Recharge at PFAS-Impacted Sites: The Other Half of the Mass Discharge Story

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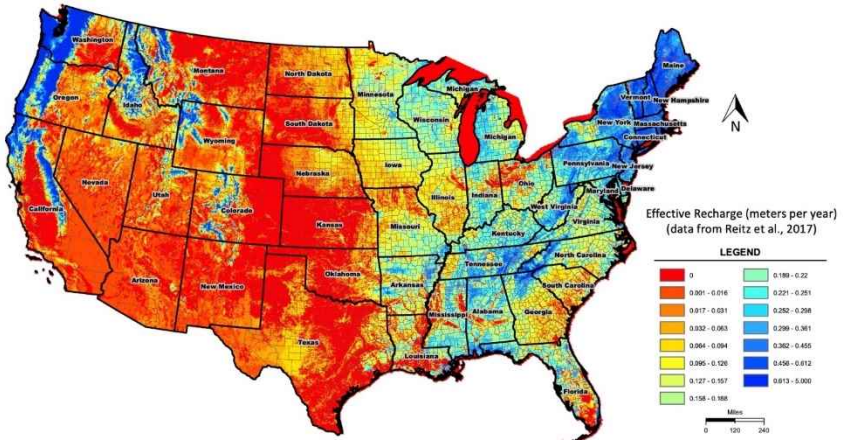
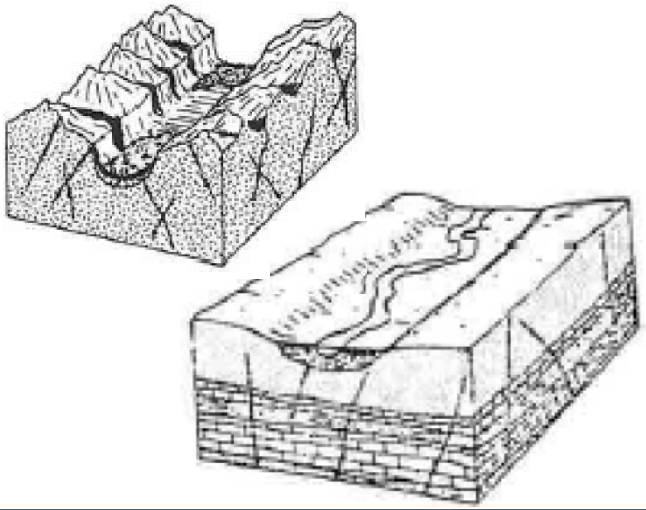
International Conference on Remediation of Chlorinated and Recalcitrant Compounds
Denver, Colorado





4 June 2024

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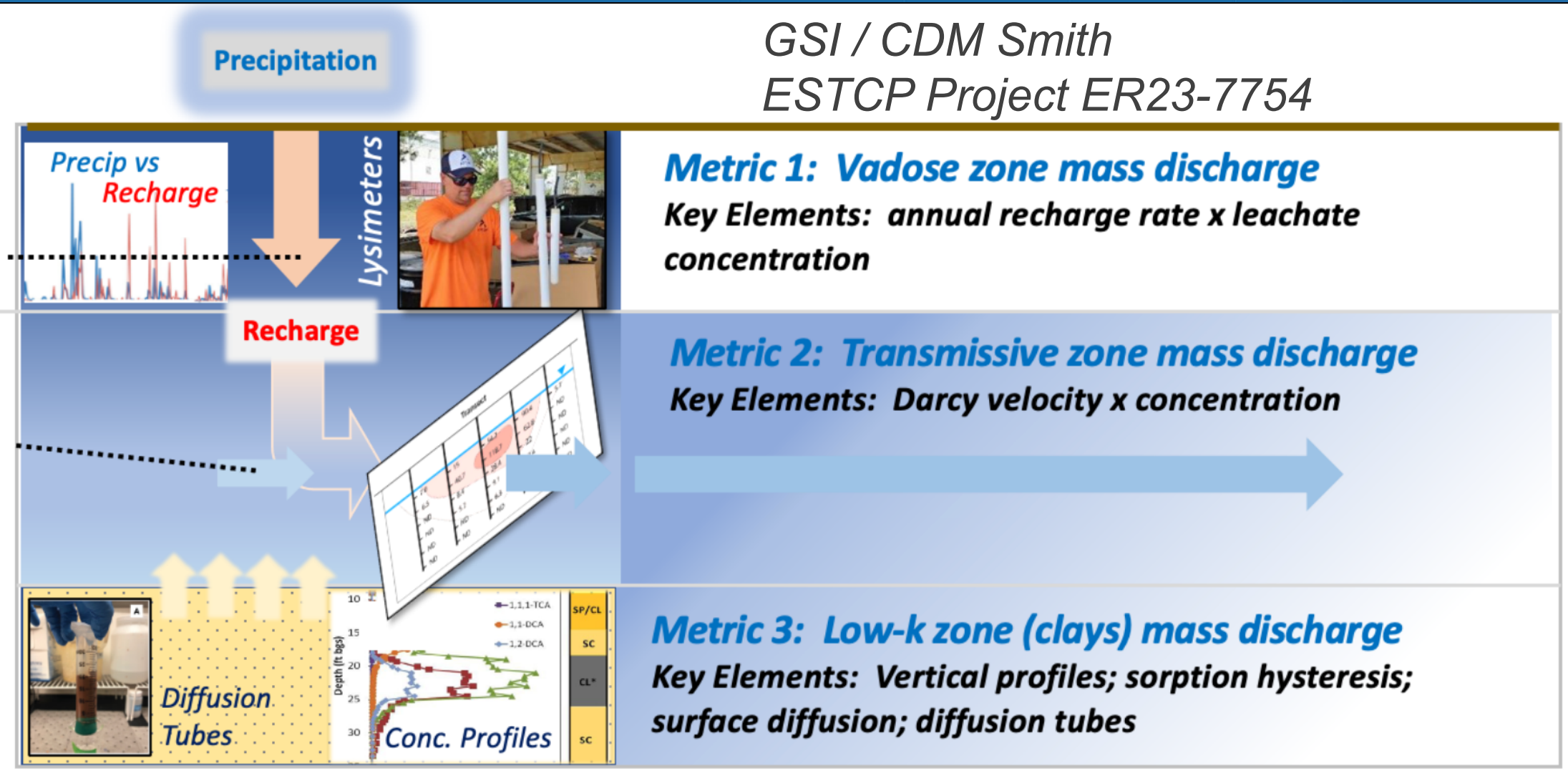
AGENDA

- The Problem
- Quantifying PFAS Mass Discharge from Unsaturated Source Zones
- Overview of Recharge Estimation Methods
- Tiered System to Estimate Recharge at PFAS Site

Mass Discharge (grams per year) is Key Metric for PFAS Sources

GSI / CDM Smith
ESTCP Project ER23-7754



Metric 1: Vadose zone mass discharge

Key Elements: annual recharge rate x leachate concentration

Metric 2: Transmissive zone mass discharge

Key Elements: Darcy velocity x concentration

Metric 3: Low-k zone (clays) mass discharge

Key Elements: Vertical profiles; sorption hysteresis; surface diffusion; diffusion tubes

Metric 4: Relative Contribution

Key Elements: Subtract Metric 1 from Metric 2

Metric 5: Change in Mass Discharge Over Time

Key Elements: Equilibrium and Diffusion Models

How much PFAS are too much?

	Flow Rate	PFOA & PFOS	PFHxS, PFNA, HPFO-DA (Gen X)
USEPA MCL	*(ng/L)*	*4*	*10*
Household	150 gpd	8.3×10^{-4} g/yr	2.1×10^{-3} g/yr
Small water supply	1000 households, 100 gpm	0.80 g/yr	2.0 g/yr
Surface Water Stream	100 cfs	357 g/yr	893 g/yr

How much PFAS are too much?

Site/Reference	Site Type	Climate	Unsaturated M_d (g/yr)		Saturated M_d (g/yr)	
			PFOS	Total PFAS	PFOS	Total PFAS
Adamson et al. (2020); Nickerson et al. (2021)	Former Fire Training Area	Humid (<10 in/yr)	--	--	310	3,600 (58 PFAS)
Anderson et al. (2022)	Former Fire Training Area	Semi-arid (10-20 in/yr)	10.2	188 (6 PFAS)	--	--
Quinnan et al. (2021) Source Area	AFFF Use/Storage	Semi-humid (20-40 in/yr)	0.4	--	22.2	227 (PFOA+PFOS)

Mass Discharge (grams per year) To Groundwater

$$M_d = QAC$$

The Problem and Two Roads to Get Mass Discharge (grams per year) To Groundwater

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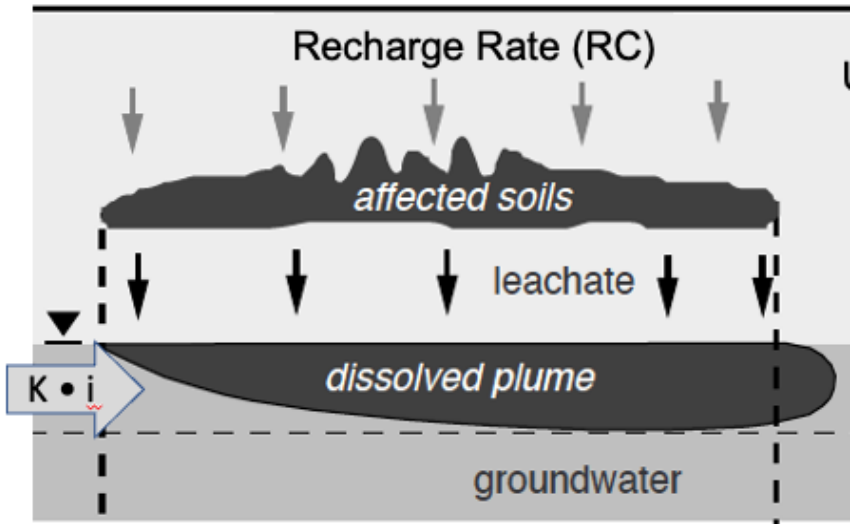
1. Soil Samples + Partitioning + Recharge



