Redox Chemistry and The Formation of Selected Field Indicators

Mike Vepraskas

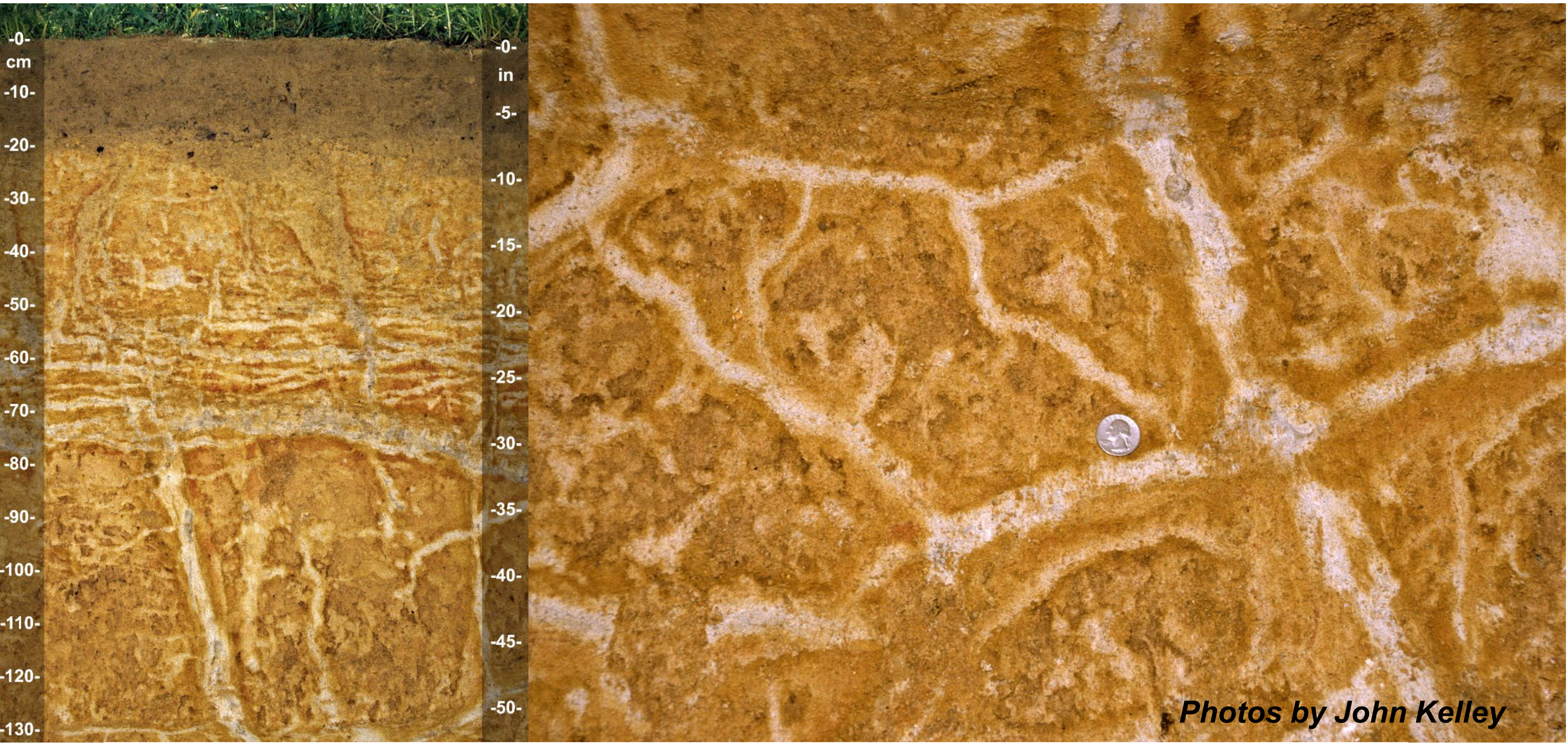
NC STATE UNIVERSITY

Photos by John Kelley

Overview

1. Discuss basic oxidation-reduction principles
2. Review how reactions form field indicators
3. Discuss F3, F6, S5, S6, and F8

What process formed this pattern?



Answer: redox chemical reactions

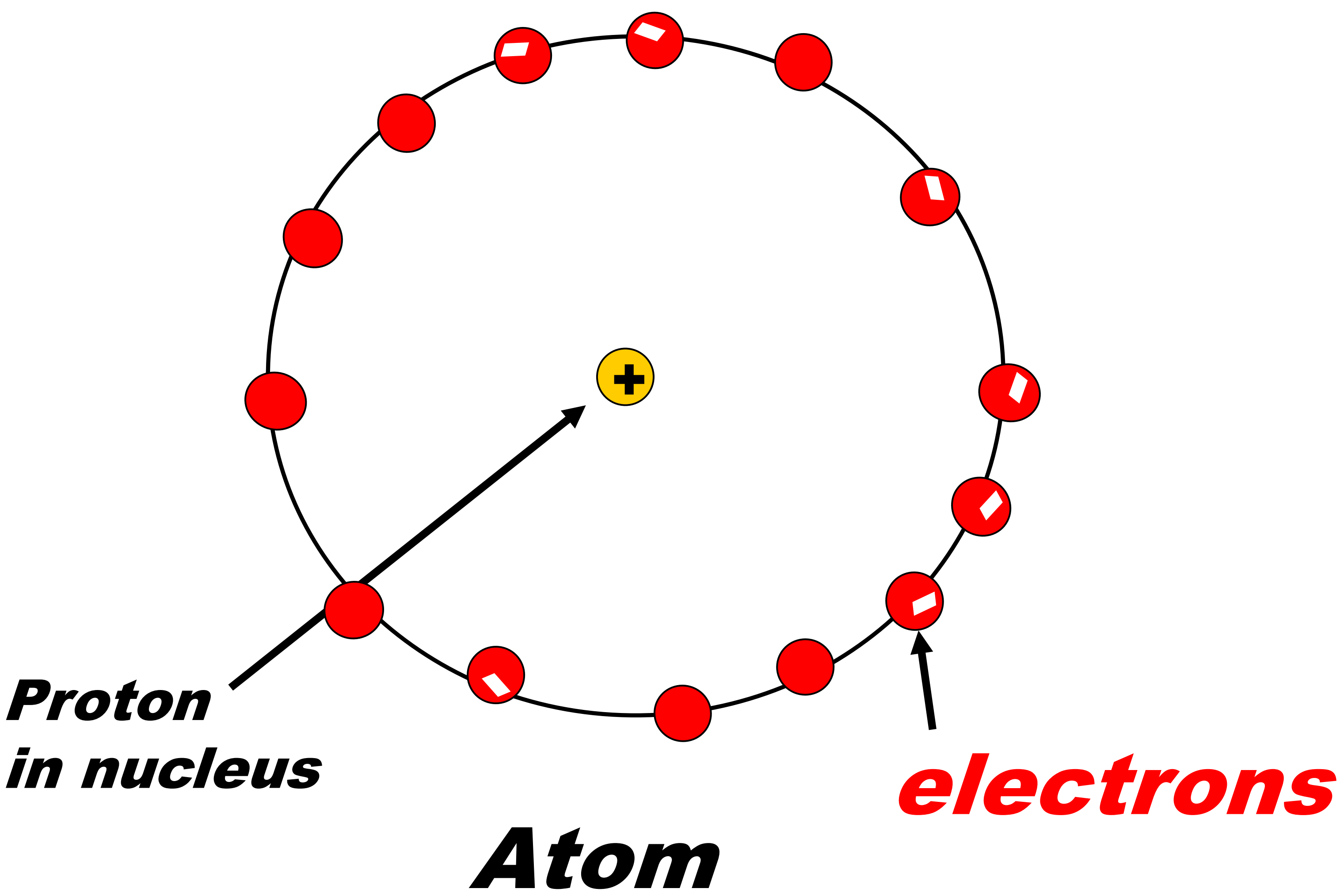
Chemistry of Saturated Soils

- ***We will focus on Oxidation-Reduction (Redox) reactions***
- ***These reactions are the most important reactions in saturated soils***

Redox Reactions influence:

- ***Soil Colors***
- ***Organic matter decomposition rates***
- ***Amounts of O_2, NO^-_3, and $SO^=_4$ in soil water***

