Assessment and Rehabilitation of Humid Region Mine Sites and Wastes

W. Lee Daniels (*and many others*)

540-231-7175; wdaniels@vt.edu

School of Plant & Environmental Sciences

VirginiaTech
1872
VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY

https://landrehab.org/

Objectives for Today

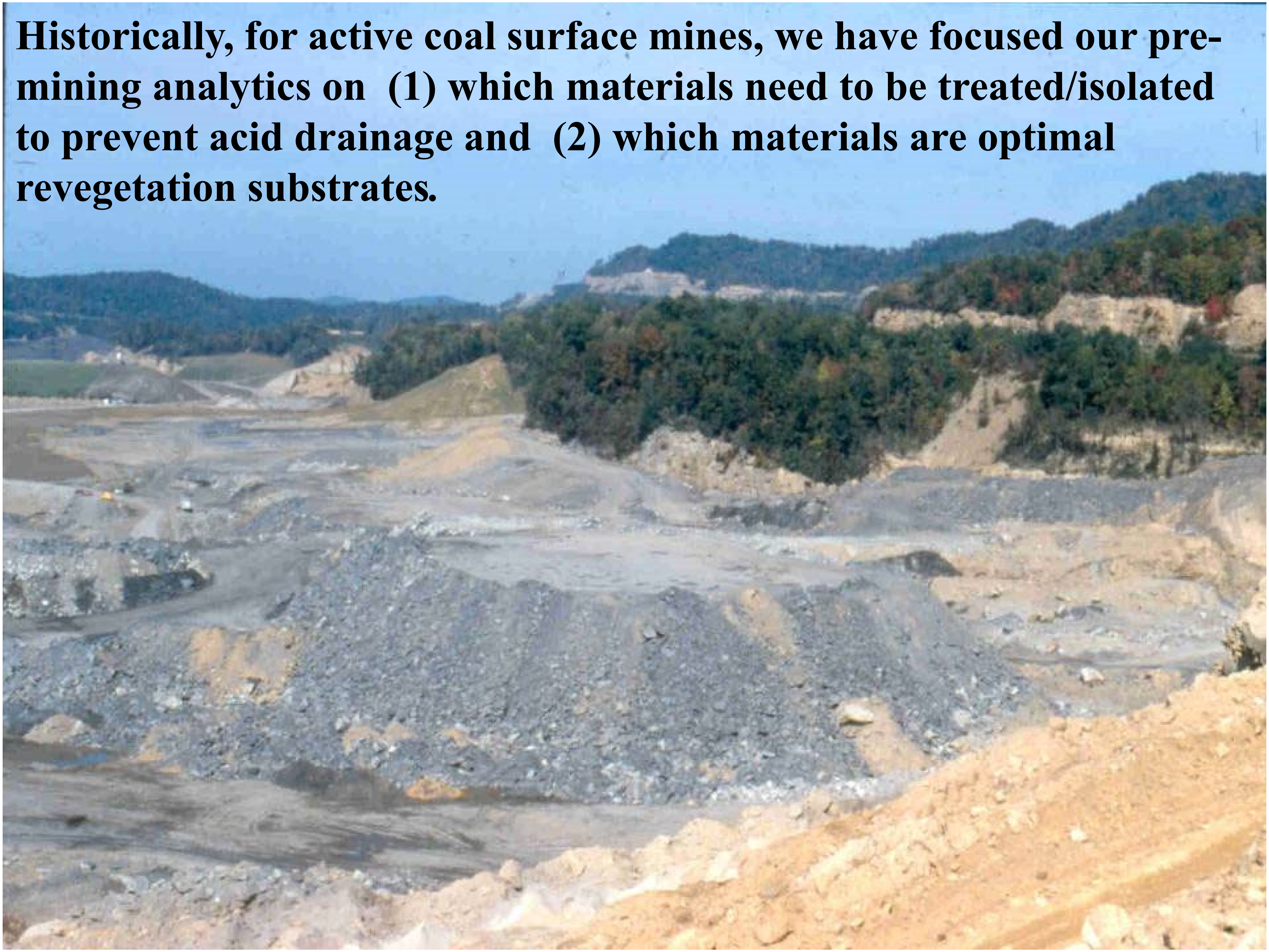
- **Review major factors affecting overall reclamation and revegetation success in humid region mining environments.**

- **Describe soil landscape reconstruction protocols for a range of mine/waste types and post-mine land uses (native forest/hayland/prime farmland).**

- **Focus on pre-mine analysis and active mine soil reconstruction protocols; not on revegetation methods per se.**

- **Review specific guidance on acid base accounting methods to limit acid mine drainage and ways to limit TDS emission in Appalachian mining environments.**

Historically, for active coal surface mines, we have focused our pre-mining analytics on (1) which materials need to be treated/isolated to prevent acid drainage and (2) which materials are optimal revegetation substrates.



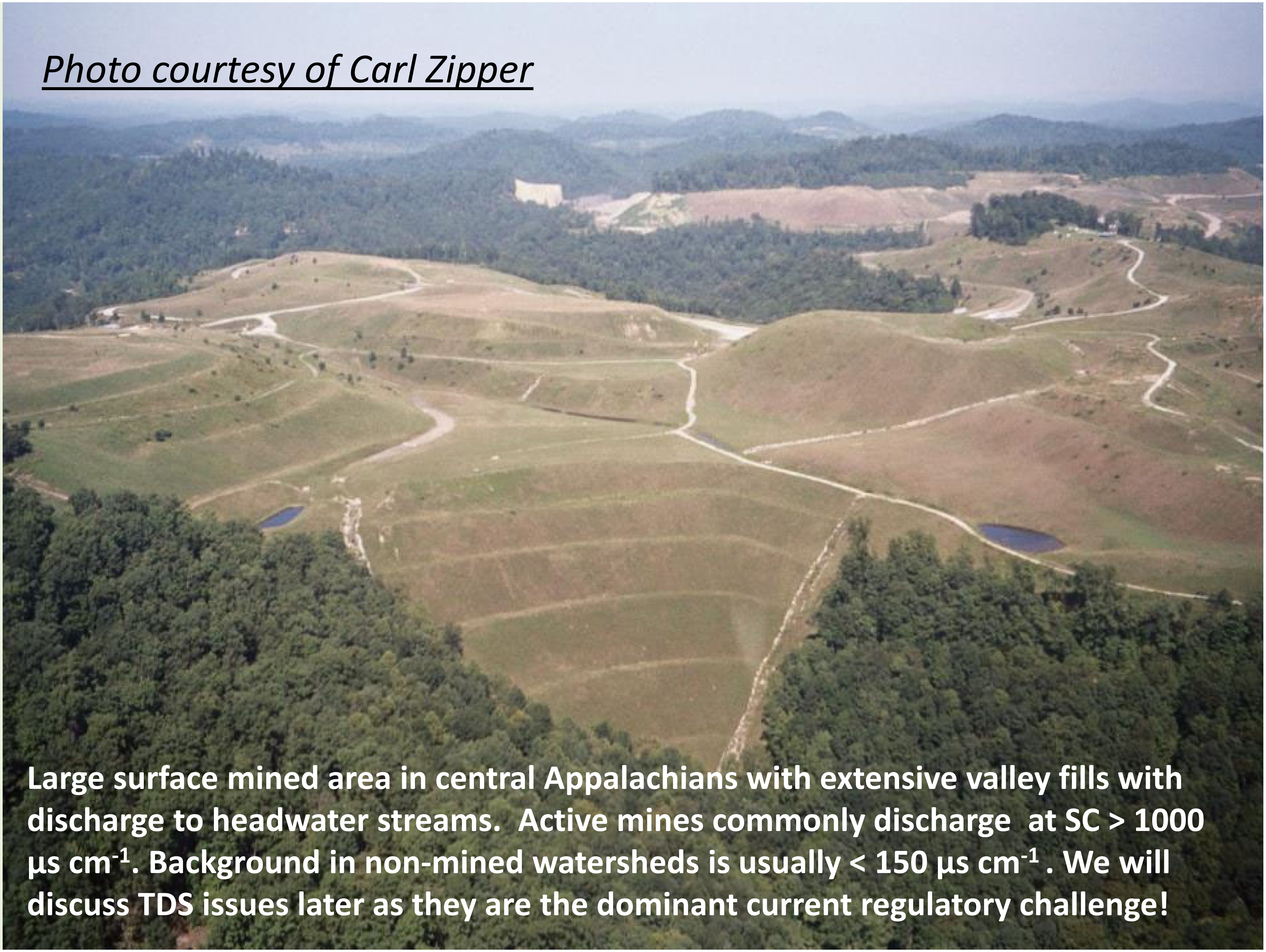
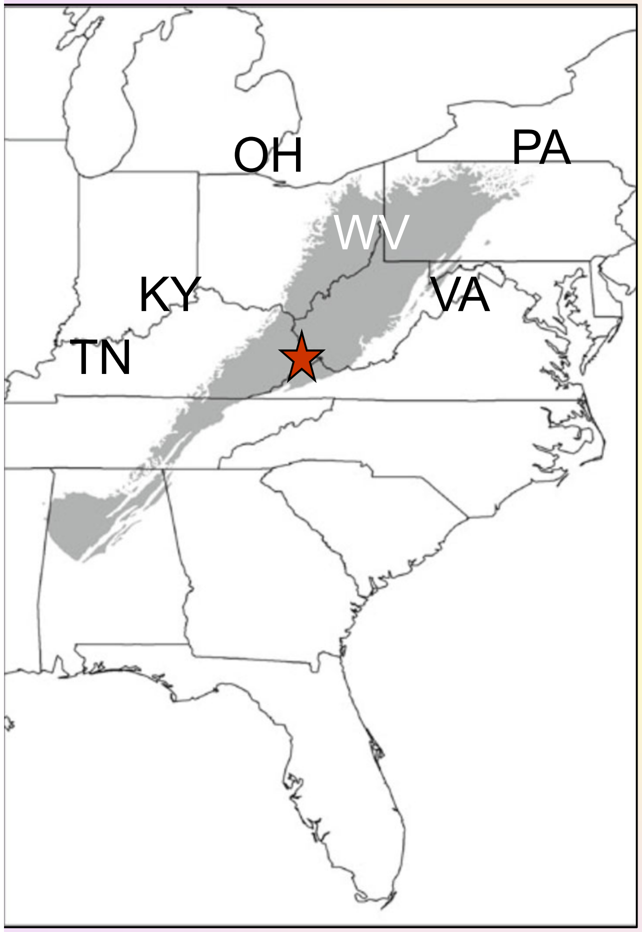


Photo courtesy of Carl Zipper

Large surface mined area in central Appalachians with extensive valley fills with discharge to headwater streams. Active mines commonly discharge at SC > 1000 µs cm^{-1}. Background in non-mined watersheds is usually < 150 µs cm^{-1}. We will discuss TDS issues later as they are the dominant current regulatory challenge!

Appalachian Forest: Among the most biodiverse non-tropical ecosystems on Planet Earth. For the past ~15 years, native forest restoration has been a primary goal (Slide by Zipper)

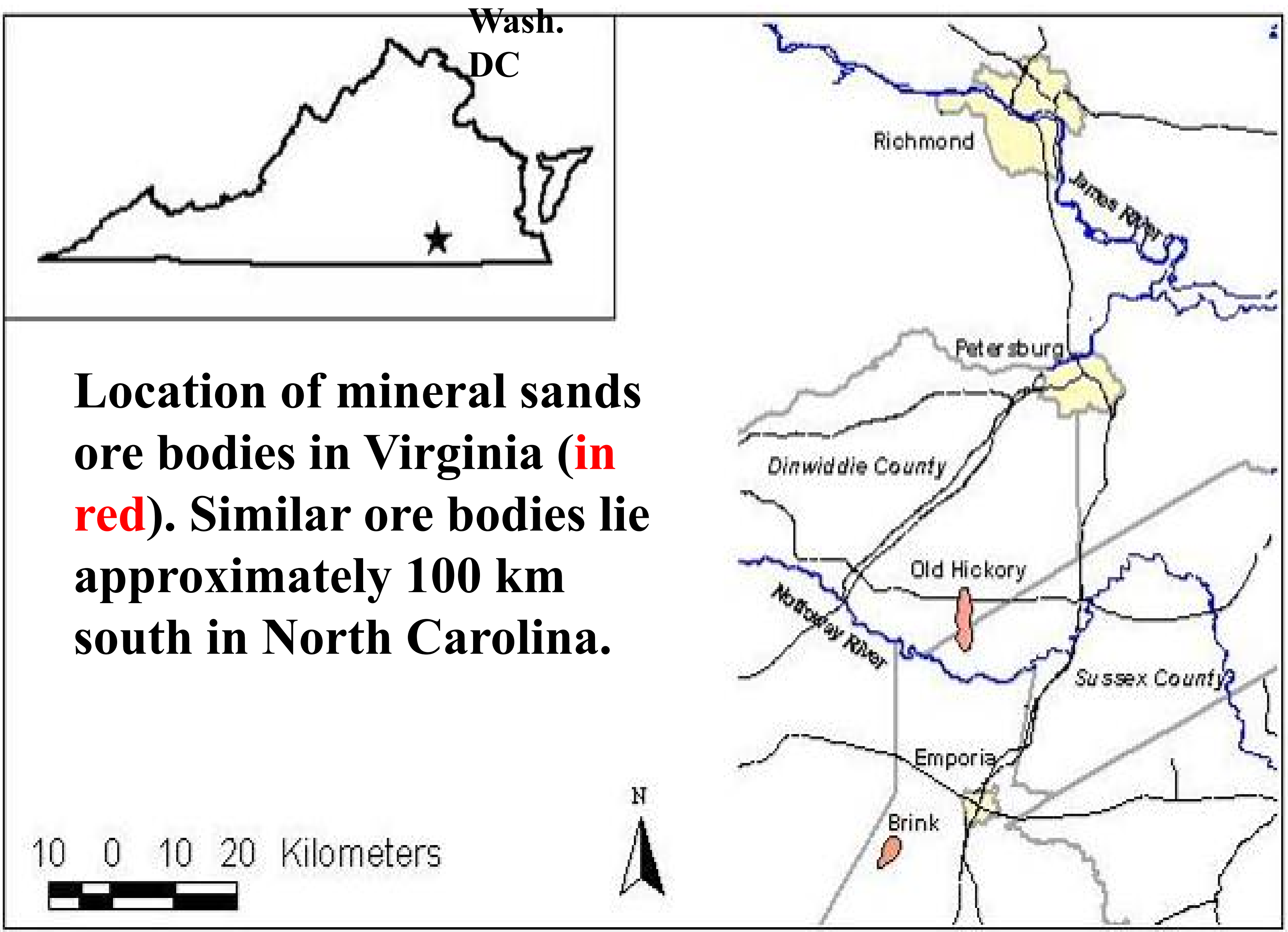


Appalachian Coalfield

Appalachian Forest

Coal Refuse Disposal Area; Up to 50% of ROM Deep Mine Coal

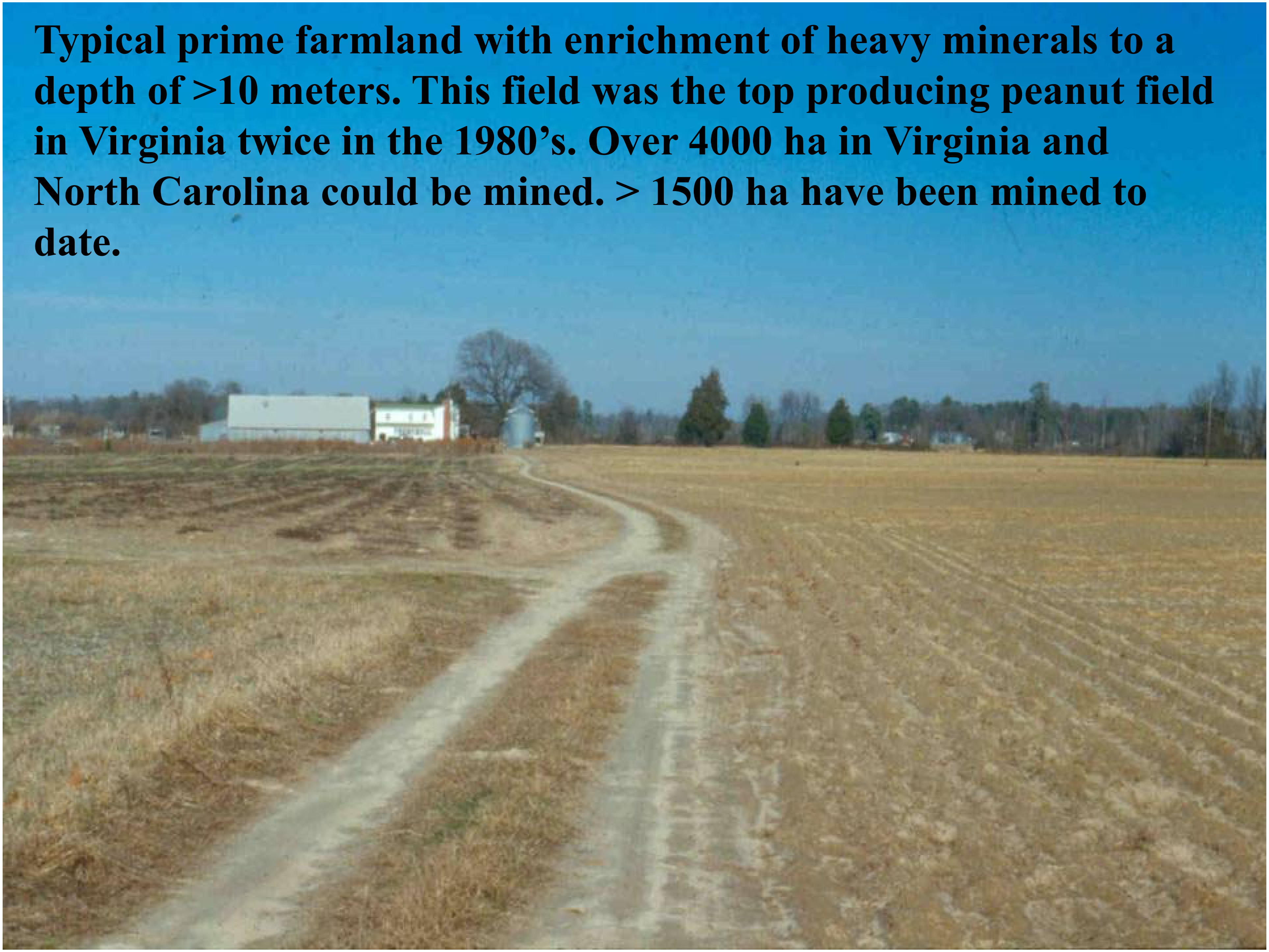
200 ha coarse coal refuse disposal facility near Pound Virginia. No topsoil was set aside for reclamation of this facility. Almost all Appalachian coal waste is net acid forming.



Location of mineral sands ore bodies in Virginia (in red). Similar ore bodies lie approximately 100 km south in North Carolina.

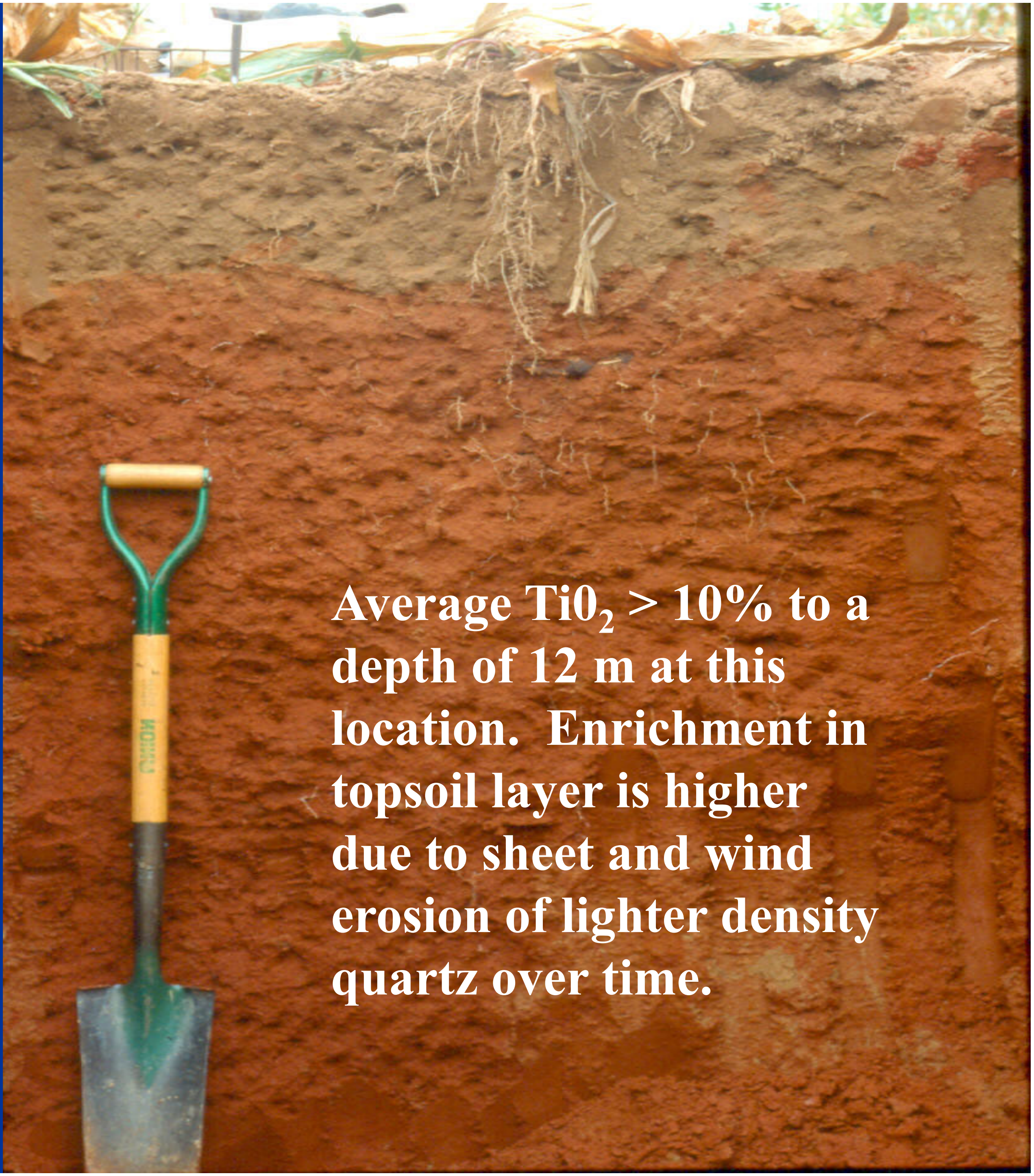
Active mining at Old Hickory. Over 2000 acres of land have been disturbed to date with approximately 600 returned to vegetation.

Typical prime farmland with enrichment of heavy minerals to a depth of >10 meters. This field was the top producing peanut field in Virginia twice in the 1980’s. Over 4000 ha in Virginia and North Carolina could be mined. > 1500 ha have been mined to date.

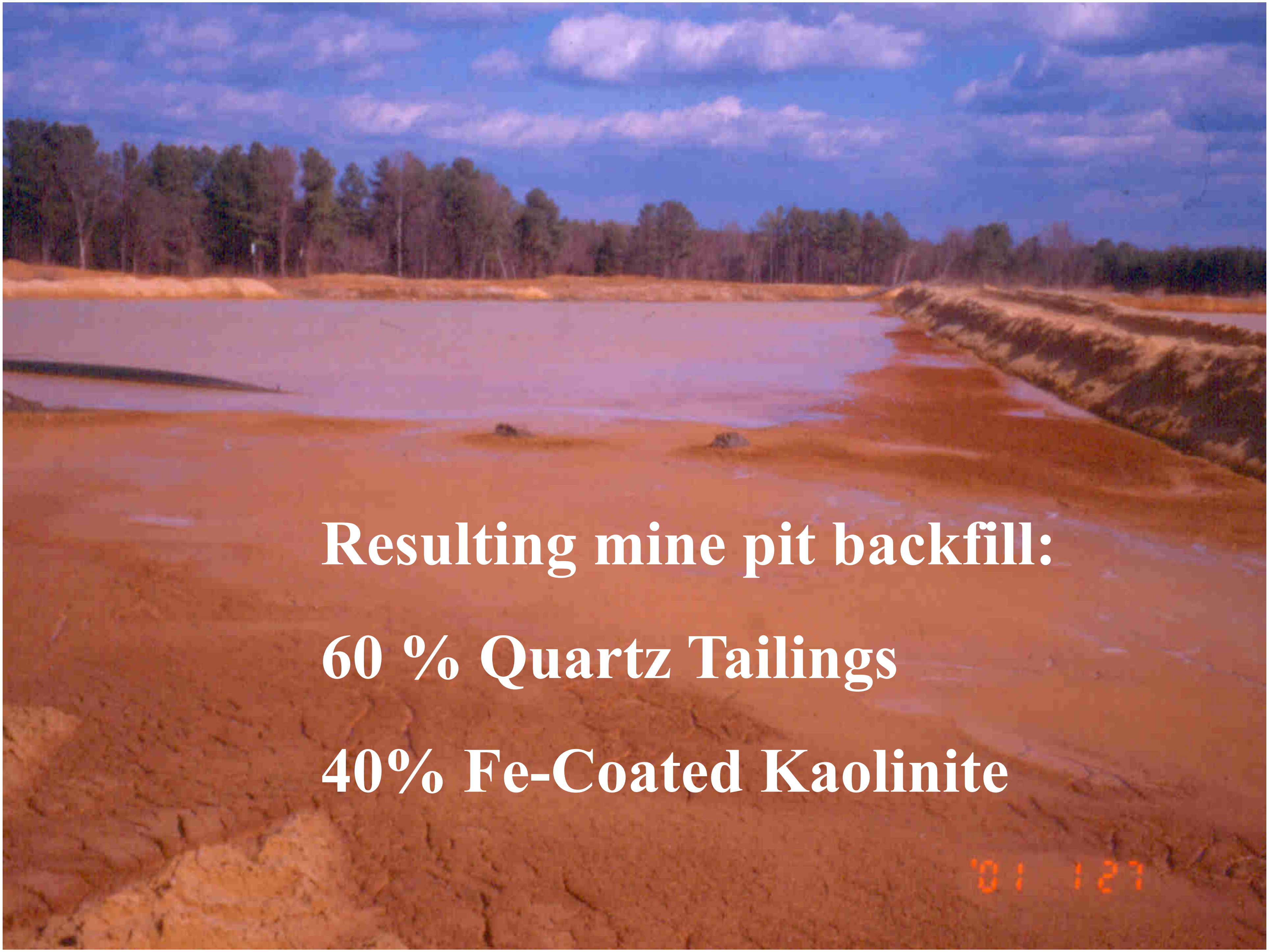


Surface (topsoil) enrichment of ilmenite+rutile+zircon is frequently > 15% W:W. Subsoil is often > 5%.

Typical highly productive soil in the Old Hickory area. Rutile-Ilmenite ($Ti0_2$) and Zirconium (Zr) are present at between 5 and > 20% w/w from the topsoil down to > 10 m in some locations.



Average $Ti0_2$ > 10% to a depth of 12 m at this location. Enrichment in topsoil layer is higher due to sheet and wind erosion of lighter density quartz over time.



Resulting mine pit backfill:

60 % Quartz Tailings

40% Fe-Coated Kaolinite

Four Things That Control Reclamation Success!