1. Analyze soil samples for **mg/kg**
2. Convert to mg/L via partitioning
3. Multiply by recharge rate and area

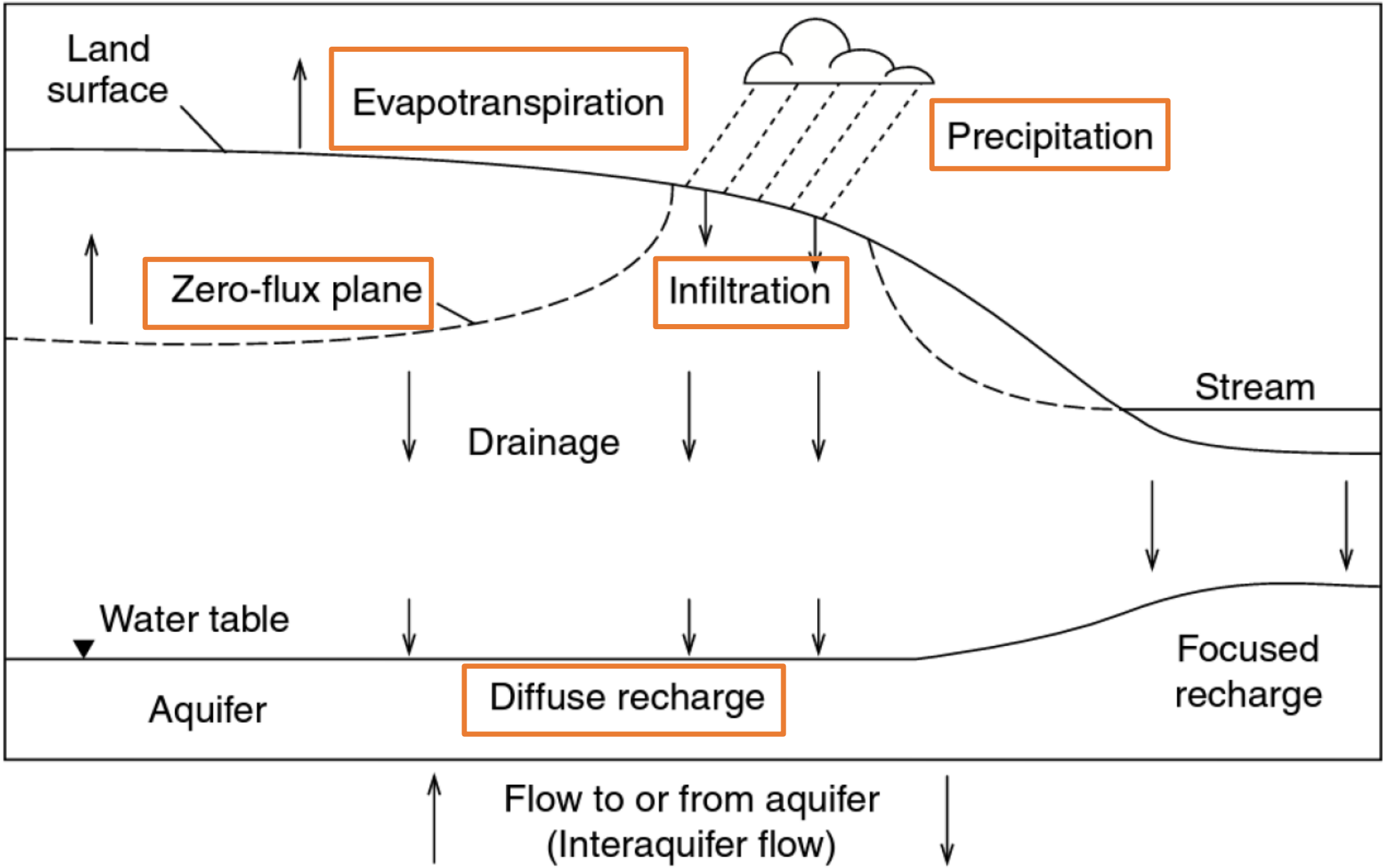
2. Suction Lysimeters + Recharge

1. Analyze porewater for **ng/L**
2. Multiply by recharge rate and area

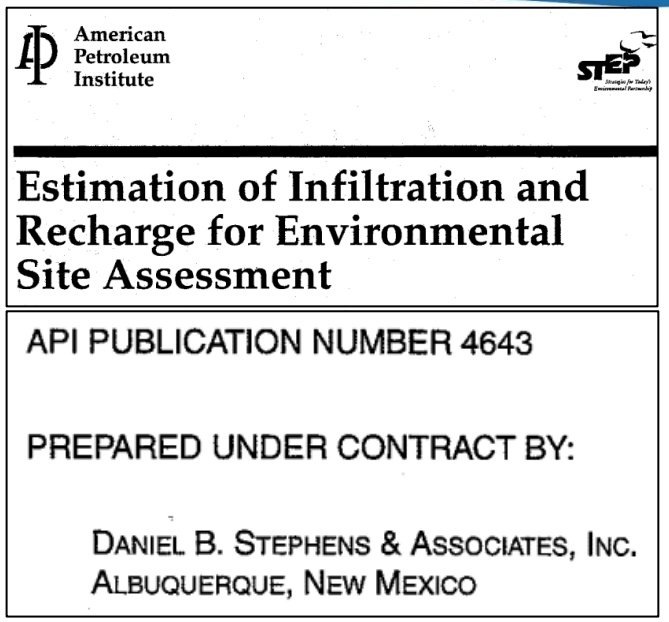
Figure: CDM Smith ER20-5088

Conceptual vertical cross section of key recharge processes *(Healy, 2010).*

There are roughly ***40 different methods*** *to estimate recharge*



Three Key Recharge References


American Petroleum Institute

STEP

Estimation of Infiltration and Recharge for Environmental Site Assessment

API PUBLICATION NUMBER 4643

PREPARED UNDER CONTRACT BY:

DANIEL B. STEPHENS & ASSOCIATES, INC.
ALBUQUERQUE, NEW MEXICO

Stephens Associates, 1996


Home › Hydrogeology Journal › Article

Paper | Published: 17 January 2002

Choosing appropriate techniques for quantifying groundwater recharge

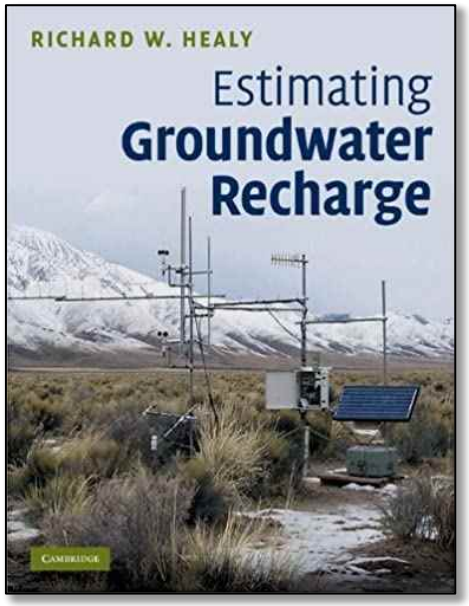
Bridget R. Scanlon, Richard W. Healy & Peter G. Cook