Redox Reactions transfer electrons and protons among atoms



Oxidation Reduction Basics

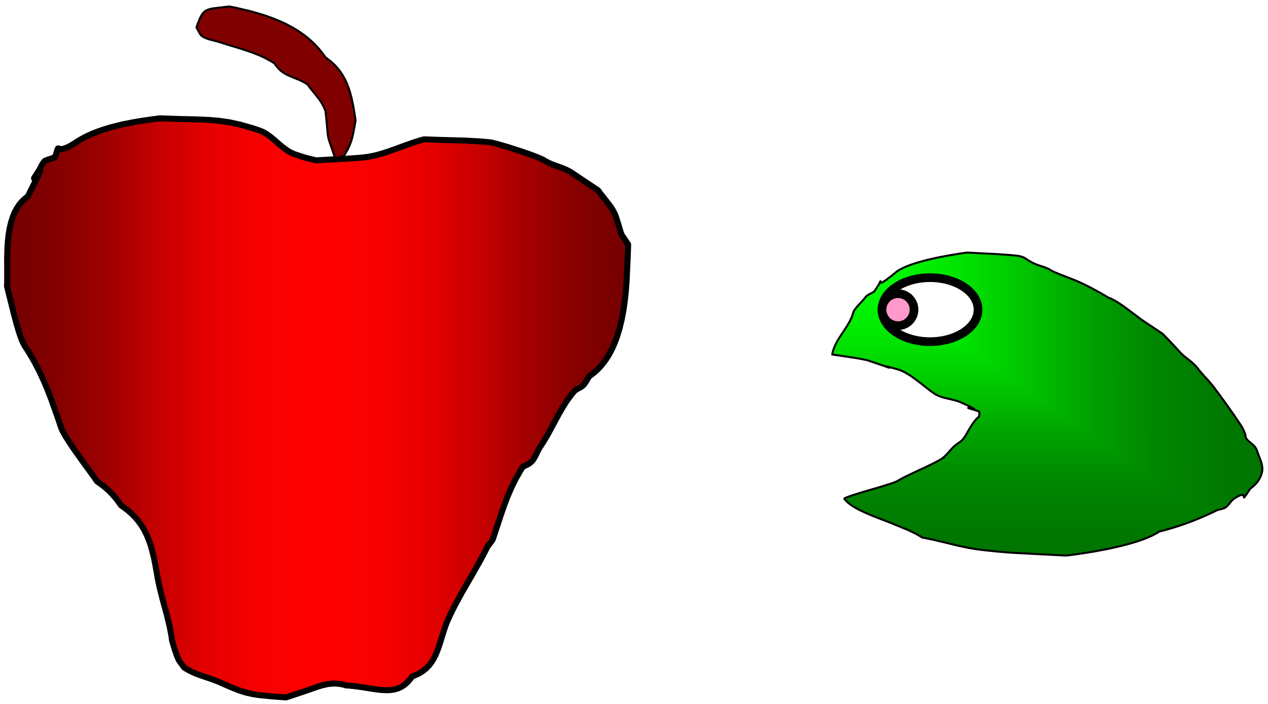
- **Electrons are taken out of one substance and given to another**
- **Most electrons (e^-) come from organic matter as it rots or decomposes**

Remember!

If organic matter is not present, then:

1. *The special redox reactions that make soils anaerobic won't occur, and*
2. *Saturated soils won't turn gray in color*

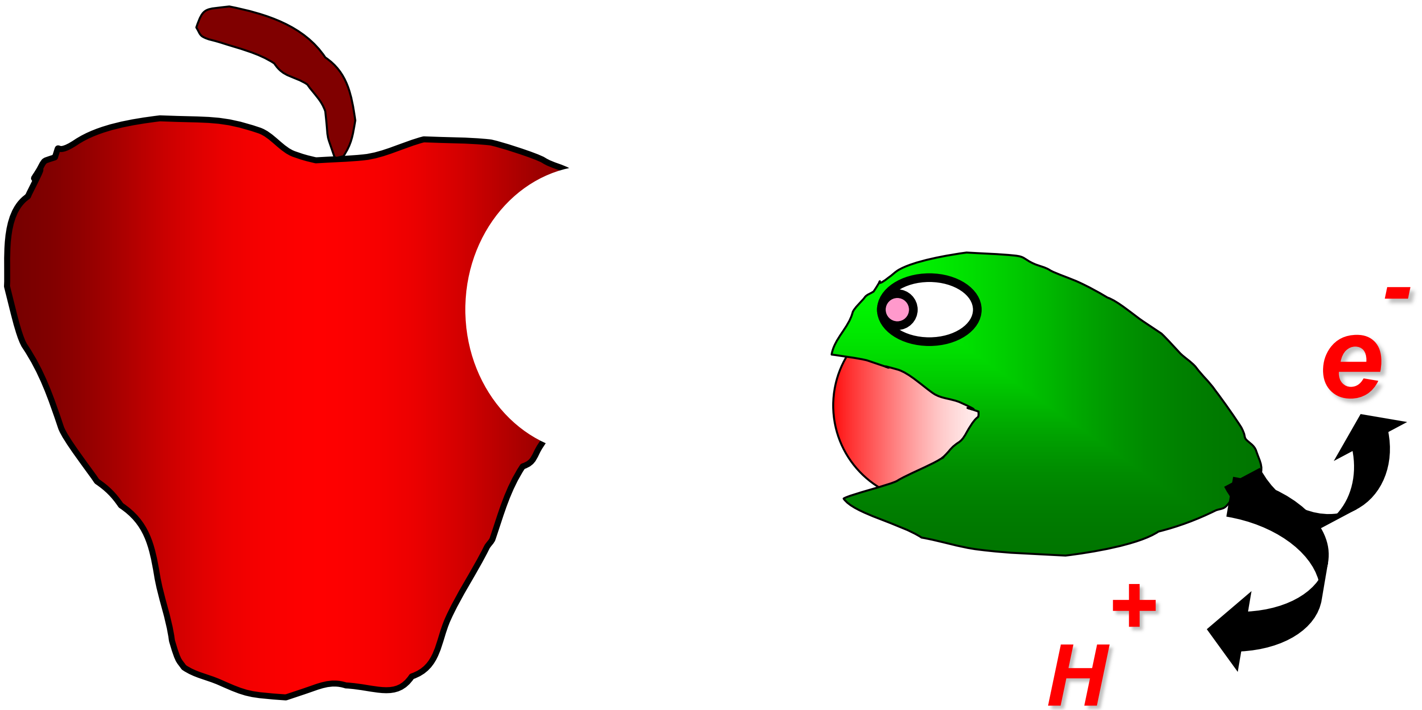
Oxidation: produces electrons when two things are present