1. **Sulfidic/Pyritic acid forming materials must be avoided or neutralized for any successful stabilization project. Worldwide, there is no doubt that acid-sulfate weathering processes are the dominant risk (*if present*) to environmental quality from any drastic land disturbance.**

Acid-forming materials on 1970's "pre-SMCRA" surface mine in Virginia

“Simple” Pyrite Oxidation

(Singer & Stumm 1970; Nordstrom, 1982)

$FeS_2 + 7/2O_2 + H_2O \longrightarrow Fe^{II} + 2SO_4{}^{2-} + 2H^+$ (1)

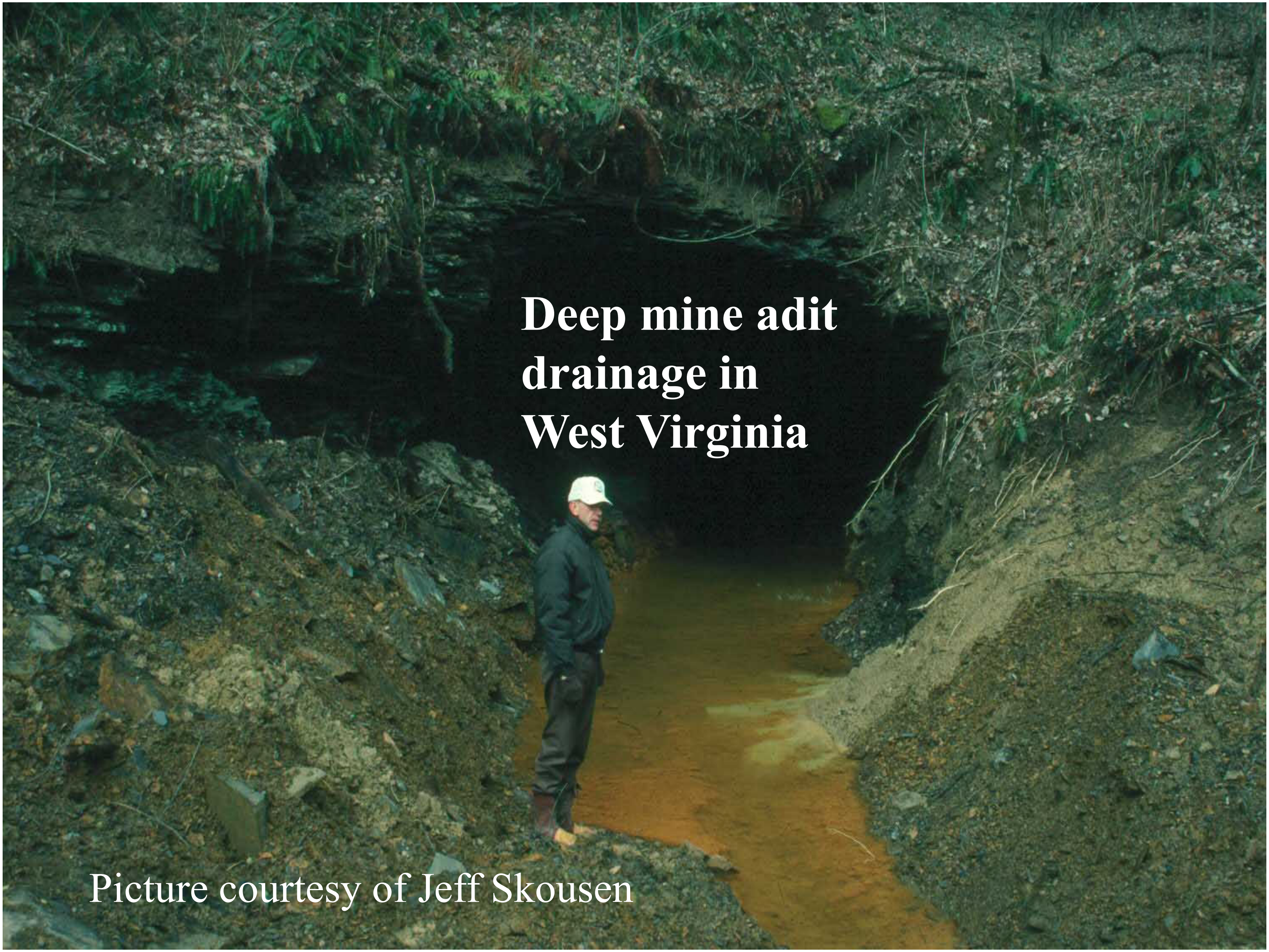
$Fe^{II} + ¼\ O_2 + H^+ \longrightarrow Fe^{III} + ½\ H_2O$ (2)

(Direct oxidation; relatively slow)

$Fe^{III} + H_2O \longrightarrow Fe(OH)_3 + 3\ H^+$ (3)

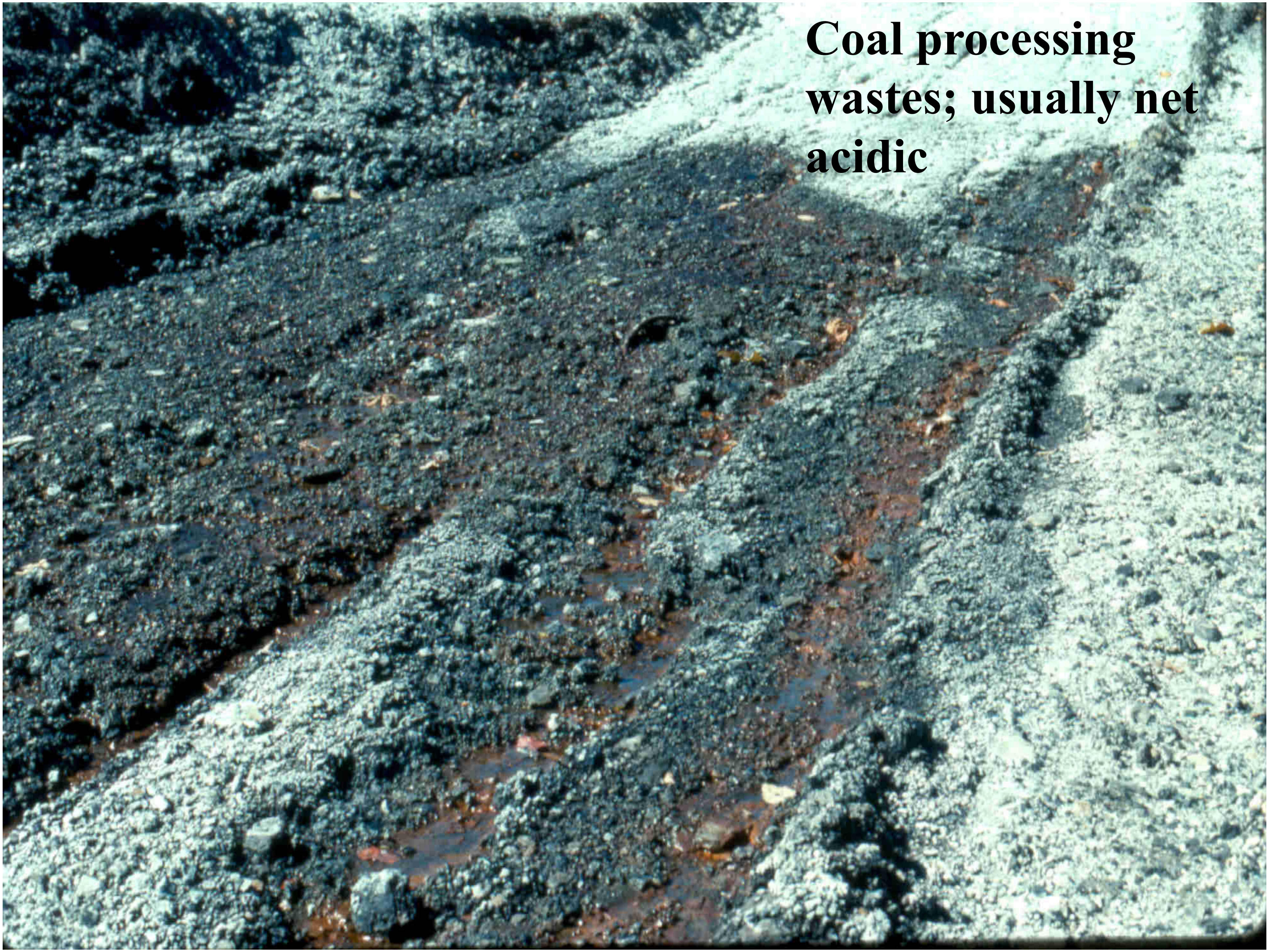
$FeS_2 + 14Fe^{III} + 8H_2O \longrightarrow 15Fe^{II} + 2SO_4{}^{2-} + 16H^+$

(Oxidation by Fe^{III}; very fast under pH < 4.5) (4)



Deep mine adit
drainage in
West Virginia

Picture courtesy of Jeff Skousen



Coal processing wastes; usually net acidic

Potential Acidity Estimators for Water Quality Prediction

Acid-Base Accounting - *Smith et al., 1976* - WVU

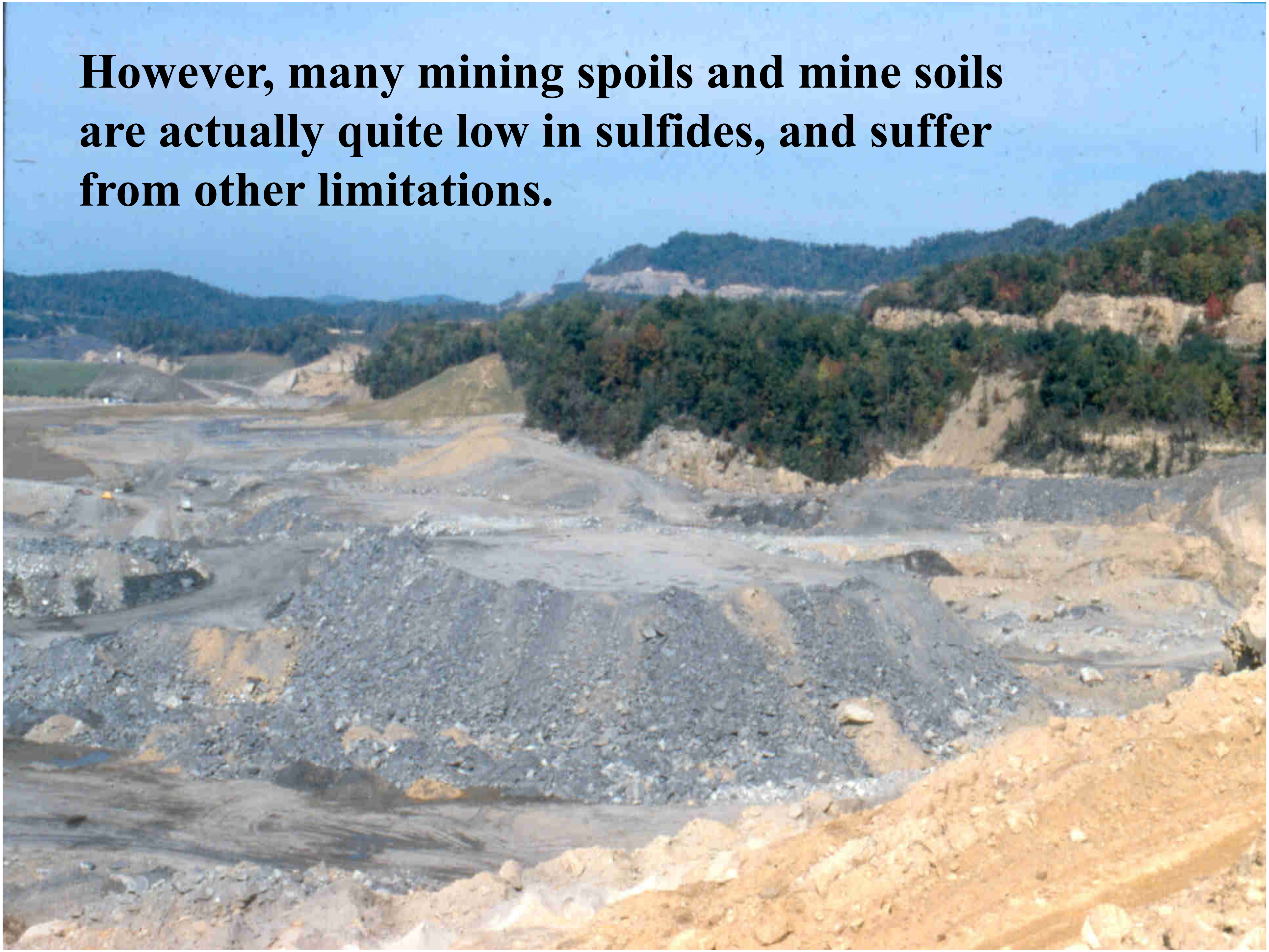
ABA is the most commonly used technique worldwide to estimate the tendency of a given material to generate acid soil conditions and associated drainage. The resultant estimate is termed "***Potential Acidity***", and hopefully gives a conservative estimate of how much lime demand a given strata or waste will require to fully mitigate or neutralize over extended periods.

Theoretical Maximum Potential Acidity (MPA) via Carbonate Neutralization *(Skousen et al., 2002)*

$FeS_2 + 2CaCO_3 + 3.75O_2 + 1.5H_20 \longrightarrow$

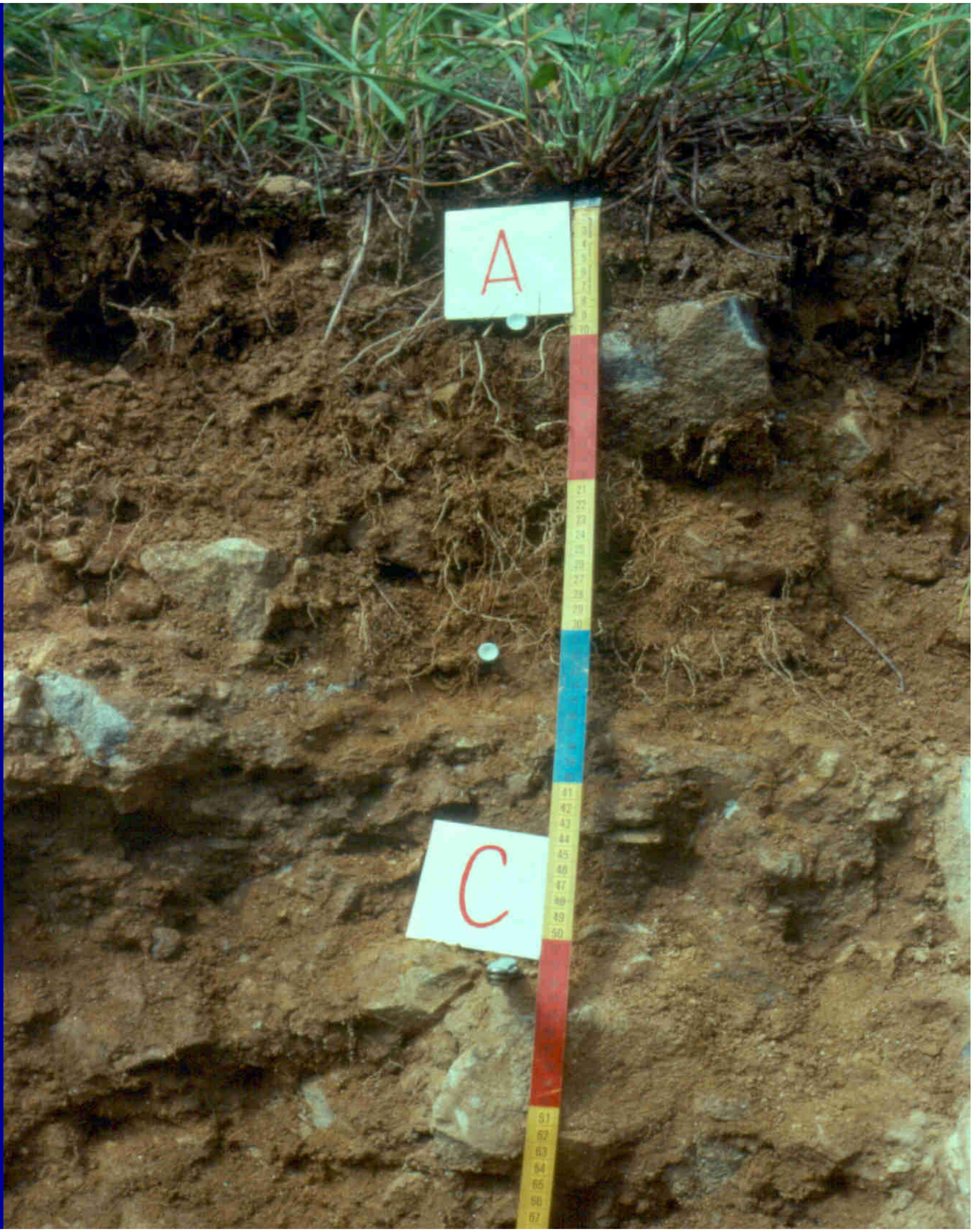
$2SO_4{}^{2-} + 2Ca^{2+} + 2CO_2$ (Neutralization Products)

Result: *1000 Mg of waste at 1% pyritic-S requires 31.25 Mg of CCE to neutralize. Also = 31 T of lime per acre six inches of spoil or soil. TDS is dominated by Ca and* SO_4



However, many mining spoils and mine soils are actually quite low in sulfides, and suffer from other limitations.

Regardless of their overall acidity and fertility status, the most common limitation to plant growth in mine soils worldwide is ***severe compaction.***



Four Things That Control Reclamation Success!

2. **Compaction is the most common limiting factor in disturbed lands worldwide.** Many mine soils with otherwise suitable chemical and physical properties are of very low quality due to severe compaction.

3. **Very coarse textures (sands) or high rock contents** limit the water holding and effective rooting volume of many disturbed land soils.


Mixed Topsoil + Weathered Overburden (A+B+C+R)
Rocky (15% fines), High pH (7.5) Sandstone Spoil

Benefits of Topsoil

Whenever it is economically feasible, native topsoils should be salvaged and re-applied to final reclamation surfaces.

In general, native soil materials will be much higher in organic matter, available N and P, and perhaps most importantly, beneficial microbial populations than any topsoil substitute materials.

Four Things That Control Reclamation Success!

4. Assuming you've avoided acid forming materials, compaction, and excessively sandy/rocky materials, the last "big thing" you really have to be concerned about is slope/aspect/albedo effects. For example, black coal waste on a 35% south-facing slope is going to be very, very difficult to stabilize without significant soil amendments due to heat loads and drought stress.

Other Important Chemical Properties (esp. in arid regions)

- Salinity (estimated by EC/SC)
- High EC usually associated with pyritic materials in humid regions
- Sodium content (estimated by ESP or SAR)
- Toxic Metals/Oxyanions

The Relatively Easy Part: Mine Soil Amendments

Once you take care of the four basic challenges pointed out earlier, you can start working towards really improving the quality of drastically disturbed soils via the addition of appropriate soil amendments such as compost, manures, biosolids, waste limes, alkaline fly ash, etc..

100 Mg/ha Yardwaste Compost + Deep Ripping, + 400 kg/ha P, + 8 Mg/ha Lime applied to Tailings/Slimes

30 cm of Topsoil
over Ripped/Limed
Tailings/Slimes

Topsoil Management

- Isolation, salvage, storage and reuse of native topsoil (O+A+E horizons) is always a BMP!
- Direct haul of topsoil from donor/stripping sites to active reclamation areas is always preferable.
- If direct haul is not feasible, topsoil should be stored in low (< 3 m deep) vegetated, well drained berms away from active mine pits.
- Keep topsoil berms well-drained and vegetated with deep rooted species. Even with that, expect significant degradation of soil quality within three to six months.

In our Appalachian coal mining environment, native topsoils are typically quite thin and difficult to safely and economically strip before mining.

Therefore, the vast majority of reclamation in the Appalachians since 1980 has utilized appropriately selected *mine spoils* as *topsoil substitutes*.

Topsoil Substitute Selection

- Potential Acidity (PA) or Lime Requirement must be less than 5 Mg per 1000 Mg Spoil (or < 5 T lime per acre 6”).
- Post-placement pH must be > 5.0 and soluble salts < 4.0 mmhos/cm. However, these goals are usually met if PA standard above is adhered to.

Topsoil Substitute Selection

- The selected strata should generate a spoil that contains ≥ 20% soil sized (< 2mm) material and few rocks > 0.5 m in size.

- Perhaps most importantly, the selected strata must (1) be thick enough to generate at least 0.5 m of final mine soil cover, and (2) occur in the mining column in a position which allows it to be readily utilized.

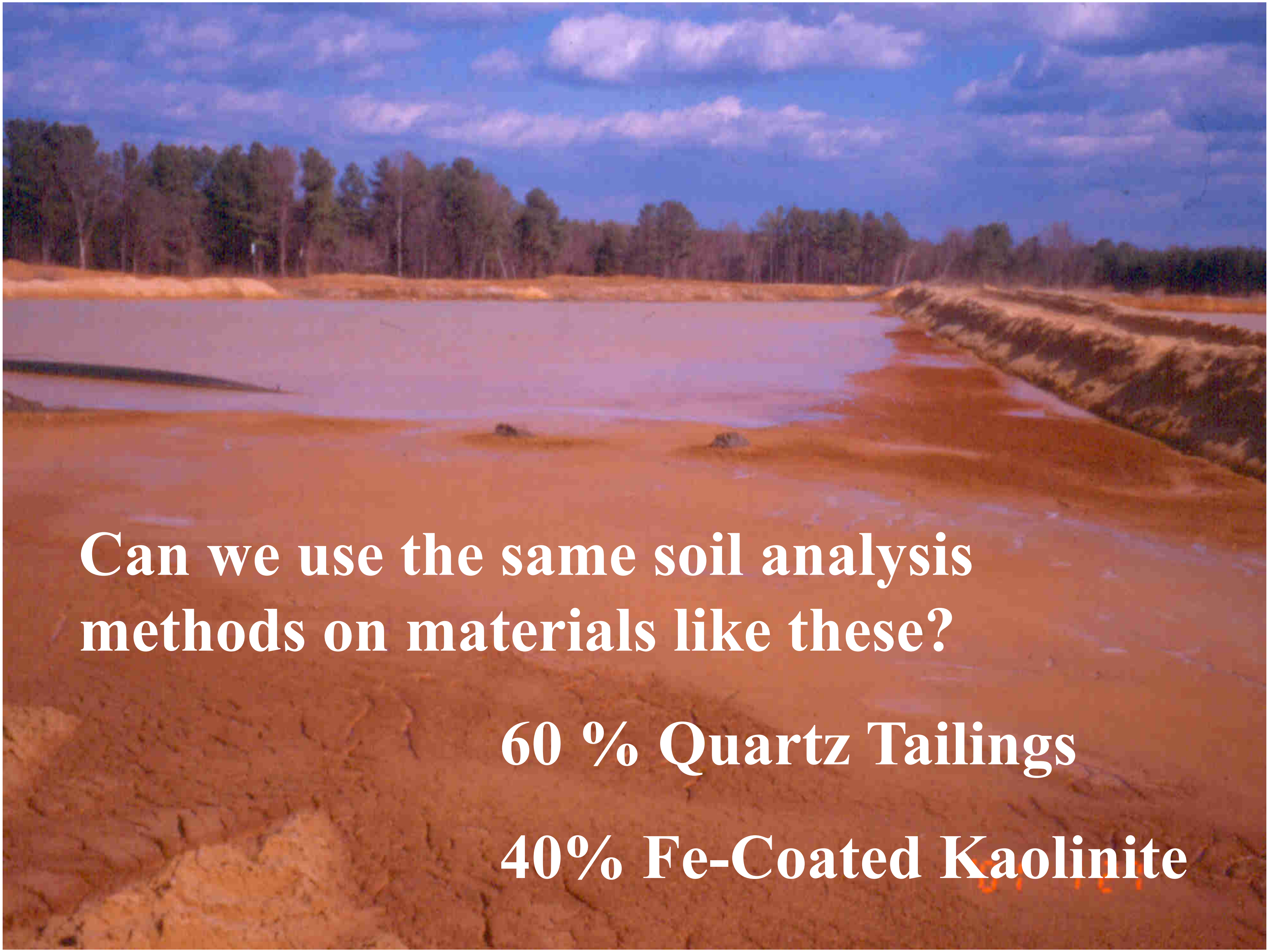
Topsoil Substitute Selection

- **Conventional soil testing parameters like extractable nutrients (P, Ca, etc.) are of very limited value in evaluating hard rock spoils for reclamation potential**

- **In certain instances, such as the return of native forest species, it is *much* better to utilize pre-weathered, oxidized, and more acidic (pH 4.5 to 5.0) overburden materials**

Mixed Topsoil + Weathered Overburden (A+B+C+R horizons)

Rocky (15% fines), High pH (7.5) Sandstone Spoil



Can we use the same soil analysis methods on materials like these?

60 % Quartz Tailings

40% Fe-Coated Kaolinite

Soil Testing Results for Contrasting Materials

Material	Sandstone Spoils	Ti Tailings/Slimes
pH	7.5	5.0
N (%)	0.0	0.0
Ext. Ca (mg/kg)	1150	27
Ext. P (mg/kg)	38	1

Issues with Overburden Placement

- The volume of suitable or optimal material must be accurately estimated and then the mining plan must be adjusted/manipulated to ensure the timing and availability of “the right stuff”.

- The mining industry never wants to handle any material twice! Therefore, you ideally pick and move the suitable material to the reclaim area in one operation.

- Topsoil isolation and reuse almost always involves “double handling” unless you can time pre-mine stripping and post-mine placement via “direct haul”

Oxidized, pH 5.5 overburden over reduced carbonate (2%) high pH (7.5 to 8.0) overburden at depth.

Issues with Overburden Placement

- The material at the top of the mining cut is most economically handled by simply pushing it over into the adjacent empty pit. If that’s the best material available (as may be the case for forest species), added cost is involved in isolating it.
- Materials deep in a mining cut must be hauled up and out of the pit anyway, so the industry prefers to use these as reclaim materials rather than materials high in the column.

Issues with Overburden Placement

- Asking the operator to blend two different strata or layers usually poses enormous coordination problems on site.

- All aspects of overburden handling and placement must be clearly worked out before mining, and then adjusted as necessary during mining.