Hydrogeology Journal **10**, 18–39 (2002) | Cite this article

8106 Accesses | **1092** Citations | **22** Altmetric | Metrics

doi: 10.1007/s10040-001-0176-2

Scanlon et al., 2002



Healy, 2010

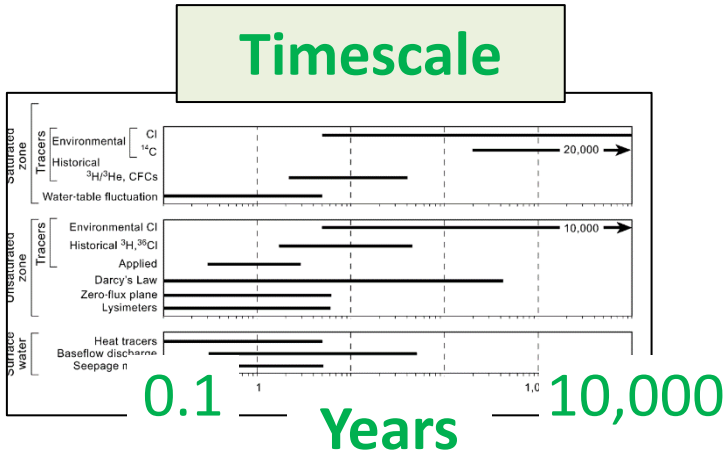
Recharge Methods
Scanlon et al., 2002

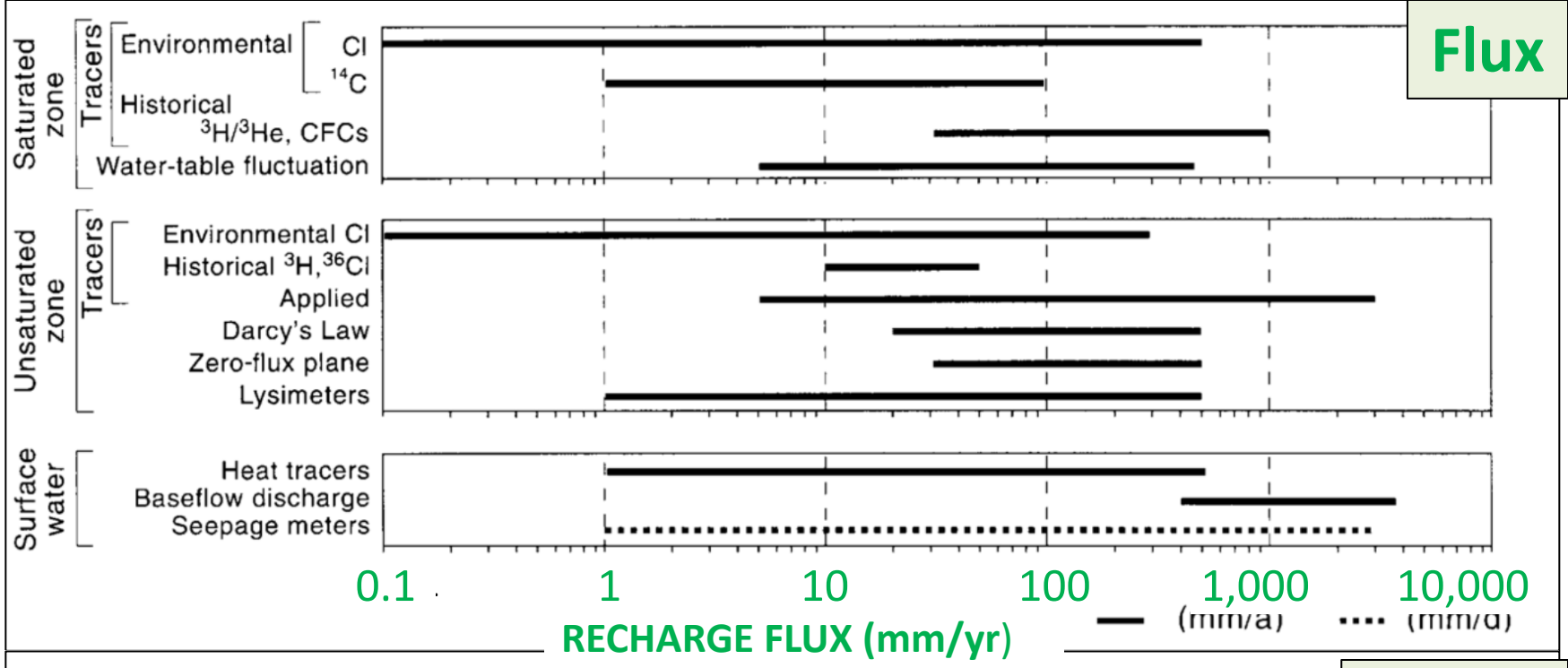
THREE METRICS, THREE GRAPHS

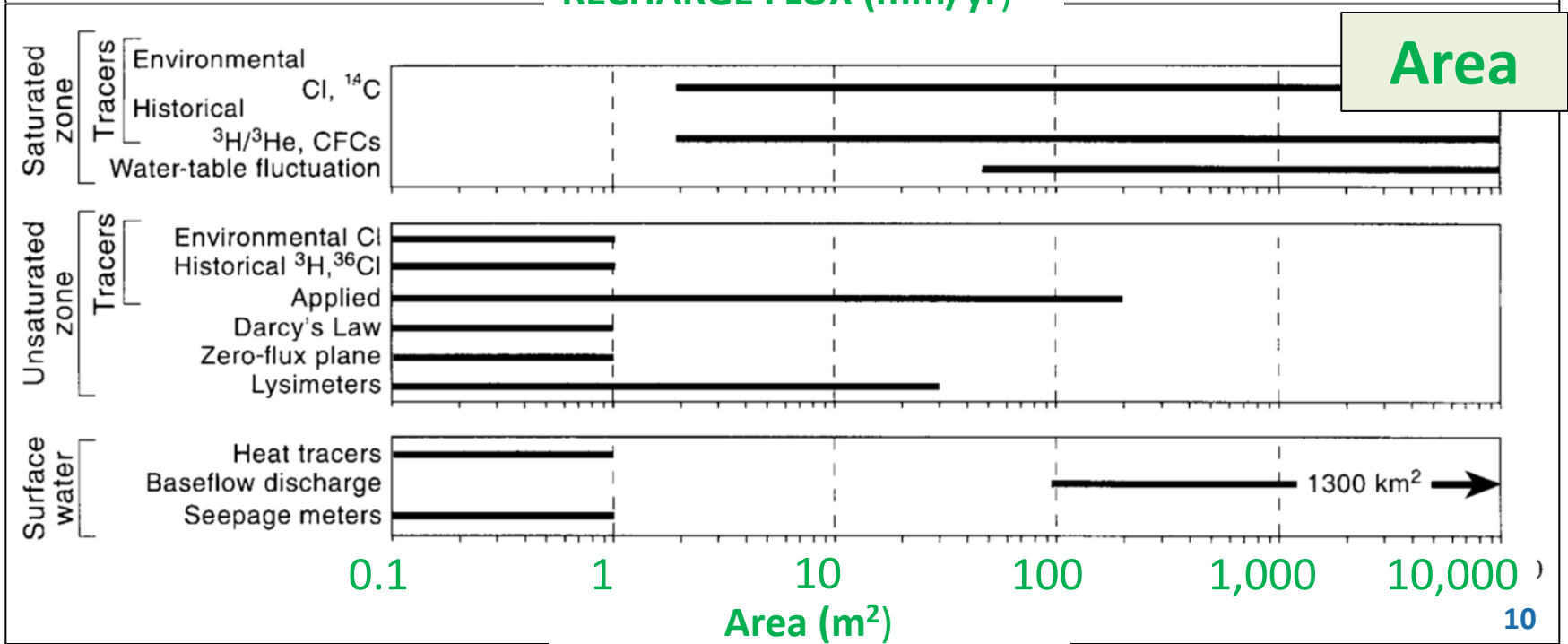
S-1: Recharge Flux Range

S-2: Measurement Area Range

S-3: Time Range (years)