Organic Matter

Bacterium

e^- produced when organic matter is eaten



Organic Matter

Bacterium

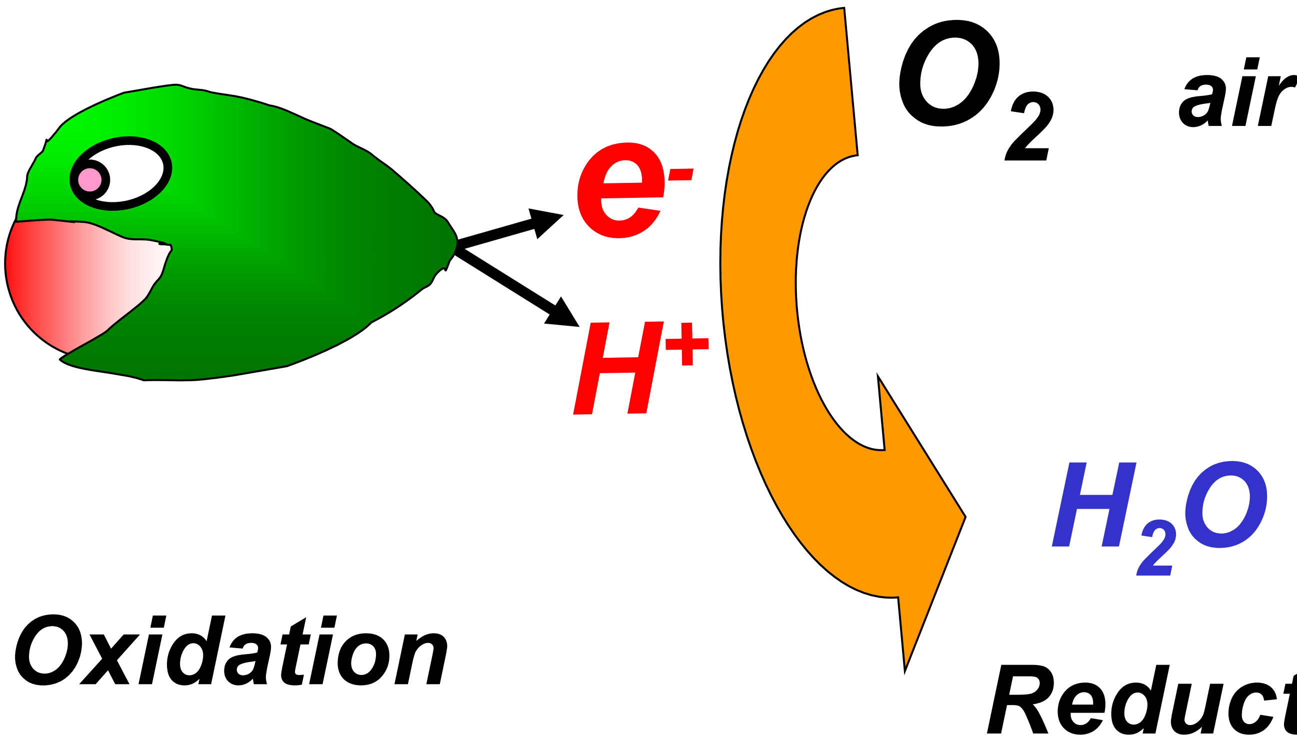
Reduction-reactions with e^- and H^+

$$O_2 + 4e^- + 4H^+ \longrightarrow 2H_2O$$

air

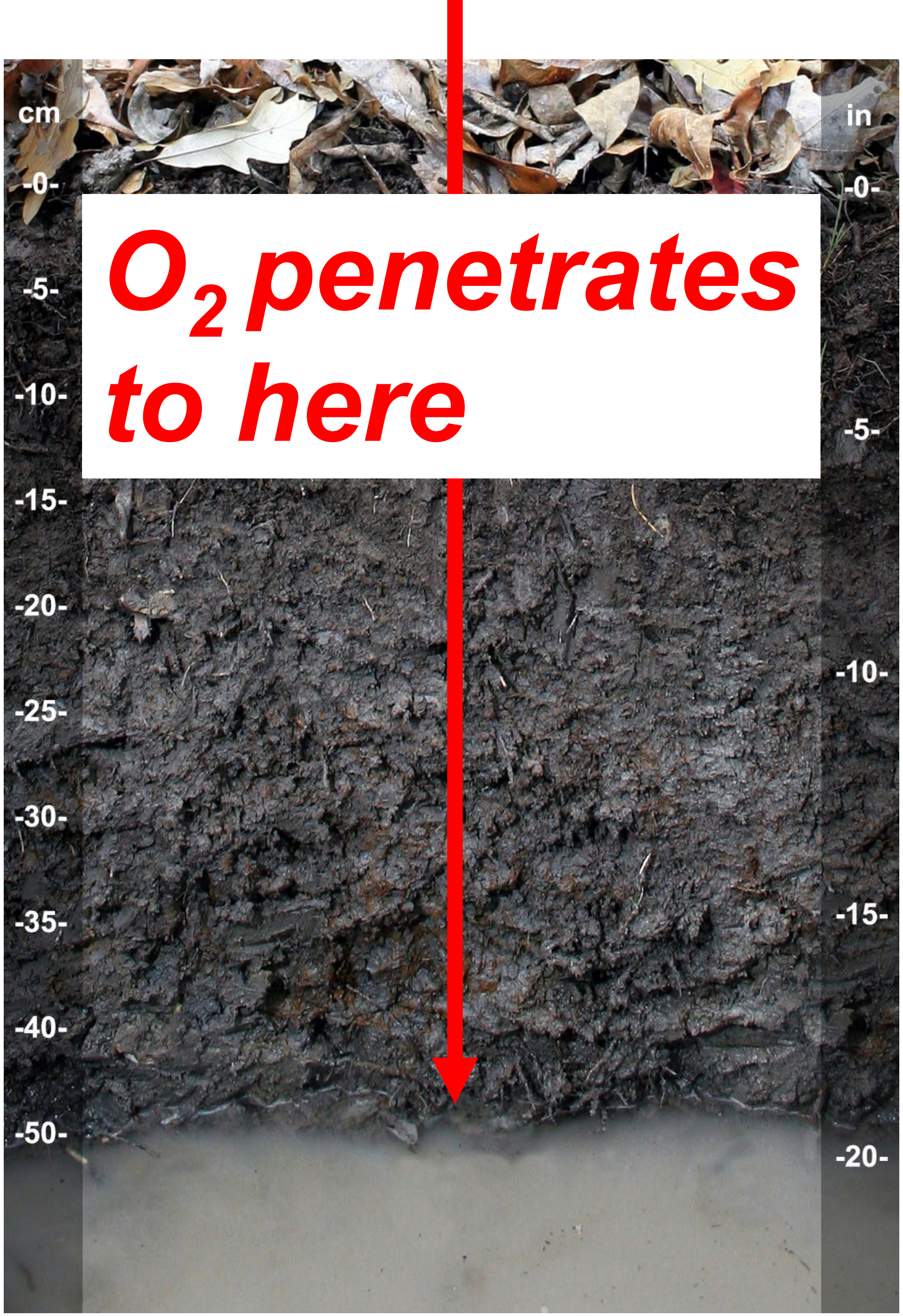
water

Oxidation and Reduction occur together



When air is present in soil, then

All e^- produced by organic matter decomposition are grabbed by O_2 to make water



Air can't enter saturated soil

Photo by John Kelley

What happens in waterlogged soils?

In waterlogged soils,

O_2 (air) does not enter soil because soil pores are filled with water

But……

Organic matter continues to decompose in waterlogged soils, but e^- produced are grabbed by:

NO_3^-, MnO_2, Fe_2O_3, $SO_4^=$, and CO_2

These are used instead of O_2

Remember

The electron acceptors are reduced in a specific order:

1. O_2 –*Strongly holds e*$^-$
2. NO_3^-
3. MnO_2
4. Fe_2O_3
5. $SO_4^=$
6. CO_2 –*Weakly holds e*$^-$

To Help You Remember the Order of Reduction

<u>O</u>h <u>N</u>o, <u>M</u>y <u>F</u>eet

<u>S</u>mell <u>C</u>rappy

Courtesy of a form student

Iron Reduction

$$Fe_2O_3 + 2e^- + 6H^+ \longrightarrow$$

Iron oxide
(Red solid)

$$2Fe^{2+} + 3H_2O$$

Reduced iron
(Colorless in solution)

Sulfate Reduction

$$SO_4^{2-} + 8e^- + 10H^+ \longrightarrow$$

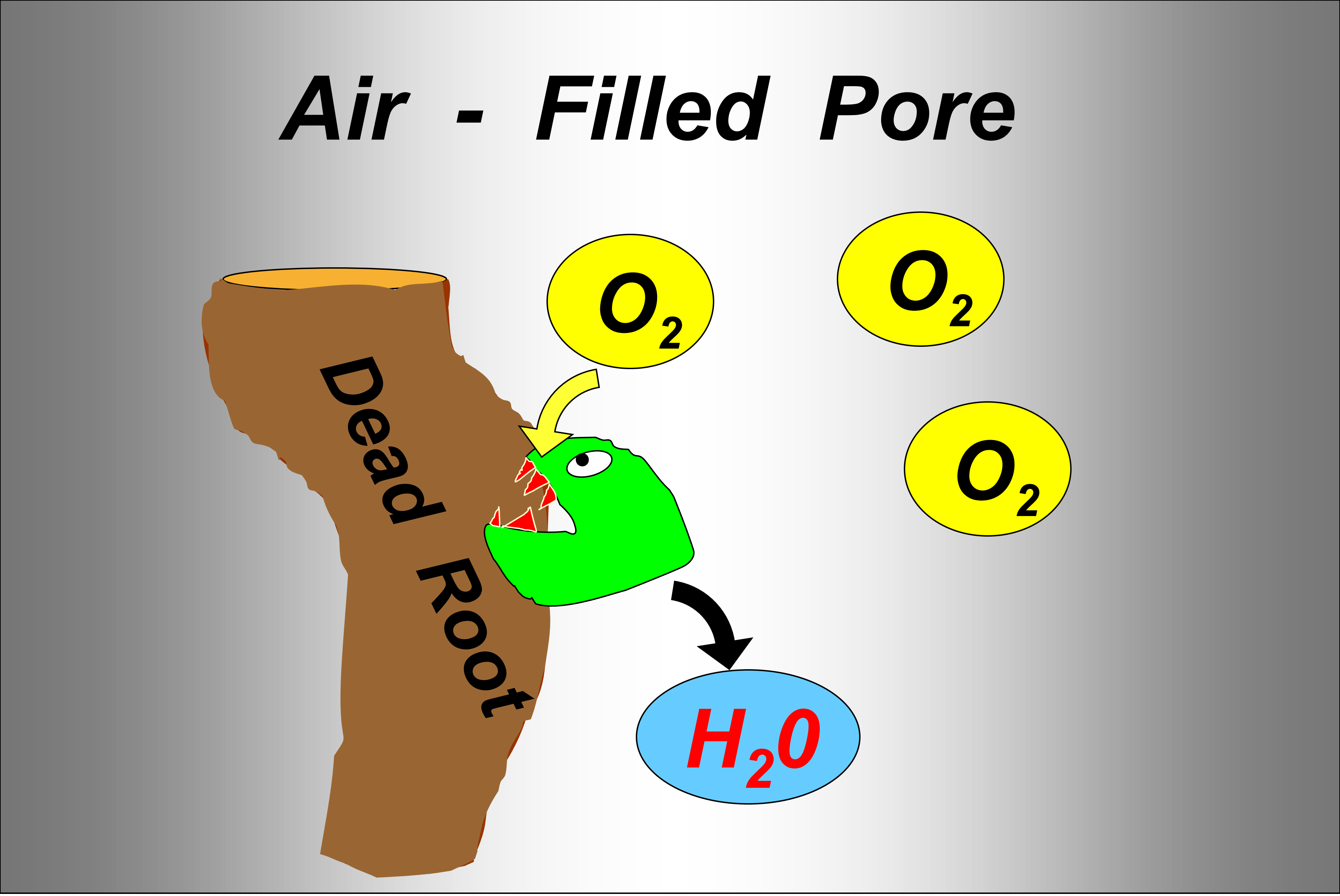
(in solution)

$$H_2S + 4H_2O$$

(smelly gas)

