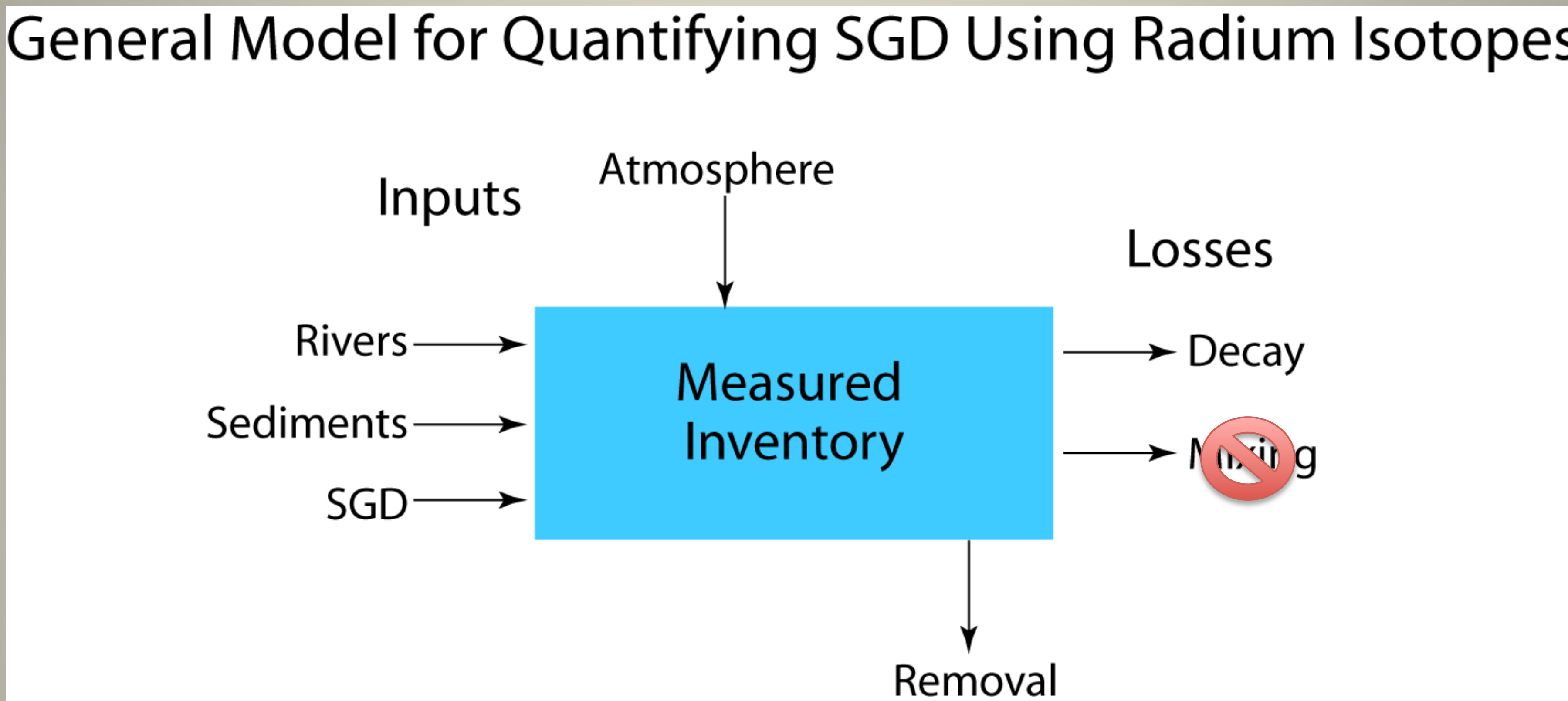
Average per km of coastline = 3.4×10^{8} m^3/yr

Apply the same model to the Atlantic Ocean



Using ^{228}Ra ($t_{1/2}$ = 5.7 yr) on a 85,000 km coastline

Apply the same model to the Atlantic Ocean



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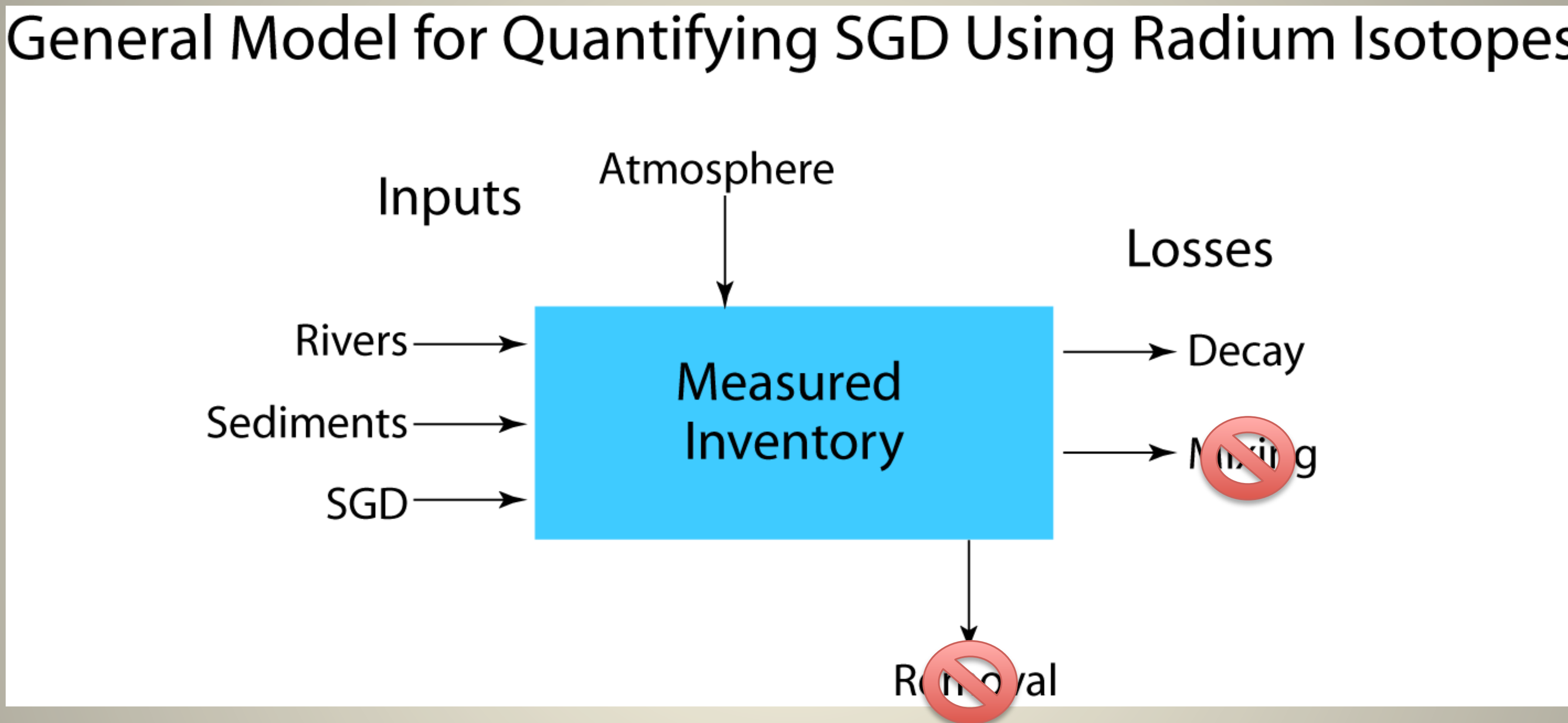

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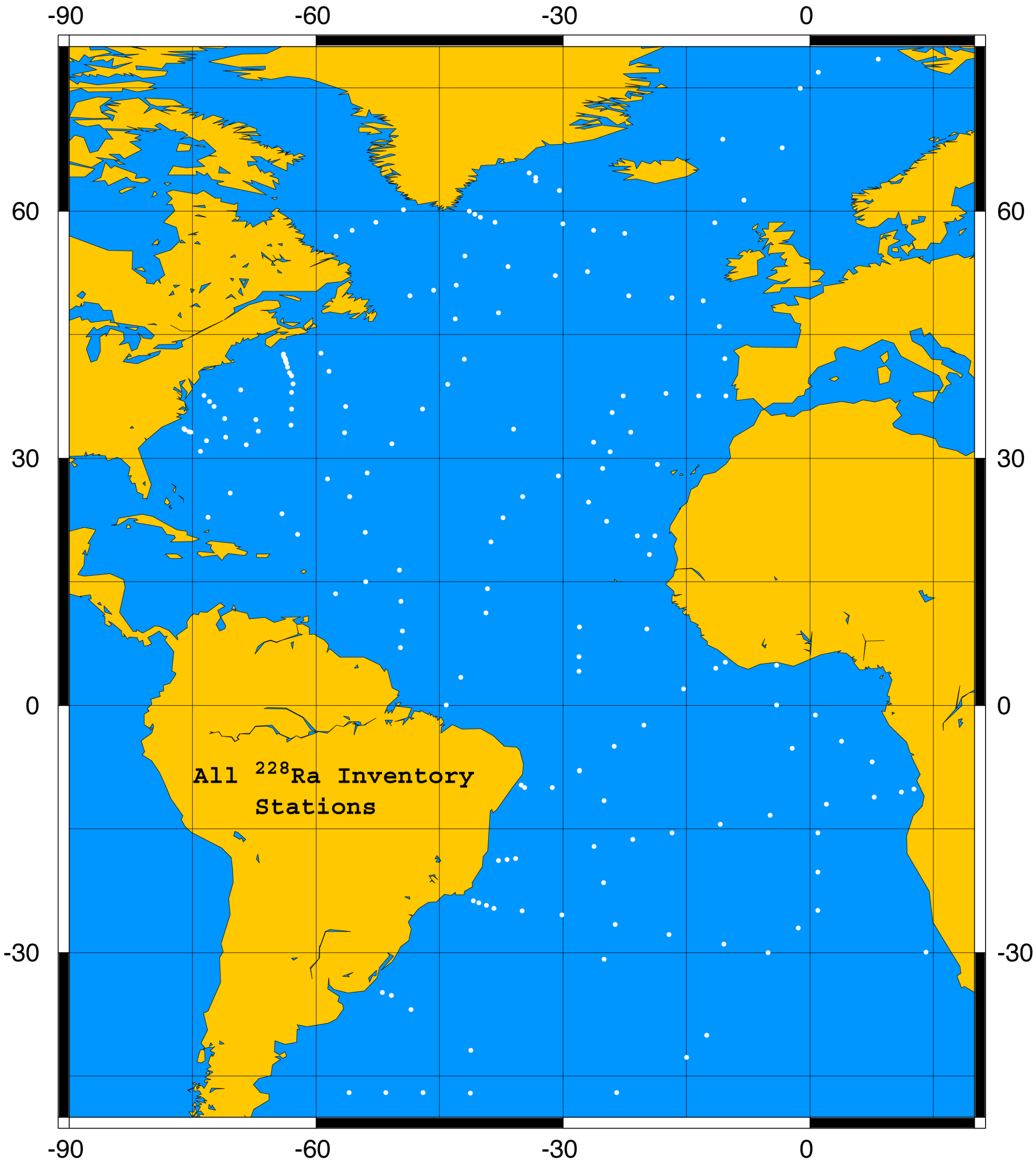