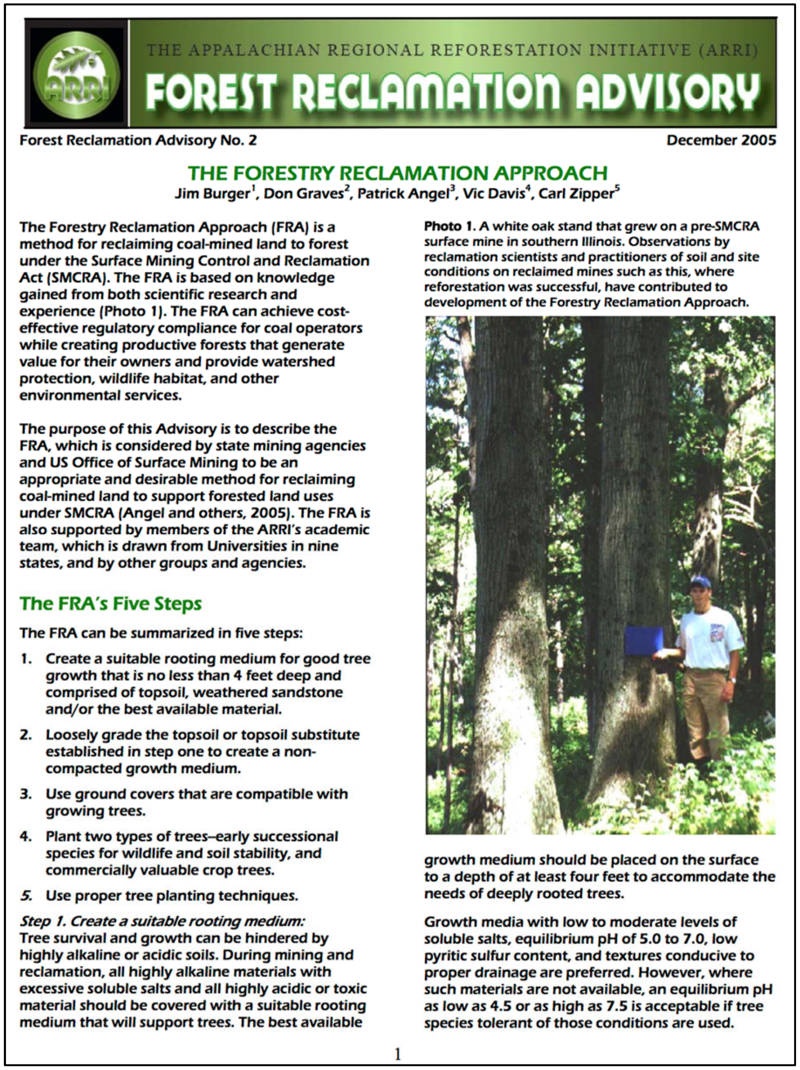
- Wherever possible, the final lift should be end-dumped, minimally graded and left rough to the extent compatible with final landuse.



Common Reclamation
Technique in Appalachia
for Three Decades
following SMCRA’s
Passage:
Smooth Grading,
Herbaceous Seeding

Depending on permit/landowner objectives, areas may be reclaimed to actively managed pasture/hayland, mixed vegetation types for "wildlife habitat", or more commonly today, return to native forest vegetation. This scene contains all three. Higher pH, less weathered materials are favored for hayland/pasture areas. The band in the middle is unmined native forest. Photo by Carl Zipper

Reforestation and the Forestry Reclamation Approach (FRA)



THE APPALACHIAN REGIONAL REFORESTATION INITIATIVE (ARRI)

FOREST RECLAMATION ADVISORY

Forest Reclamation Advisory No. 2 December 2005

THE FORESTRY RECLAMATION APPROACH

Jim Burger[1], Don Graves[2], Patrick Angel[3], Vic Davis[4], Carl Zipper[5]

The Forestry Reclamation Approach (FRA) is a method for reclaiming coal-mined land to forest under the Surface Mining Control and Reclamation Act (SMCRA). The FRA is based on knowledge gained from both scientific research and experience (Photo 1). The FRA can achieve cost-effective regulatory compliance for coal operators while creating productive forests that generate value for their owners and provide watershed protection, wildlife habitat, and other environmental services.

The purpose of this Advisory is to describe the FRA, which is considered by state mining agencies and US Office of Surface Mining to be an appropriate and desirable method for reclaiming coal-mined land to support forested land uses under SMCRA (Angel and others, 2005). The FRA is also supported by members of the ARRI's academic team, which is drawn from Universities in nine states, and by other groups and agencies.

The FRA's Five Steps

The FRA can be summarized in five steps:

1. Create a suitable rooting medium for good tree growth that is no less than 4 feet deep and comprised of topsoil, weathered sandstone and/or the best available material.
2. Loosely grade the topsoil or topsoil substitute established in step one to create a non-compacted growth medium.
3. Use ground covers that are compatible with growing trees.
4. Plant two types of trees–early successional species for wildlife and soil stability, and commercially valuable crop trees.
5. Use proper tree planting techniques.

Step 1. Create a suitable rooting medium: Tree survival and growth can be hindered by highly alkaline or acidic soils. During mining and reclamation, all highly alkaline materials with excessive soluble salts and all highly acidic or toxic material should be covered with a suitable rooting medium that will support trees. The best available growth medium should be placed on the surface to a depth of at least four feet to accommodate the needs of deeply rooted trees.

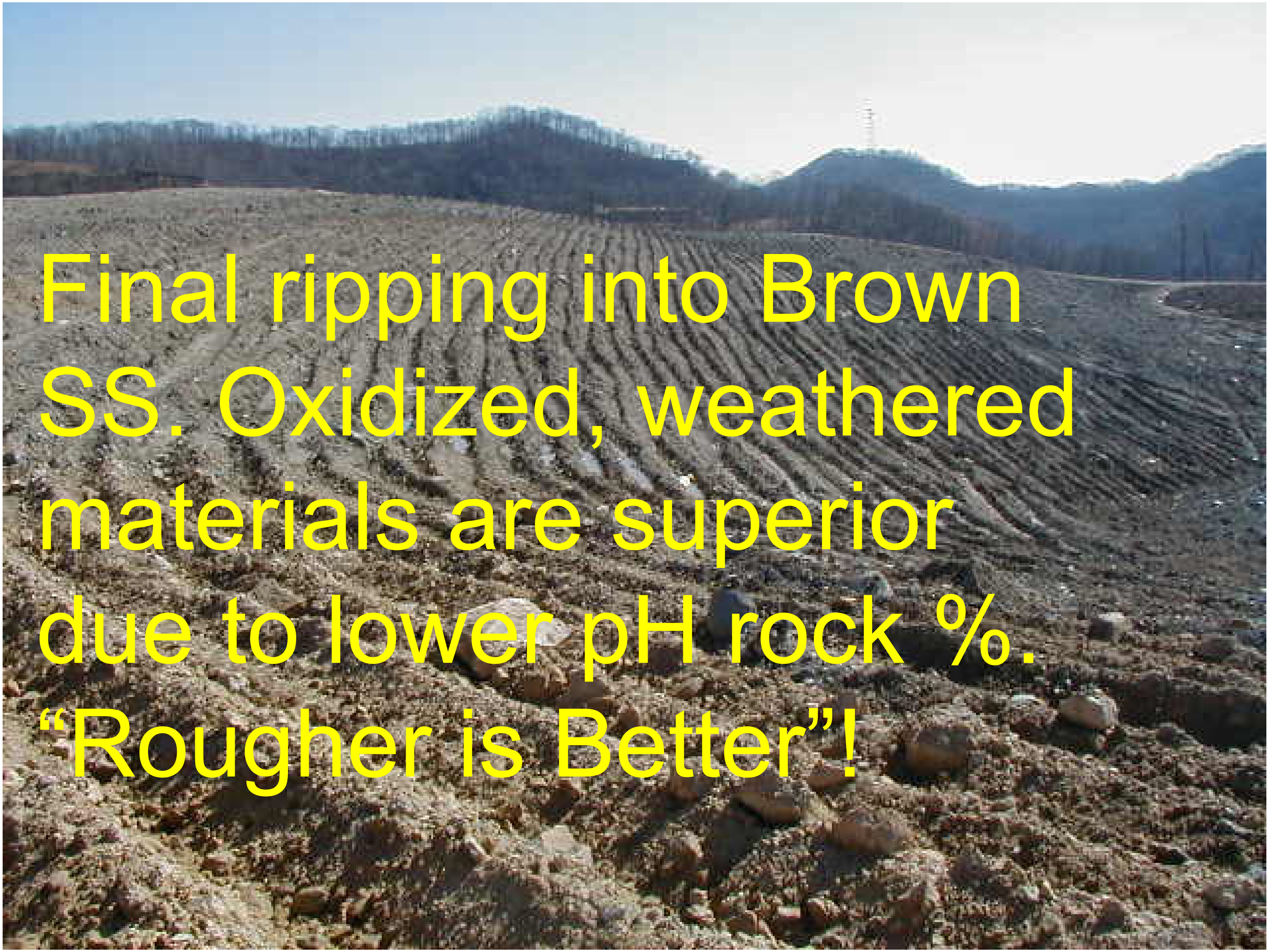
Photo 1. A white oak stand that grew on a pre-SMCRA surface mine in southern Illinois. Observations by reclamation scientists and practitioners of soil and site conditions on reclaimed mines such as this, where reforestation was successful, have contributed to development of the Forestry Reclamation Approach.

Growth media with low to moderate levels of soluble salts, equilibrium pH of 5.0 to 7.0, low pyritic sulfur content, and textures conducive to proper drainage are preferred. However, where such materials are not available, an equilibrium pH as low as 4.5 or as high as 7.5 is acceptable if tree species tolerant of those conditions are used.

The FRA's Five Steps:

1. Create a suitable rooting medium for good tree growth that is no less than 4 feet deep and comprised of topsoil, weathered sandstone and/or the best available material.
2. Loosely grade the topsoil or topsoil substitute established in step one to create a non-compacted growth medium.
3. Use ground covers that are compatible with growing trees. Reduce N fertilizer rates.
4. Plant two types of trees--early successional species for wildlife and soil stability, and commercially valuable crop trees.
5. Use proper tree planting techniques.

Step 2. Leave surfaces loose and un-compacted.

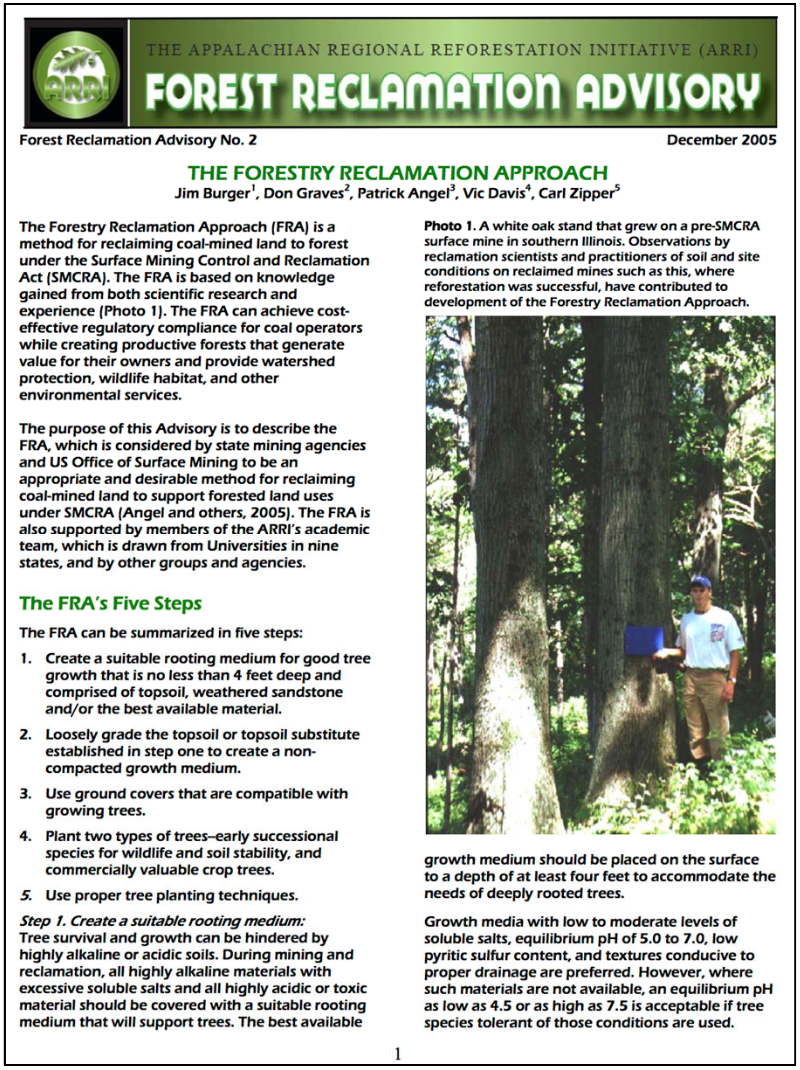


Final ripping into Brown SS. Oxidized, weathered materials are superior due to lower pH rock %. "Rougher is Better"!

Herbaceous revegetation strategies also influence reforestation success.

FRA Step 3. Use herbaceous ground covers that are compatible with growing trees.

Reforestation and the Forestry Reclamation Approach (FRA)



THE APPALACHIAN REGIONAL REFORESTATION INITIATIVE (ARRI)

FOREST RECLAMATION ADVISORY

Forest Reclamation Advisory No. 2

December 2005

THE FORESTRY RECLAMATION APPROACH

Jim Burger[1], Don Graves[2], Patrick Angel[3], Vic Davis[4], Carl Zipper[5]

The Forestry Reclamation Approach (FRA) is a method for reclaiming coal-mined land to forest under the Surface Mining Control and Reclamation Act (SMCRA). The FRA is based on knowledge gained from both scientific research and experience (Photo 1). The FRA can achieve cost-effective regulatory compliance for coal operators while creating productive forests that generate value for their owners and provide watershed protection, wildlife habitat, and other environmental services.

The purpose of this Advisory is to describe the FRA, which is considered by state mining agencies and US Office of Surface Mining to be an appropriate and desirable method for reclaiming coal-mined land to support forested land uses under SMCRA (Angel and others, 2005). The FRA is also supported by members of the ARRI's academic team, which is drawn from Universities in nine states, and by other groups and agencies.

The FRA's Five Steps

The FRA can be summarized in five steps:

1. Create a suitable rooting medium for good tree growth that is no less than 4 feet deep and comprised of topsoil, weathered sandstone and/or the best available material.
2. Loosely grade the topsoil or topsoil substitute established in step one to create a non-compacted growth medium.
3. Use ground covers that are compatible with growing trees.
4. Plant two types of trees–early successional species for wildlife and soil stability, and commercially valuable crop trees.
5. Use proper tree planting techniques.

Photo 1. A white oak stand that grew on a pre-SMCRA surface mine in southern Illinois. Observations by reclamation scientists and practitioners of soil and site conditions on reclaimed mines such as this, where reforestation was successful, have contributed to development of the Forestry Reclamation Approach.

Step 1. Create a suitable rooting medium: Tree survival and growth can be hindered by highly alkaline or acidic soils. During mining and reclamation, all highly alkaline materials with excessive soluble salts and all highly acidic or toxic material should be covered with a suitable rooting medium that will support trees. The best available growth medium should be placed on the surface to a depth of at least four feet to accommodate the needs of deeply rooted trees.

Growth media with low to moderate levels of soluble salts, equilibrium pH of 5.0 to 7.0, low pyritic sulfur content, and textures conducive to proper drainage are preferred. However, where such materials are not available, an equilibrium pH as low as 4.5 or as high as 7.5 is acceptable if tree species tolerant of those conditions are used.

The FRA's Five Steps:

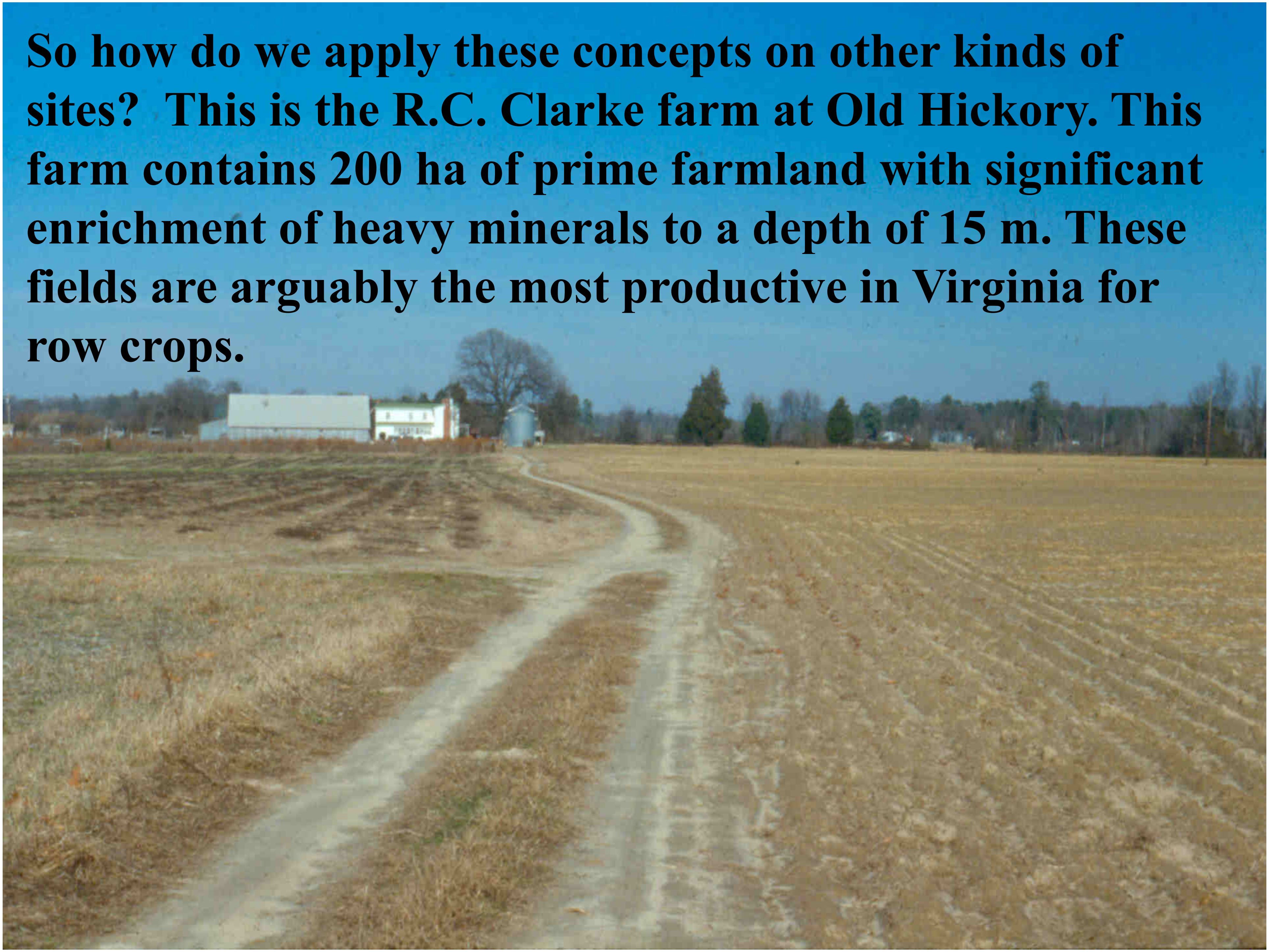
1. Create a suitable rooting medium for good tree growth that is no less than 4 feet deep and comprised of topsoil, weathered sandstone and/or the best available material.
2. Loosely grade the topsoil or topsoil substitute established in step one to create a non-compacted growth medium.
3. Use ground covers that are compatible with growing trees. Reduce N fertilizer rates.
4. Plant two types of trees--early successional species for wildlife and soil stability, and commercially valuable crop trees.
5. Use proper tree planting techniques.

Eight-year-old mixed native hardwood stand growing on blasted rock

Incorporation of 45 Mg/ha lime on sulfidic coal waste materials. Many require topsoil covers of 25 to 50 cm combined with lime at contact.

Effects of 10 Mg/ha Lime plus 50 Mg/ha Papermill Sludge on Acidic Coal Refuse

Direct seeding results after 3 years with lime 25 T/ha, high P and 35 T/Ac biosolids and acid/salt tolerant seed mix. The tall plants are native annual invading into the plots. Similar results can be obtained with stable yard waste composts and other suitable organics.

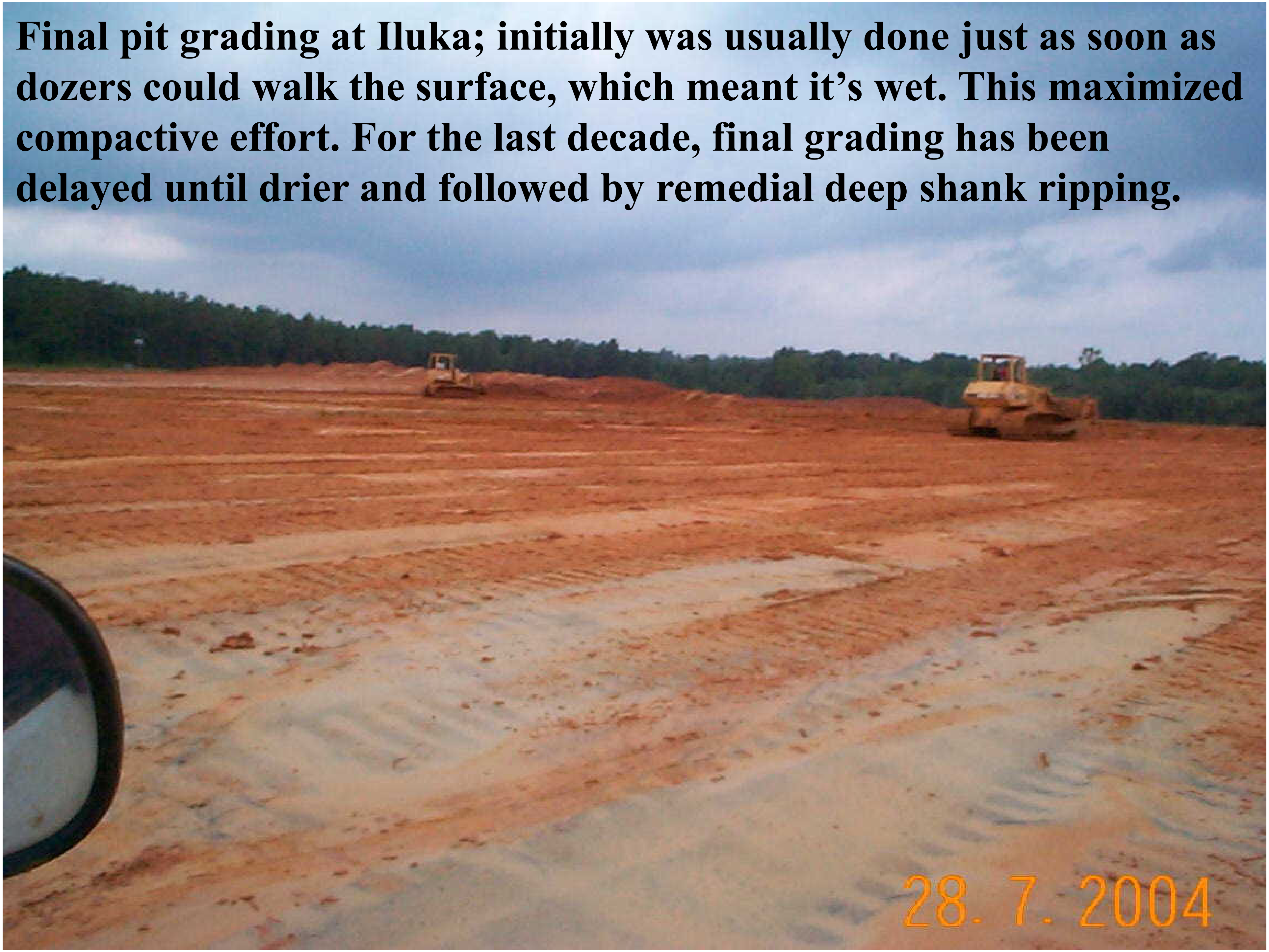


So how do we apply these concepts on other kinds of sites? This is the R.C. Clarke farm at Old Hickory. This farm contains 200 ha of prime farmland with significant enrichment of heavy minerals to a depth of 15 m. These fields are arguably the most productive in Virginia for row crops.

Typical tails+slimes pit dewatering. Material in foreground is clayey slimes; background is sandy tailings

18. 5. 2004

Final pit grading at Iluka; initially was usually done just as soon as dozers could walk the surface, which meant it's wet. This maximized compactive effort. For the last decade, final grading has been delayed until drier and followed by remedial deep shank ripping.



28. 7. 2004

Surface of mine soil at Old Hickory in 2004. Note dense, massive layered appearance. No structure or roots with depth.

This is the “appropriate ripper” for these kinds of soil problems! Clint Zimmerman (pictured) was primarily responsible for recognizing the need and implementing routine ripping.

Sequence of photos (by Chuck Stilson/Iluka) showing ripping of subsoil and application of topsoil for final reclamation. The topsoil is spread with dozers and then tilled/ripped again to loosen compaction. Ripping usually occurs below topsoil; not through it.

Lime + P are added to the subsoil before ripping and then lime + N-P-K are added to the topsoil based on soil test results.

2005 Corn Yields (bu/ac)

Topsoil/Lime/NPK 61 c*

Tail + Biosolids: 174 a

Tails + Lime + NPK: 136 b

Unmined adjacent: 224

County Average: 98

(2000 – 2005)

Adjacent prime farmland – Orangeburg Soil with same management as plot area.

**Yields within experiment followed by different letters were different at p > 0.01*

First year topsoil yields were reduced by compaction and heavy crusting. Remediated via chisel plowing.

13. 7. 2005

2006 Wheat Yields (Mg/ha)

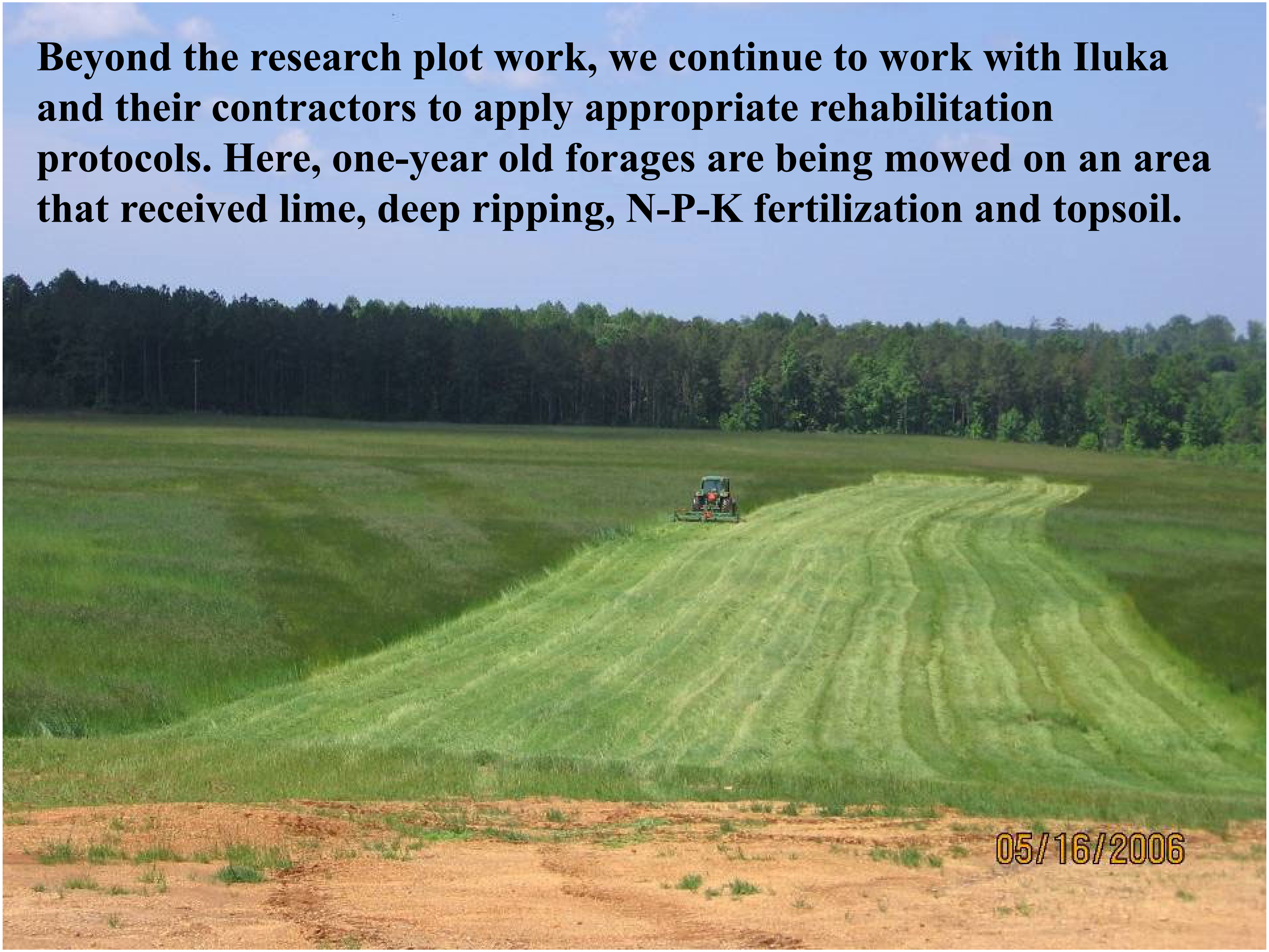
Topsoil/Lime/NPK	4.3
Tails + Biosolids:	4.8
Tails + Lime + NPK:	4.1

Unmined adjacent:	6.9
County Average: (2000 – 2005)	3.8

Adjacent prime farmland – Orangeburg Soil with same management as plot area.