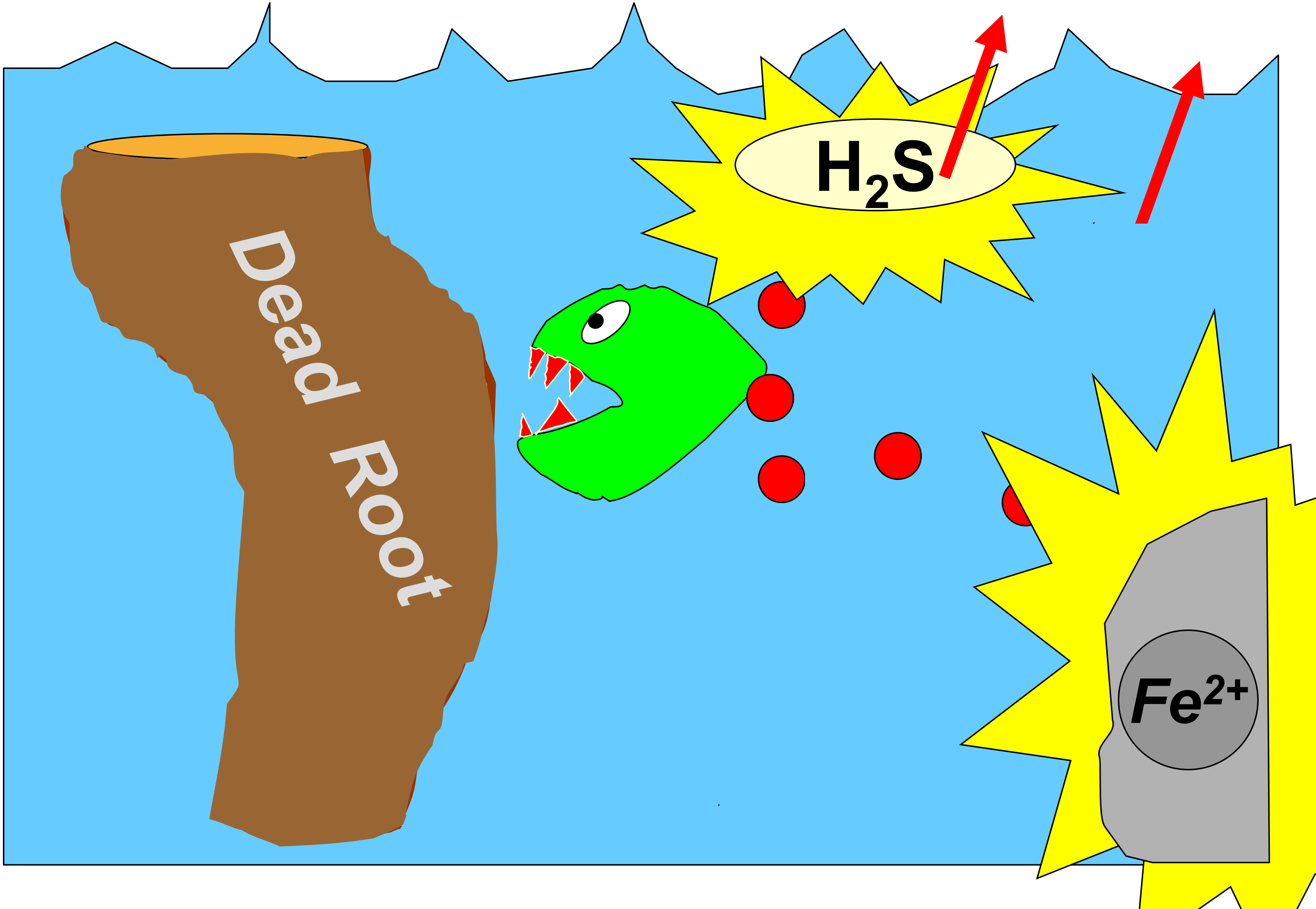
H_2S smells like eggs


Fe Sulfides
(FeS)
May also
Be Formed



O_2 only Electron Acceptor

Water - Filled Pore



What is needed for soil to become anaerobic?

1. ***Organic matter must be present (source of e-)***
2. ***Air must not enter soil***

    (soil must be saturated)

Conditions needed to create anaerobic conditions.

3. **Bacteria** *must decompose organic matter (Temps.> 42º F)*

4. *Dissolved O_2 in water must be removed (soil is **anaerobic**).*

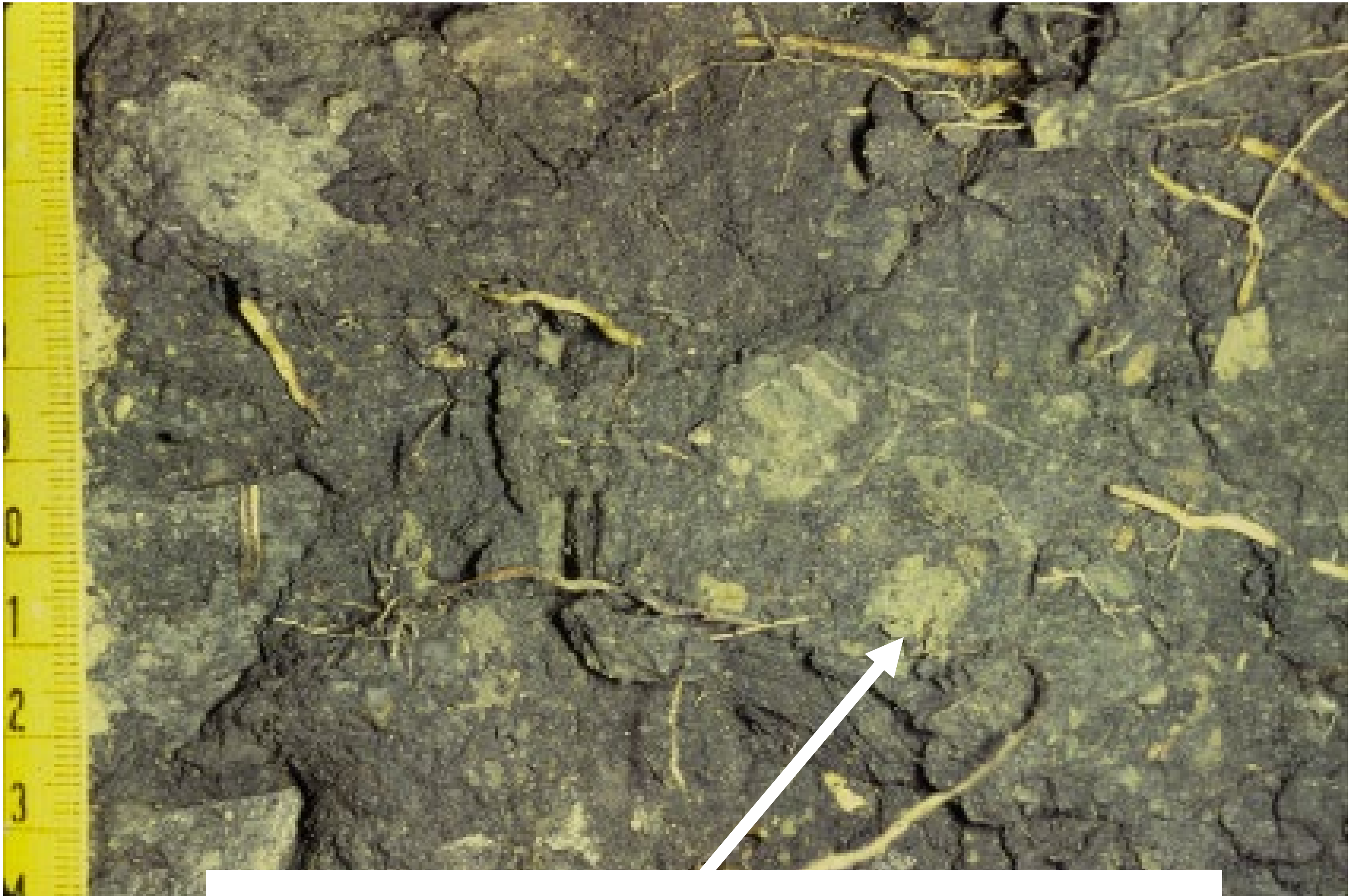
O_2 will be removed if conditions 1-3 met and water is stagnant.