TTO
1981-1989

Stations with ^{228}Ra profiles

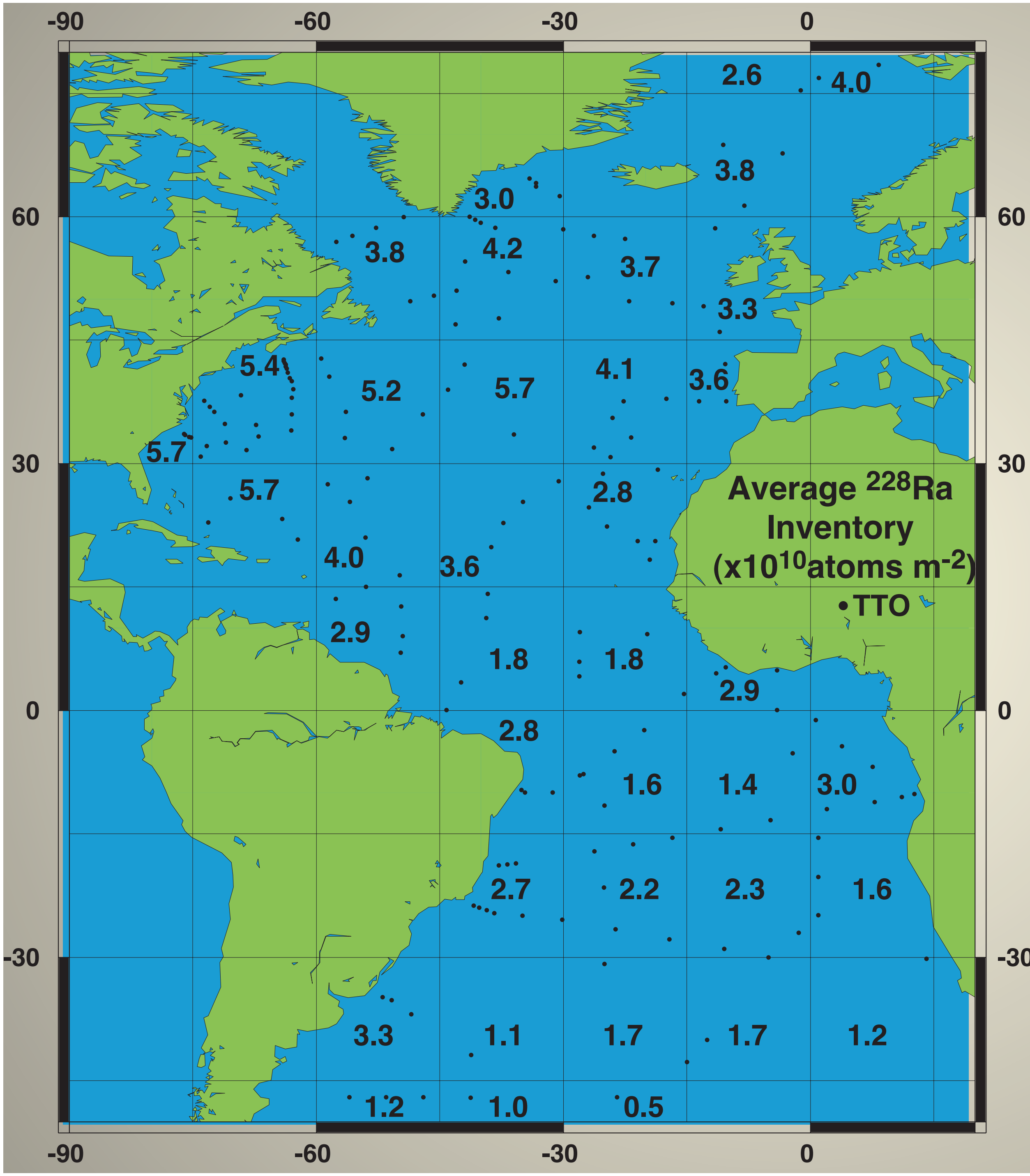
$^{232}Th \longrightarrow {}^{228}Ra \longrightarrow$

half life = 5.7 years

$\lambda = 0.12\ yr^{-1}$

Bob Key,
Jorge Sarmiento
Princeton

Nature Geoscience 1, 309-311, 2008.