Winter Wheat on Carraway-Winn Farm in May of 2006

Beyond the research plot work, we continue to work with Iluka and their contractors to apply appropriate rehabilitation protocols. Here, one-year old forages are being mowed on an area that received lime, deep ripping, N-P-K fertilization and topsoil.



05/16/2006

Summary

- The vast majority of mine wastes, overburden material, or returned soil-like materials can be successfully reclaimed and revegetated once the appropriate suite of analyses have been conducted.

- However, it is absolutely essential that sulfidic wastes (> 0.2% pyritic-S) be isolated away from the final reclamation surface, or very high rates of suitable liming materials must be applied and incorporated, or thick soil or overburden covers employed.

Summary

- **Assuming you avoid sulfidic materials, compaction, rockiness/texture/water holding, and slope/aspect issues become the most challenging in succession.**
- **In most instances, manipulating soil pH and fertility (e.g. NPK) is relatively simple compared to these four major limitations.**
- **Apriori testing of all proposed revegetation strata is critical, particularly for ABA.**
- **Rock type, weathering/oxidation extent, and estimated fine earth (< 2mm) size consist are also important to predict.**

Summary

- Interpretation of conventional soil testing procedures (e.g. Mehlich, Bray) for mine spoils and wastes is “complicated”. In particular, estimates of “available nutrients” out of hard rock mixed mineral spoils are of limited value.

- While not discussed in great detail here, we highly recommend the use of combined organic amendments (e.g. composts/ biosolids, etc.), particularly when they can be incorporated.

- Most reclamation specialists tend to be overly concerned with managing fertility etc., when time and time again, compaction is really the ***major limitation***. You need to rip compaction; winter freeze/thaw, gypsum or other “magic potions” will not remediate it.

Summary

- **Final Advice**: **Never** tell a local landowner or stakeholder "*your soil and land will look just the same after mining and will be just as productive as it is today*".

- I cannot tell you how many projects I have worked on where these assertions "came back to bite the speaker"!

Time for a Break!

- **Questions on the first half of the presentation?**
- **Let’s take a 10 minute break?**
- **I will remain online and answer any continuing questions**
- **We will cover detail on acid base accounting and TDS prediction issues when we return!**

Acid Base Accounting and Infrastructure Damage from ASS

W. Lee Daniels and Zenah Orndorff (ABA example)

540-231-7175; wdaniels@vt.edu

COLLEGE OF AGRICULTURE AND LIFE SCIENCES
SCHOOL OF PLANT AND
ENVIRONMENTAL SCIENCES
VIRGINIA TECH™

http://www.landrehab.org

“Simple” Pyrite Oxidation

(Singer & Stumm 1970; Nordstrom, 1982)

$FeS_2 + 7/2O_2 + H_2O \longrightarrow Fe^{II} + 2SO_4^{2-} + 2H^+$ **(1)**

$Fe^{II} + ¼\ O_2 + H^+ \longrightarrow Fe^{III} + ½\ H_2O$ **(2)**

(Direct oxidation; relatively slow)

$Fe^{III} + H_2O \longrightarrow Fe(OH)_3 + 3\ H^+$ **(3)**

$FeS_2 + 14Fe^{III} + 8H_2O \longrightarrow 15Fe^{II} + 2SO_4^{2-} + 16H^+$

(Oxidation by Fe^{III}; very fast under $pH < 4.5$) **(4)**

Some “standard” procedures

Static tests:

- Acid-Base Accounting (ABA; USEPA 1978)
  - -neutralization potential - NP
  - -maximum potential acidity – MPA
  - - NNP = NP – MPA (- is acidic; + is alkaline)

- Potential Peroxide Acidity (PPA) – Rxn with 30% H_2O_2

Kinetic tests (e.g., *Let’s take time into account?):*

- Columns
- Humidity cells
- Soxhlet extractors
- Mesocosms/barrels
- Field scale studies

Acid-Base Accounting (ABA)

- Developed during the late 1960’s and 1970’s at West Virginia University – the first approach (*and still the most widely used*) to predicting quantity of acid-producing materials prior to mining.
- A system of balancing the neutralization potential and acid producing potential of a given geologic material. Neutralization Potential (NP) – Maximum Potential Acidity (MPA) = Net Neutralization Potential (NNP)
- Commonly used in the mining industry to characterize overburden and predict post-mining drainage quality.

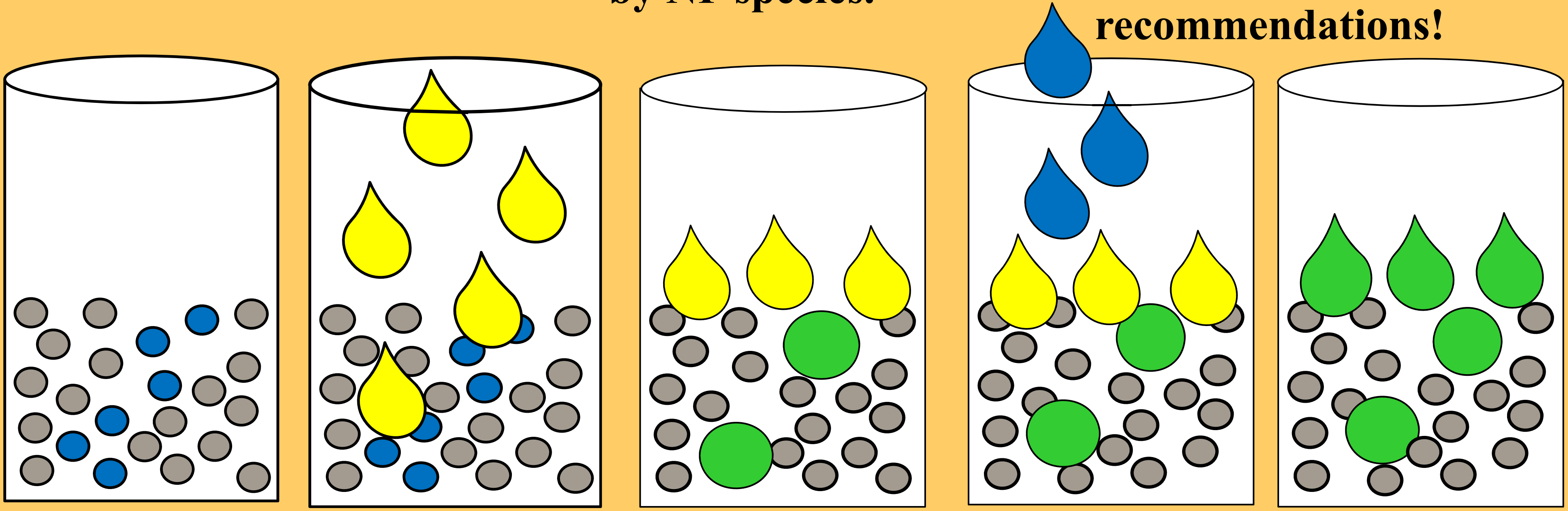
Neutralization Potential (NP)

Soil or crushed rock sample; Blue = carbonates or other +NP Minerals like feldspars?

Add known amount of acid (HCl) to be > NP; based on the “HCl fizz test”

Wait for neutralization reactions to complete. Note that not all the acid here reacts, but 2/5 of added acid is consumed by NP species.

Now, we add the amount of base (NaOH) needed to neutralize the non-reacted acid in order to calculate how much acid was consumed by NP (e.g. “back titration”). Results are expressed as: tons $CaCO_3$ equivalent / 1000 tons material. *Why*? This dry mass is close to 1 acre of soil, 6” deep = “AFS” for routine liming recommendations!



🔵 Grains with neutralizing potential ○ Minerals without neutralizing or acid potential

Neutralization Potential (NP)

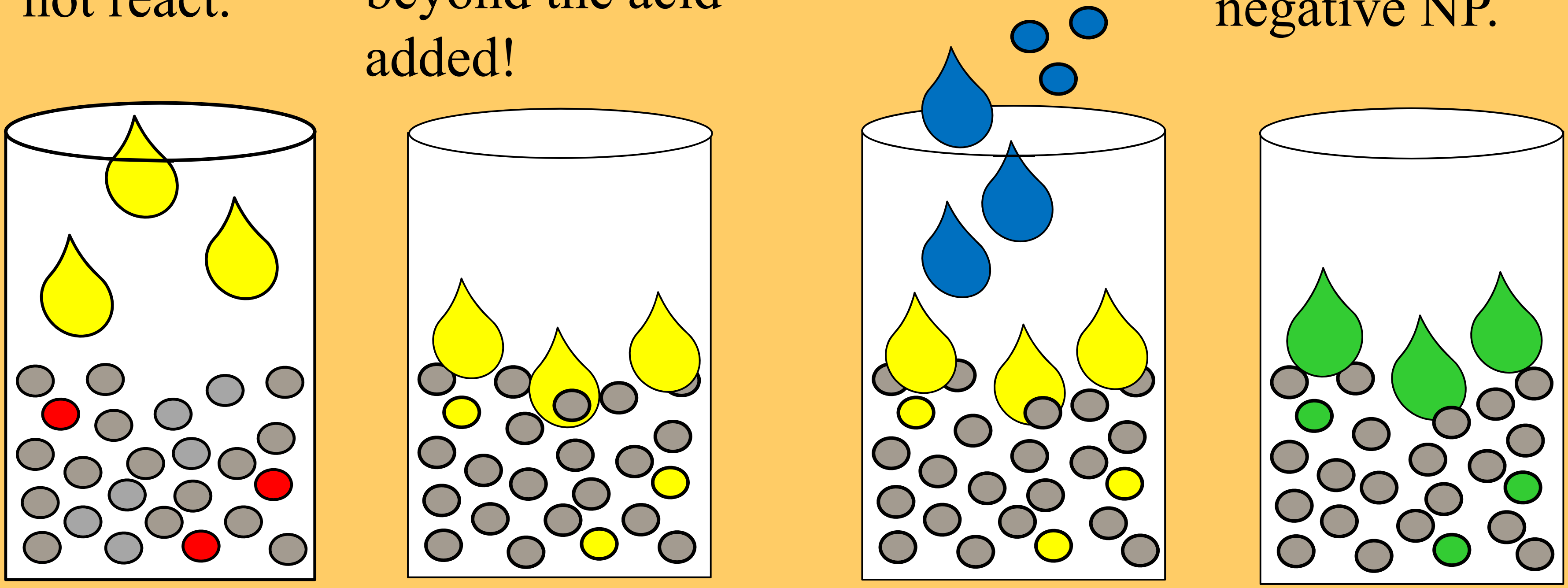
NP Results may be actually be “negative” (lime demand) if sample contains readily soluble sources of acidity (such as some sulfate minerals).

Material is acid with no NP; acid added does not react.

Dissolution of readily soluble ASS minerals produces acidity beyond the acid added!

More base is needed to neutralize the acidity.

Acidity initially added is less than acidity neutralized; = negative NP.



● Soluble source of acidity ● NO neutralizing or acid potential

Maximum Potential Acidity (MPA)

Maximum Potential Acidity (MPA):
Measure %S content (proxy to measure pyrite content)

Calculate, based on stoichiometry, how much acidity is produced from pyrite oxidation.

Result expressed as liming requirement (T CCE/1000).

Can be calculated using Total- *or* Pyritic-S

Use of Total-S generates more conservative results

Pyritic S values more expensive to obtain, but more "accurate"

1% S = 31.25 tons $CaCO_3$ equivalent /1000 tons material

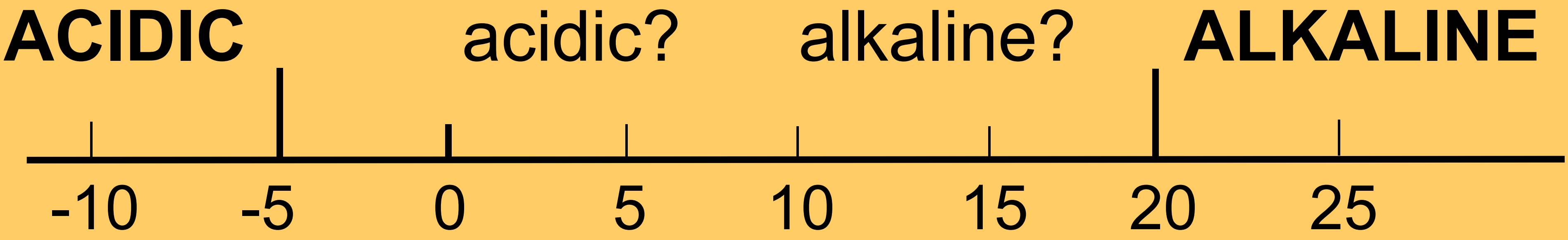
Net Neutralization Potential (NNP) Example

- NP in lab determined = 22 T $CaCO_3$/1000 T (*determined in lab; could also be reported as 2.2% CCE depending on method*)
- MPA: sample contains 1.2% Total-S

  MPA = (1.2) * 31.25 = 37.5 T $CaCO_3$/1000T
- **NNP** = 22 - 37.5 = -15.5 T $CaCO_3$/1000T

ABA interpreting results: NNP vs NPR?

NNP: Net Neutralization Potential (NP – MPA)

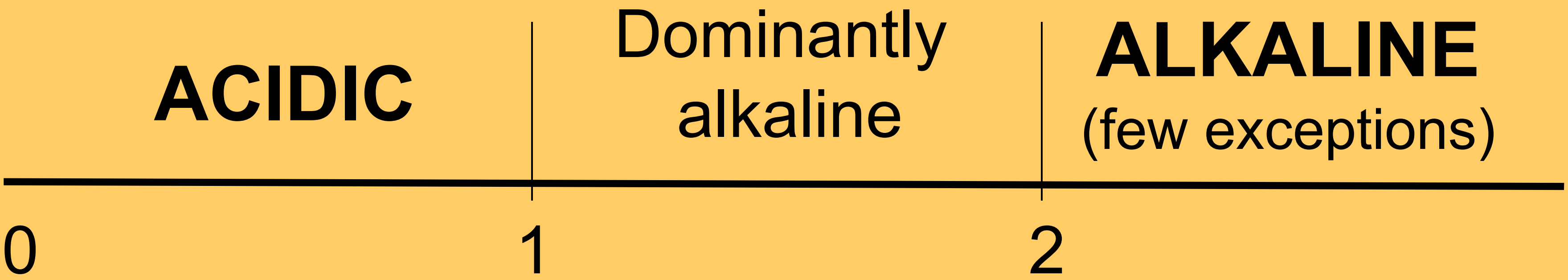


ACIDIC acidic? alkaline? **ALKALINE**

-10 -5 0 5 10 15 20 25

Toxic (most regs) = < -5

NPR: Neutralization Potential Ratio = NP/MPA



ACIDIC

Dominantly alkaline

ALKALINE (few exceptions)

0 1 2

ABA complicating factors

- The MPA calculation assumes all S is sulfide-S (specifically pyrite)

  3 common forms of sulfur:
  sulfide-S sulfate-S organic-S

  Sulfide-S (pyritic) is the primary acid producer, so using total-S will “conservatively overpredict” MPA if significant amounts of sulfate and/or organic-S are present

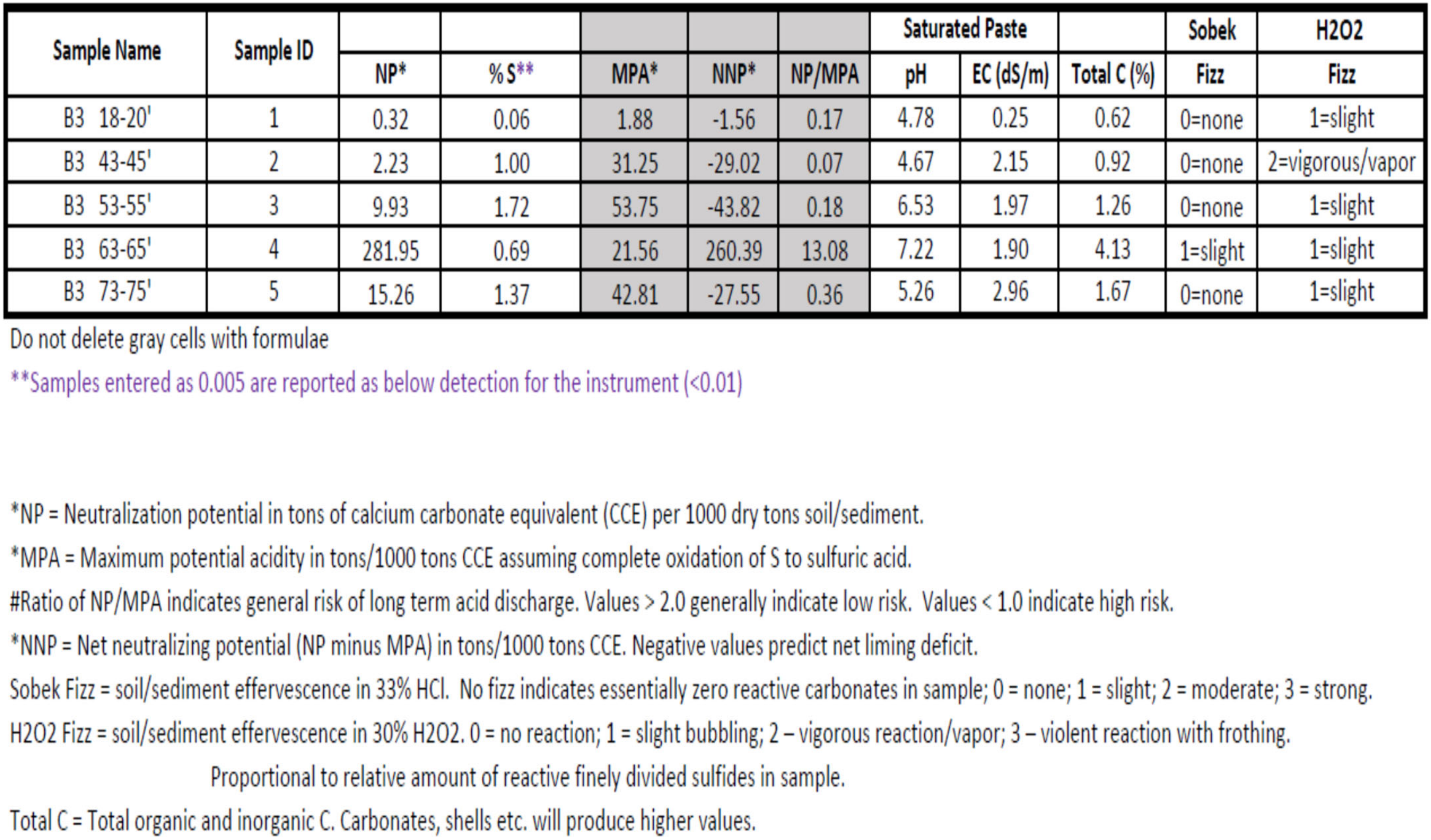
- Assumes complete reaction of sulfide-S and reaction with NP components and “similar reaction kinetics”.

- Presence of siderite ($FeCO_3$) overestimates NP; Most labs use modified Sobek/Skousen-NP to account for siderite

ABA complications and assumptions!

- The HCl fizz test for NP is somewhat subjective, may have discrepancies among workers and labs.
- Assumes materials which consume acid in the lab will generate alkalinity in the field
- Assumes rate of acid production from sulfide oxidation will be similar to rate of alkalinity production and neutralization reactions from neutralizing materials. Carbonate solub. is << than acid salts.
- Can we really compare what happens in the lab to what happens in the field?

A typical recent ABA example for “real world sediments” near Richmond!



Sample Name	Sample ID						Saturated Paste			Sobek	H2O2
		NP*	% S**	MPA*	NNP*	NP/MPA	pH	EC (dS/m)	Total C (%)	Fizz	Fizz
B3 18-20'	1	0.32	0.06	1.88	-1.56	0.17	4.78	0.25	0.62	0=none	1=slight
B3 43-45'	2	2.23	1.00	31.25	-29.02	0.07	4.67	2.15	0.92	0=none	2=vigorous/vapor
B3 53-55'	3	9.93	1.72	53.75	-43.82	0.18	6.53	1.97	1.26	0=none	1=slight
B3 63-65'	4	281.95	0.69	21.56	260.39	13.08	7.22	1.90	4.13	1=slight	1=slight
B3 73-75'	5	15.26	1.37	42.81	-27.55	0.36	5.26	2.96	1.67	0=none	1=slight

Do not delete gray cells with formulae

**Samples entered as 0.005 are reported as below detection for the instrument (<0.01)

*NP = Neutralization potential in tons of calcium carbonate equivalent (CCE) per 1000 dry tons soil/sediment.

*MPA = Maximum potential acidity in tons/1000 tons CCE assuming complete oxidation of S to sulfuric acid.

#Ratio of NP/MPA indicates general risk of long term acid discharge. Values > 2.0 generally indicate low risk. Values < 1.0 indicate high risk.

*NNP = Net neutralizing potential (NP minus MPA) in tons/1000 tons CCE. Negative values predict net liming deficit.

Sobek Fizz = soil/sediment effervescence in 33% HCl. No fizz indicates essentially zero reactive carbonates in sample; 0 = none; 1 = slight; 2 = moderate; 3 = strong.

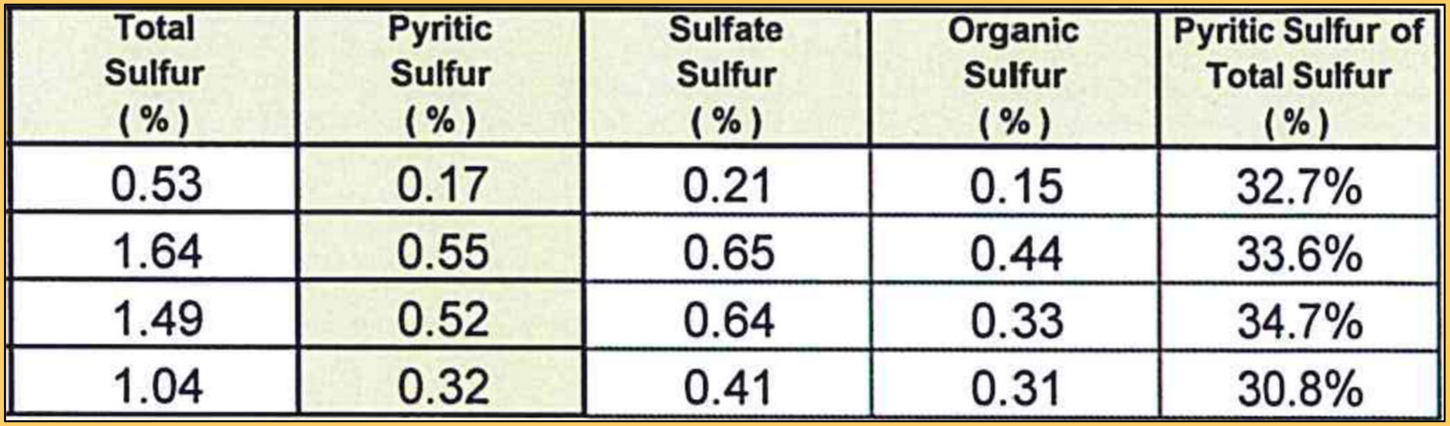
H2O2 Fizz = soil/sediment effervescence in 30% H2O2. 0 = no reaction; 1 = slight bubbling; 2 – vigorous reaction/vapor; 3 – violent reaction with frothing.

Proportional to relative amount of reactive finely divided sulfides in sample.

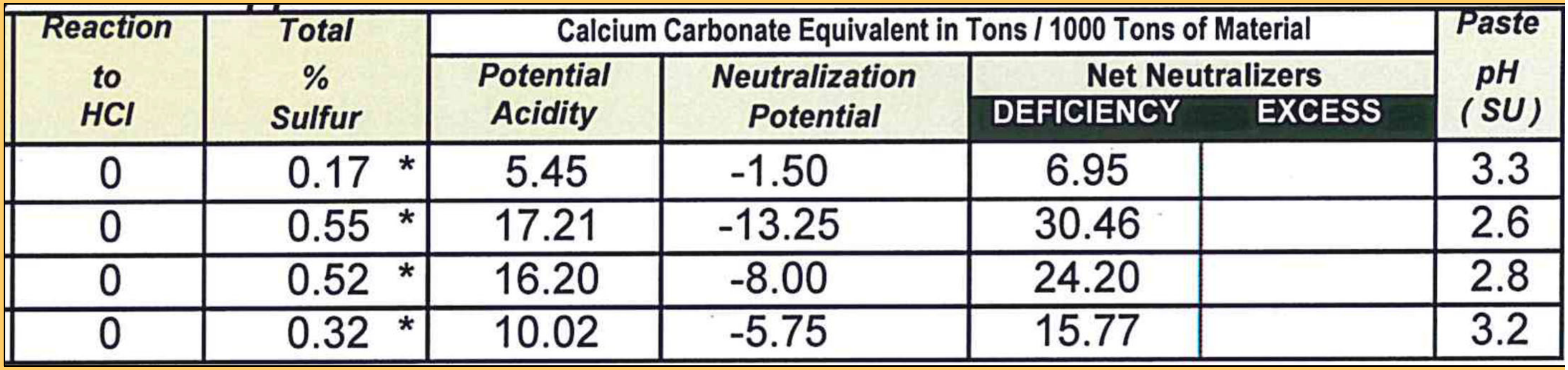
Total C = Total organic and inorganic C. Carbonates, shells etc. will produce higher values.

Another ABA example

Relatively low proportion of pyritic-S and high proportion of organic-S suggests this material is partially weathered leading to very low pH (< 3.5)



Total Sulfur (%)	Pyritic Sulfur (%)	Sulfate Sulfur (%)	Organic Sulfur (%)	Pyritic Sulfur of Total Sulfur (%)
0.53	0.17	0.21	0.15	32.7%
1.64	0.55	0.65	0.44	33.6%
1.49	0.52	0.64	0.33	34.7%
1.04	0.32	0.41	0.31	30.8%



Reaction to HCl	*Total % Sulfur*	Calcium Carbonate Equivalent in Tons / 1000 Tons of Material				*Paste pH (SU)*
		Potential Acidity	*Neutralization Potential*	Net Neutralizers		
				DEFICIENCY	EXCESS	
0	0.17 *	5.45	-1.50	6.95		3.3
0	0.55 *	17.21	-13.25	30.46		2.6
0	0.52 *	16.20	-8.00	24.20		2.8
0	0.32 *	10.02	-5.75	15.77		3.2

MPA = %S (pyritic) X 31.25.
Note all of these materials are very Acidic with negative NPs.