Good Kinds of Organic Matter for Reduction

1. Dead roots (still squishy)
2. Plant debris (leaves)
3. Dissolved organic matter

Reduction occurs where bacteria eat organic matter

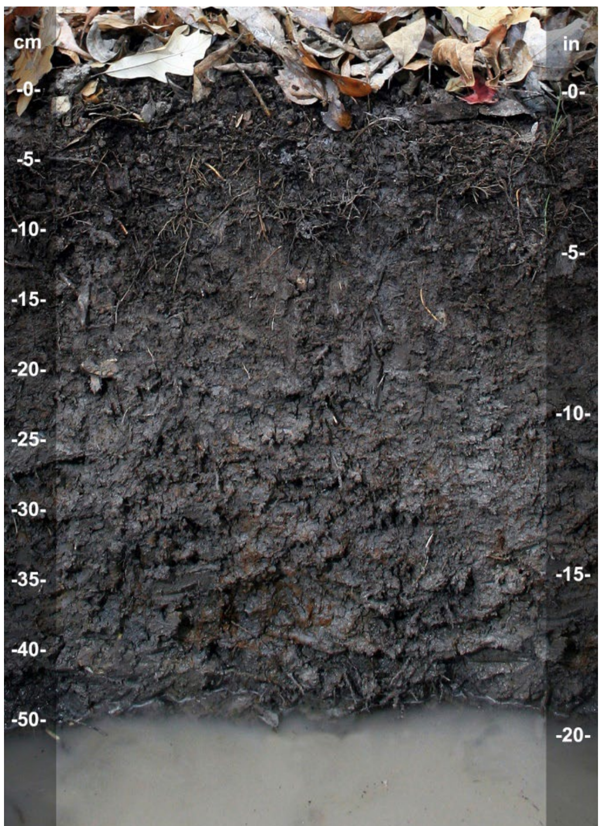
- *This can be in spots (microsites) or around roots*
- *Entire horizons will not be reduced at one time—unless saturated for long periods*



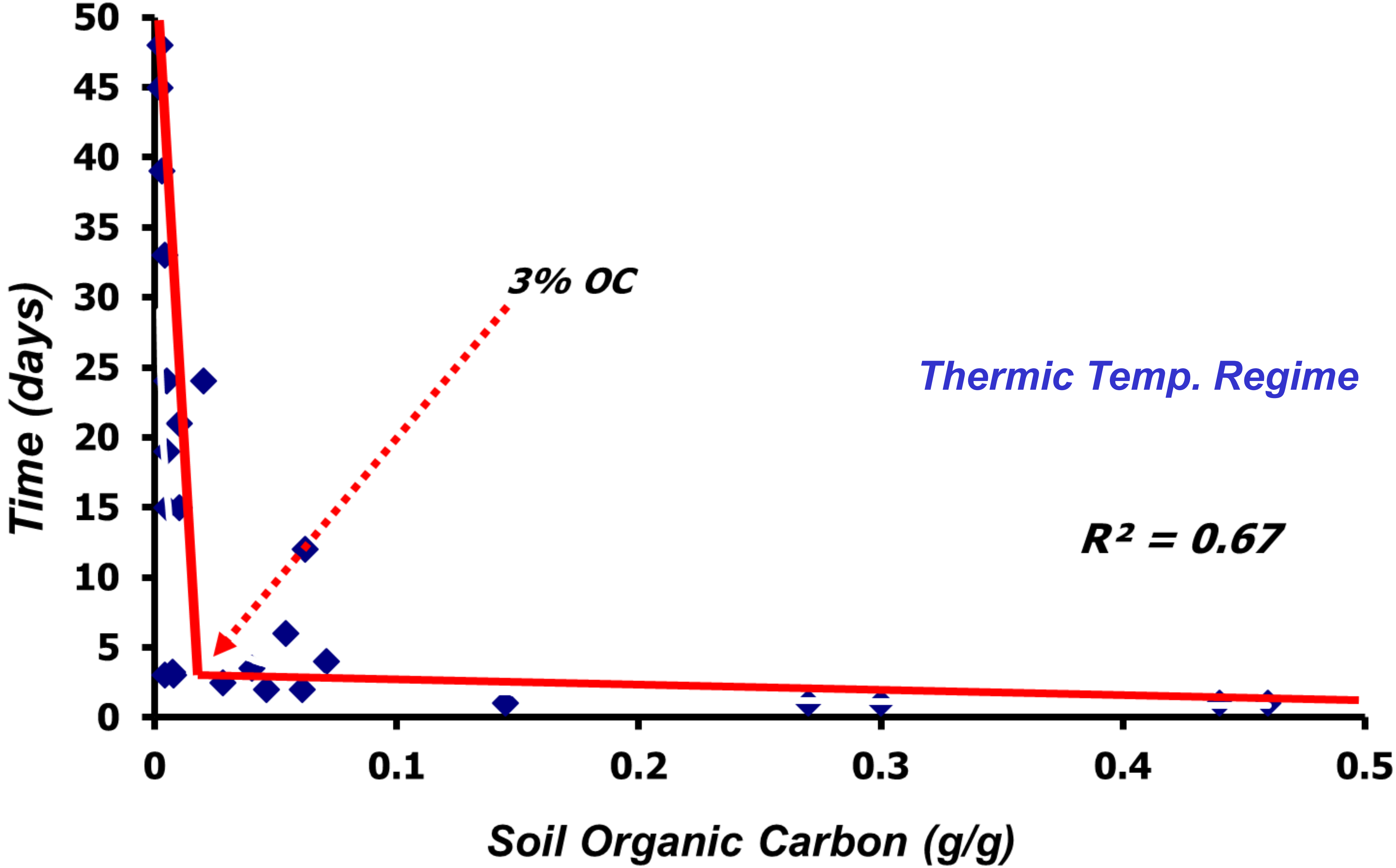
Fe reduction occurred here

Fe reduction occurred around roots

How long does it take a soil to become anaerobic once it saturates?



Time Required to Develop Anaerobic Conditions Following Saturation in a Horizon



Is this water Fe-reduced or anaerobic?

*Reduction occurs where water moves through soil **slowly***

- ***Reduction is slowed when water is flowing***
- ***Reduction occurs quickest in stagnant water on flat ground***