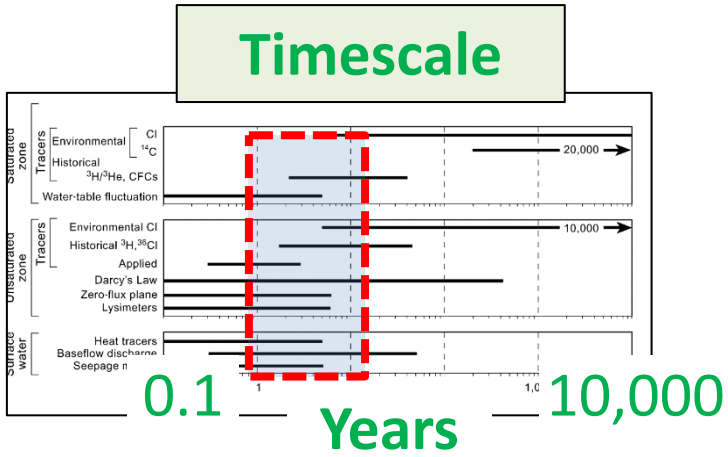


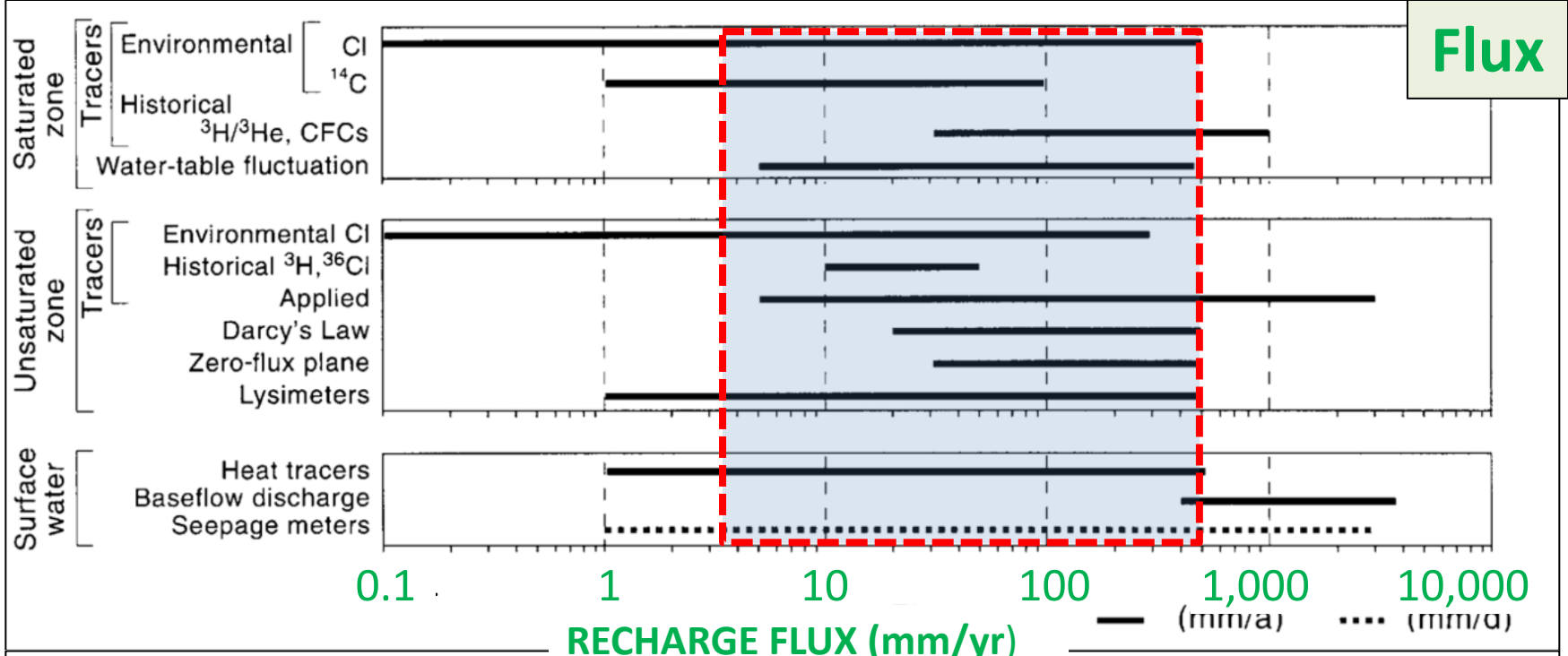
Recharge Methods For PFAS Sites

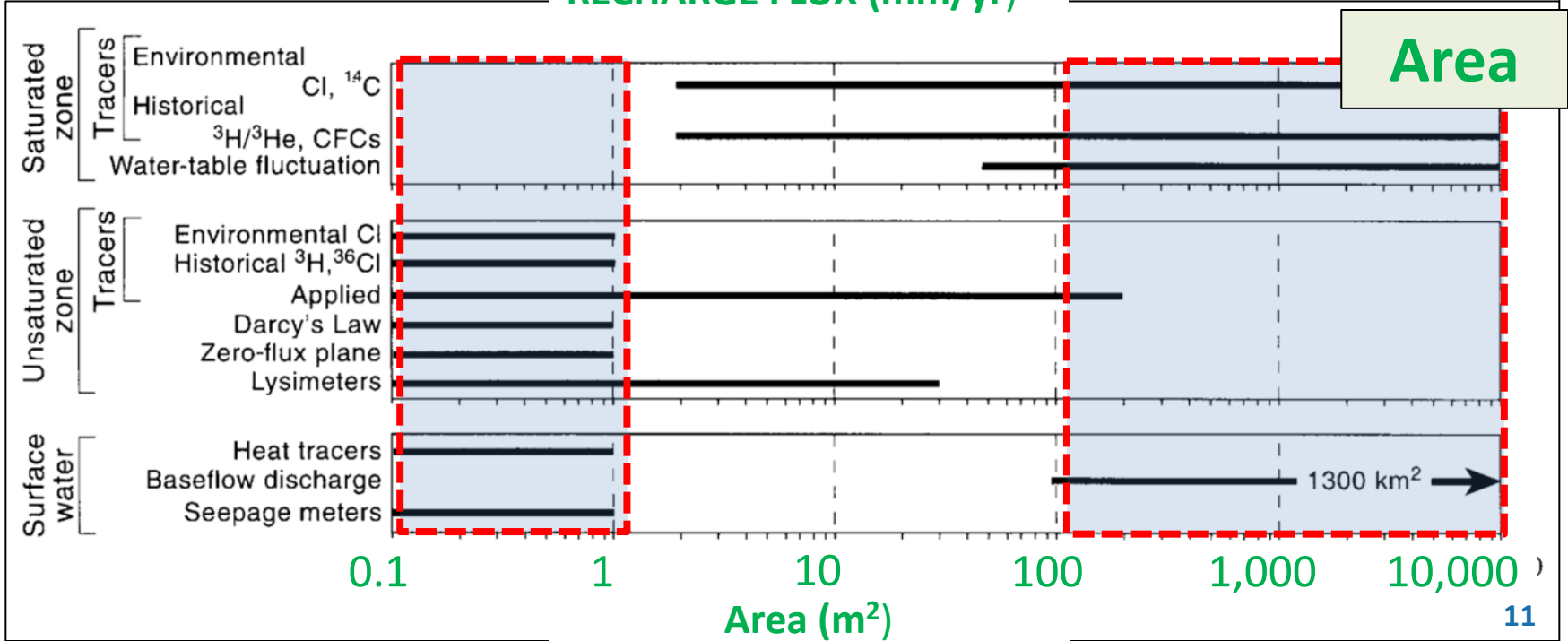
(Newell et al., 2023)

Key Point:

We narrowed down list of methods to ones ***most applicable for PFAS sites***







Tiered Approach To PFAS Recharge

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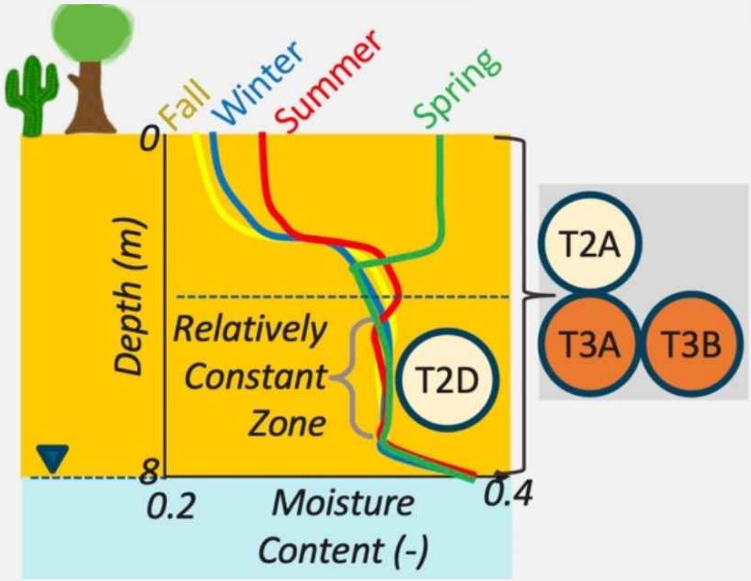
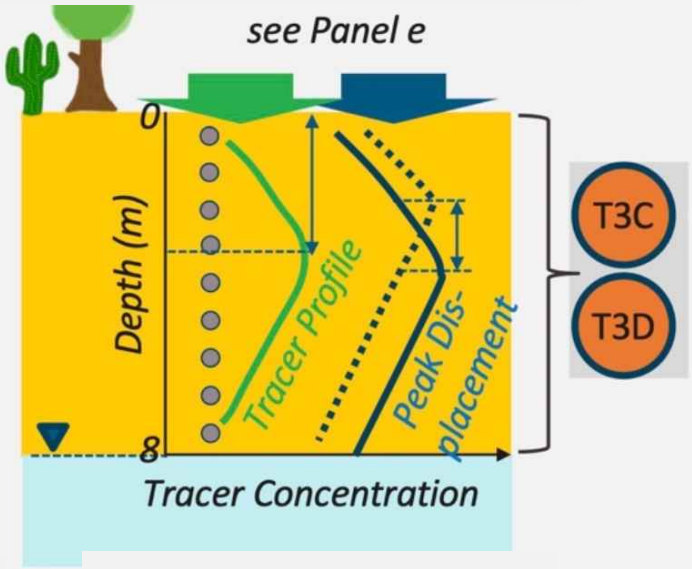
Tier (# of Methods)	Objective	Target PFAS Sites	Need Field Data?	Level of Effort
Tier 1 (4)	Simple source zone recharge estimate	Smaller, low risk	No	Little or no field time. A few hours for analysis.
Tier 2 (6)	Moderate level of effort	Moderate risk	Limited	A few days in the field and a few days for analysis.
Tier 3 (5)	Detailed recharge estimates	Most complex, important sites	Extensive	More extensive field and analysis time than Tier 2 methods.

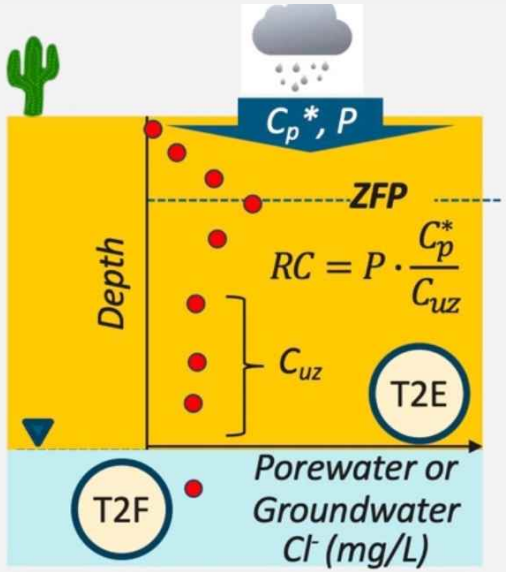
Soil Moisture



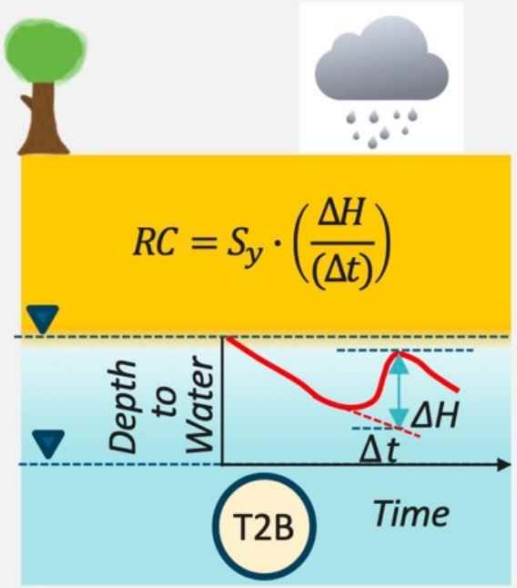
Unsat. Zone Tracers



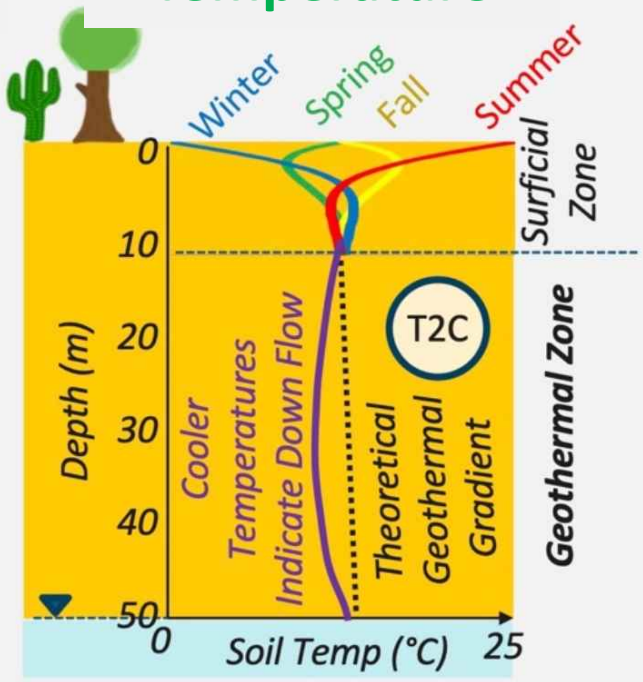
Meteoric Chloride



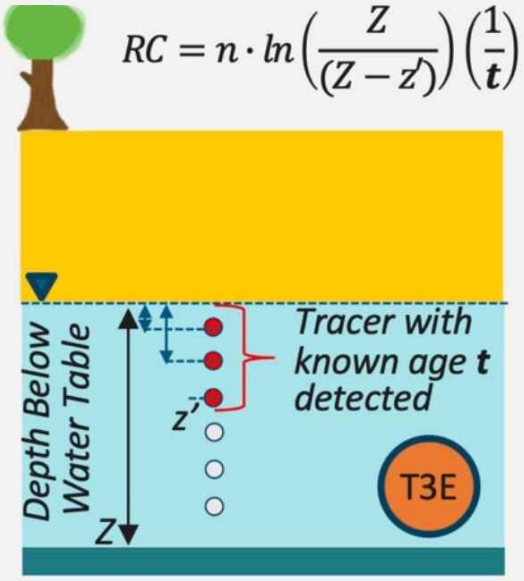
Water Table Fluctuation (WTF)