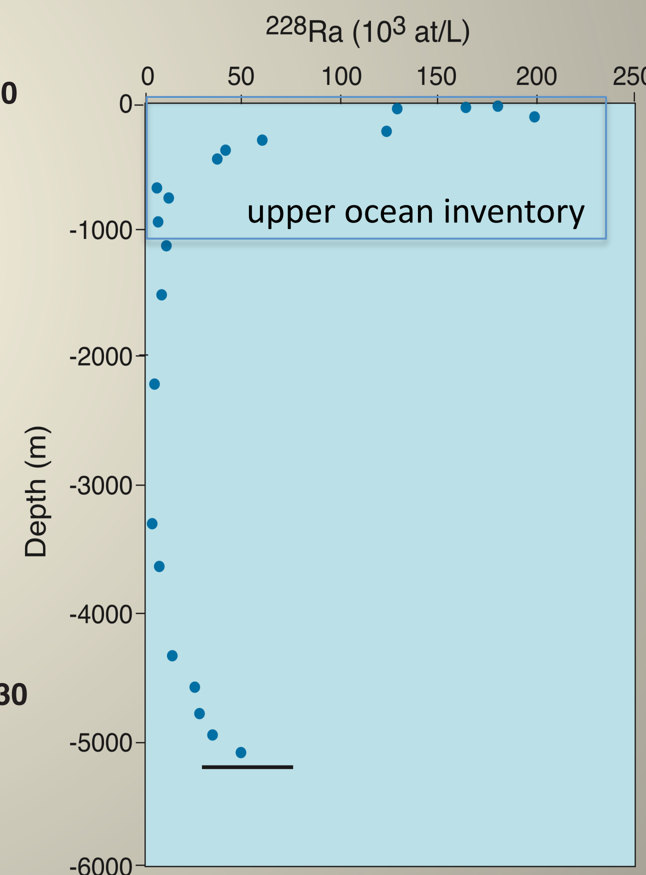


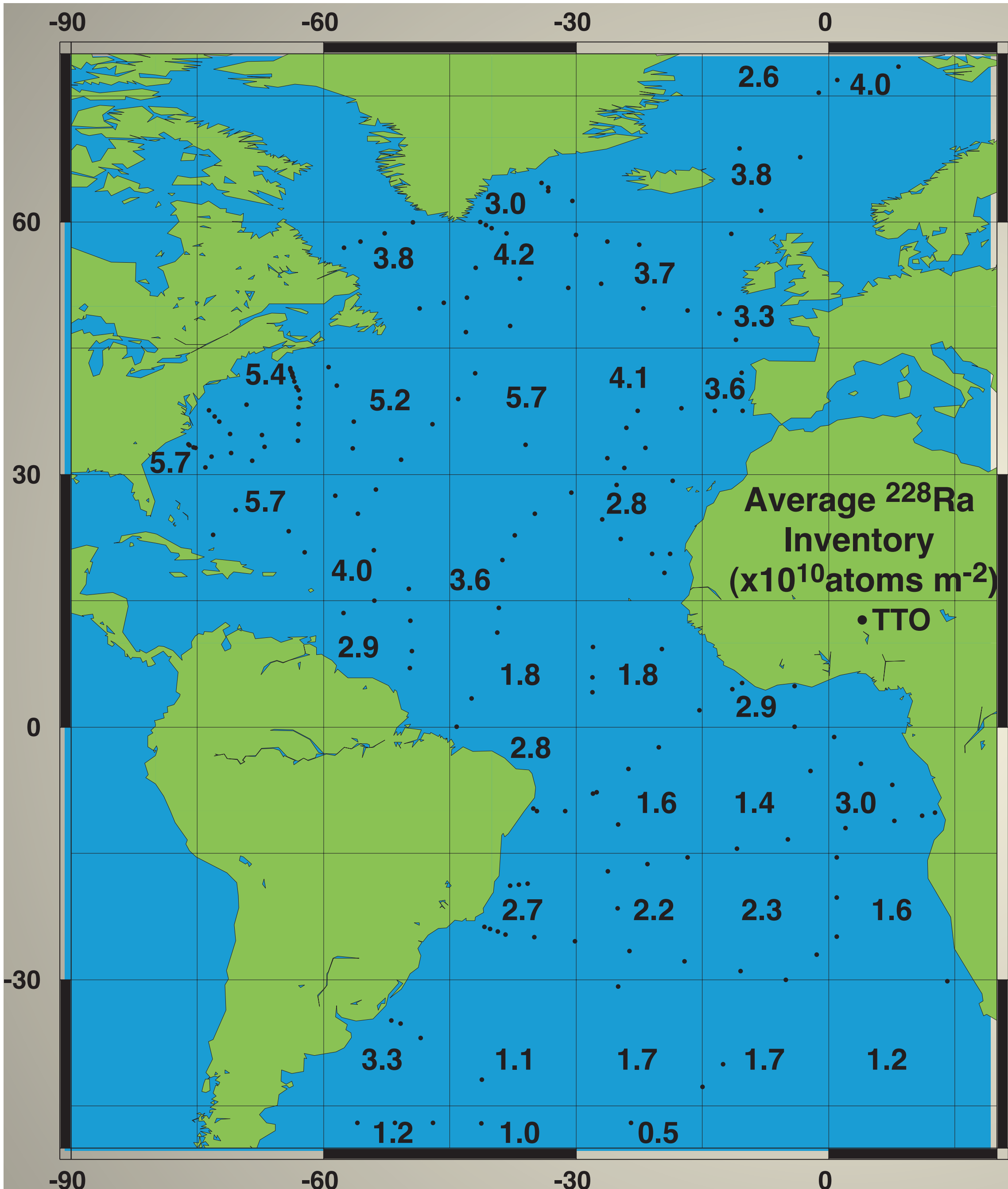
surface-1000 m

Average ^{228}Ra Inventory
$= 3.0 \times 10^{10}$ atoms/m^2

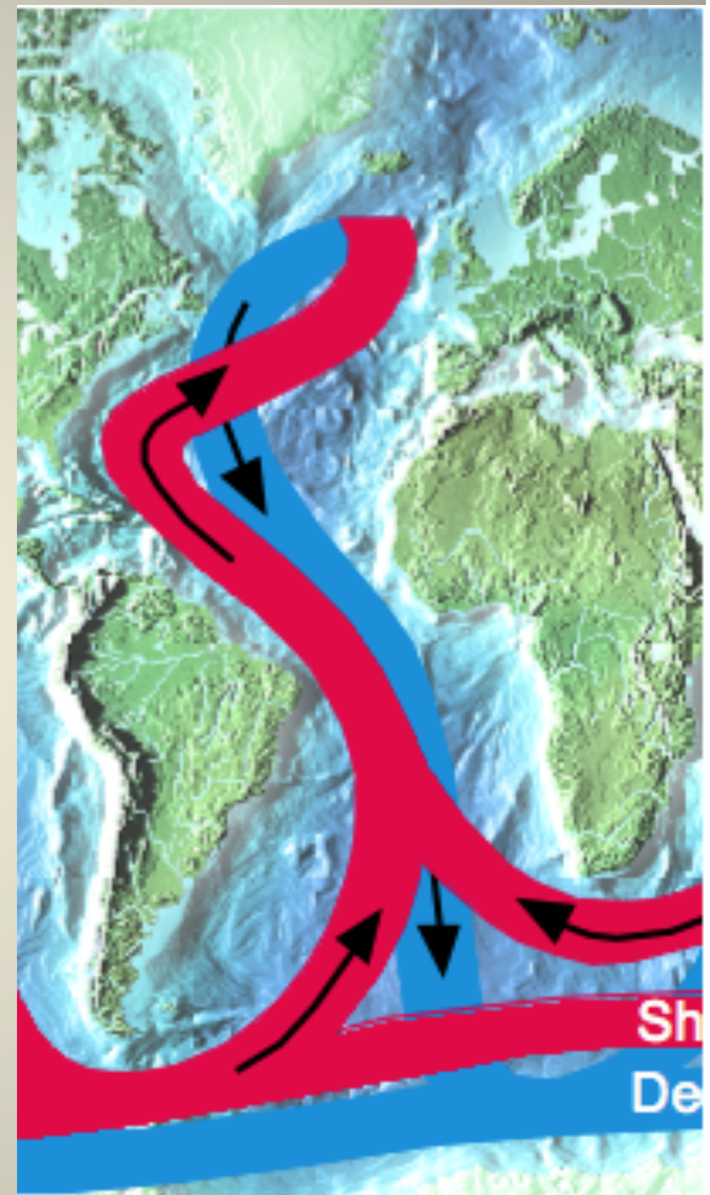
1 dpm = 4.36×10^6 atoms

1 Bq = 2.62×10^8 atoms





-90 -60 -30 0
60 30 0 -30
Average ^{228}Ra Inventory
(x10^{10}atoms m^{-2})
•TTO
2.6 4.0
3.8
3.0
3.8 4.2 3.7 3.3
5.4 5.2 5.7 4.1 3.6
5.7
5.7 2.8
4.0 3.6
2.9
1.8 1.8
2.9
2.8
1.6 1.4 3.0
2.7 2.2 2.3 1.6
3.3 1.1 1.7 1.7 1.2
1.2 1.0 0.5



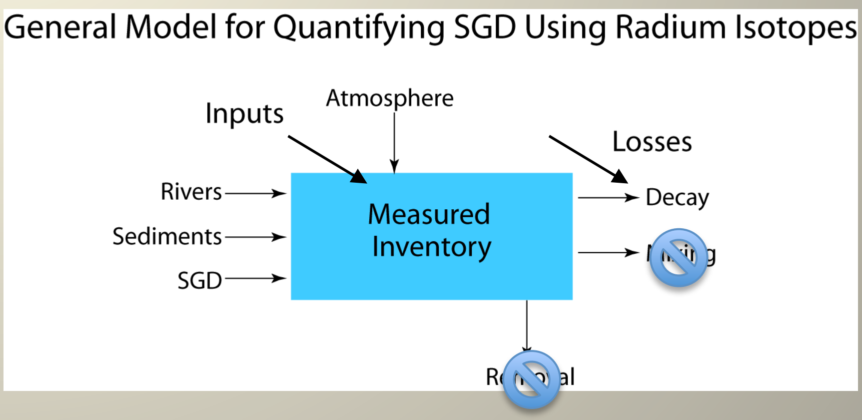
Total inventory $^{228}Ra = 2.9 \times 10^{24}$ atoms in upper 1000 m

12% of the ^{228}Ra inventory decays each year.

^{228}Ra loss = Inventory x decay rate (λ)

$= 2.9 \times 10^{24}$ atoms x 0.12 year^{-1}

$= 3.5 \times 10^{23}$ atoms year^{-1}



If we know the total inventory of ^{228}Ra in the upper water column, we know how much of that inventory is lost by decay each year.

If the distribution is steady state, this gives us the flux from the continents required to balance the decay.

Is ^{228}Ra in steady state in the ocean?

The TTO samples were collected during the 1980's.
Almost all of the ^{228}Ra that was in the ocean at that time has decayed.

$A = A_0 e^{-\lambda t}$

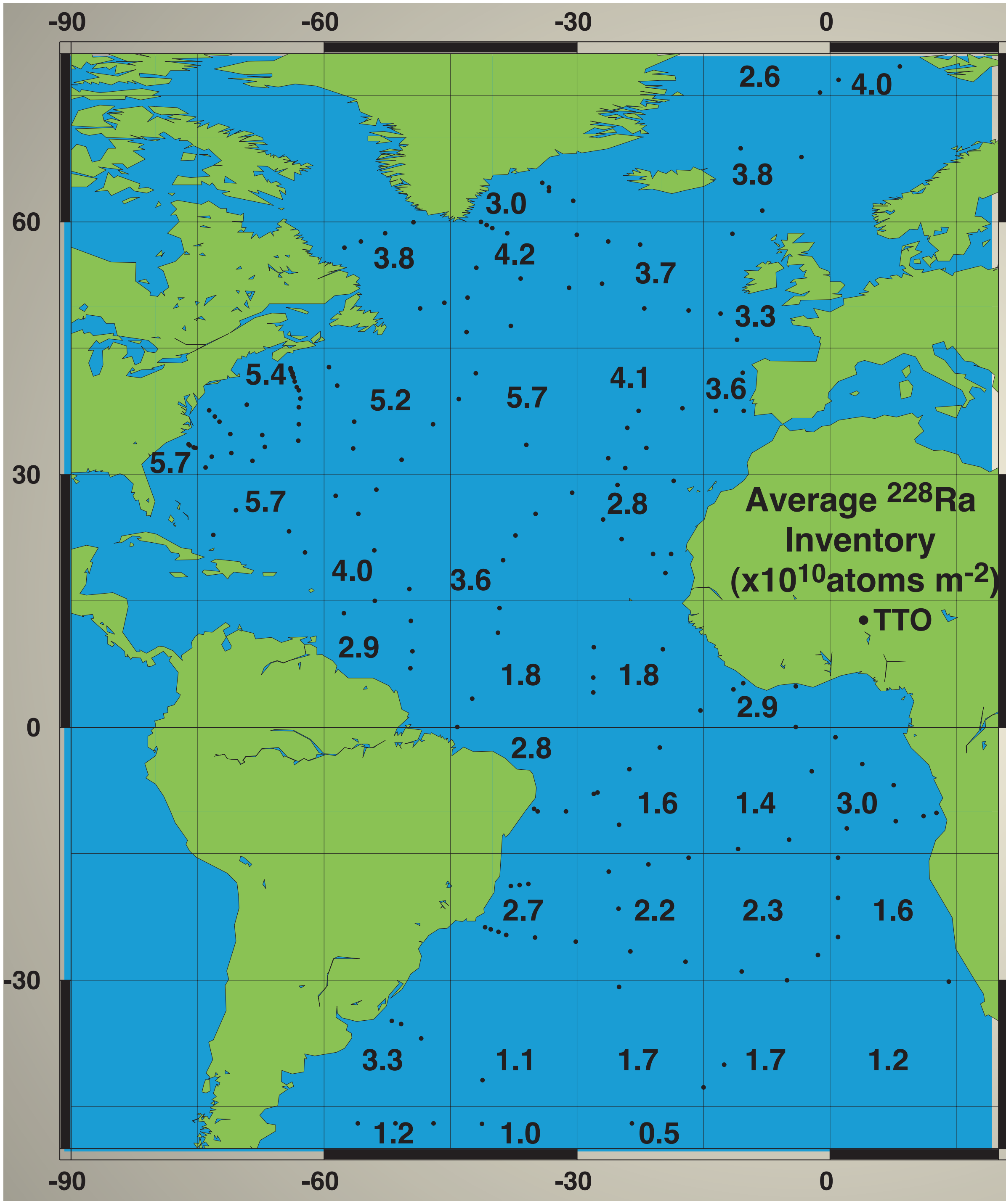
$t = \sim 25$ years, $\lambda = 0.12\ yr^{-1}$, $e^{-\lambda t} = 0.049$, only ~5% remains.