Lets put it all together and watch features form

Photo by John Kelley

Examining Root Decomposition under Saturated Conditions

- ***Rhizotrons***
  (ant farms) constructed to watch changes around roots

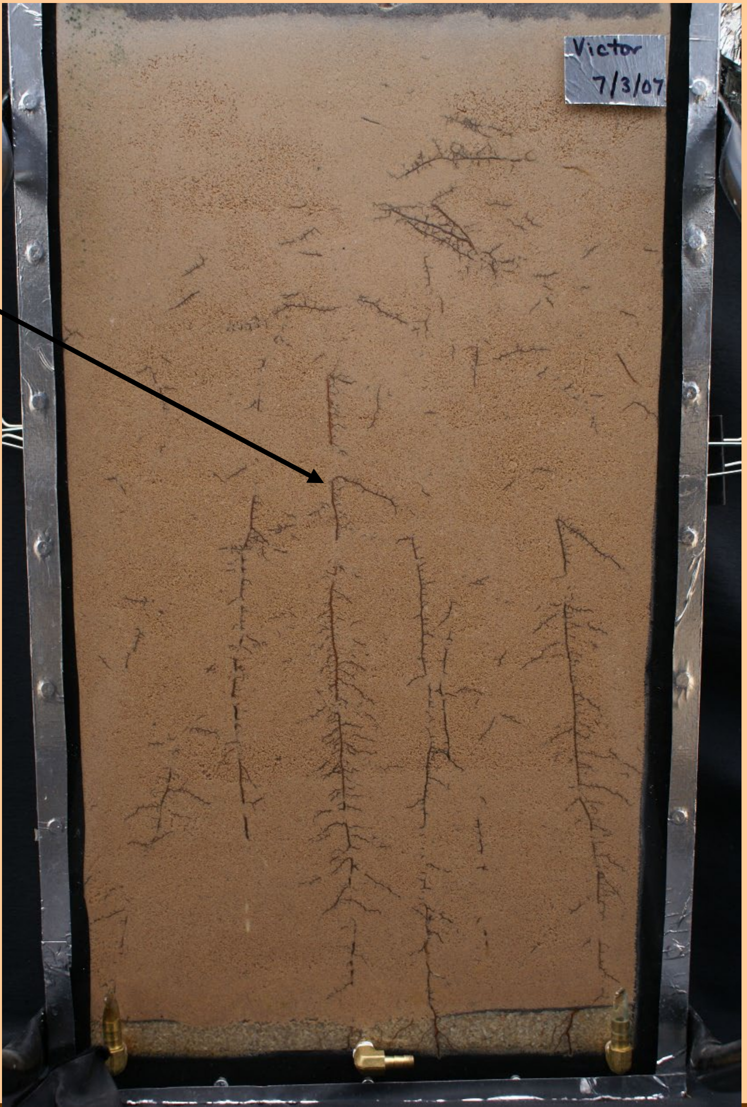
24″ × 14″ @ 30° angle

Procedure

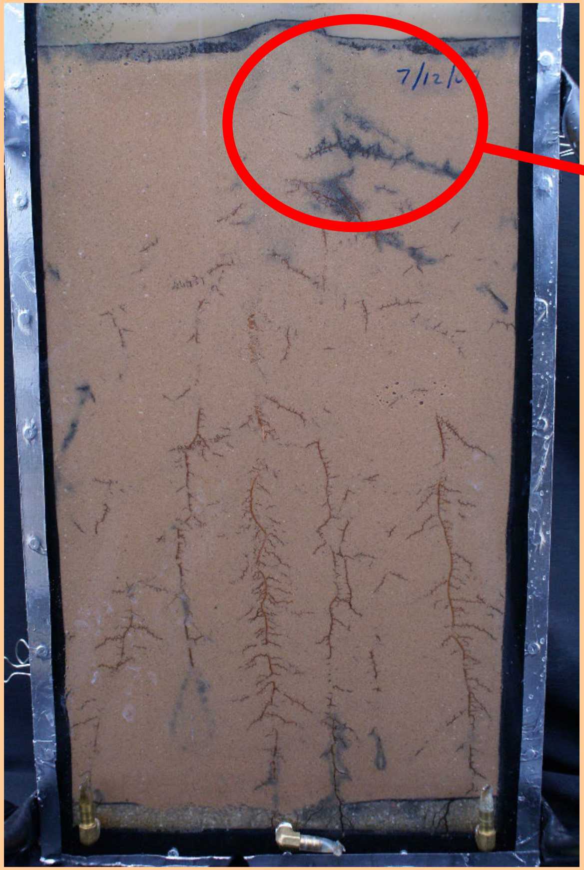
- ***Pine tree roots grown in moist sand until roots reached bottom of rhizotron***
- ***Soil saturated and ponded***
- ***Ponding maintained for 126 days***
- ***Morphology described every 2 weeks***
- ***Root examined every 2 weeks***