Temperature



Groundwater Tracers



Legend

Generally better for:

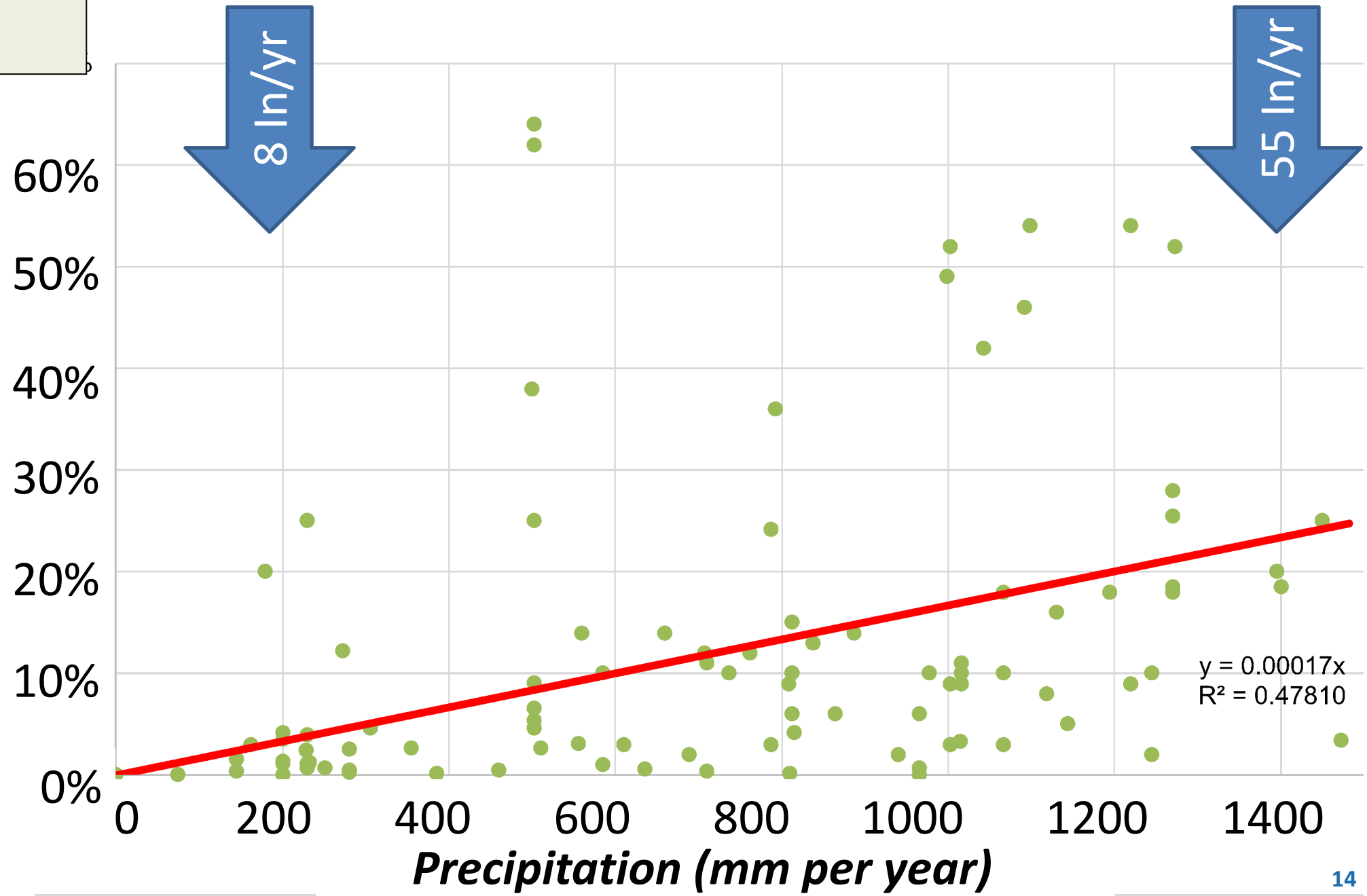
- More Humid Climates
- More Arid Climates

PFAS Recharge Methods:

- T1D Tier 1
- T2C Tier 2
- T3B Tier 3

Method T1-A
Tier 1 Method

Groundwater Recharge as % of Precipitation



Data from Stephens et al., 1996

Method T1-A
Tier 1 Method

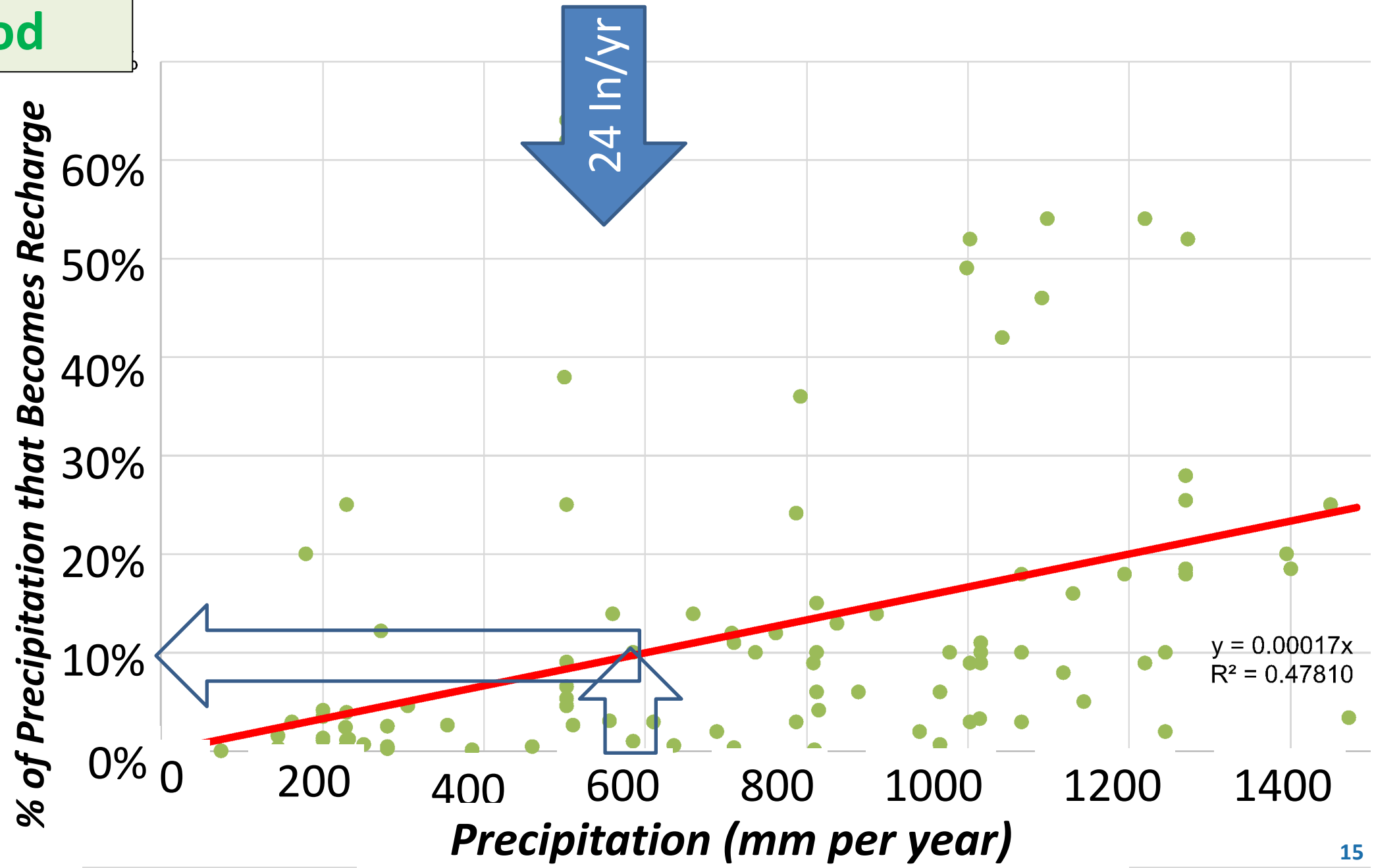
Groundwater Recharge as % of Precipitation