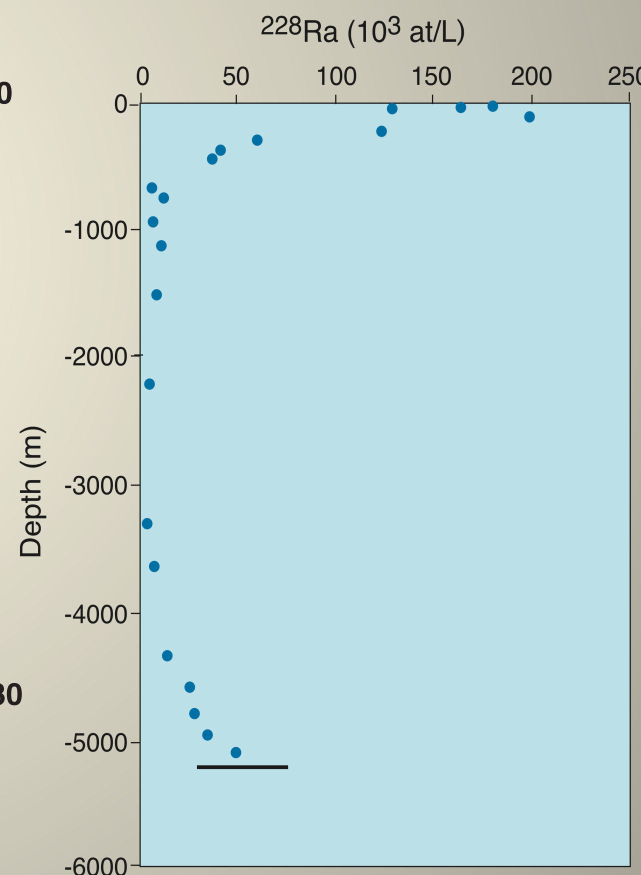
GEOTRACES (2011) provides a new data set for part of the Atlantic. Is ^{228}Ra in steady state in the upper Atlantic?

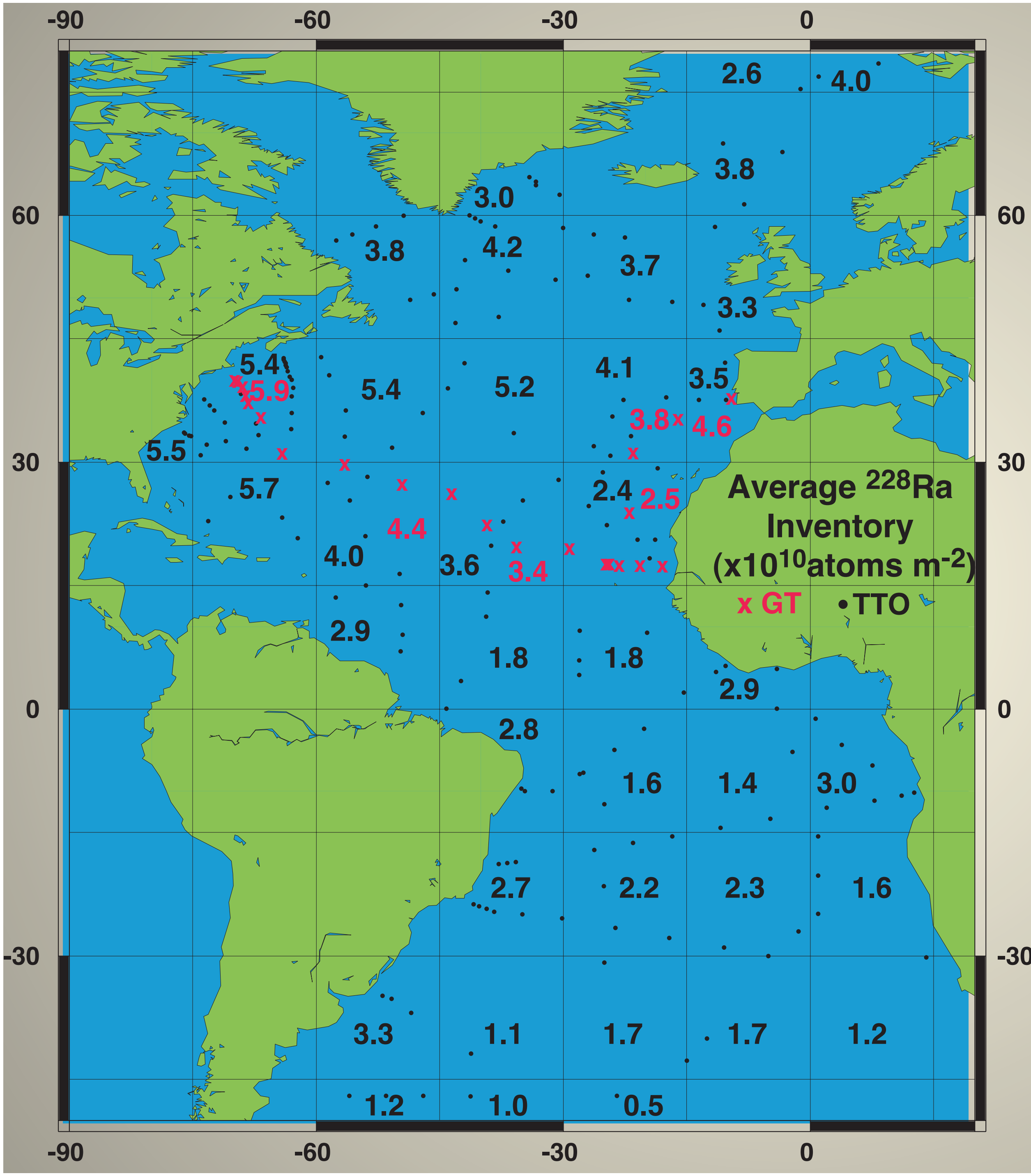
surface-1000 m

Average ^{228}Ra Inventory
$= 3.0 \times 10^{10}$ atoms/m^2

1 dpm = 4.36×10^6 atoms
1 Bq = 2.62×10^8 atoms

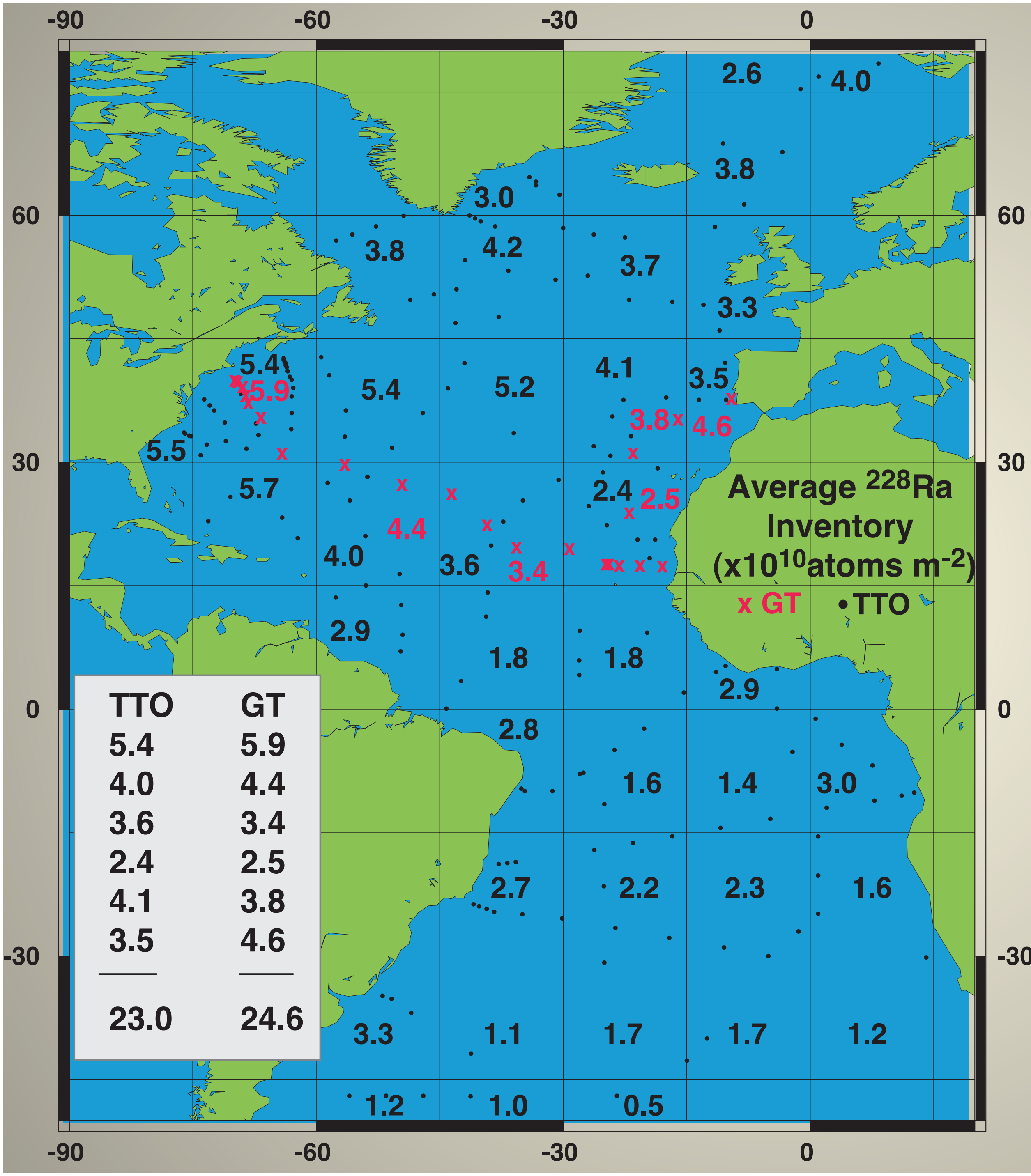






Add US Atlantic GEOTRACES Data

95% of the ^{228}Ra atoms present during TTO decayed before the 2011-2012 GT cruises.