Before Ponding

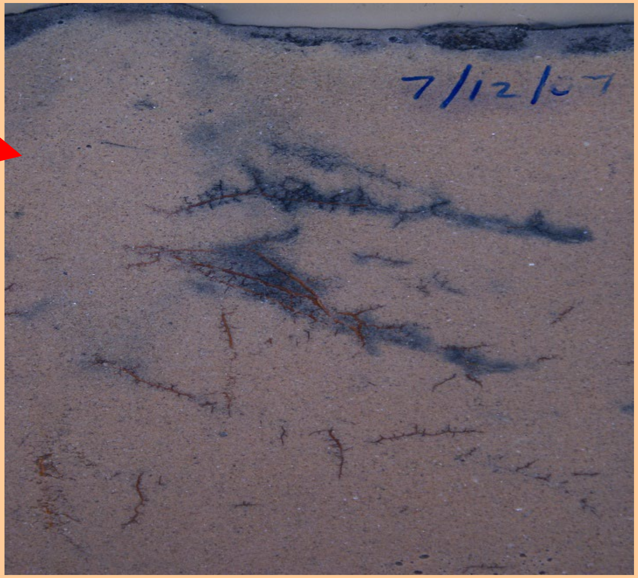
Main tap root



10 Days After Ponding:
Roots begin to die



8% root death

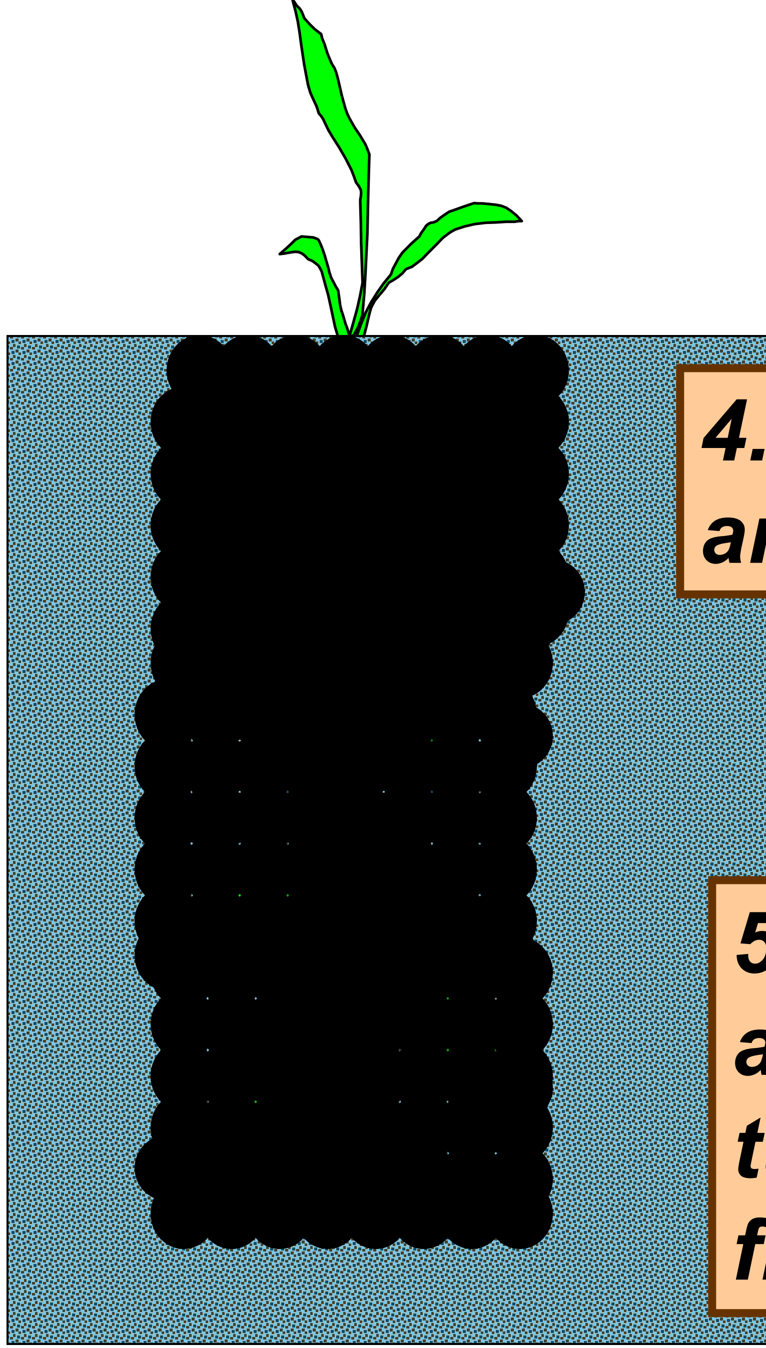


Root death noticed in smaller roots

1. Soil saturates

2. Root dies

3. Bacteria eat root

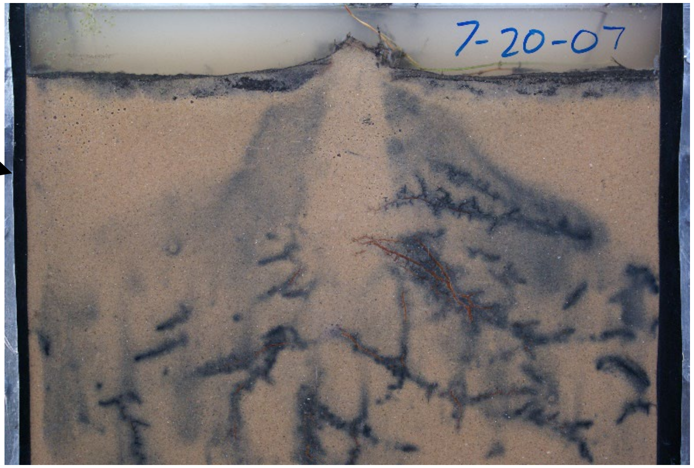


4. Fe^{2+} and S^{2-}

5. Area around root turns black from FeS

Black Color shows where bacteria are active

23% root death

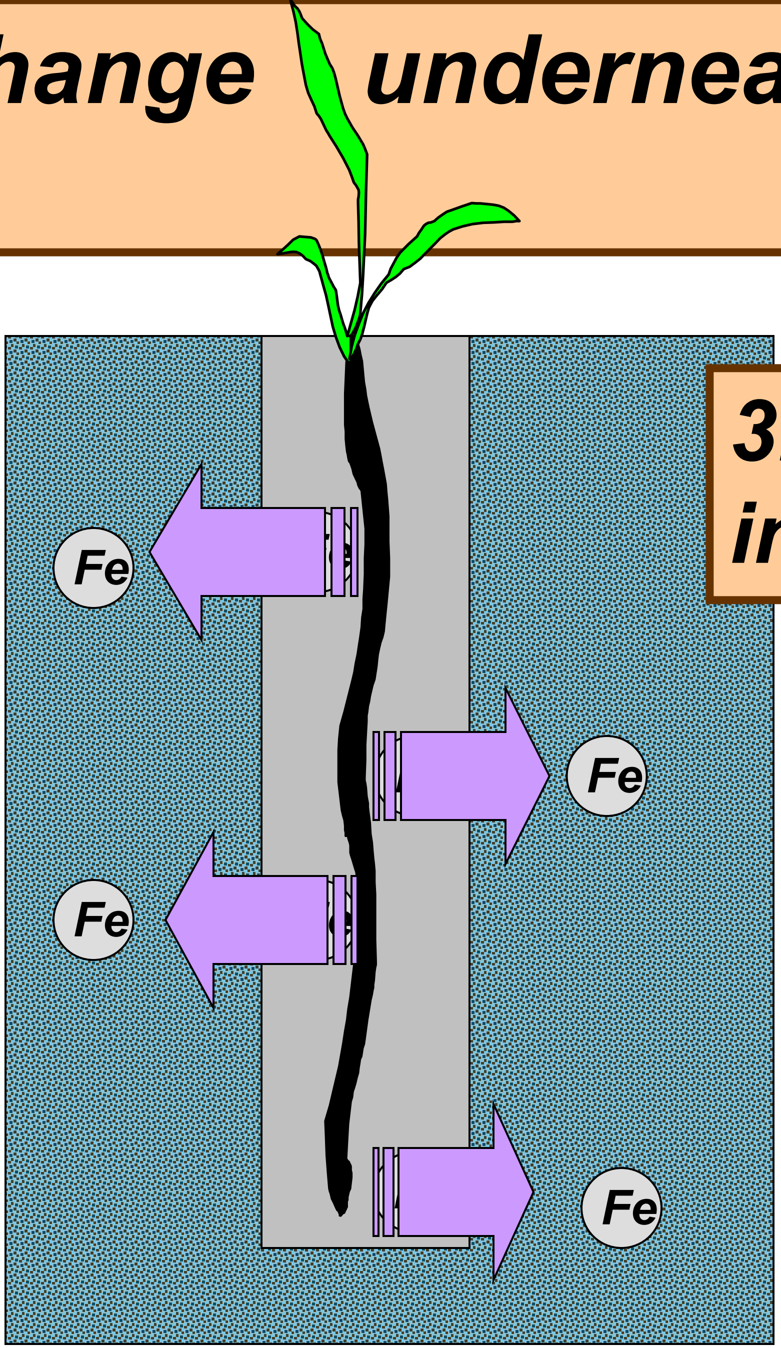


18 days after ponding

Soil colors change underneath the Fe Sulfides

1. Fe is reduced

2. Soil around root turns gray



3. Fe moves into matrix

4. Redox depletion forms around root

If saturation ended after 18 days then this is what would be seen

80 Days of Ponding

52% root death

Live root, getting oxygen into rhizosphere

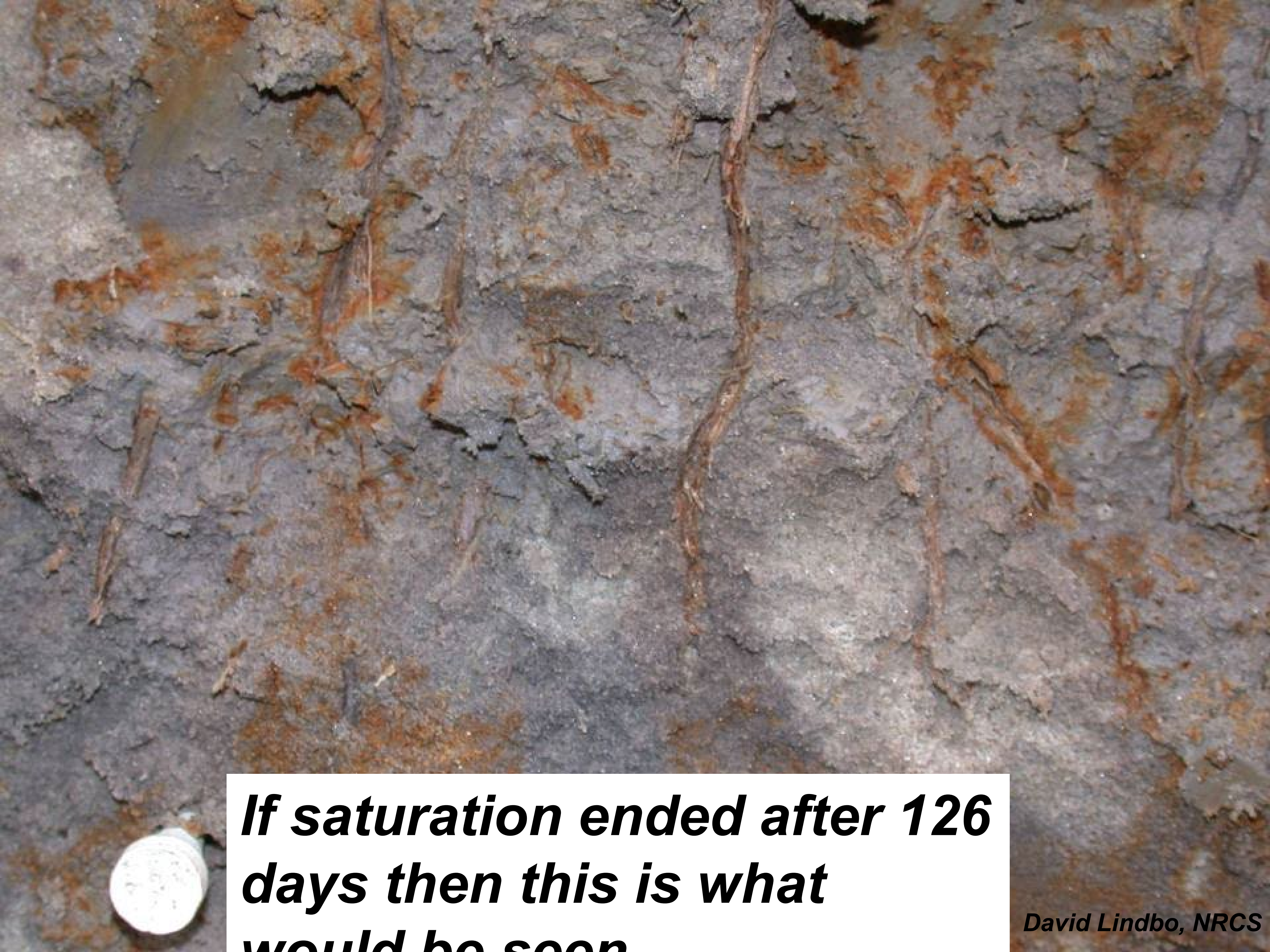
Reduction occurring in matrix away from root channels

126 Days After Ponding

A lot of FeS present after 126 days of saturation.