Example:
Precip = 600 mm/yr (24 in/yr

10% becomes recharge

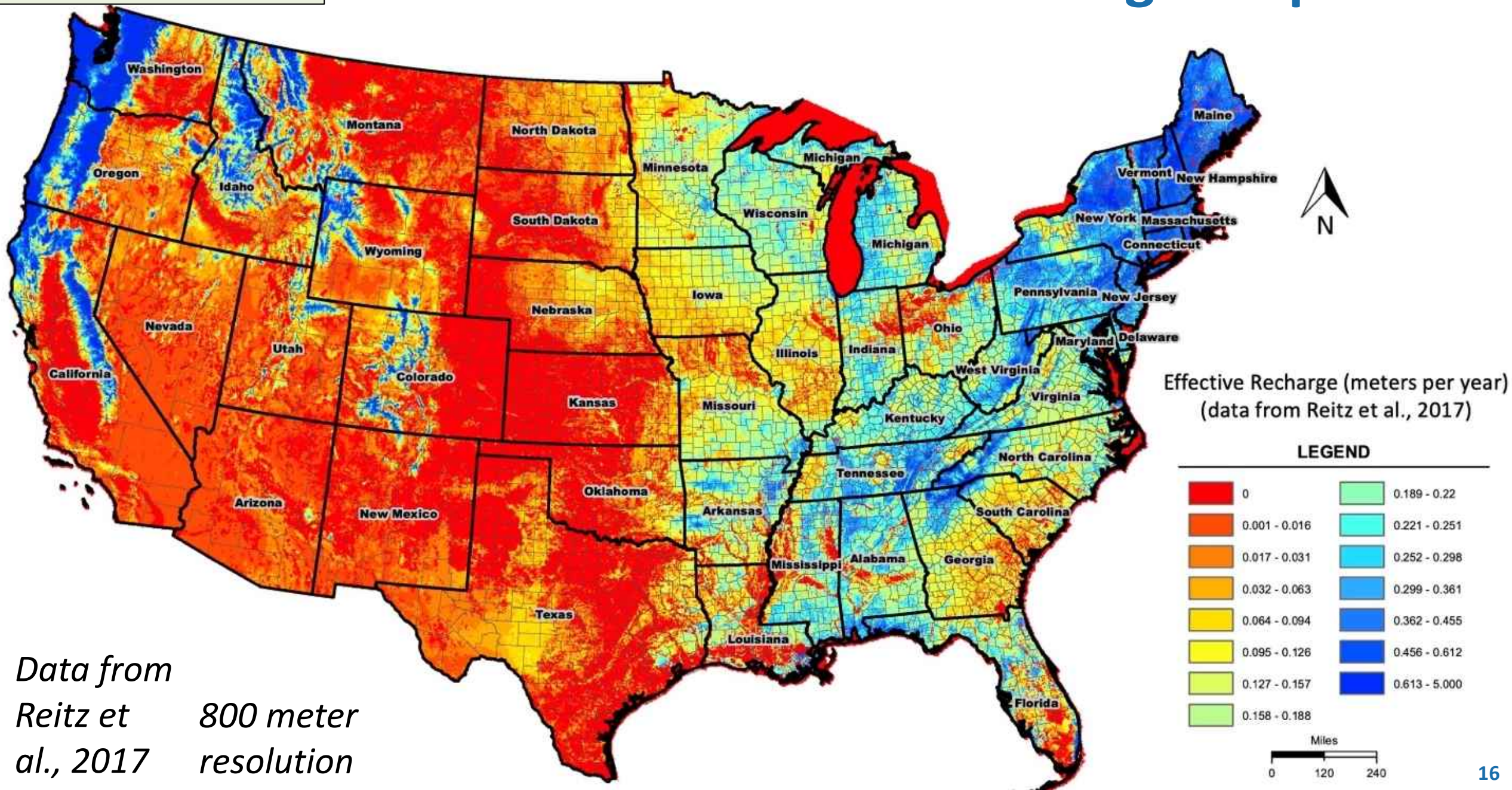
Recharge = 2.4 in/yr

Data from Stephens et al., 1996



Method T1-B

Groundwater Recharge Map

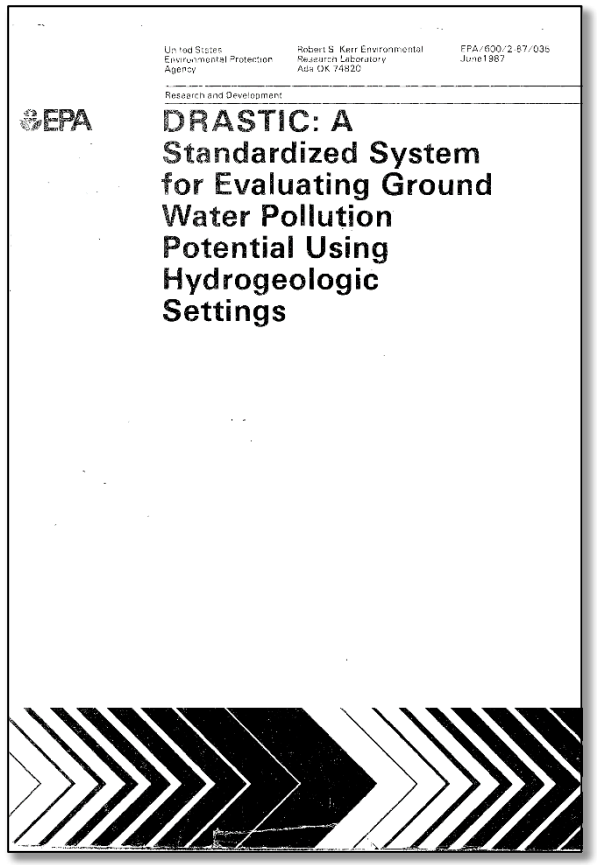


Data from Reitz et al., 2017

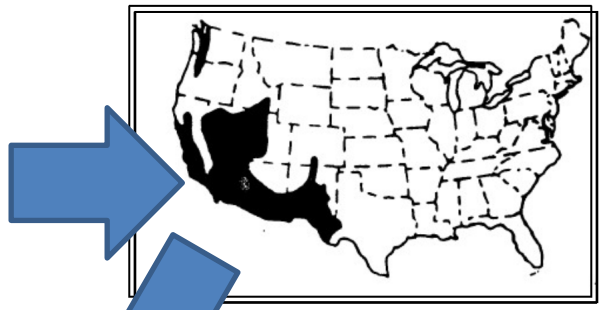
800 meter resolution

Method T1-C

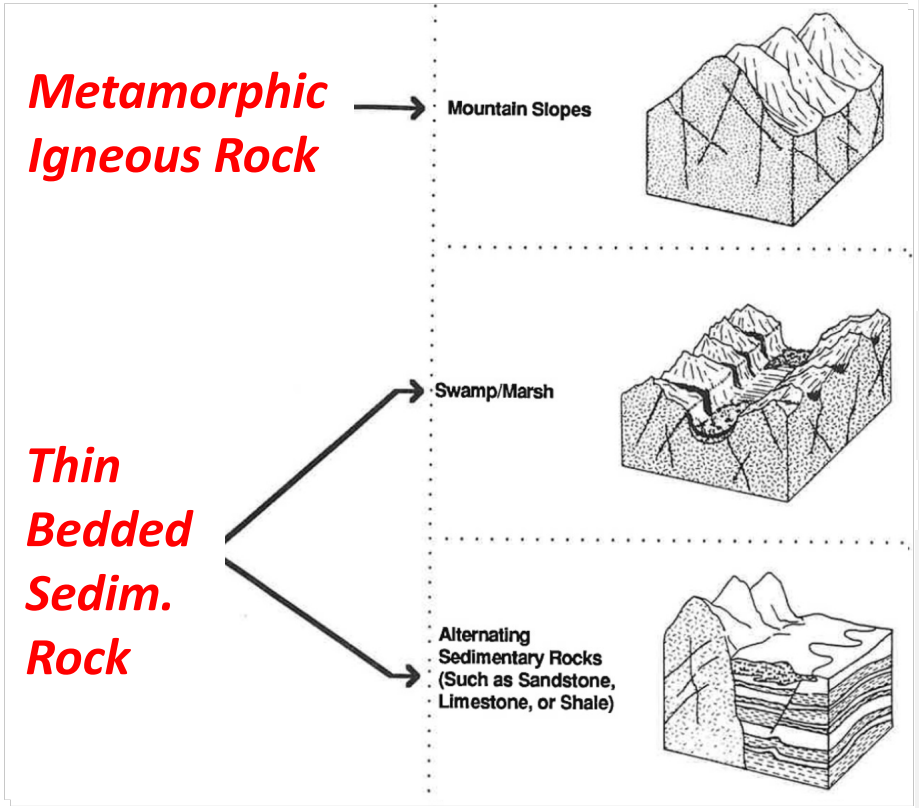
DRASTIC HEURISTIC METHOD



b)



Alluvial Basins Region
(2 Total Hydrogeologic Settings, 3 Shown below)



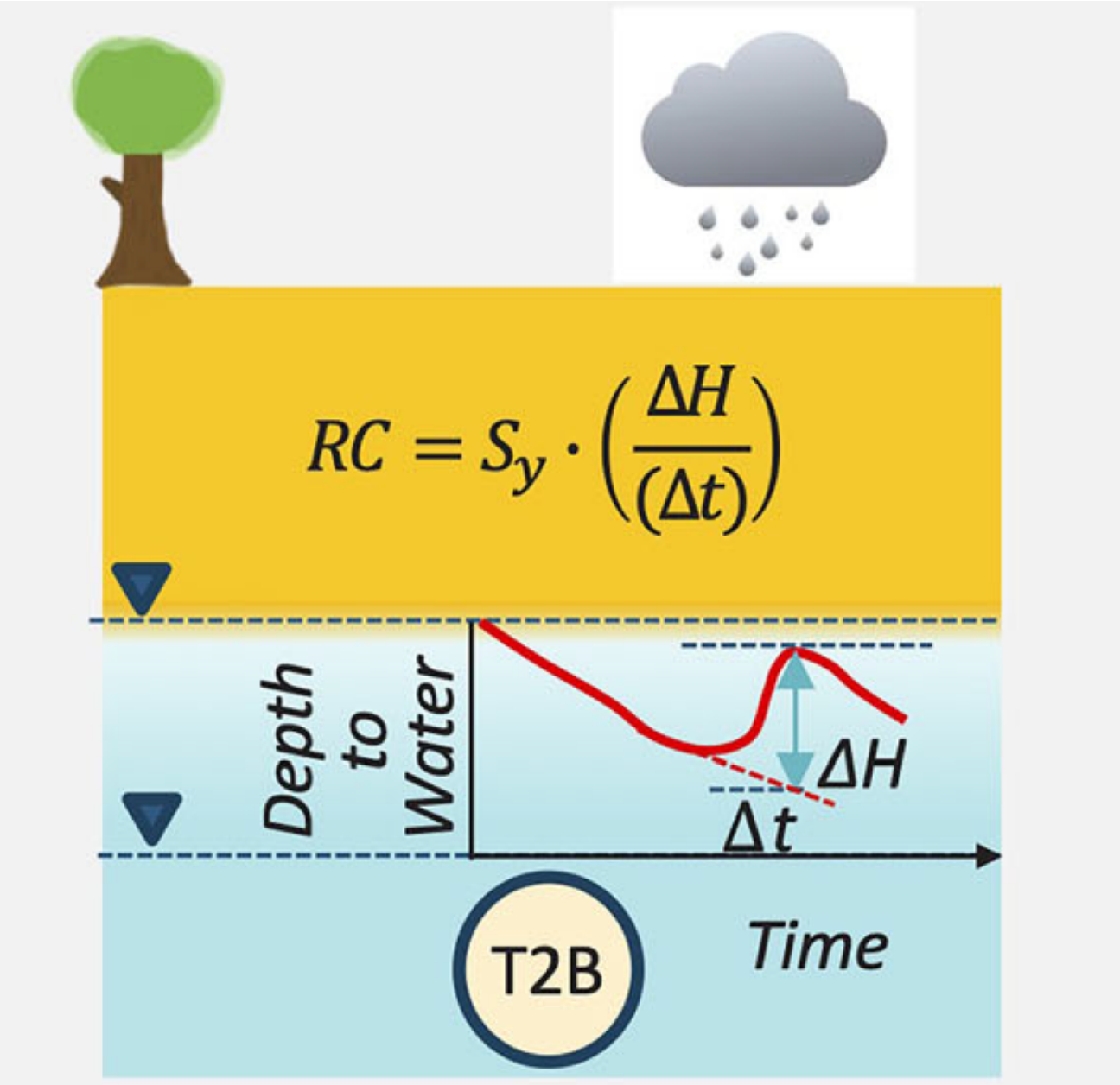
Mountain Slopes
Recharge:
0-2 Inches Per Year