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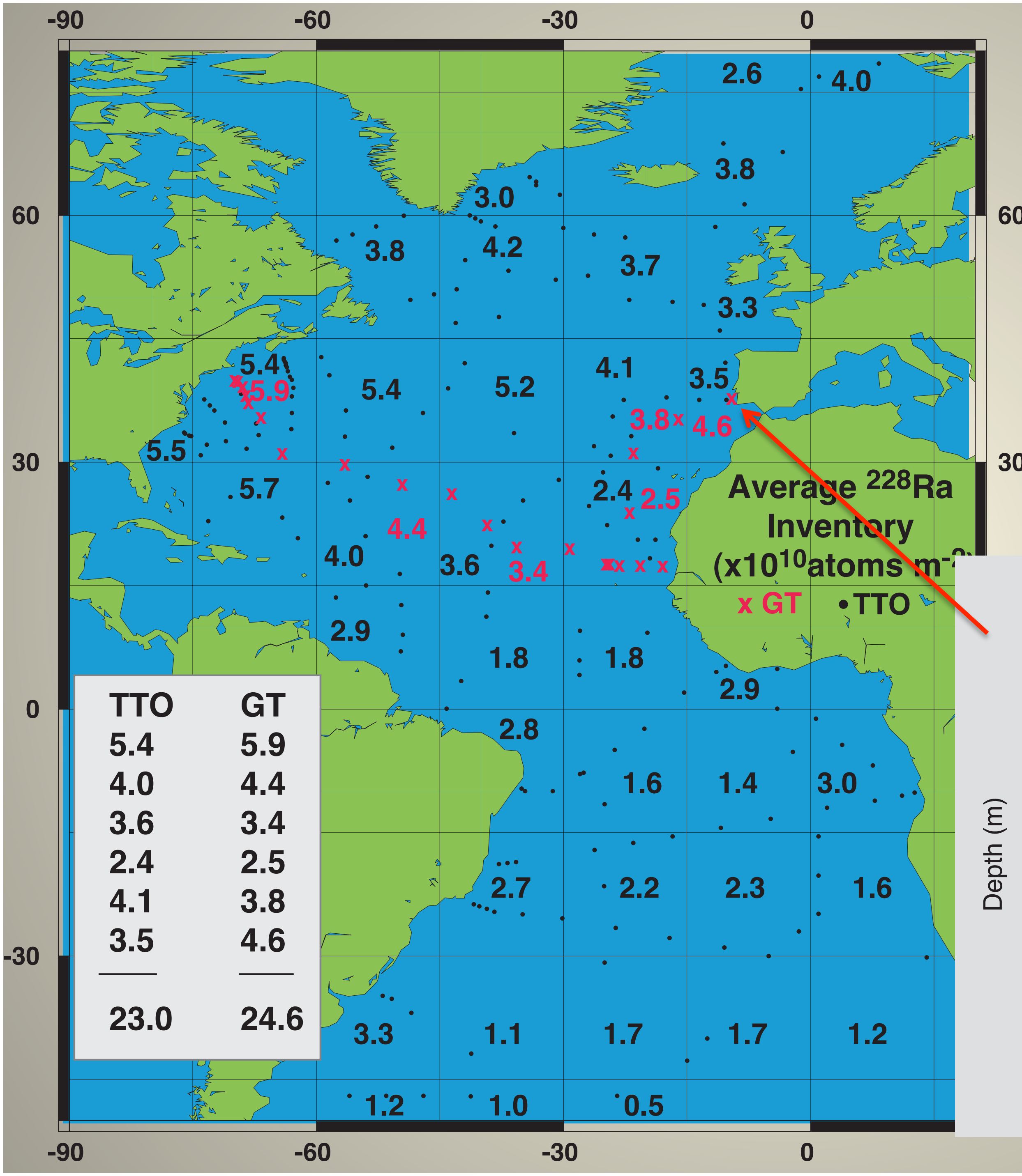

TTO	GT
5.4	5.9
4.0	4.4
3.6	3.4
2.4	2.5
4.1	3.8
3.5	4.6
23.0	24.6

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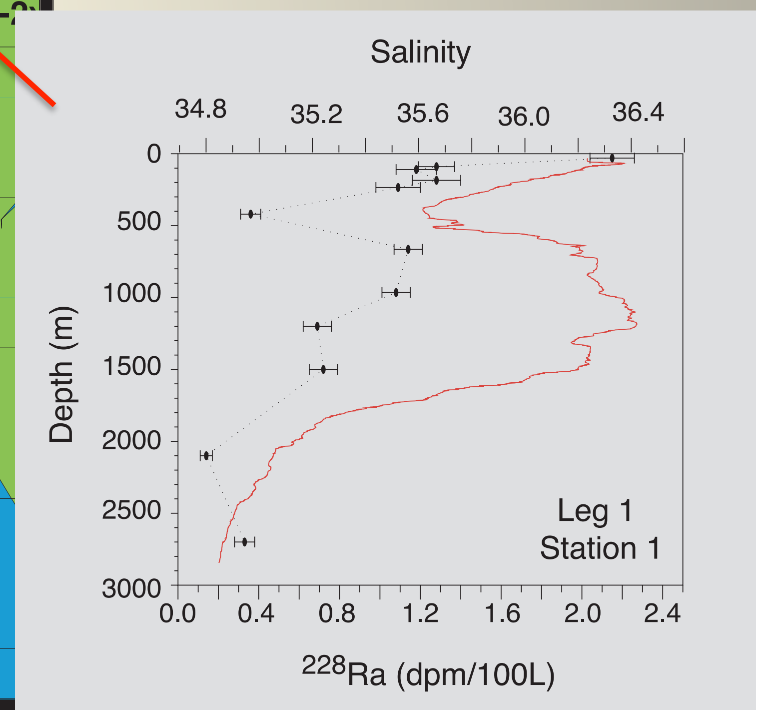