NNP = NP - MPA
Be cognizant of how +/- signs are being used!!! Labs vary.

Potential Peroxide Acidity (PPA)

- **Standard method used at Va Tech, UK and others. Original method also in 1978 EPA document.**
- **120 ml of 30% hydrogen peroxide (H_2O_2) are added in numerous small increments to a 1 g sample.**
- **The H_2O_2 oxidizes sulfides in the sample and acidity is produced. We also assume the acidity produced reacts with internal neutralizers present in the relatively short reaction time (hours).**
- **The amount of acidity produced is determined by titration with NaOH.**
- **Results expressed in tons CCE demand / 1000 tons material**

Kinetic tests

- Time-consuming
- More expensive analysis

- Produce effluent which may be tested and compared to mine drainage (i.e. acidity, sulfates, metals…..)
- Evaluate how sample changes over time

COLUMN SETUP

Capped with 5 cm sand

- Sample volume: 1200 cm^3
- Inside diameter = 7.5 cm
- Height of spoil = ~ 27 cm
- Inside bottom of column:

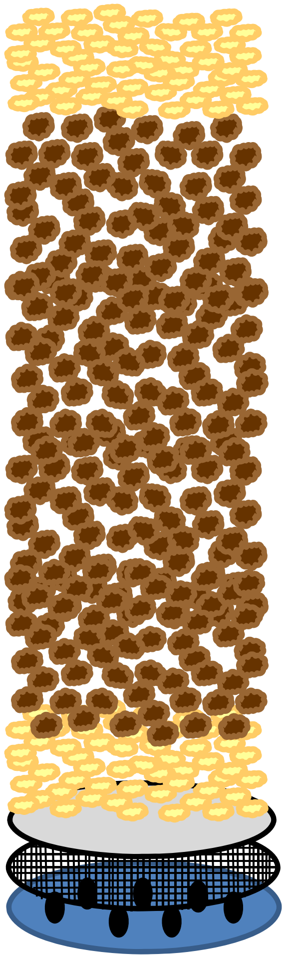
  -- 5 cm (2”) sand

  -- Whatman #1 filter

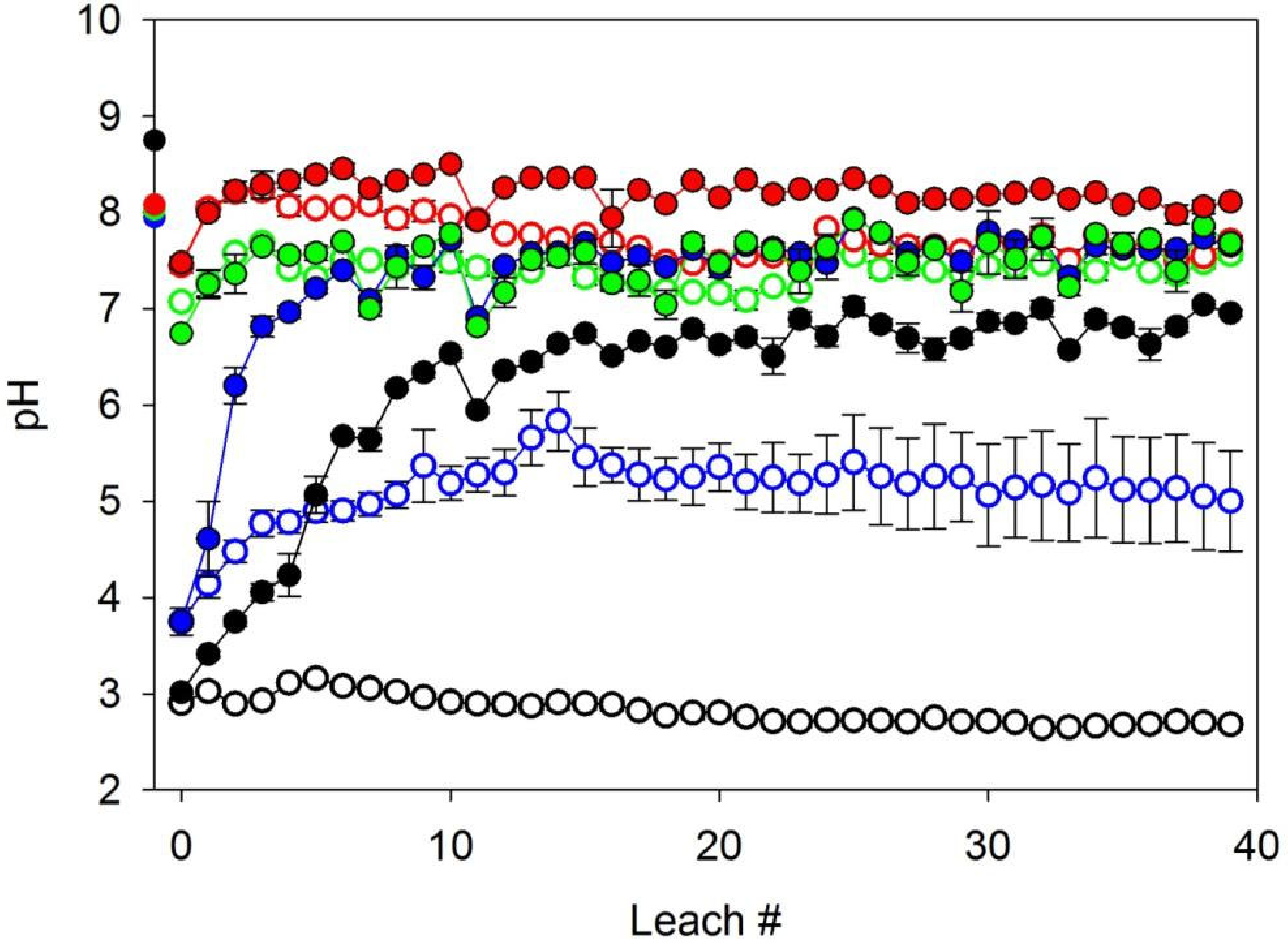
  -- 0.1 mm nylon mesh

  -- perforated plastic disc

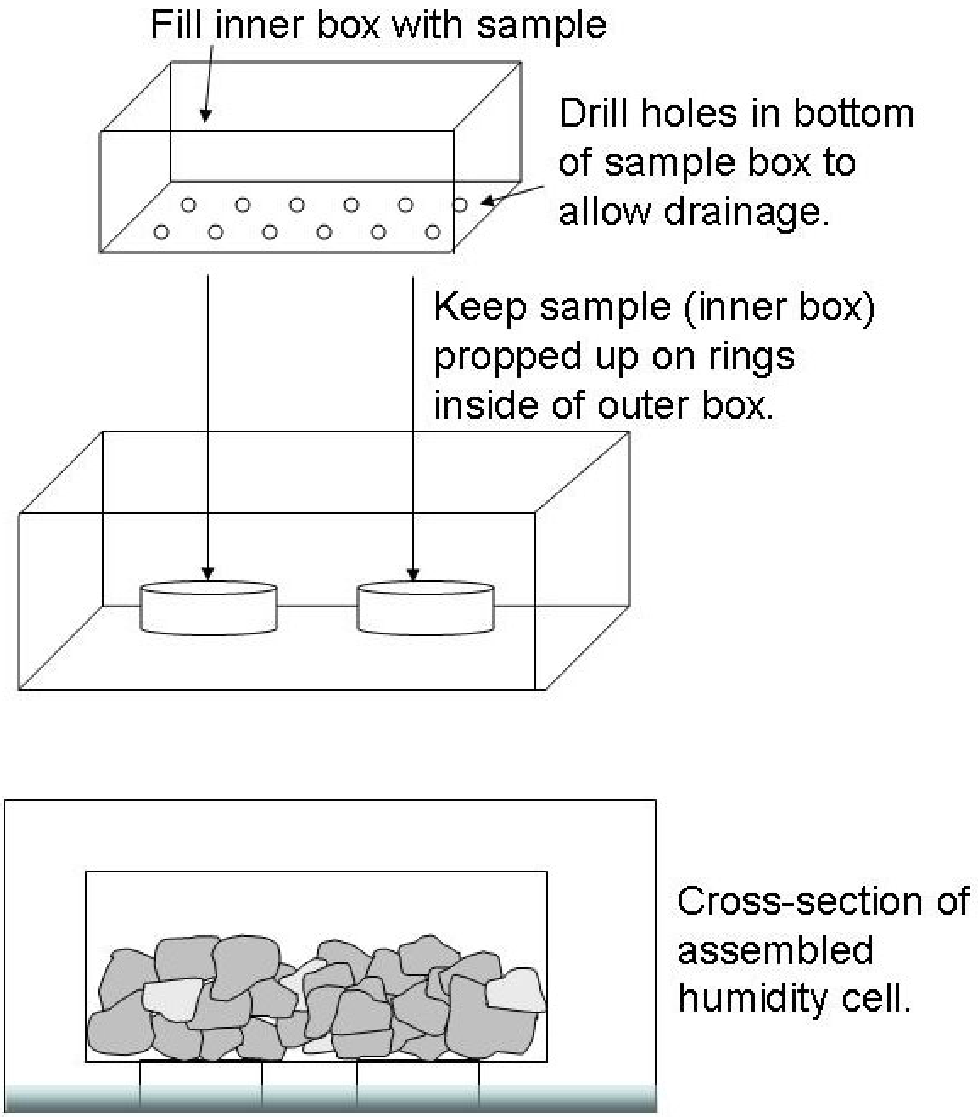
- PVC pipe nipple and Tygon tubing for drainage



Example of data over time (2 leach cycles/week)



Humidity Cells



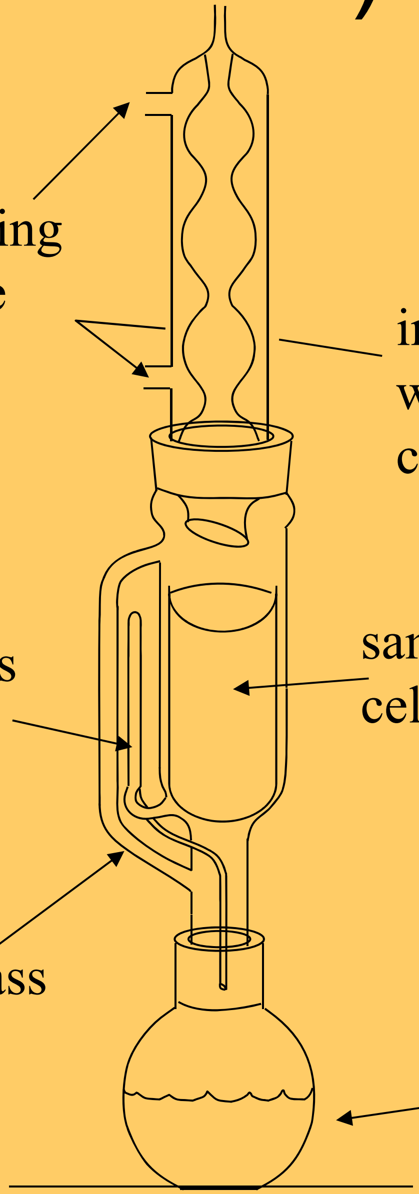
Fill inner box with sample

Drill holes in bottom of sample box to allow drainage.

Keep sample (inner box) propped up on rings inside of outer box.

Cross-section of assembled humidity cell.

Soxhlet Extractors (aka reflux)



outlet for cooling water from the condenser

inlet for cooling water to the condenser

siphon drains leachate in extractor to the reservoir

sample is held in cellulose thimble

vapor by-pass tube from reservoir to condenser

water reservoir

hot plate

Leaching mesocosms/barrels

Same idea as columns and humidity cells, but larger size and exposed to real climatic conditions.


3 6'02

Acid Attack on Concrete

(1) Direct dissolution of cementitious materials due to their high solubility in acids,

(2) formation and expansion of highly hydrated Ca-sulfates like ettringite under moderate to high pH,

(3) formation and expansion of hydrated Ca-Si-sulfates like thaumasite, and

(4) formation of complex Fe-hydroxy sulfates which may also infiltrate the concrete structure leading to significant swell and matrix shatter.

Compiling a state-wide sulfide hazard map for Virginia: Devonian black shales.

Inside the culvert at Clifton Forge.

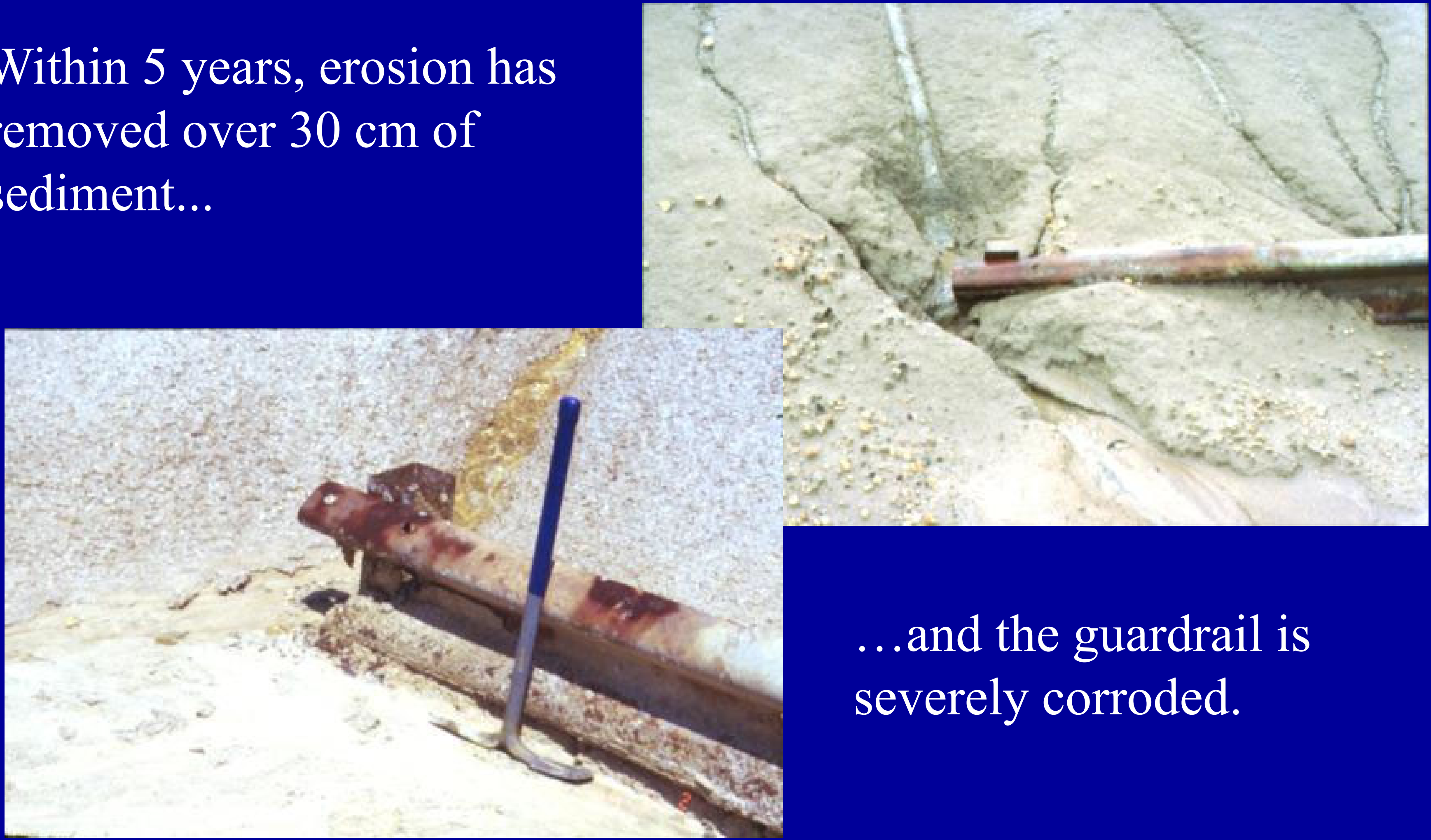
Acid-S Attack on Metal

Direct dissolution of metals at low pH.

Salt induced corrosion.

Compiling a state-wide sulfide hazard map for Virginia: Tertiary marine sediments.

Within 5 years, erosion has removed over 30 cm of sediment...



…and the guardrail is severely corroded.

Sulfate Minerals -- Expansive

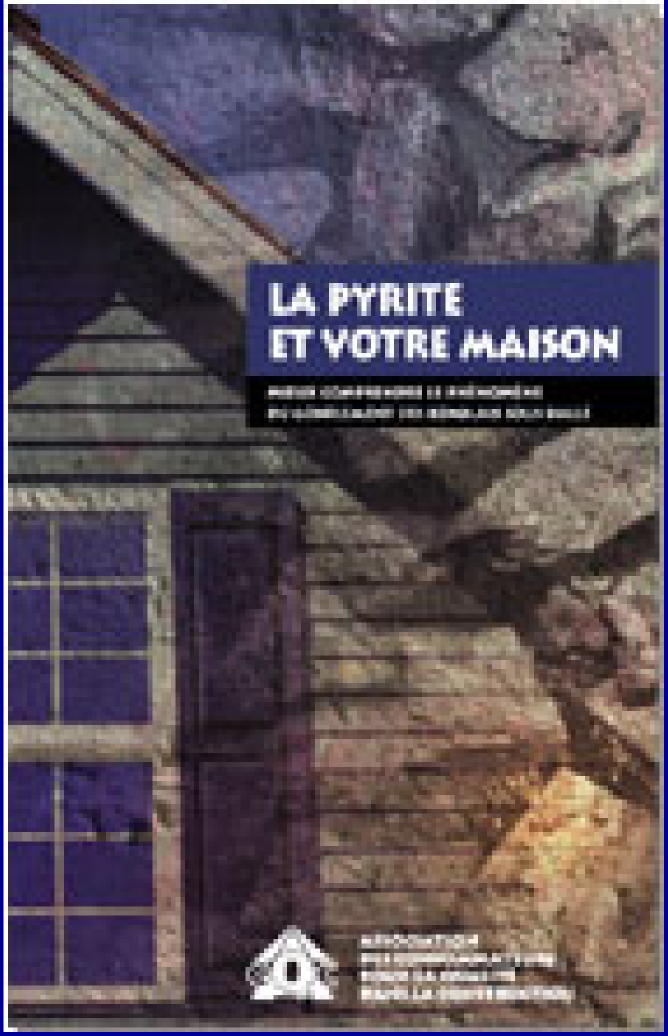
Ettringite

$(Ca_6Al_2(SO_4)OH_{12}\text{-}26H_2O)$

Thaumasite

$(Ca_3Si(CO_3)(SO_4)(OH)_6\text{-}12H_2O)$

Expansive pyritic shales are notably problematic around Montreal, Canada



LA PYRITE
ET VOTRE MAISON

A Canadian consumers group (ACQC) publishes this pamphlet to promote public awareness of expansive pyritic shales. According to this group about 10,000 houses in eastern Canada are thought to be affected by pyrite oxidation.

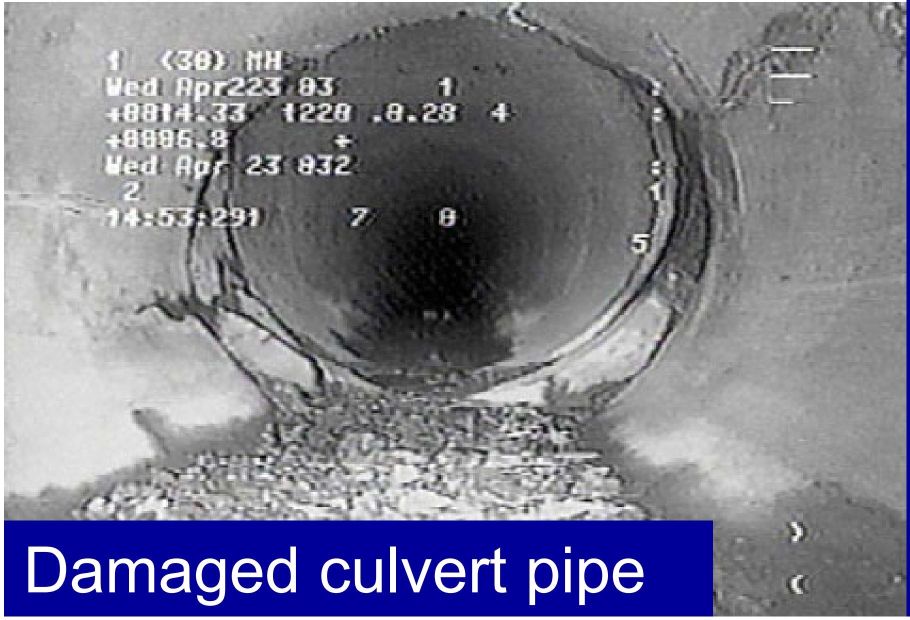
Cracks in basement floor due to sulfide/sulfate-induced shale heave.


Pavement surface distortion


Displaced curb and gutter above culvert

Sulfide-induced shale heaving in Bristol, VA

Pictures from report to VDOT by Thomas E. Freeman P.E., available online



Damaged culvert pipe

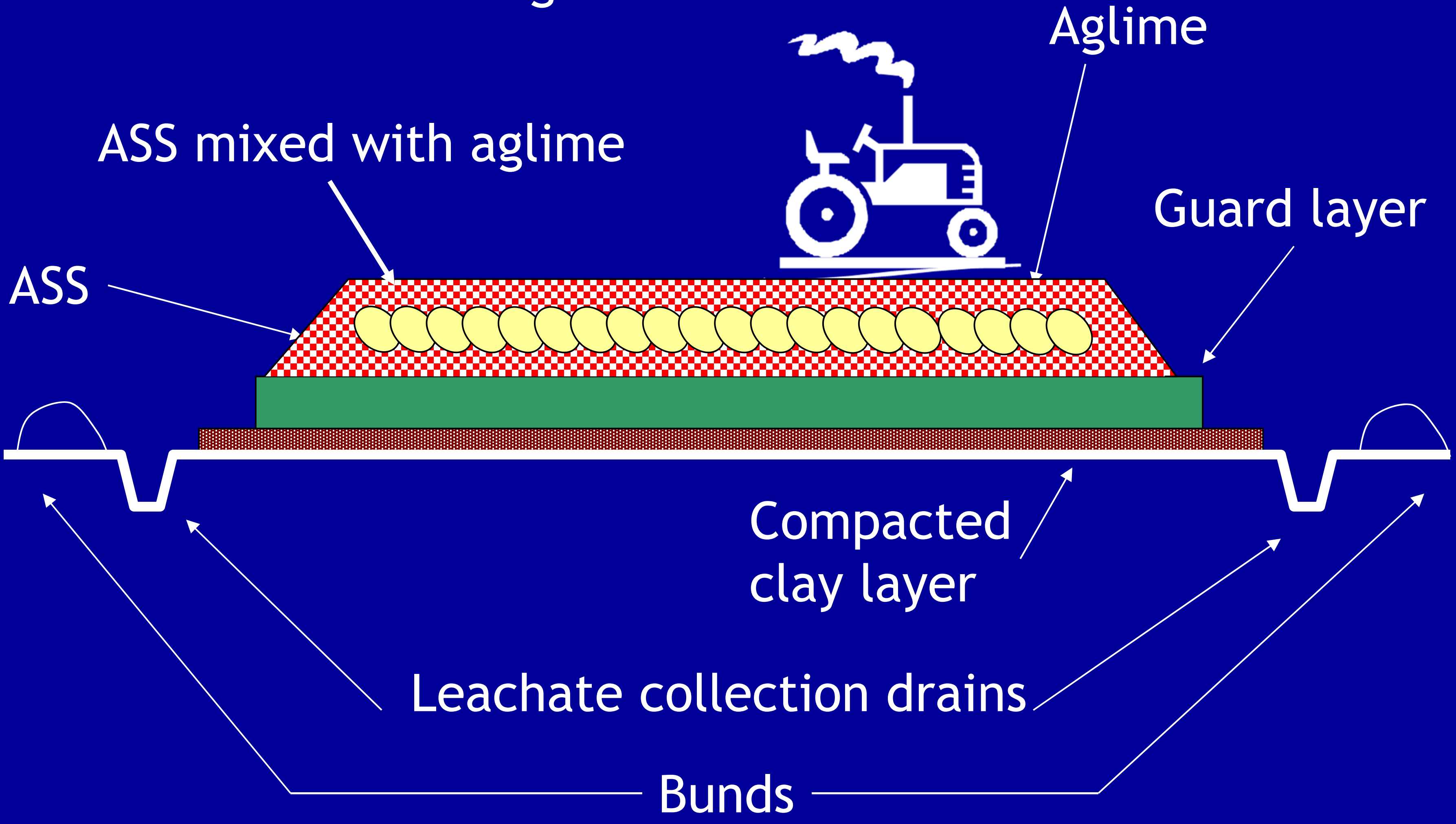

Shale borrow site

Remediation Alternatives

- Avoid it whenever possible!
- Remove and place it below the water table and/or an impermeable cap as soon as possible.
  - Don't leave ASS exposed more than several weeks
  - Add a lime coating to exposed surfaces immediately to retard onset of "fast reaction" when pH drops below 4.5.
  - Ensure that the fill will not receive oxygenated groundwater from upgradient; isolate it.
  - Simply placing it below a vegetated cap will not keep long-term acidic water from moving downgradient. *The bugs that catalyze the "rapid step" only need 1% O_2 p.p.*

Acid sulfate materials from dredging in Queensland mangrove area.

- Verification testing
- Compact soil
- Go again



Aglime

ASS mixed with aglime

Guard layer

ASS

Compacted clay layer

Leachate collection drains

Bunds

Spread the aglime, mix it in, verification testing & then go again!

guard layer

Mitigation of Direct Acid Attack on Concrete and Metal

(1) Utilization of sulfate resistant concrete (e.g. Type V) to minimize direct sulfate hydroxy salt hydration effects.

(2) Use of appropriate coatings to limit acid dissolution of cement and infiltration of mixed cation-sulfate solutions.

(3) Use PVC where possible?