Swamp/Marshes Recharge:
2-4 Inches Per Year

Alternating Sandstone – Shale Sequences
Recharge:
7-10 Inches Per Year

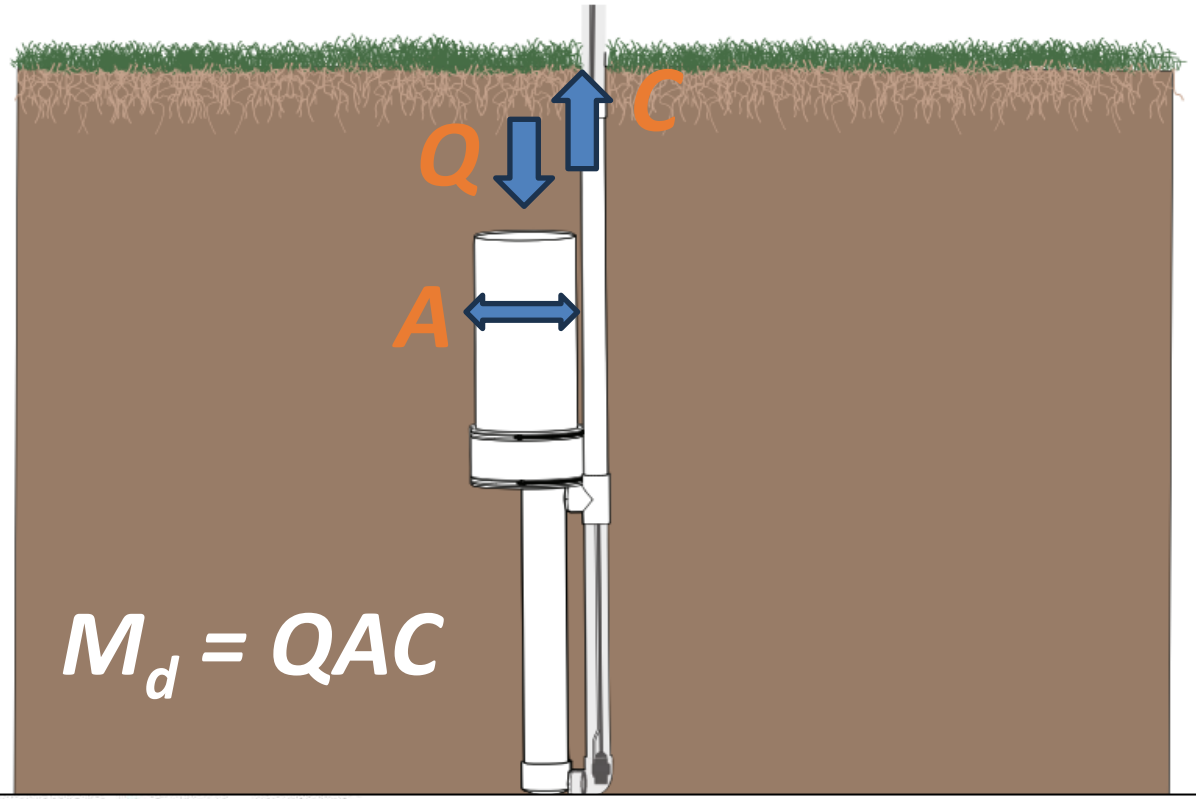
Method T2-B

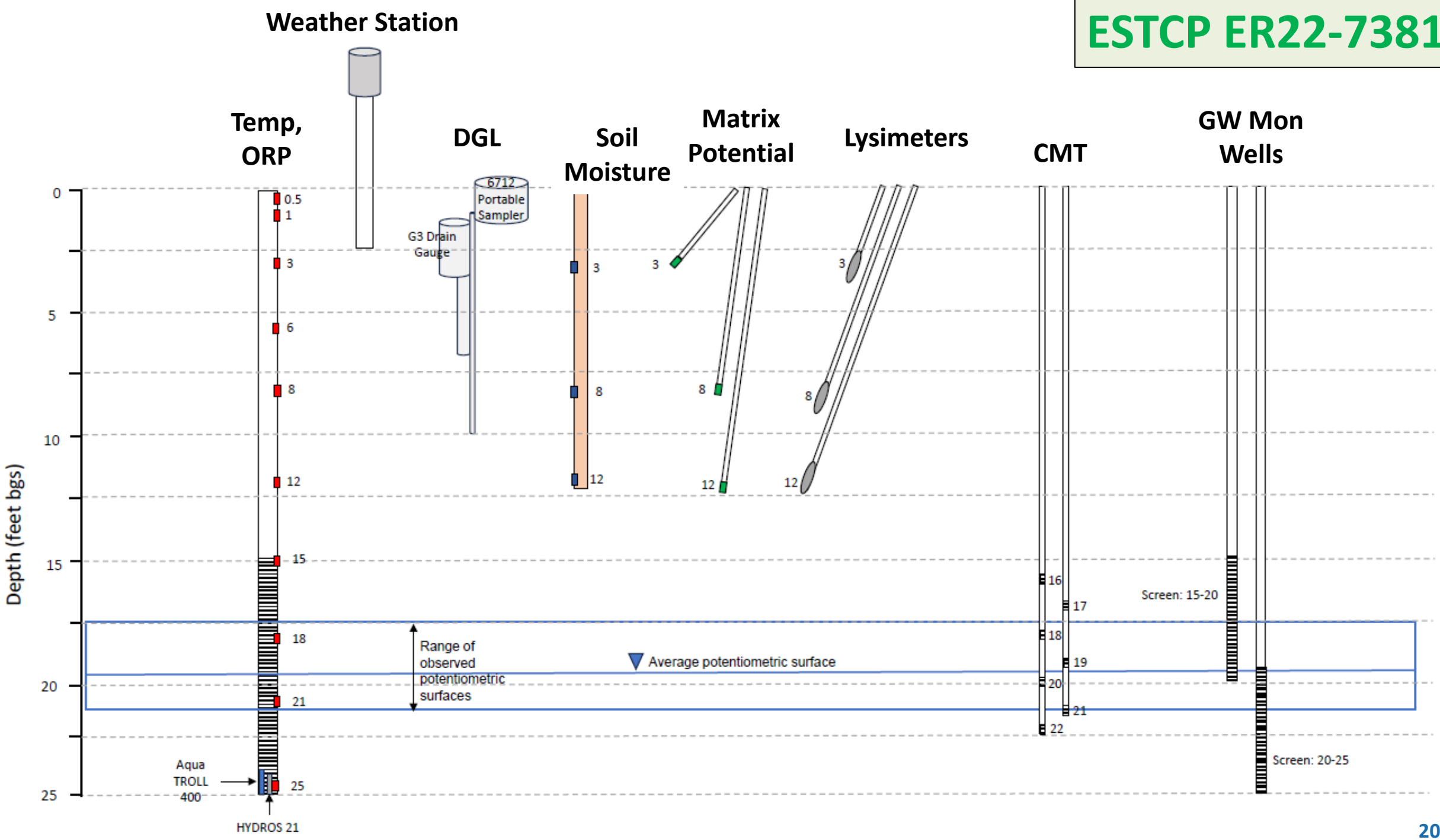
WATER TABLE FLUCTUATION METHOD (WTF?)



Method T3-B

Unsat. Zone Flow Lysimeters
(e.g., Drain Gage Lysimeter)



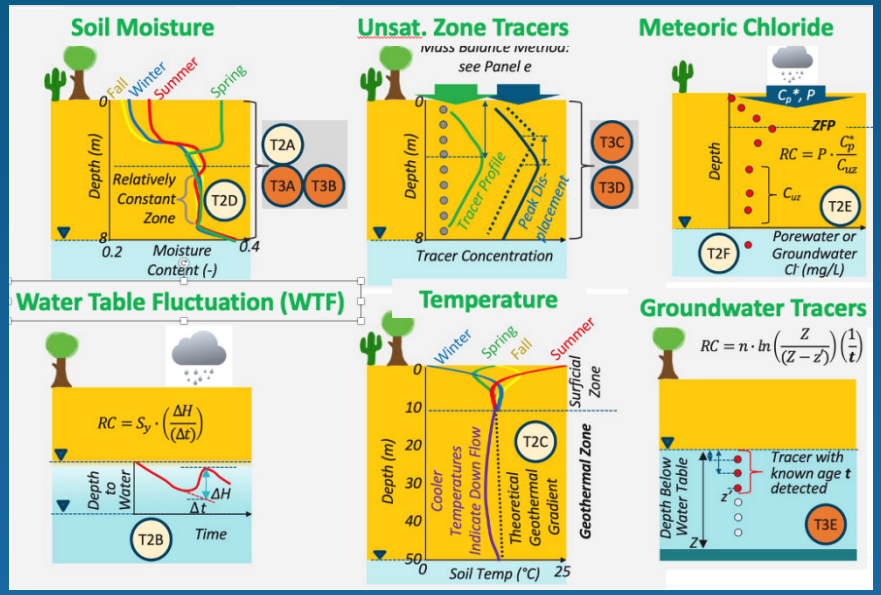

Weather Station
Temp, ORP
DGL
Soil Moisture
Matrix Potential
Lysimeters
CMT
GW Mon Wells
Depth (feet bgs)
0
5
10
15
20
25
0.5
1
3
6
8
12
15
18
21
25
6712 Portable Sampler
G3 Drain Gauge
3
8
12
3
8
12
3
8
12
16
17
18
19
20
21
22
Screen: 15-20
Screen: 20-25
Range of observed potentiometric surfaces
Average potentiometric surface
Aqua TROLL 400
HYDROS 21