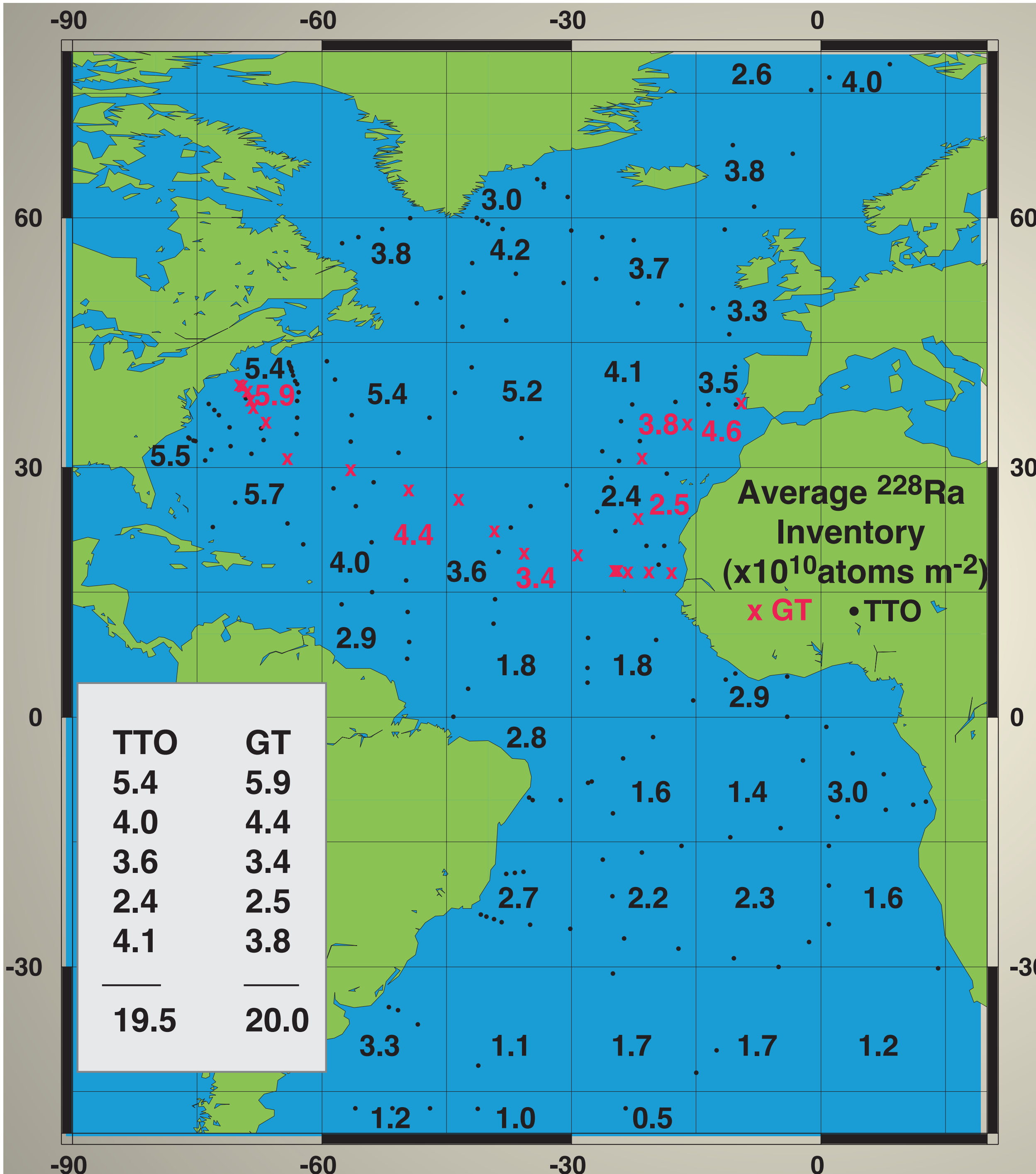

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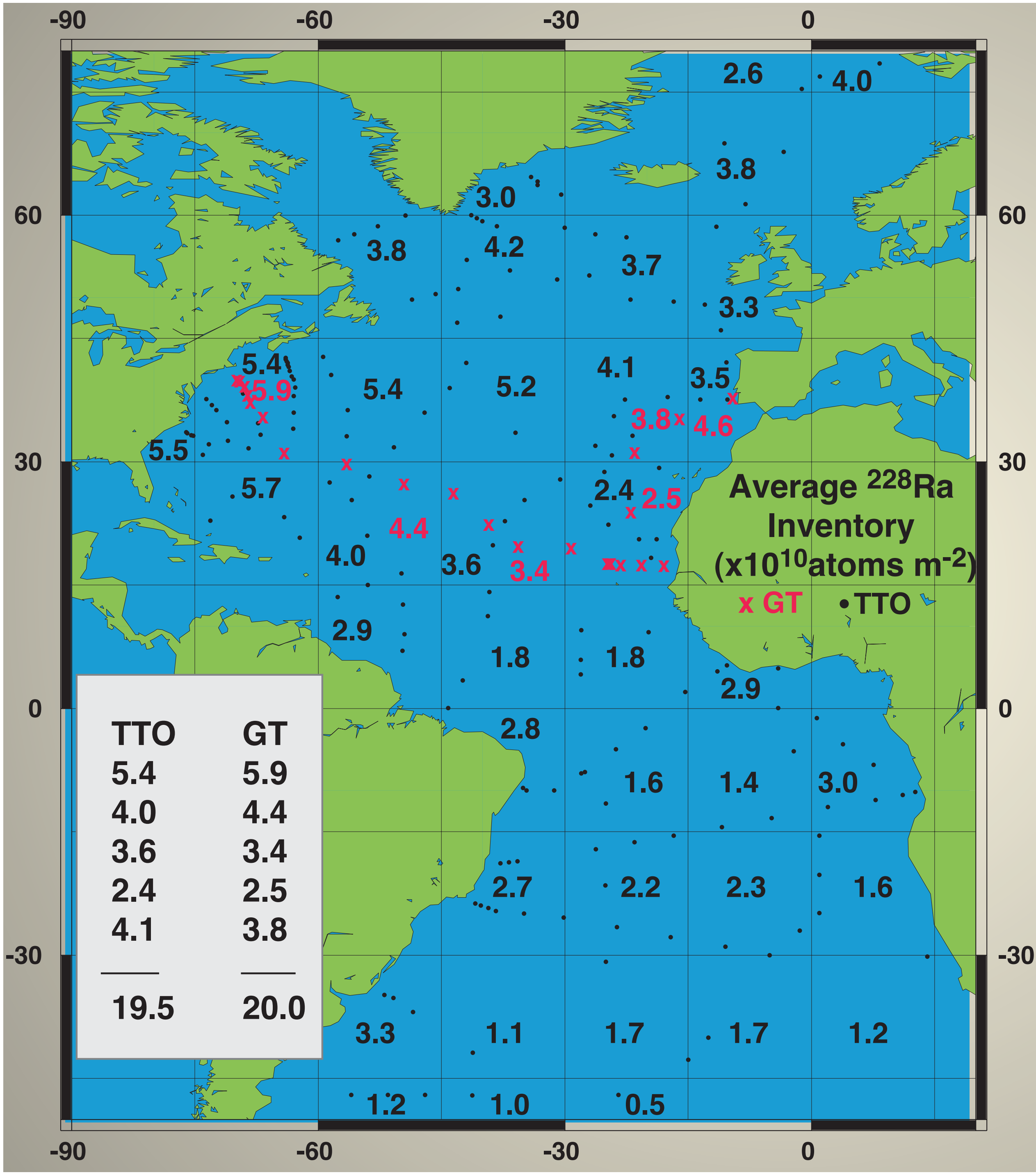


Add US Atlantic GEOTRACES Data

95% of the ^{228}Ra atoms present during TTO decayed before the 2011-2012 GT cruises.

^{228}Ra appears to be at steady state in the upper North Atlantic.

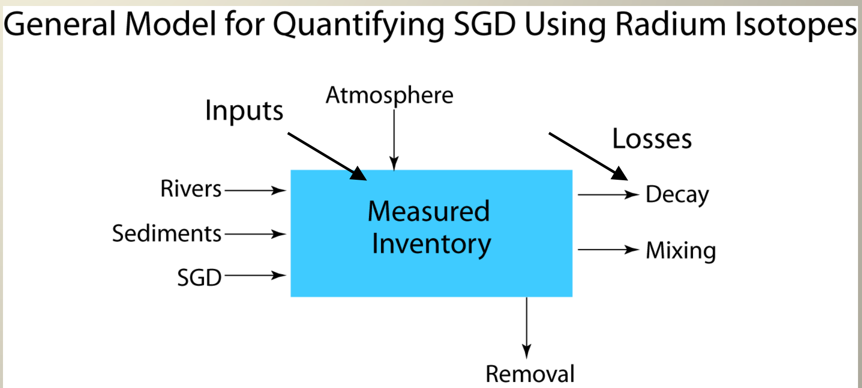
Total inventory $^{228}Ra = 2.9 \times 10^{24}$ atoms in upper 1000 m

12% of the ^{228}Ra inventory decays each year. This must be replaced by a similar flux from the continents **to maintain steady state.**

^{228}Ra flux = Inventory x decay rate (λ)

$= 2.9 \times 10^{24}$ atoms $\times 0.12$ year^{-1}

$= 3.5 \times 10^{23}$ atoms year^{-1}

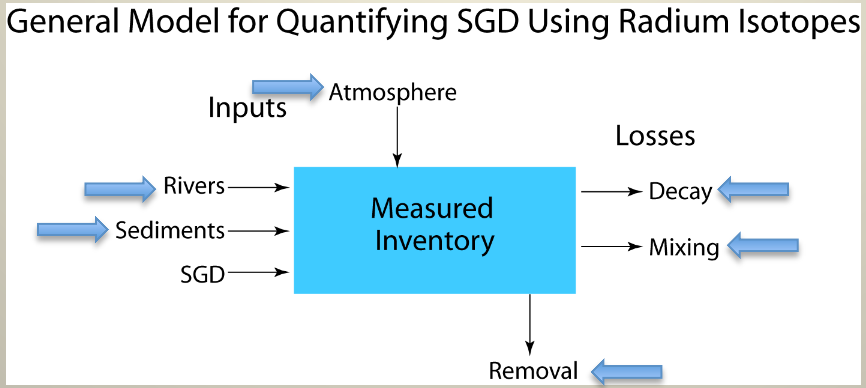


^{228}Ra Balance

Total ^{228}Ra loss = 3.5×10^{23} atoms/yr

Sediment input = 1.3×10^{23} atoms/yr
River input = 2.5×10^{22} atoms/yr
Dust input = 2.8×10^{21} atoms/yr

Difference = 1.9×10^{23} atoms/yr



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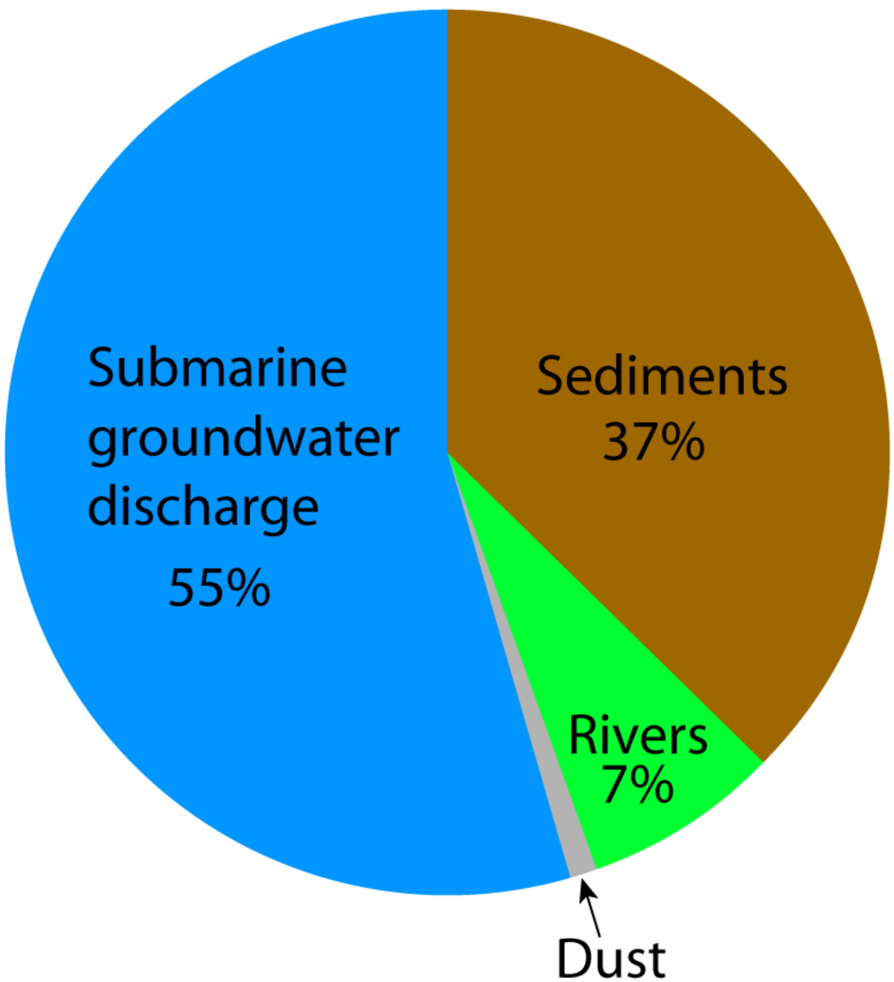
Dust input = 2.8×10^{21} atoms/yr

Difference = 1.9×10^{23} atoms/yr

This must come from SGD.