Concrete Coatings

Various asphalt formulations; VOC issues with many

Epoxy resins with fillers or glass fibers,

Plasticized PVC,

Polyester resins,

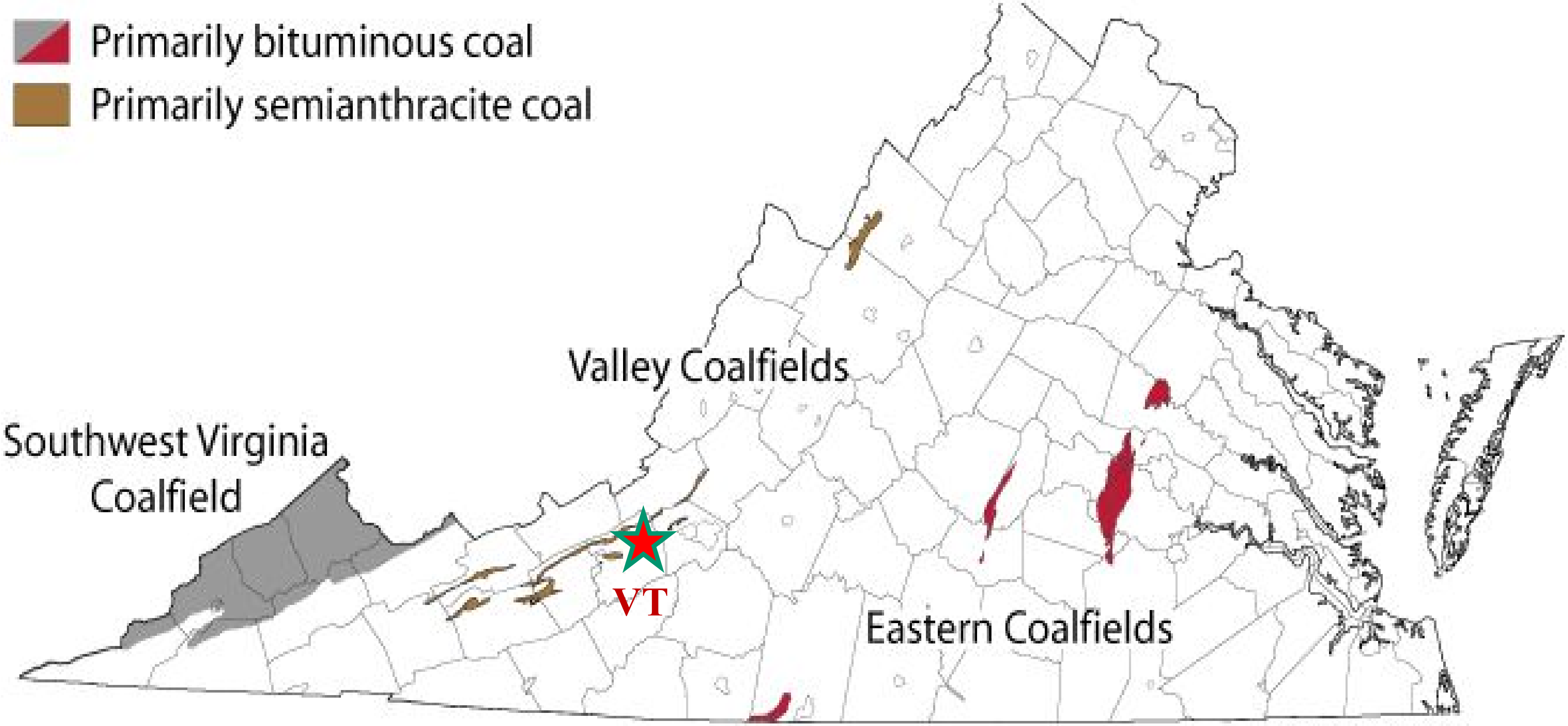
Multiple coats of linseed oil.

Predicting Water Quality Impacts of Appalachian Coal Mine Spoils and Valley Fills

W. Lee Daniels & Carl Zipper
and many, many others!
wdaniels@vt.edu
https://landrehab.org

COLLEGE OF AGRICULTURE AND LIFE SCIENCES
SCHOOL OF PLANT AND ENVIRONMENTAL SCIENCES
VIRGINIA TECH.

Location of Southwest Virginia Coalfield and Virginia Tech



Compiled by S. Williams

Historically, for active coal surface mines, we spent 20+ years focusing our pre-mining analytics on (1) which materials need to be treated/isolated to prevent acid drainage and (2) which materials are optimal revegetation substrates. ***However, we now need to consider (3) what TDS components will each release?***

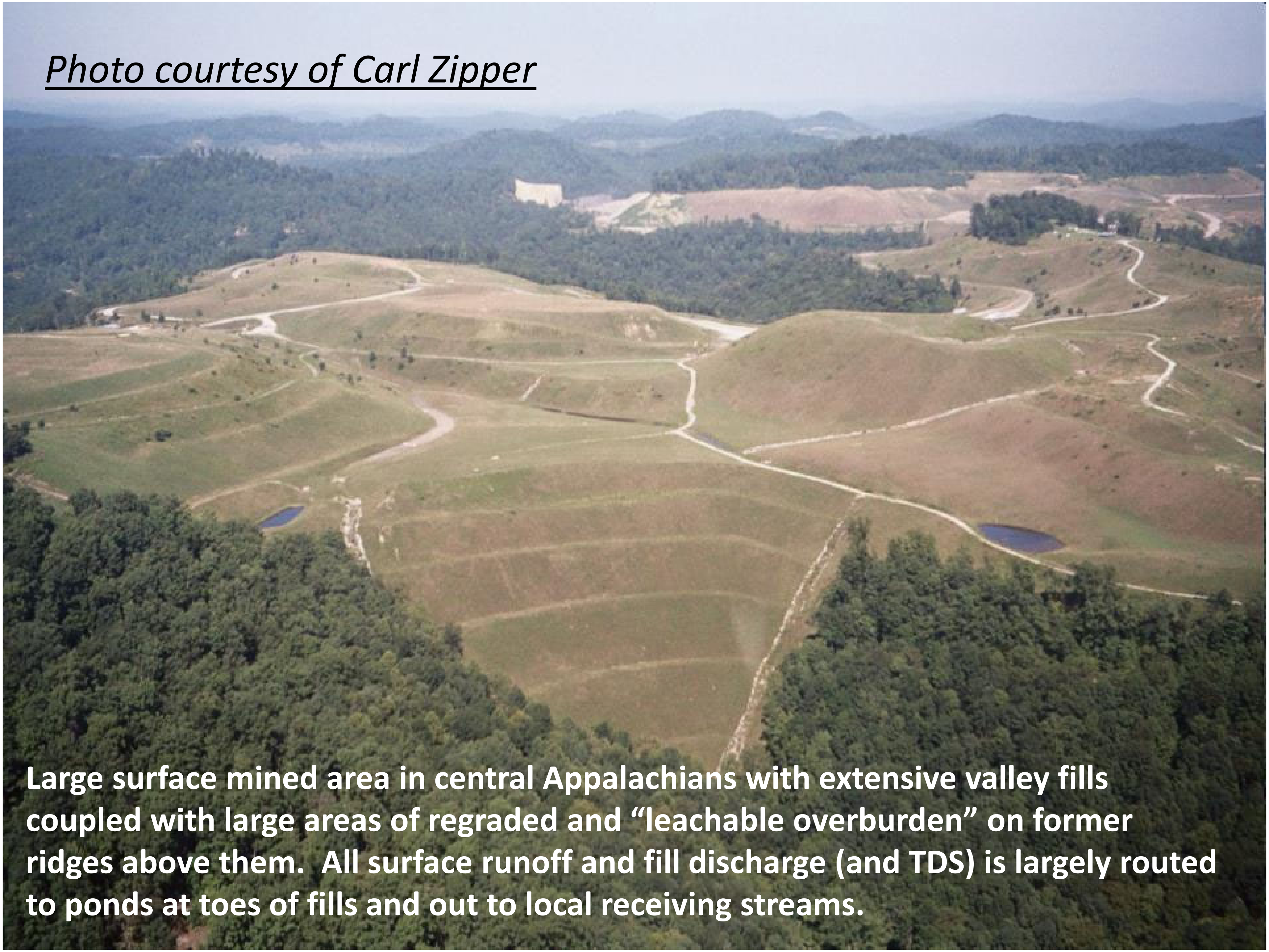


Photo courtesy of Carl Zipper

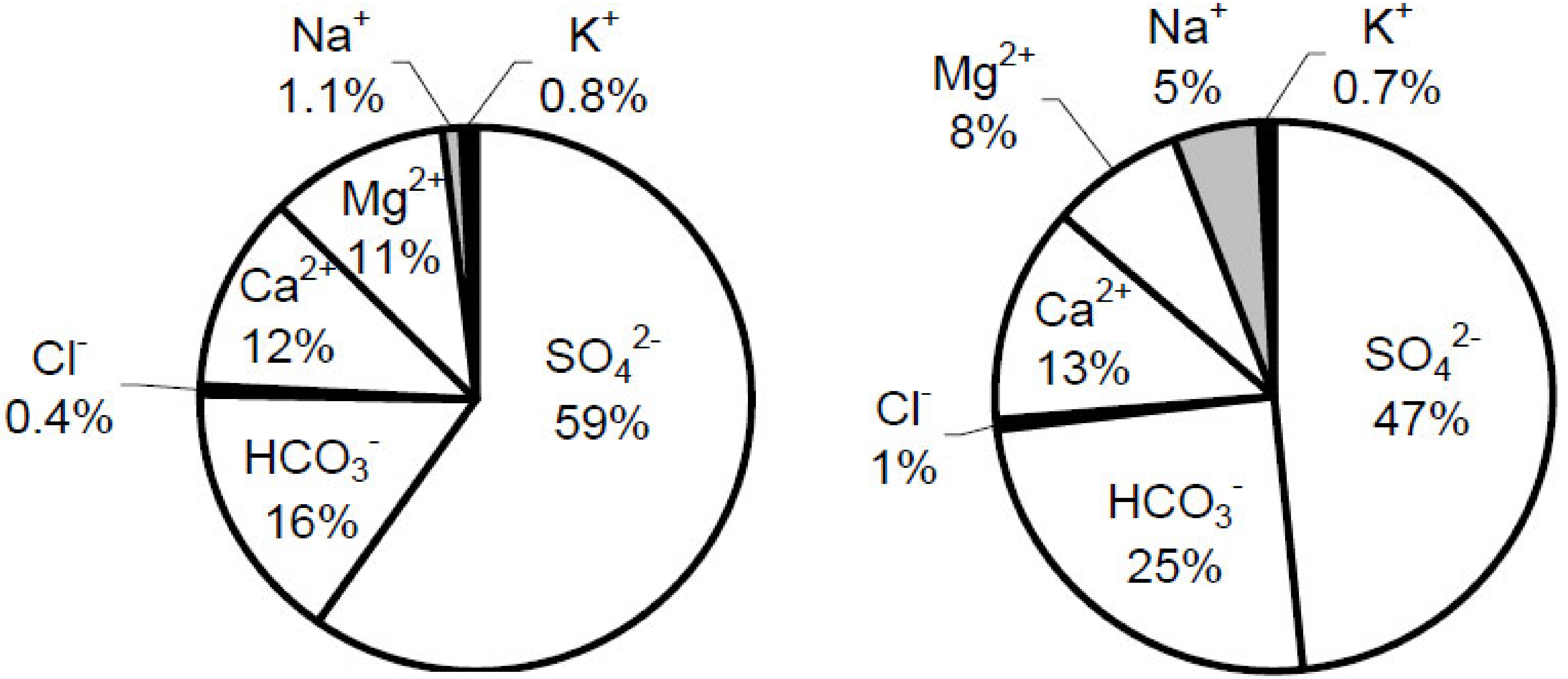
Large surface mined area in central Appalachians with extensive valley fills coupled with large areas of regraded and "leachable overburden" on former ridges above them. All surface runoff and fill discharge (and TDS) is largely routed to ponds at toes of fills and out to local receiving streams.

What are we talking about?

- TDS = **Total Dissolved Solids** expressed as mg/L. Sum of Ca+K+SO_4 etc. in solution. Laborious to analyze for!
- Typically field estimated by electrical conductance (EC) in µS/cm and then corrected to specific conductance (SC) at 25^o C. **TDS = ~ 0.7 SC**.
- So, **500 µS/cm = 350 mg/L**
- However, conversion factors range from 0.64 for Cl to > 0.90 for SO_4 dominated waters. DI = 0.56

Where's it come from?

- **Acid-base reactions**; sulfide oxidation and carbonate neutralization reactions.
- Background **carbonation reactions** in non-sulfidic materials.
- **Hydrolysis** of primary mineral grains.
- **Entrained Cl and SO_4** in rocks (minor).
- **Other minor weathering reactions** like K release from micas, Mg from chlorite etc.



Pond et al. 2008

Timpano 2011

J. N. Am. Benthol. Soc., 2008, 27(3):717–737DOI: 10.1899/08-015.1

M.S. Thesis; VT

Dominant constituents of total dissolved solids (TDS) in circumneutral water released by coal mine valley fills in the central Appalachian USA coalfields.

TDS/EC Discharge Standards?

Several widely cited studies (e.g. Pond et al., 2008), found that streams with high conductivity -- above ~ 500 µs/cm -- were biologically impaired. Impacts are primarily to sensitive macroinvertebrates (mayflies etc.)

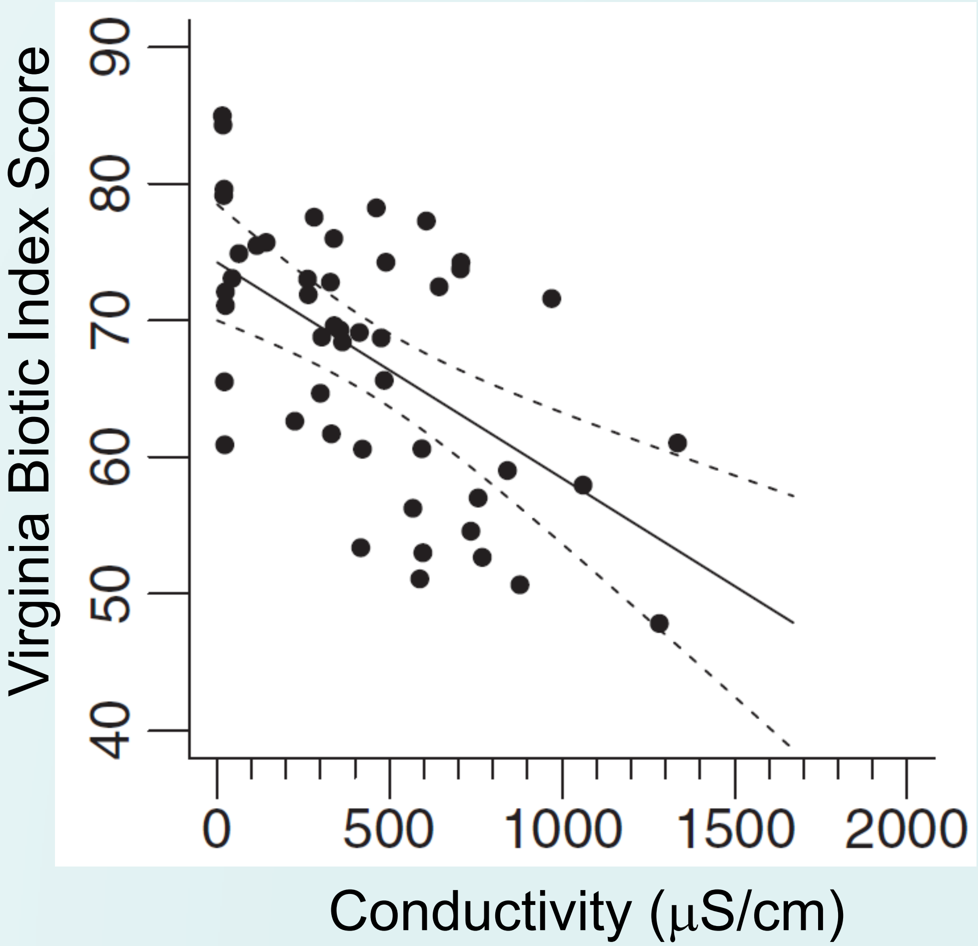
On April 1, 2010, USEPA issued new "guidance" requiring measures to mitigate discharges above 300 µs/cm, and a reduction in mine size or cancellation of active or future fills if above 500 µs/cm.

While this guidance was overturned in DC federal court in 2012, TDS remains a dominant state & federal regulatory concern.

Summary of In-Stream Effects Reports

- There are numerous consistent reports of a negative association between increasing stream SC/EC and abundance of sensitive taxa, particularly *Ephemeroptera* (mayflies).
- Few studies have controlled for other factors affecting macroinvertebrates such a shade, litter inputs, water temperature, etc.
- Species richness appears to be more responsive to elevated SC than relative abundance.

Virginia Biomonitoring Macroinvertebrates & Salinity



Family-level Biotic Index declines as salinity increases

But, highly variable

Note: Coal mine discharges not regulated by SC levels, but via VBI scores which are primarily based on stream macro-invertebrate sampling

Timpano et al. 2015 *JAWRA*

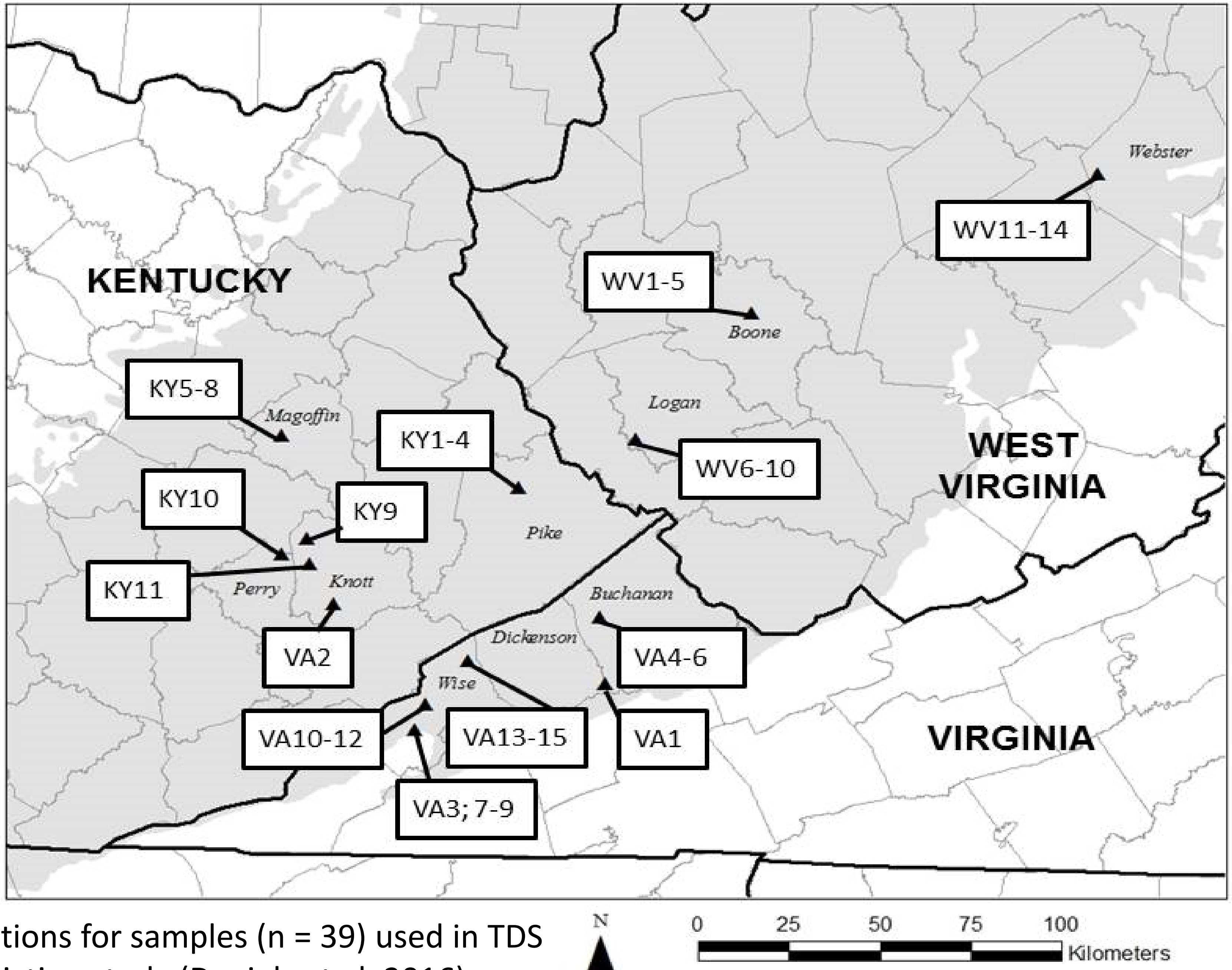
Summary of In-Stream Effects Reports

- It is not clear to what extent the absence of these sensitive taxa is actually influencing in-stream functions such as litter processing and nutrient spiraling.
- The actual cause-effect relationship of how SC (or any component ions like (SO_4) has not been well established.
- Effects of higher salt levels on osmoregulation by organisms adapted to (selected for) very low TDS waters appears likely.
- Regardless, there does appear to be a significant relationship between receiving stream SC and abundance of sensitive macroinvertebrates at much lower levels than those cited (1,000–3,000 µS/cm) by Cañedo-Argüelles et al. (2013) for similar effects in other world ecosystems.

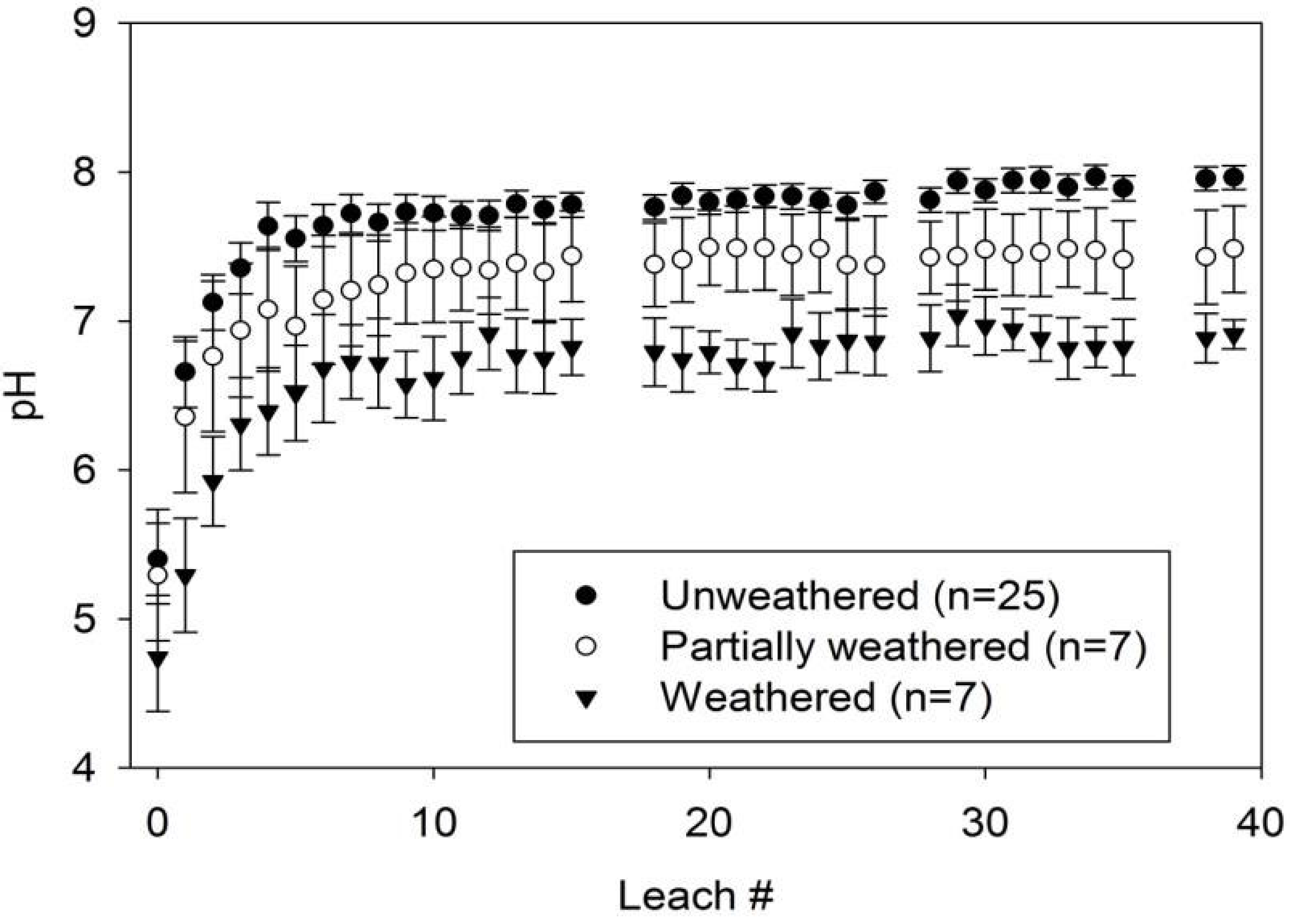
TDS Prediction Study Cooperators (*most but not all!*)

- **Virginia Tech** – *Carl Zipper, Zenah Orndorff, Sara Klopf, Mike Beck and Clay Ross*
- **University of Kentucky** – *Chris Barton, Carmen Agouridis, Richard Warner and Pat Angel (OSM)*
- **West Virginia University** – *Jeff Skousen, Louis McDonald and Jessica Odenheimer*

- Over 70 regional spoils have been run in triplicate for various studies under unsaturated conditions (3 columns per sample) with simulated rain.
- Whole spoil crushed & screened to < 1.25 cm.
- Typically run for minimum of 20 weeks (40 cycles) with 2 x 2.5 cm of simulated rain (pH 4.6) per week (1 cycle = 2.5 cm)

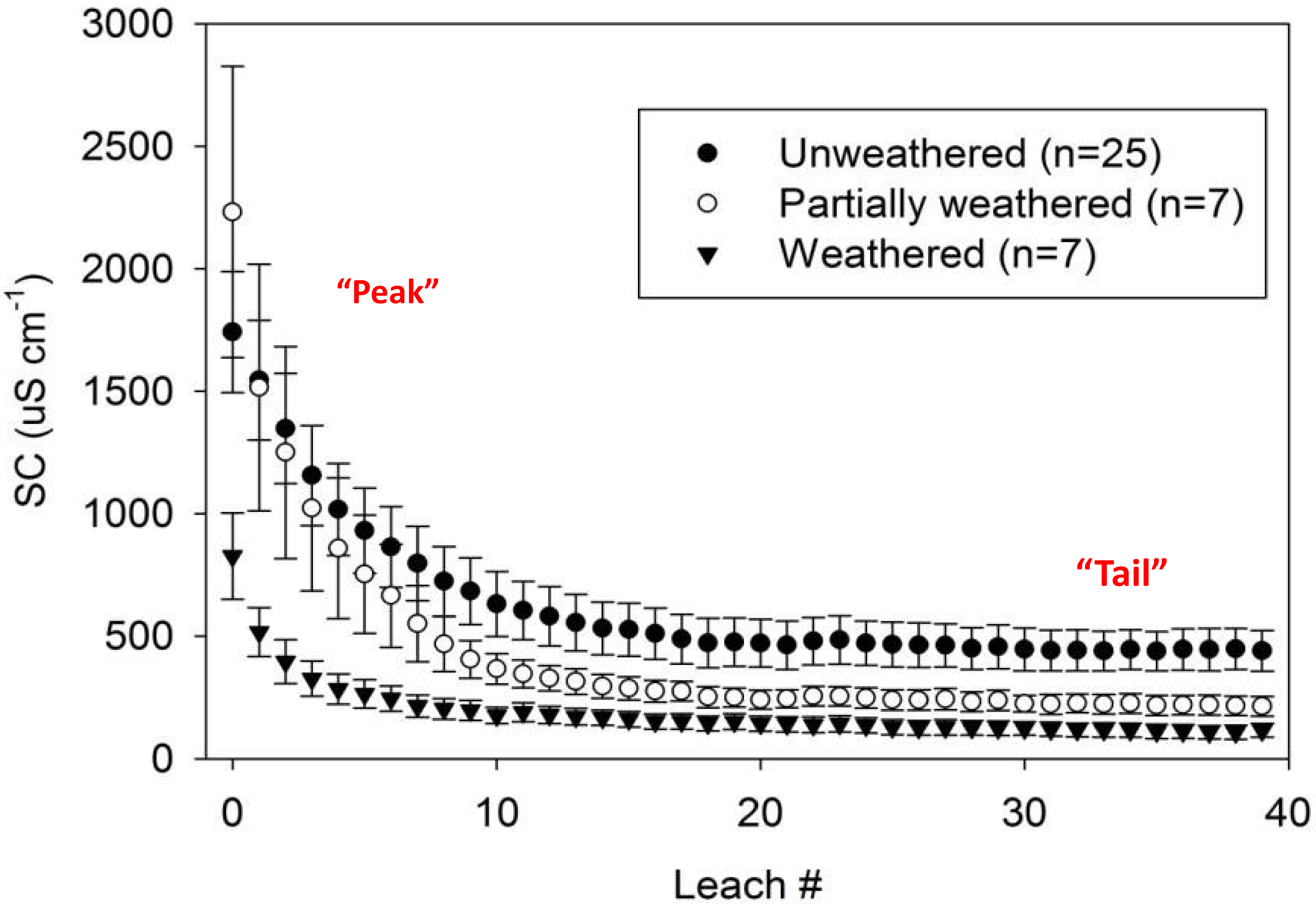


Locations for samples (n = 39) used in TDS Prediction study (Daniels et al. 2016)