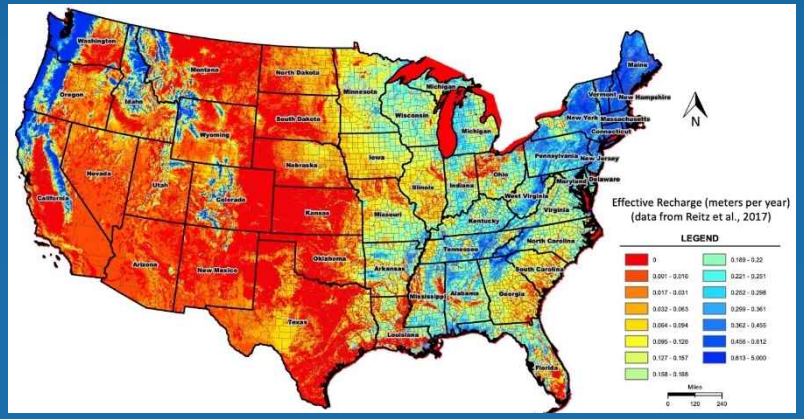
Comparison of 4 Recharge Estimation Methods

Site	Regression Method (T1-A)	Reitz Baseflow Method (T1-B)	DRASTIC Heuristic Method (T1-C)	Unsat. Zone Meteoric Chloride Tracer (T2-E)
	Recharge (mm per year; 1 inch = 25.4 mm)			
Arid Site, Wyoming	**25**	**18**	**0-51**	**2.1**
Humid Site, Tennessee	**380**	**236**	**178-254**	**>33.8**

WRAP UP

- Key metric to manage and prioritize sites:
  - PFAS Mass Discharge (Md) from the unsat. zone
- Recharge needed to quantify Md
- Reviewed 40 recharge methods from literature based on Flux, Area, and Timescale
  - Identified 15 potentially useful recharge estimation methods identified for PFAS sites
- Developed Tiered Approach for PFAS sites:
  - From simple to complex recharge methods





QUESTIONS

Newell et al. 2023

https://doi.org/10.1002/vzj2.20262

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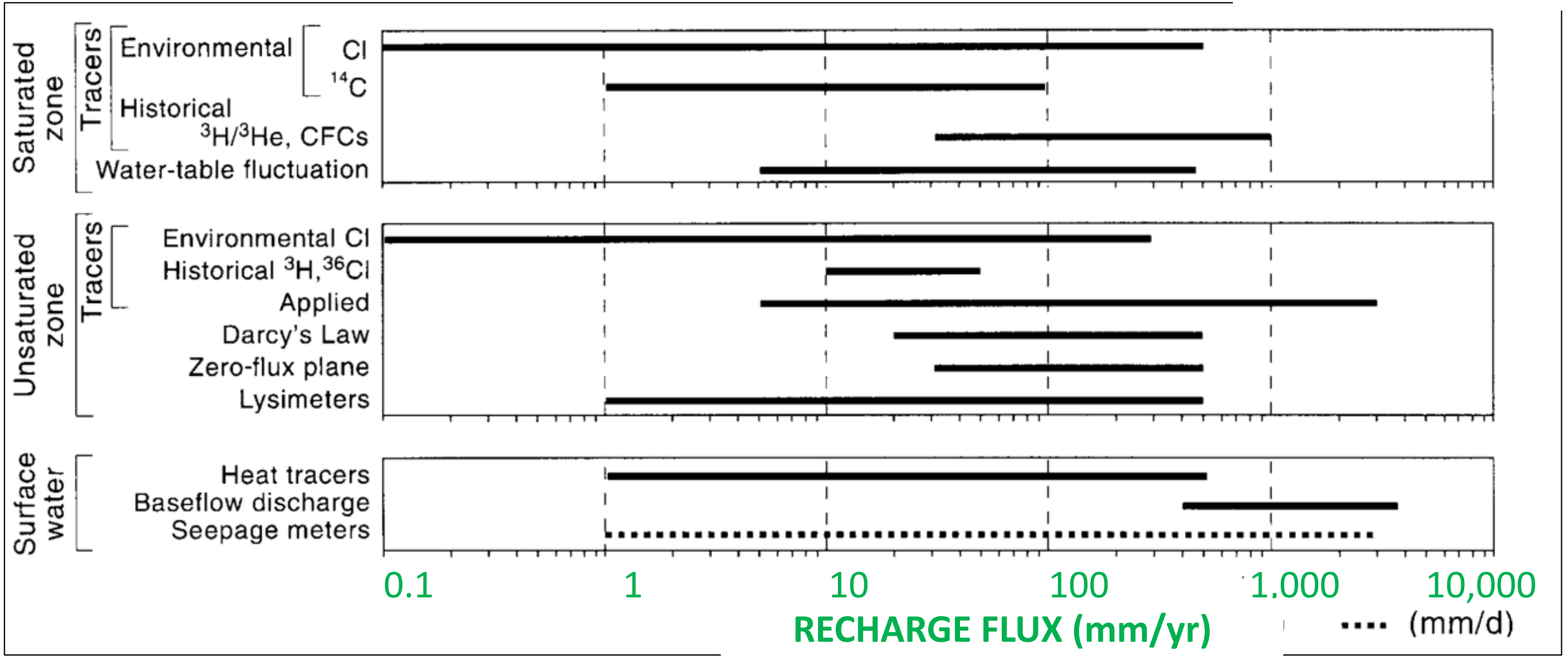
Methods by Amount of Recharge Flux

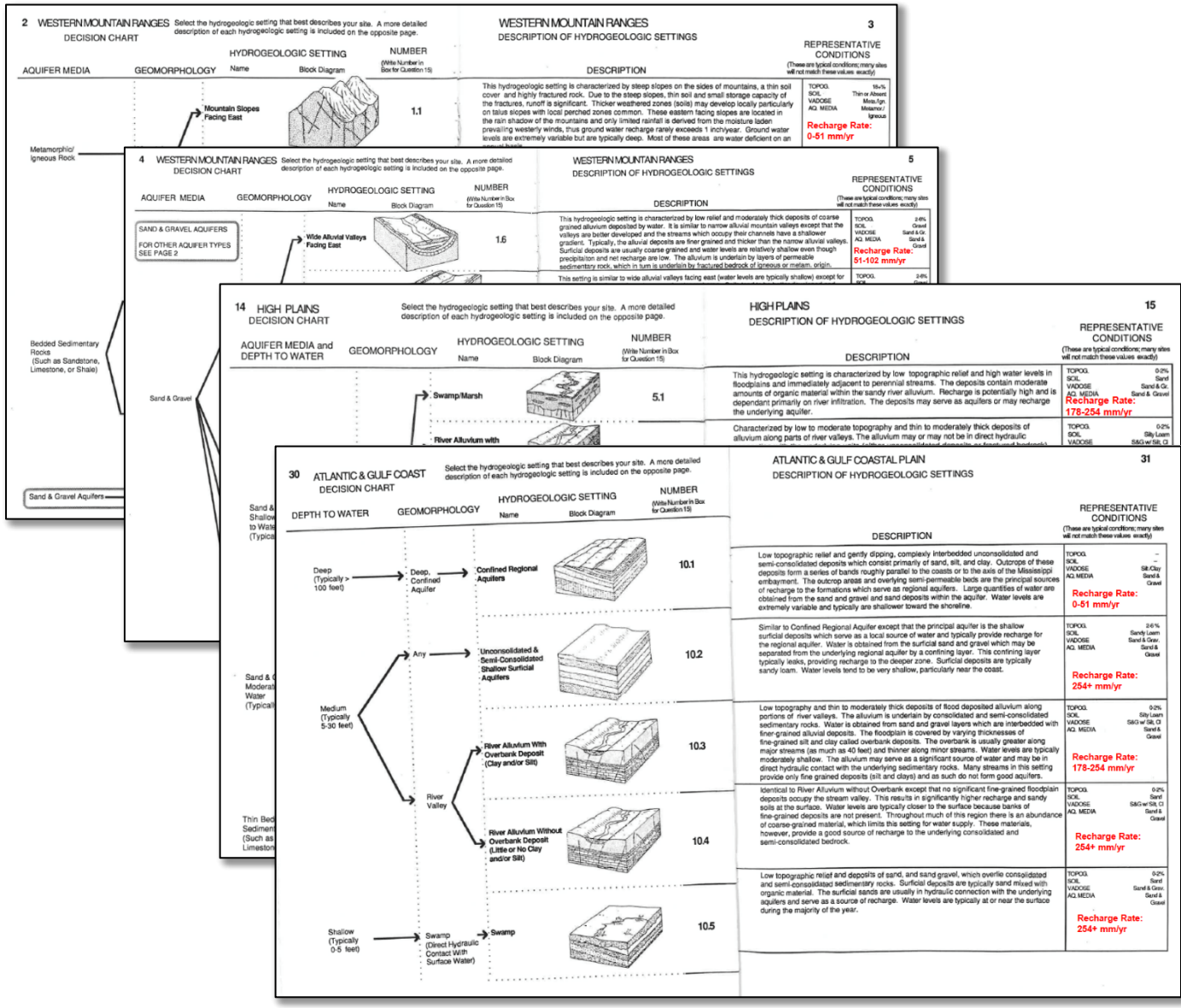
Scanlon et al., 2002



Method T1-C

DRASTIC HEURISTIC METHOD

111 Different Hydrogeologic Recharge Estimates (30 Pages)



The Problem and Two Roads to Get Mass Discharge (grams per year) To Groundwater

	1. Soil Samples + Partitioning + Recharge	*2. Suction Lysimeters + Recharge*
PROS	• Used for most other organic COCs • Collect soil sample any time • Can be incorporated in models	• No need for partitioning calcs • Direct measurement of porewater
CONS	• PFAS Air/water partitioning increases complexity, variability	• Unfamiliar to many practitioners • Some questions about temporal change on concentration

Key Point: Guidance on Estimating Recharge at PFAS Sites Would be Beneficial