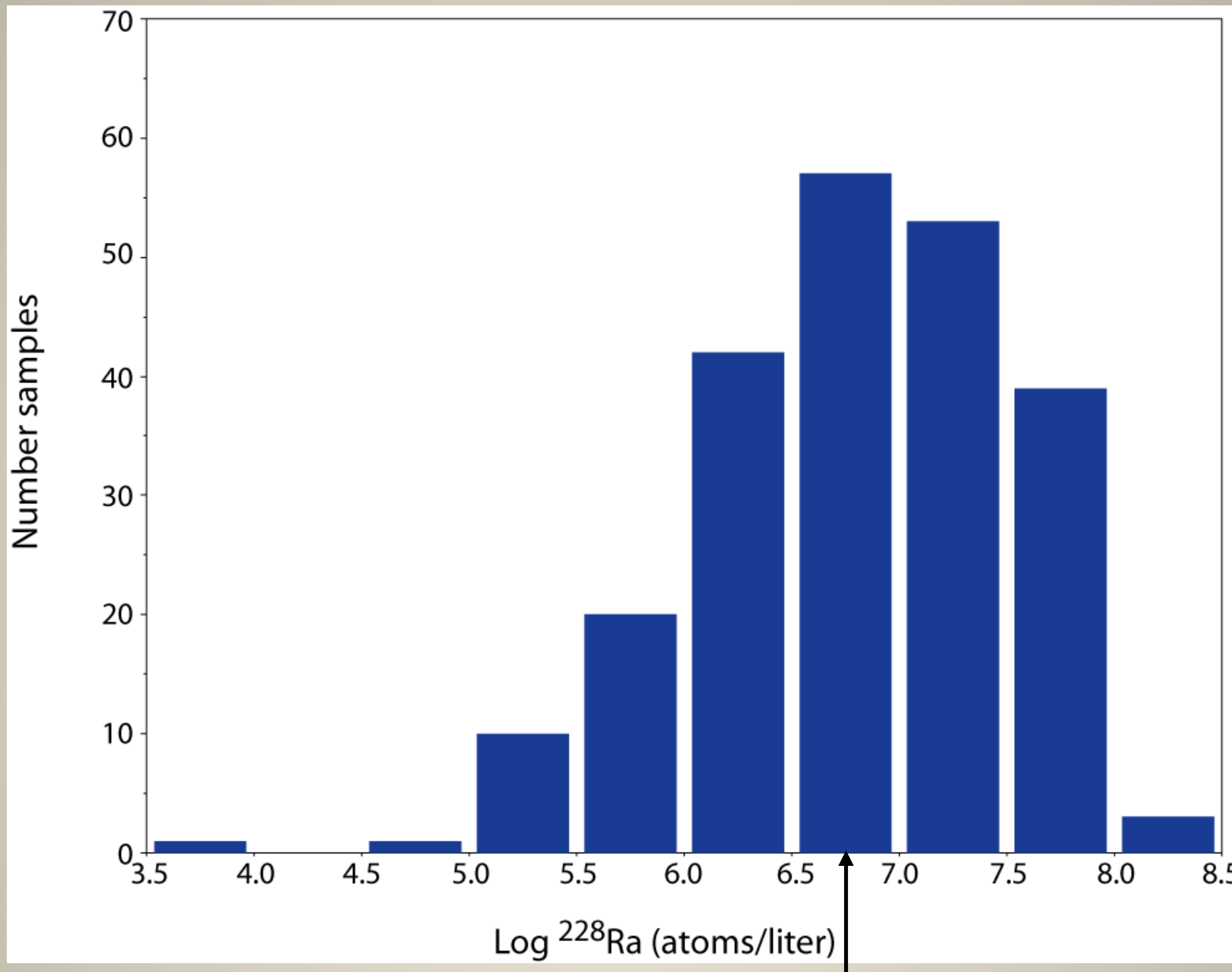
Inputs of ^{228}Ra to the upper Atlantic Ocean



Need the concentration of ^{228}Ra in SGD to convert the ^{228}Ra flux to the SGD flux.

$$\text{SGD Flux (L/yr)} = \frac{^{228}\text{Ra Flux (atoms/year)}}{[^{228}\text{Ra}]_{SGD} \text{ (atoms/L)}}$$

Distribution of ^{228}Ra in Atlantic SGD (226 samples)



unbiased estimate of the mean = 6.2 x 10^6 at/L (1.5 dpm/L)

standard error bounds (5.6 - 6.9) x 10^6 at/L

assuming there is no bias in sampling

SGD ^{228}Ra flux = (1.9±0.8) x 10^{23} atoms/yr

Measured ^{228}Ra in SGD = (5.6 - 6.9) x 10^{6} atoms/L

(~100 x the concentration in the surface Atlantic)

SGD flux = (2-4) x 10^{16} L/yr

River flux = 2.4 x 10^{16} L/yr

How important is SGD on a global scale?

The SGD flux to the Atlantic Ocean is similar to the river flux to the Atlantic (80-160% of the river flux).

Because SGD contains higher concentrations of many components than do rivers, this flux is probably more important in maintaining the balance of many elements in the ocean.

Comparison of large-scale (>100 km) SGD estimates based on radium or radon

Region	Date	Coast length km	SGD Flux $10^8\ m^3\ km^{-1}\ y^{-1}$	Reference
Onslow Bay, NC	Jul-02	140	2.9	McCoy et al., 2007
SE USA	Jul-94	320	2.6	Moore 2000
SE USA	Sep-98	600	4.7	Moore 2010
SE USA	Oct-98	600	3.3	Moore 2010
SE USA	Apr-99	600	4.4	Moore 2010
SE USA	Feb-00	600	2.2	Moore 2010
SE Brazil	Dec-04	240	1.5	Windom et al., 2006
S. China Sea	Jul-08	308	4.4	Liu et al., 2011
Yangtze Mouth	Aug-09	320	2.6	Gu et al., 2012
Yucatan	Jan-Nov-09	370	1.1	Null et al., 2014
Atlantic	1981-1989	85,000	3.7	Moore et al., 2008
Mediterranean	1981-2014	64,000	0.2	Rodellas et al., 2015
Global	1971-2014	1,364,700	0.4	Cho & KIm, 2016

Conceptual model for South Atlantic Bight

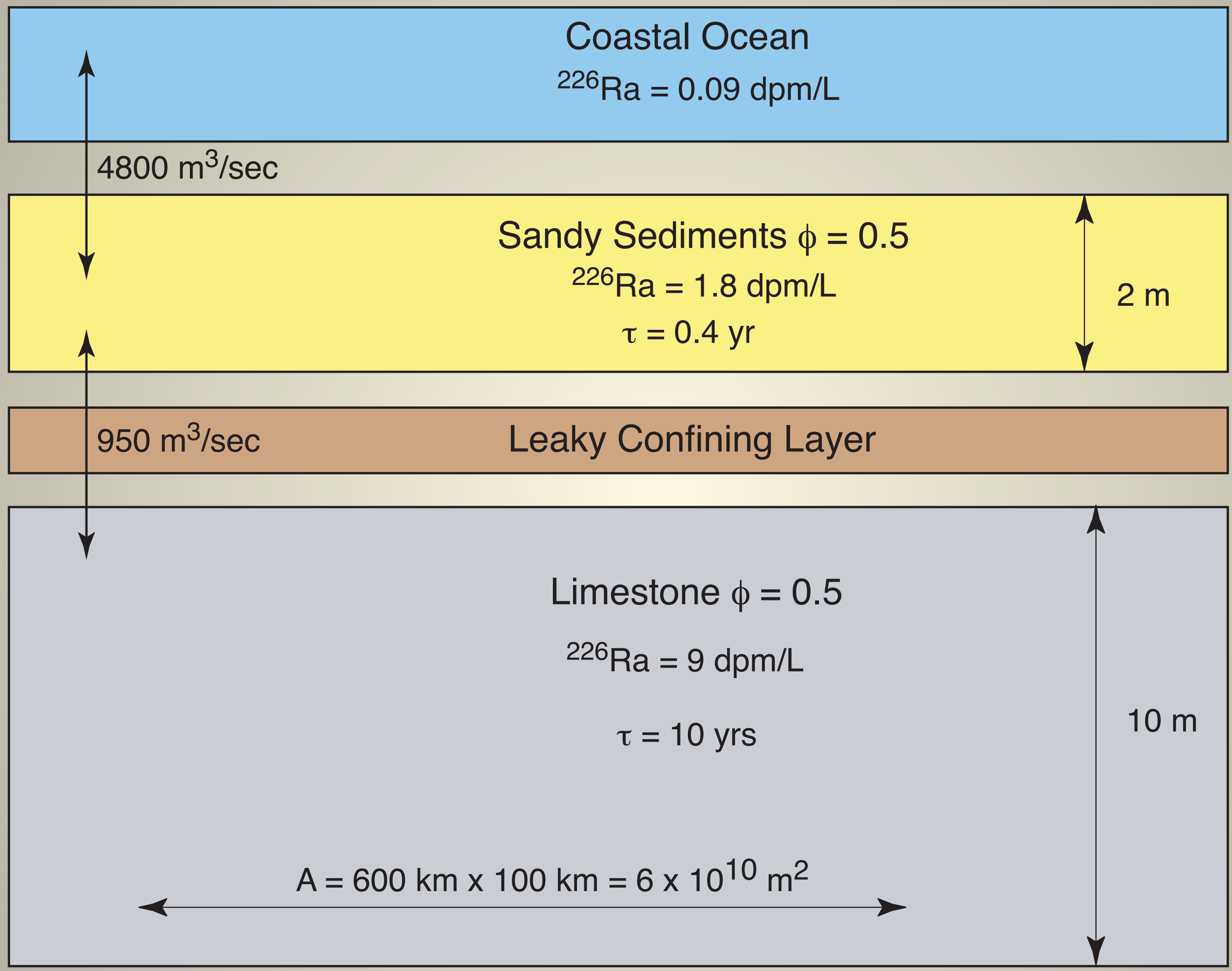
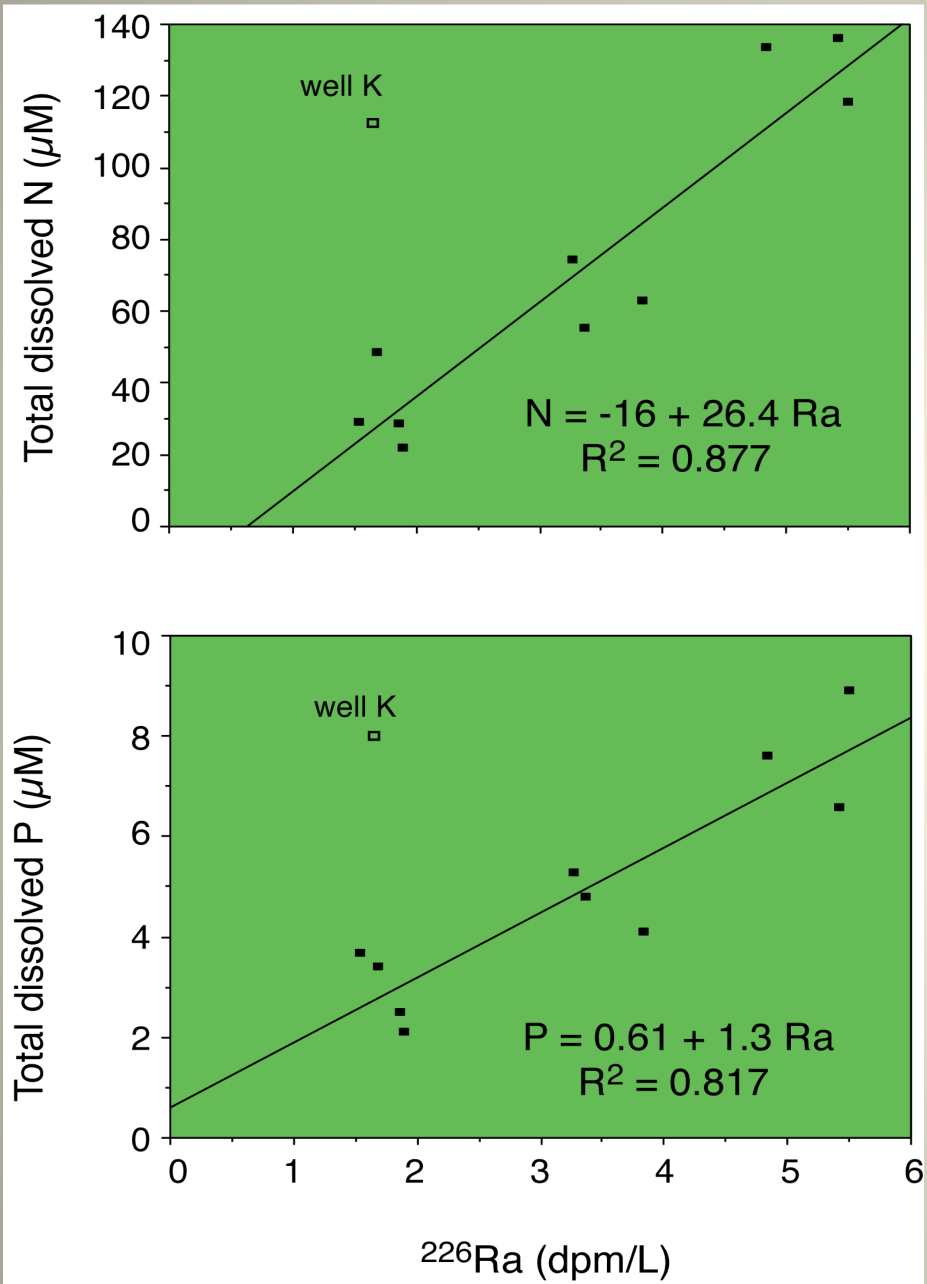