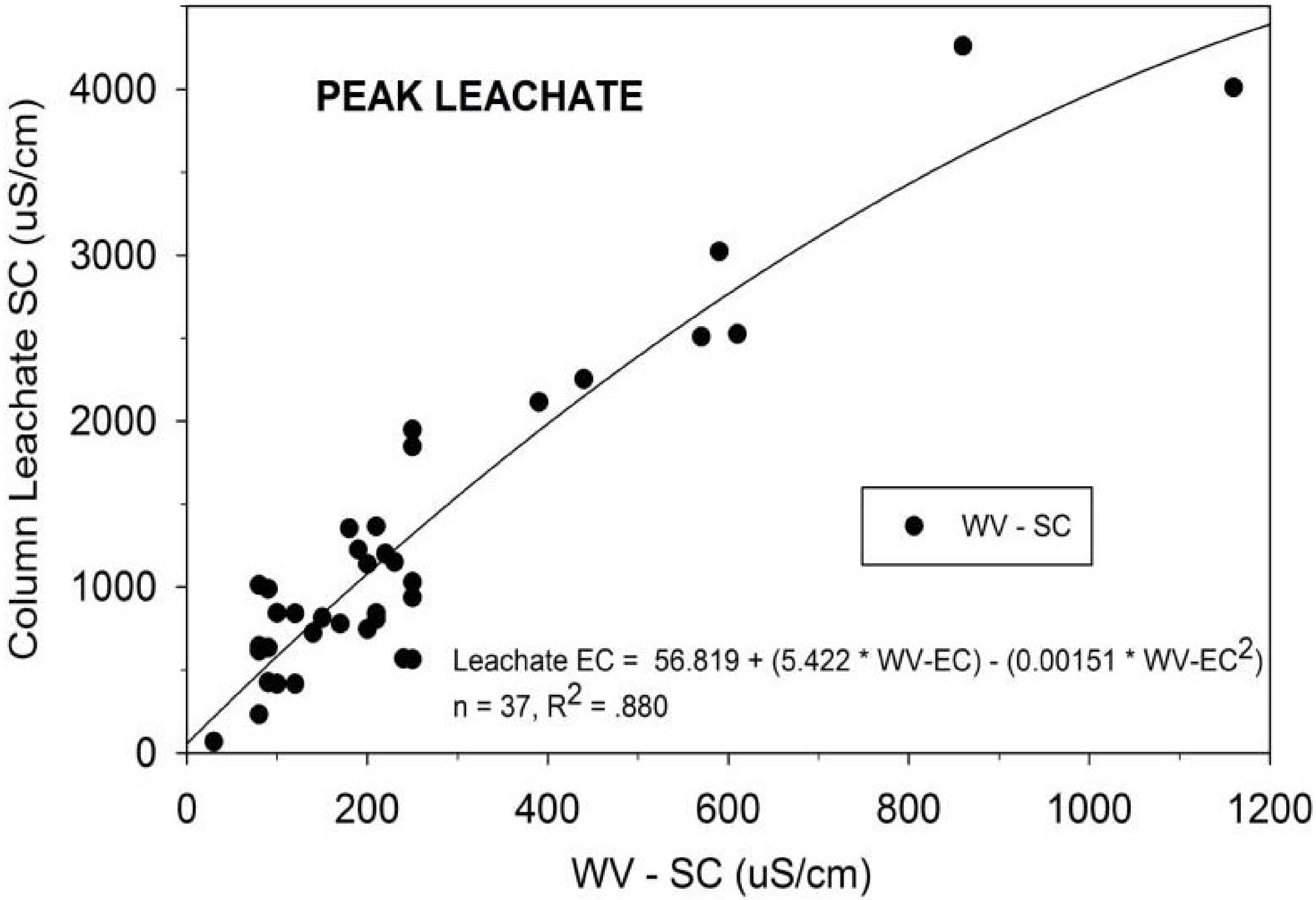
Daniels et al., 2016. Env. Poll. 216, p 371 – 379

Oxidized, pH 5.5 overburden over reduced pH 8.0 carbonate (2%) containing overburden at depth.

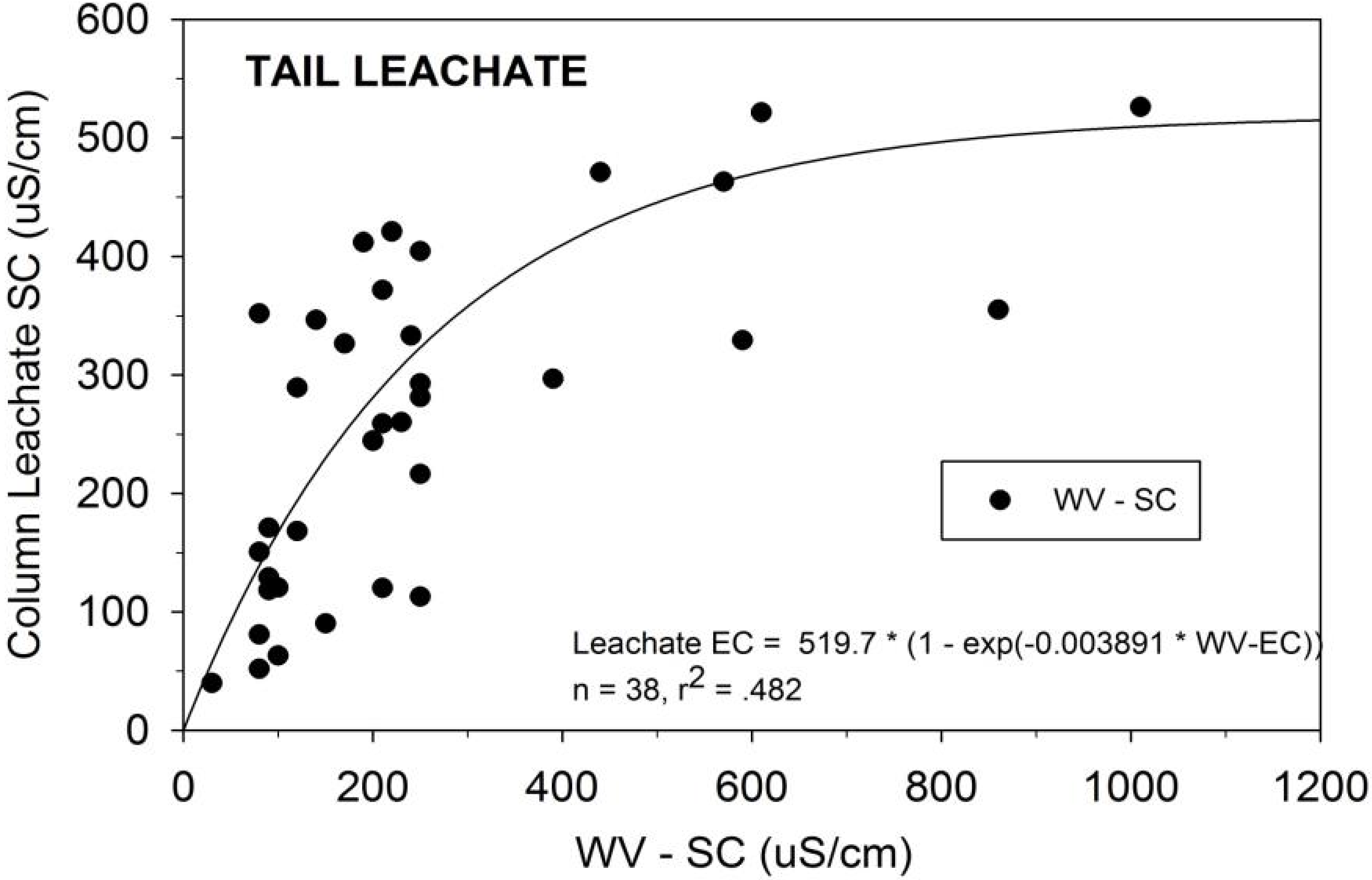

3000
2500
2000
1500
1000
500
0
SC (uS cm^{-1})
0
10
20
30
40
Leach #
● Unweathered (n=25)
○ Partially weathered (n=7)
▼ Weathered (n=7)

“Peak”

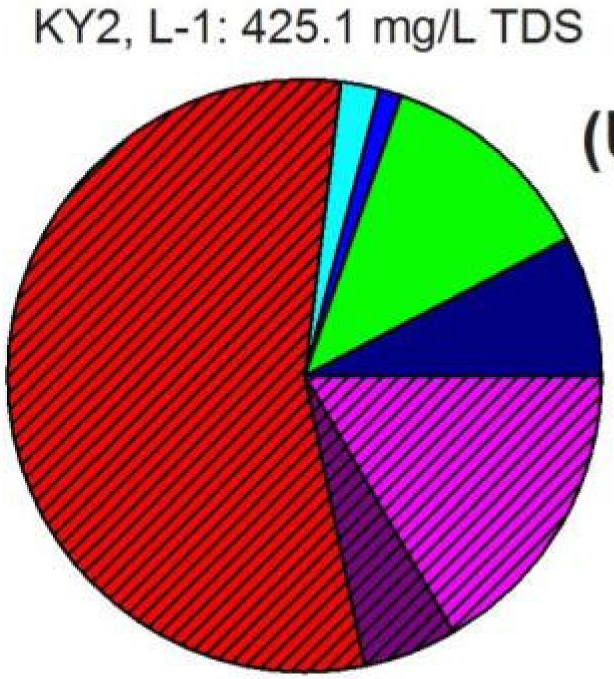
“Tail”

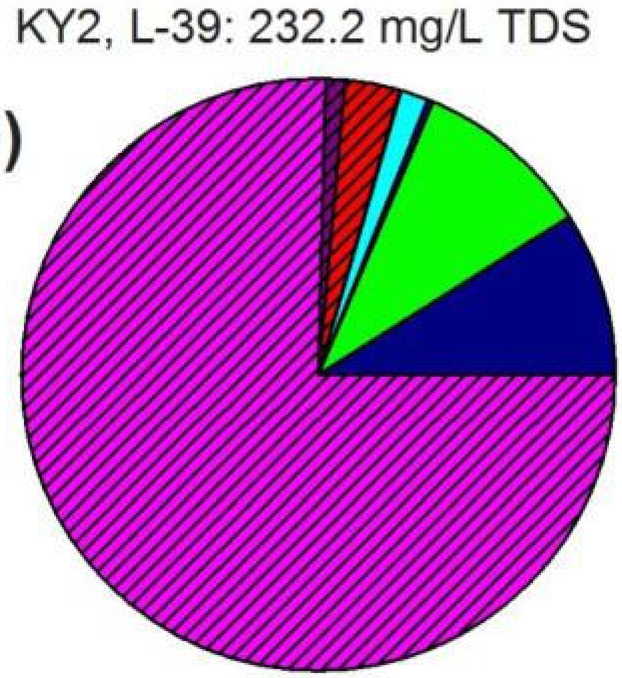


We have evaluated over 20 different static lab tests such as total-S, ABA parameters, various soluble salt (SC) extracts etc. and regressed them against "peak" SC production and longer term semi-stable "tail" SC. The best fit model above is for 2:1 water:spoil SC., but standard SSSA saturated paste extract generates a very similar model ($R^2 = 0.856$). Total-S generates models with R^2 ~0.65, but sensitive to outliers.

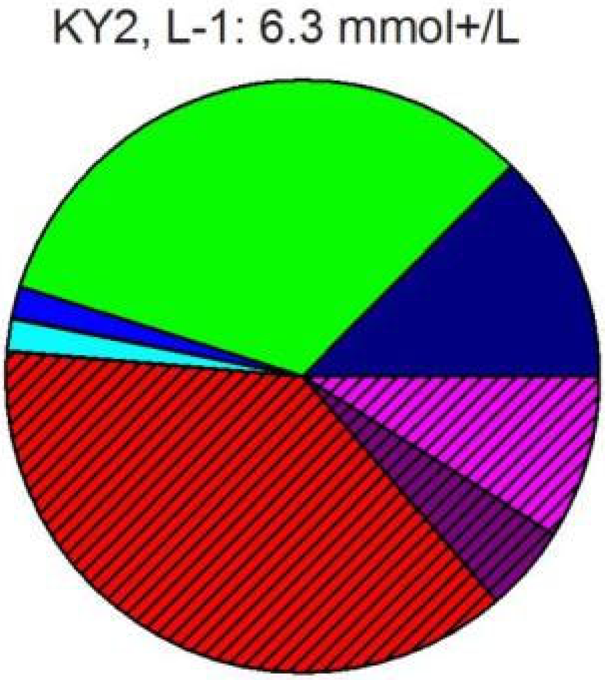

TAIL LEACHATE
Column Leachate SC (uS/cm)
WV - SC (uS/cm)
0
100
200
300
400
500
600
0
200
400
600
800
1000
1200
● WV - SC
Leachate EC = 519.7 * (1 - exp(-0.003891 * WV-EC))
n = 38, r2 = .482

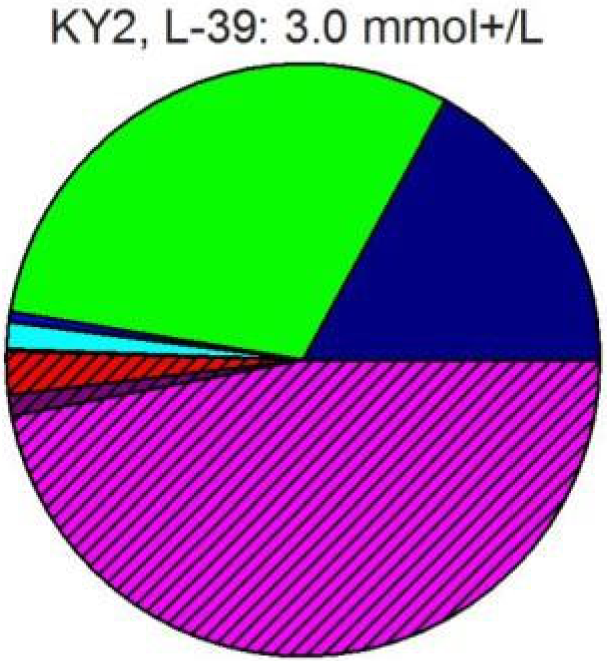
GRAY (UNWEATHERED) SANDSTONE


KY2, L-1: 425.1 mg/L TDS


KY2, L-39: 232.2 mg/L TDS

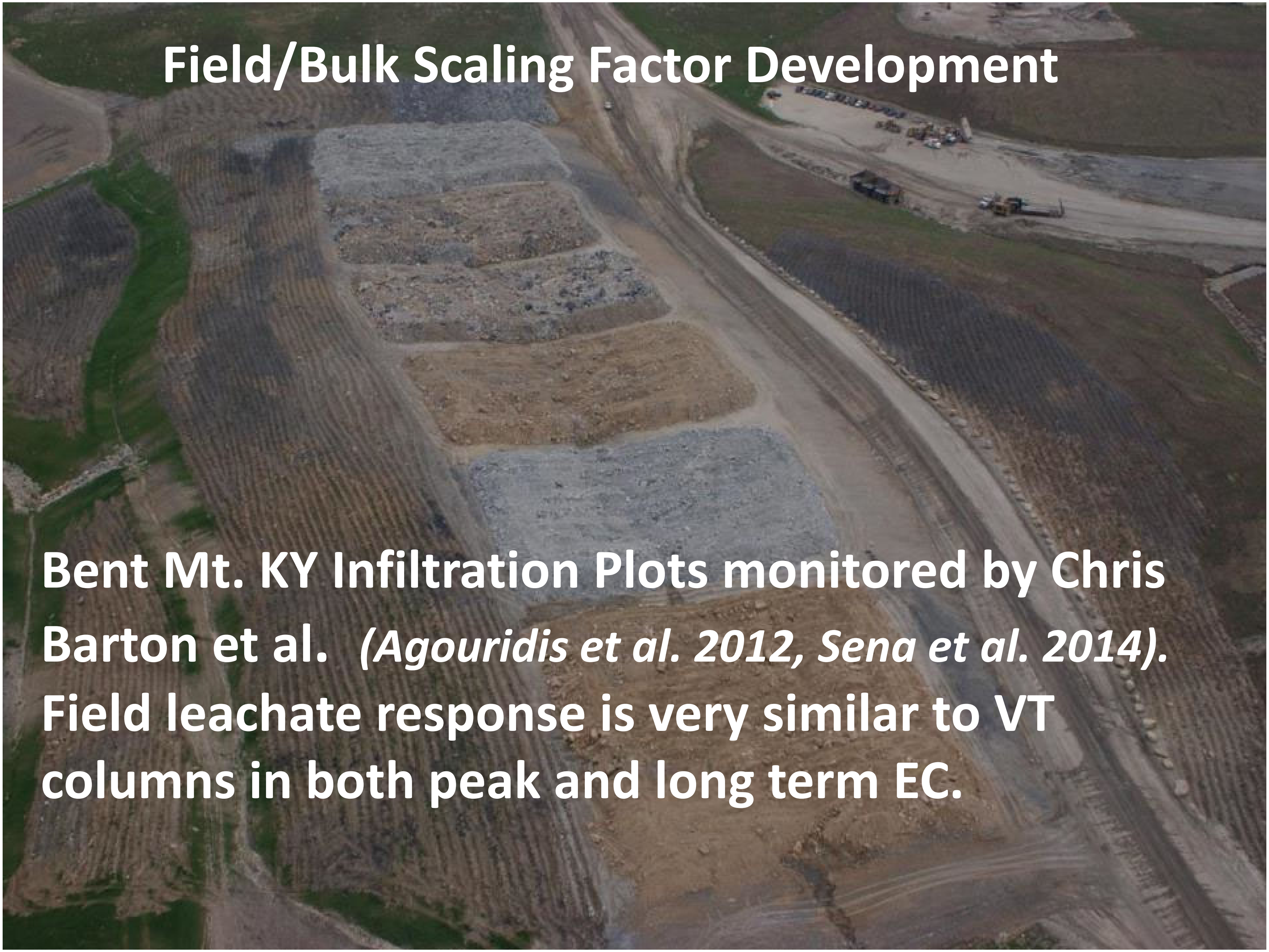
🟦 Ca
🟩 Mg
🟦 Na
🟩 Al
🟦 K
🟦 Fe
⬜ other cations
▨ sulfate
▨ chloride
▨ bicarbonate


KY2, L-1: 6.3 mmol+/L

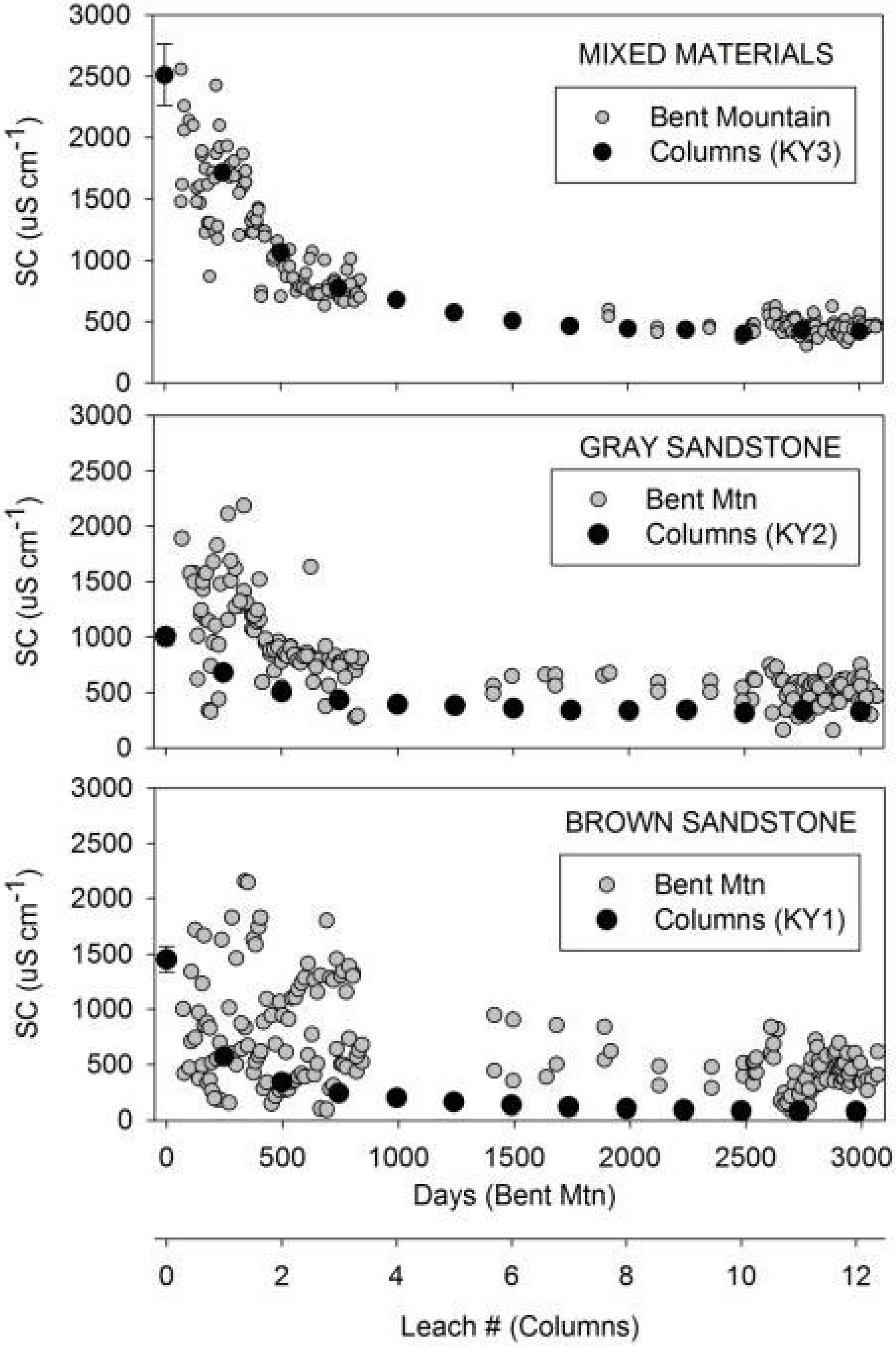

KY2, L-39: 3.0 mmol+/L

Samples from Bent Mt Ky Agouridis et al. 2010 study

Field/Bulk Scaling Factor Development



Bent Mt. KY Infiltration Plots monitored by Chris Barton et al. *(Agouridis et al. 2012, Sena et al. 2014).* **Field leachate response is very similar to VT columns in both peak and long term EC.**



Individual spoil sample leaching data from VT columns and UK Bent Mt. lysimeters. Note the very good correspondence for the mixed materials along with the (a) poorer initial fit for the "gray sandstone", and the (b) fairly consistent under-prediction for the columns vs. the "brown [weathered] sandstone".

The brown [weathered] sandstone at this particular site is higher in reactive S than the majority of those examined.

Large leaching tanks (mesocosms ~ 1.5 m^3) in September, 2012, in Blacksburg.

Results by Ross (2015) and Daniels, Klopf et al Https://powellriverproject.org/reports/

Filter fabric was placed over drainage layer and then spoils placed in tanks.

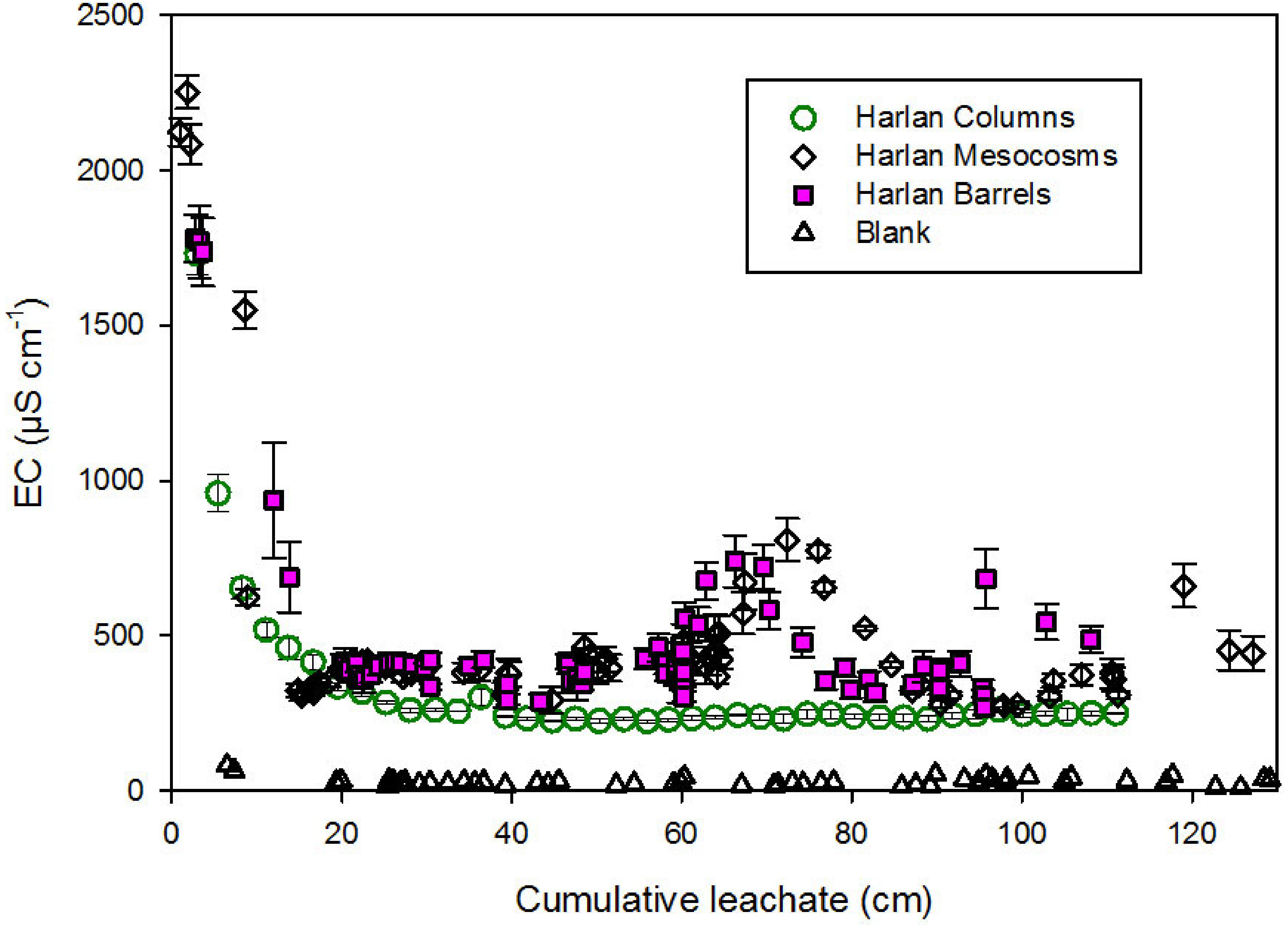
Raw spoil (up to 18”) placed into mesocosms over filter fabric and 10 cm of acid washed gravel. Initiated in October of 2012 and continued through 2021.

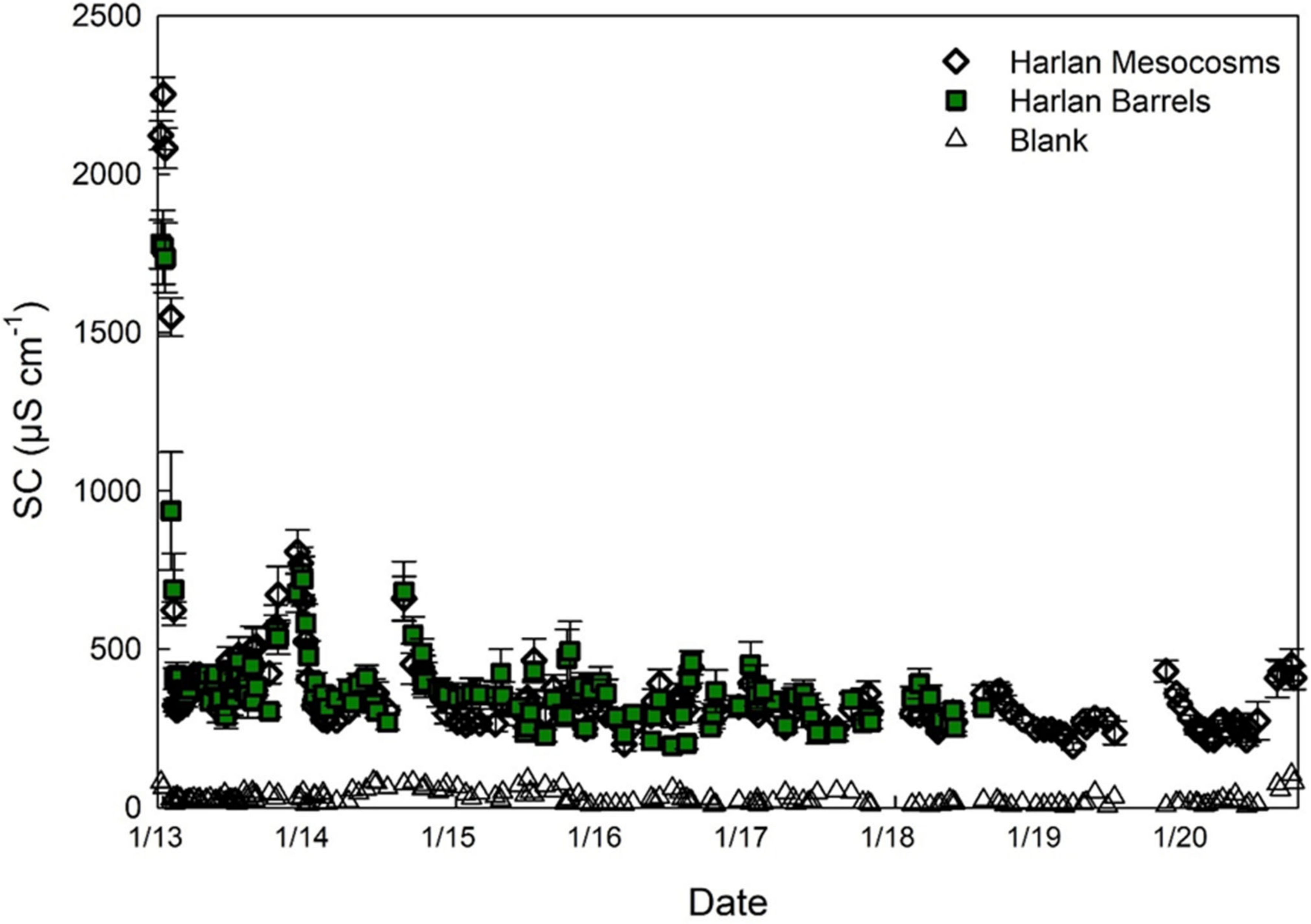
Smaller “barrels” on same site with same spoil (Harlan fm). Barrels received $\leq$ 5” screened spoils.

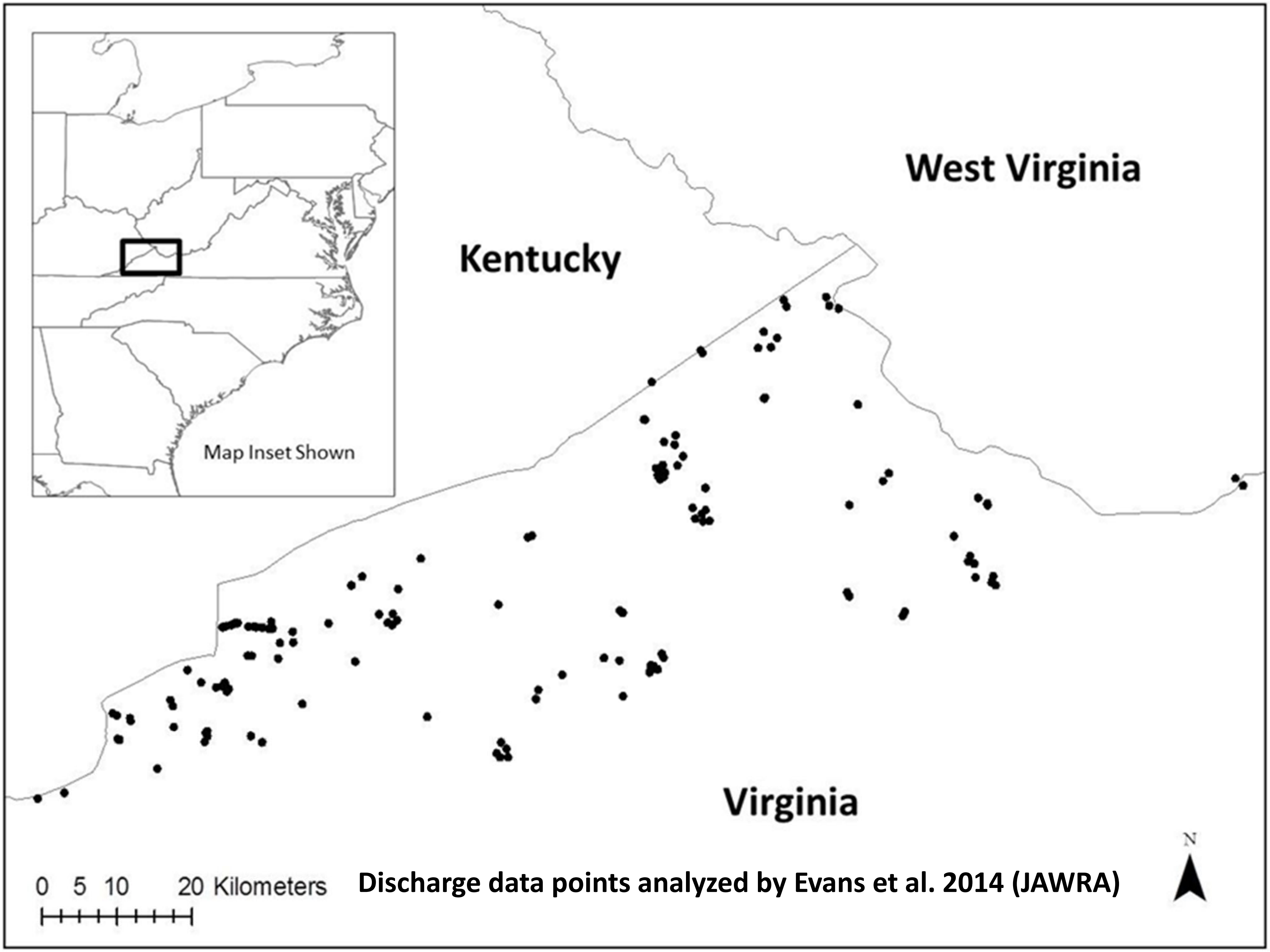
Materials are maintained without vegetation and receive ambient precipitation only.

Harlan spoil barrels (foreground) and tanks (background) with one blank barrel containing only gravel and filter fabric

Results from Ross (2015) M.S. Thesis




2500
2000
1500
1000
500
0
SC (µS cm^{-1})
1/13
1/14
1/15
1/16
1/17
1/18
1/19
1/20
Date
◇ Harlan Mesocosms
■ Harlan Barrels
△ Blank



Discharge data points analyzed by Evans et al. 2014 (JAWRA)

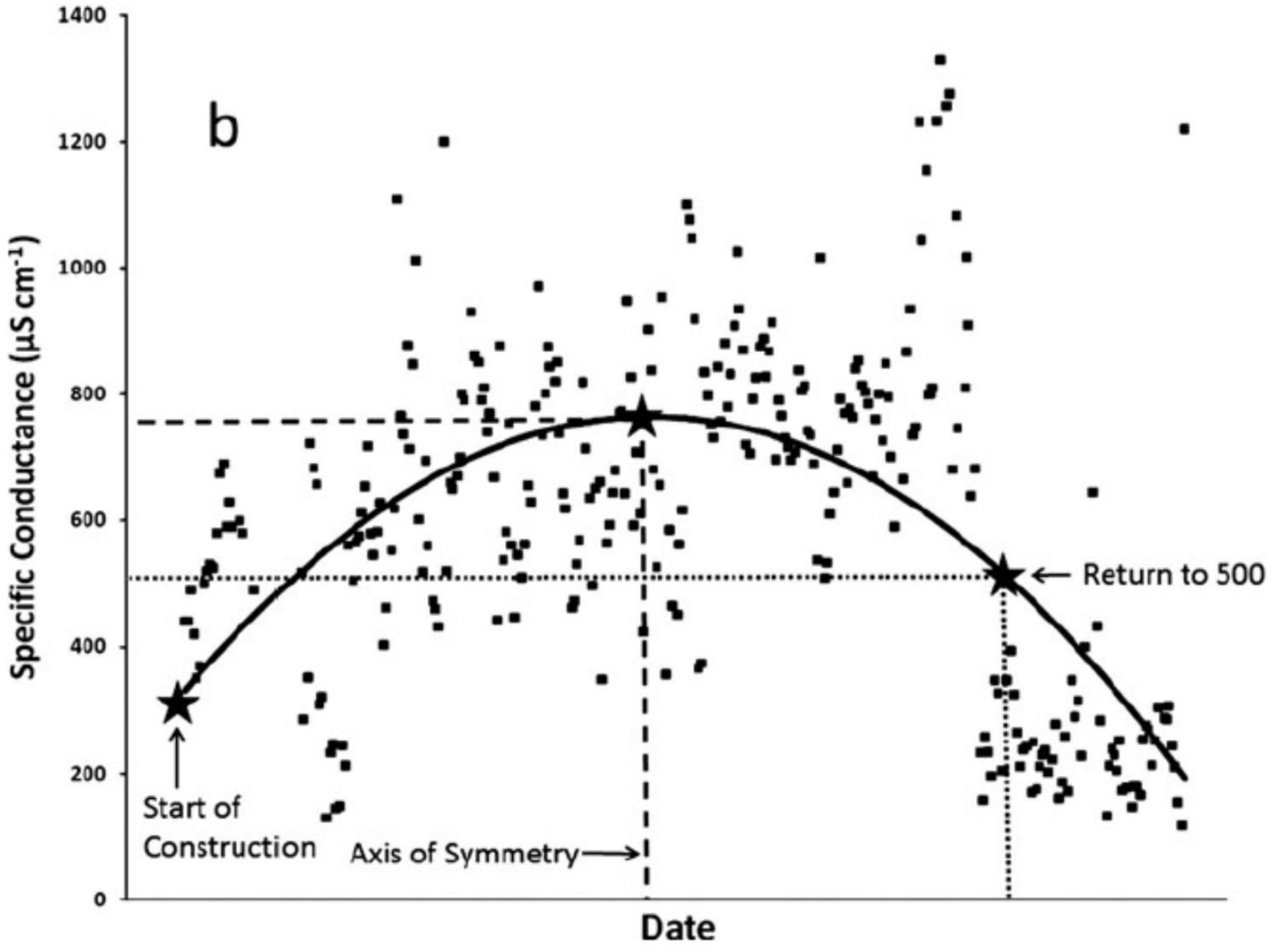


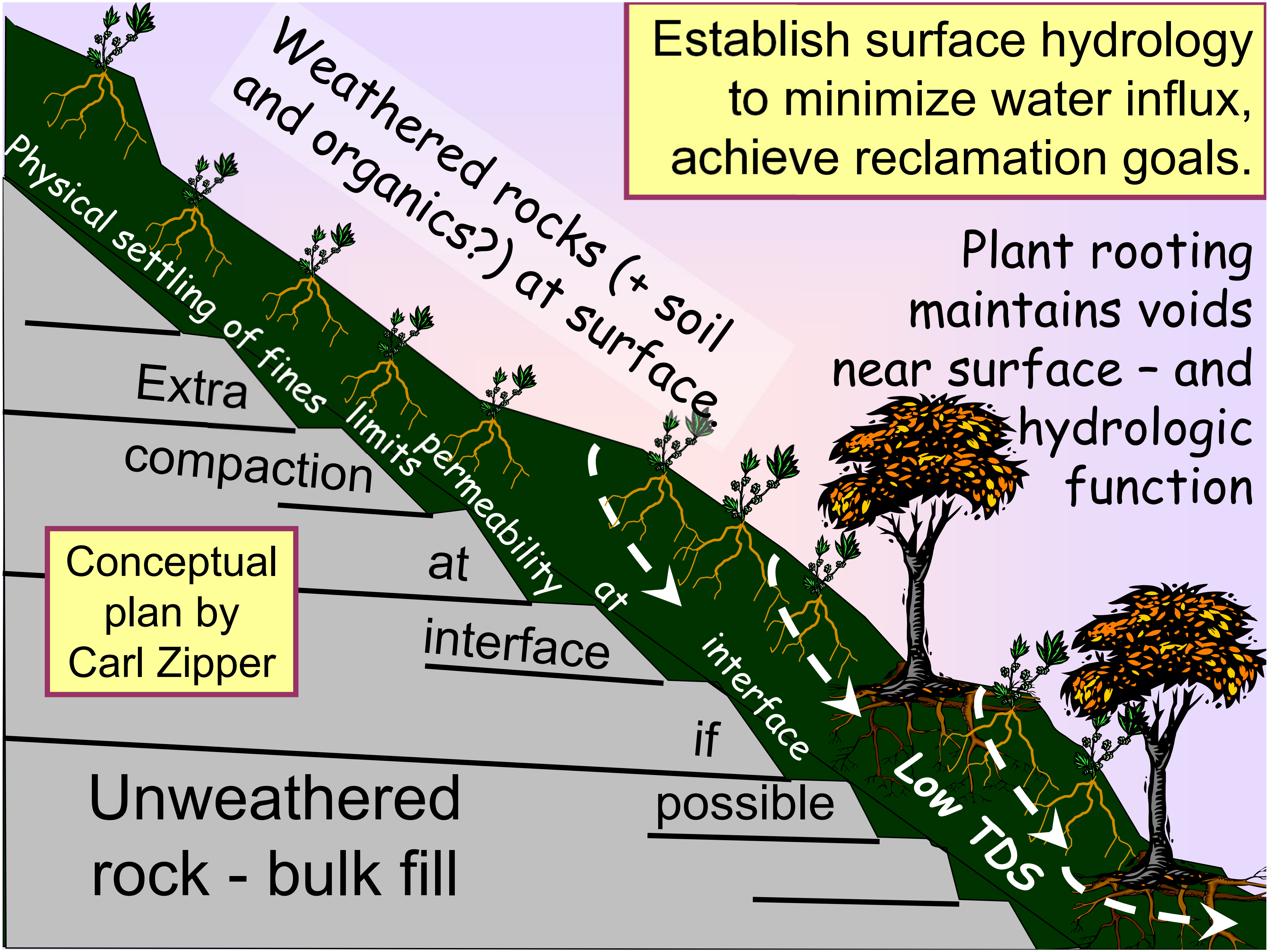
FIGURE 3. Example of Specific Conductance (SC) Data at a Valley Fill with (a) Disturbance Phases Delineated, and (b) a Quadratic Model Fit to Data (solid line), with Axis of Symmetry and the Method for Estimating the Time Required for SC to Return to 500 µS/cm Illustrated.

Field SC data for 137 valley fill discharge points in SW Virginia from Evans et al. 2014 (JAWRA).

Note (a) range of commonly observed values and (b) long term trend of decline for many locations over time.

How much time? 15 to 20 years in the field via the model, but longer for a number of locations. Why?

Establish surface hydrology
to minimize water influx,
achieve reclamation goals.



Weathered rocks (+ soil and organics?) at surface.

Plant rooting maintains voids near surface – and hydrologic function

Physical settling of fines limits permeability at interface

Extra compaction at interface if possible

Low TDS

Unweathered rock - bulk fill

Conceptual plan by Carl Zipper

Experimental Fill 1 Site

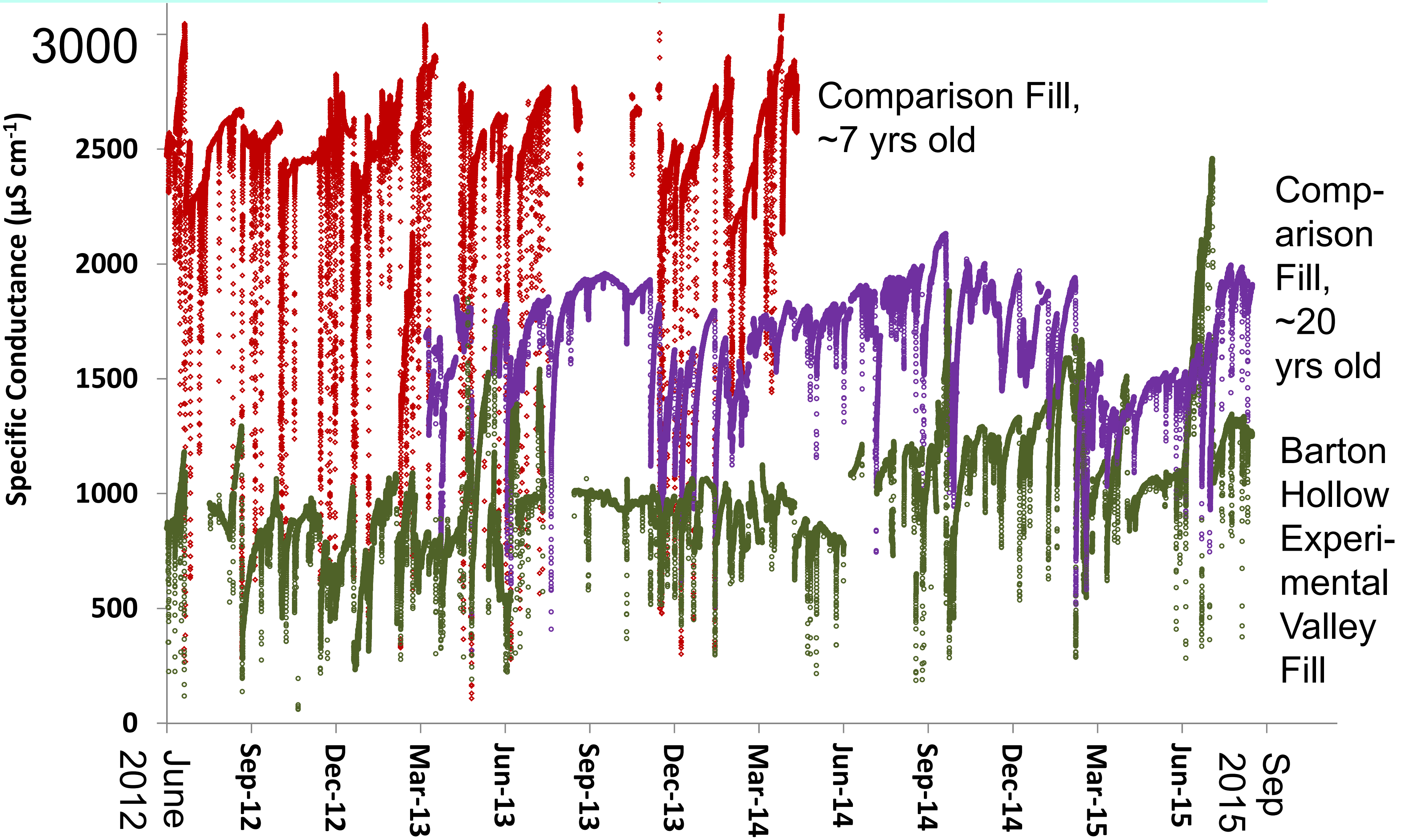

Experimental fill 1; Barton Hollow
11/14 (Teco; Cambrian; ClintwoodJOD)


Flume for water monitoring
(older conventional fill)


Conventional Fill (Younger)


Conventional Fill (older)

Specific Conductance at Barton Hollow Experimental Valley Fill and two nearby comparison fills (spoil type not controlled) over a 3-year monitoring period.



Conclusions

- A relatively simple combination of lab procedures (e.g. saturated paste EC/pH) and field indicators (rock type, color and hardness) can be used to clearly and quickly identify problematic materials.

- Assuming excessive amounts of net acid-forming materials are either excluded from valley fills or effectively isolated, the SC of discharge waters for the vast majority should decline to < 500 us cm^{-1} over time unless pre-existing acidic seeps or other confounding factors are present. However, it might take 15-20+ years?

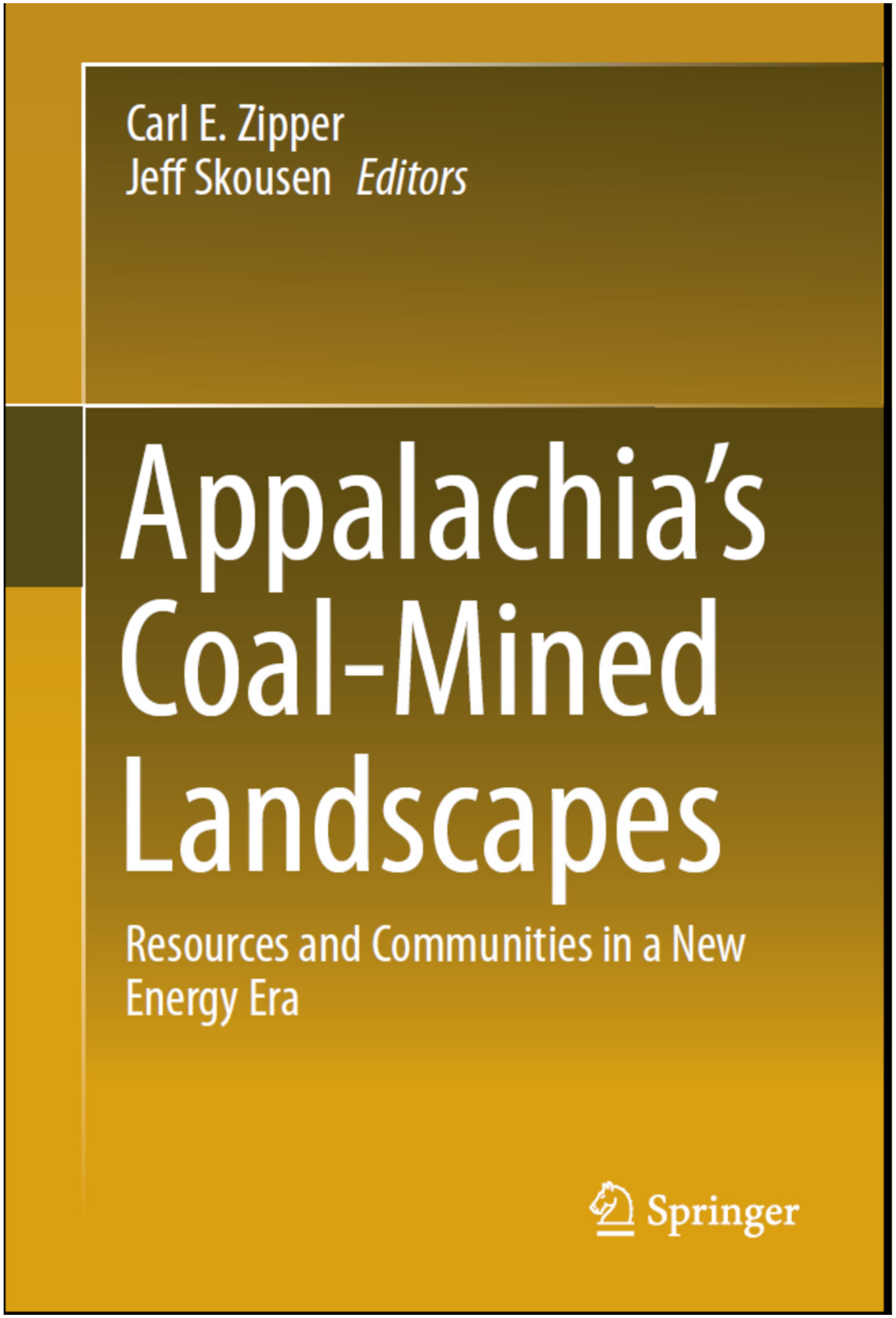
Conclusions

- In general, brown oxidized strata are lower in TDS risk than non-weathered gray materials. Risk is also related to rock texture; sandstones tend to generate lower TDS than mudrocks or shales. Avoid black shales at all costs; regardless of S content.

- New mine-spoil fill construction procedures that isolate these materials from contact with surface runoff or percolating groundwater are under development, being tested, and appear promising. Final surface soil and water conveyances must be constructed from the lowest TDS producing materials available which will generally be the surface pre-weathered soils and rock saprolites.

Conclusions

- The chemical nature of long-term bicarbonate-dominated discharge waters will be fundamentally different, however, from the sulfate-dominated discharge waters that predominate in mining-influenced Appalachian landscapes today. Net biotic effects of this shift in ionic composition are currently unknown, but presumably would be more favorable for re-establishment of sensitive macroinvertebrate taxa.



Carl E. Zipper
Jeff Skousen *Editors*

Appalachia's Coal-Mined Landscapes

Resources and Communities in a New Energy Era

Springer

Much of what I covered today (and a lot more!) is now available in this book from Springer.

13 chapters including considerable socio-economic interactions, etc.

Focus is on "how we got here and what we can do with it".

https://doi.org/10.1007/978-3-030-57780-3

TDS Research Sponsors

- **USDI -OSM**
- **VT Powell River Project**
- **ARIES – Appalachian Regional Initiative for Env. Science (Regional Coal Industry via VCCER)**
- **Deep thanks to all of our colleagues (*many not cited today*) who worked on these varied projects over time in many roles.**