Figure 3

W.S. Moore, GLOBAL BIOGEOCHEMICAL CYCLES, VOL. 24, GB4005, 2010



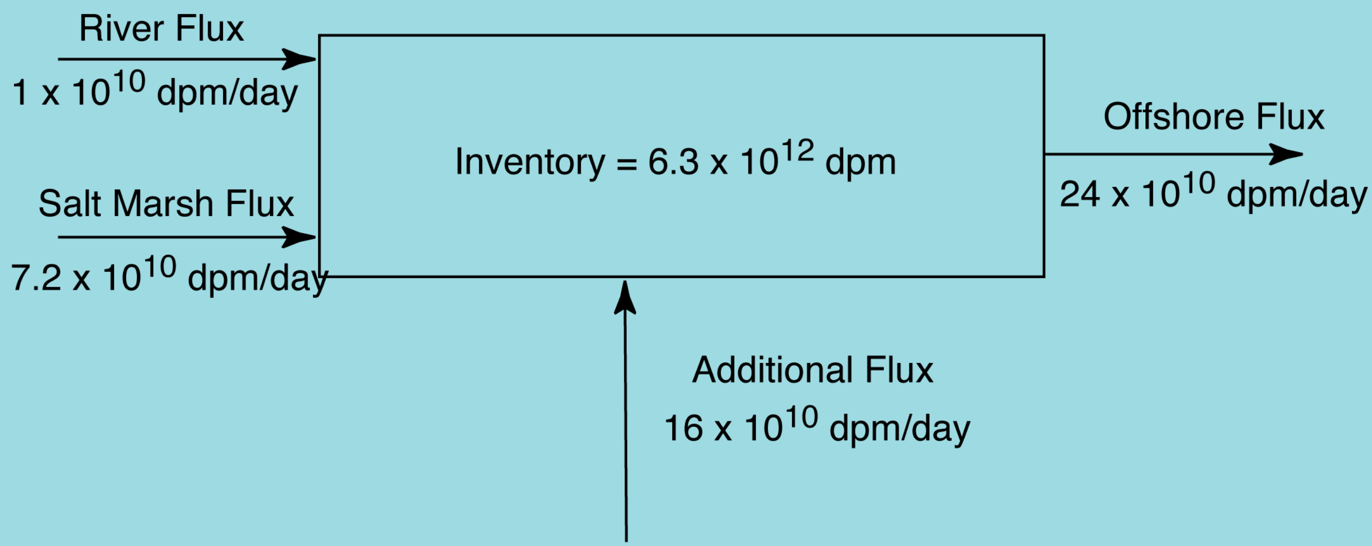
Data from offshore monitoring wells in the shallow coastal aquifer

If there is stoichiometric relation between radium and nutrients:

[Nut/Ra] x Ra flux = Nut flux

(Moore et al., 2001)

Excess ^{226}Ra in Surface Water
South Atlantic Bight (Cape Fear to Savannah) July 1994



From Radium-Nutrient Relationship in Offshore Wells

TDN/Ra = 26.4×10^{-6} mole/dpm x 16×10^{10} dpm/day = 4.2×10^{6} moles/day

TDP/Ra = 1.3×10^{-6} mole/dpm x 16×10^{10} dpm/day = 2.1×10^{5} moles/day

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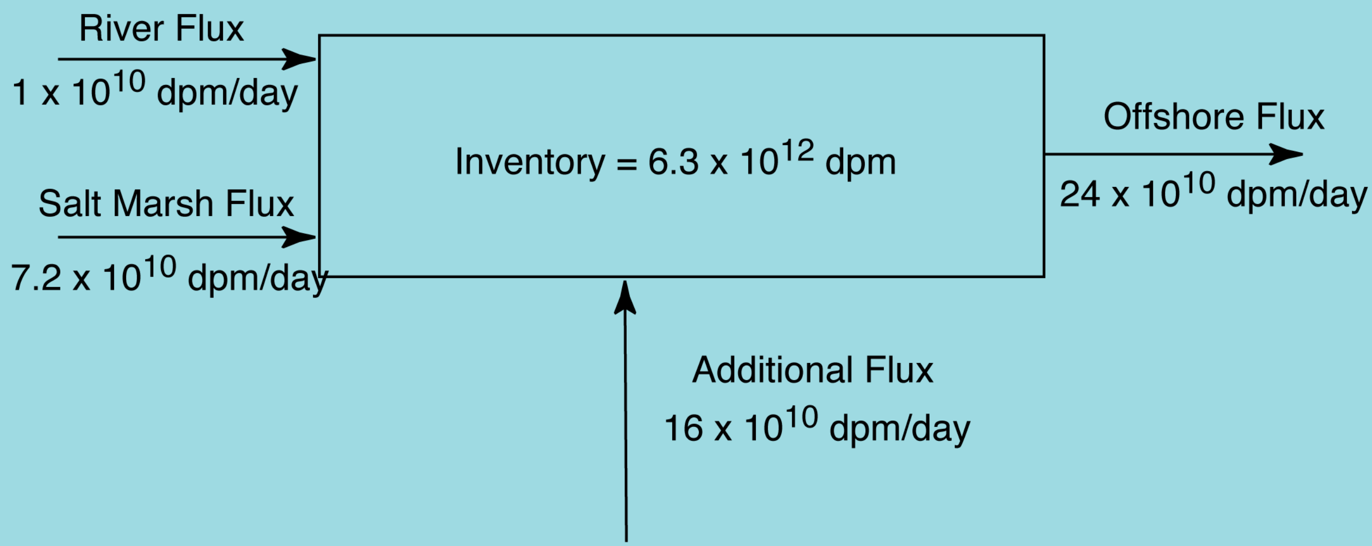

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~ 3x the river fluxes


Windom, H.L., L.F. Niencheski, W.S. Moore, R. Jahnke. Submarine Groundwater
Discharge: a Large, Previously Unrecognized Source of Dissolved Iron to the South
Atlantic Ocean. Marine Chemistry, 102: 252-266, 2006.

Conclusions

Radium isotopes effectively integrate the effects of submarine groundwater discharge over a variety of spatial scales.

The limited studies that are available on embayment and ocean scales give consistent results when normalized to shoreline length.

One of the most important outcomes of Ra isotope studies is that submarine groundwater discharge (SGD) has been recognized as an important component of the hydrologic cycle, rivaling rivers as a pathway for nutrient, carbon, and metal input to the ocean.