Much reduction occurring in matrix away from root channels

63% root death

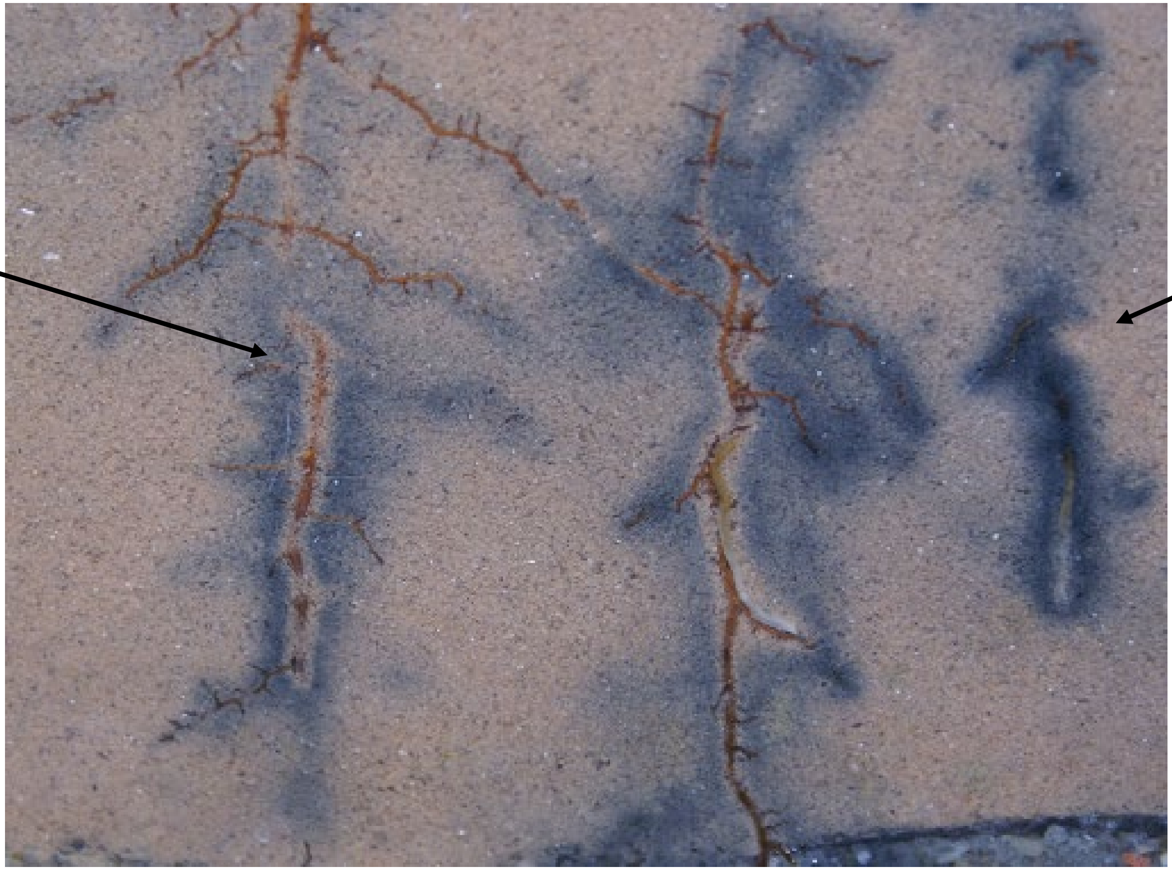


If saturation ended after 126 days then this is what would be seen

David Lindbo, NRCS

Areas Around Live Roots Lack FeS where aerobic conditions occur

FeS not present next to live root



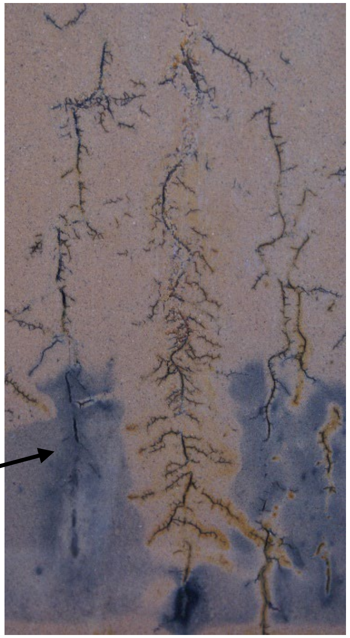
FeS present at dead root

Rhizotrons Drained

Air moves into soil along root channels

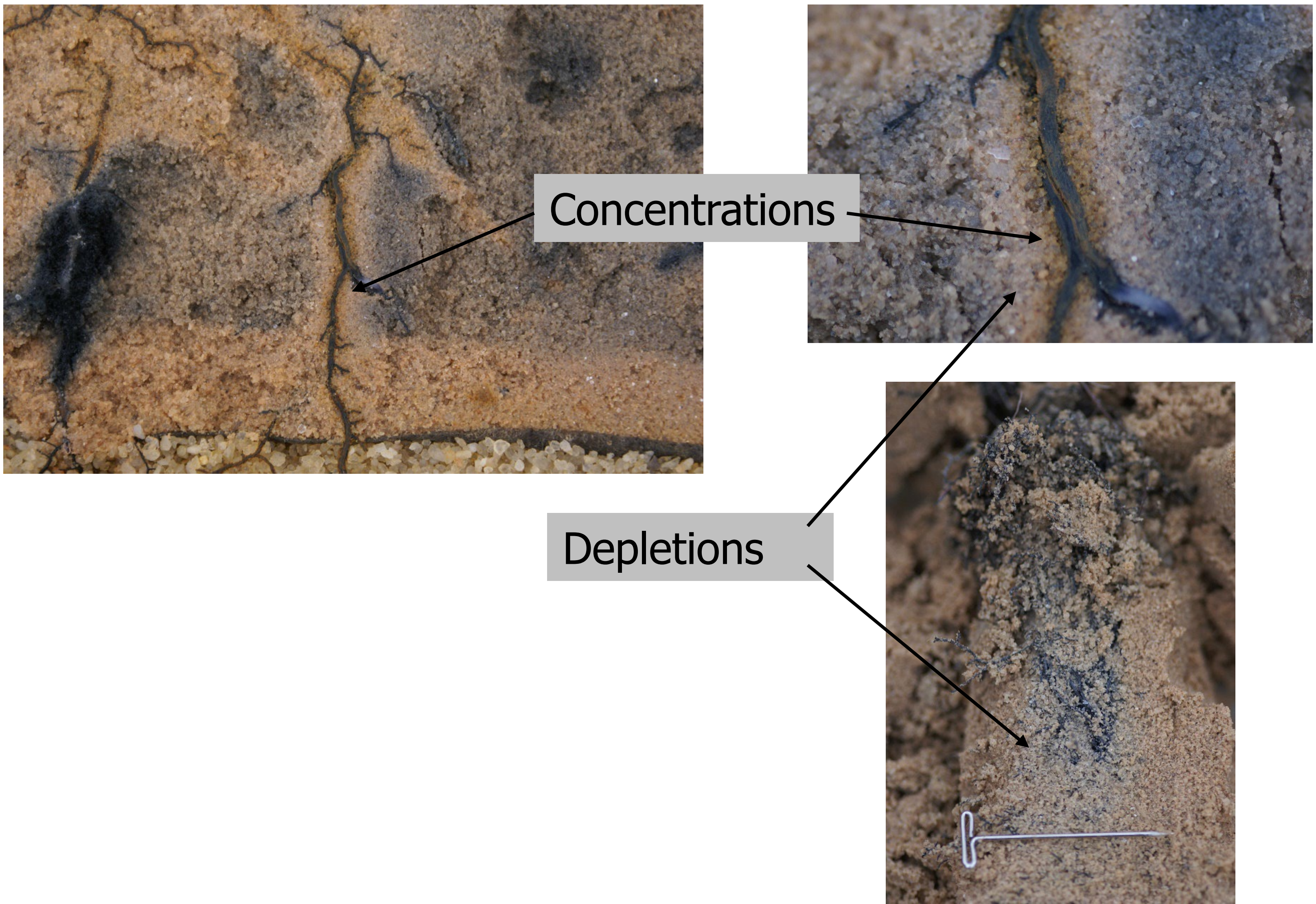
FeS is quickly oxidized to $Fe(OH)_3$ and H_2SO_4

67 Days After Aeration



Fe oxidized Around channels

Redox Concentrations formed where air entered soil



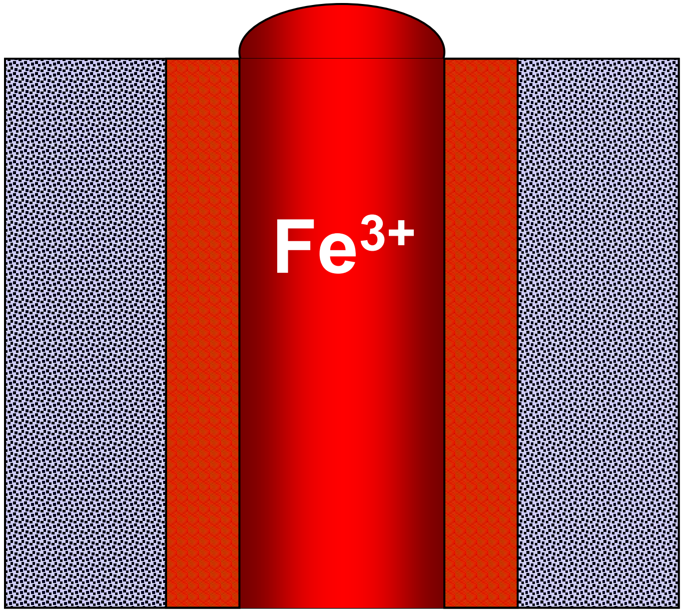
Redox Concentration in Rhizotron

Redox concentrations

Form around root channels that contain air

Pore Linings

Channel



The root channel becomes encased with “hardened” Fe^{3+}

How long does it take to form redoximorphic features?

- ***Reduced matrix- 7 days***
- ***Redox concentrations-***
  30 days
- ***Redox depletions- 8 days***

"These times are for "perfect conditions"

Field Indicator Formation: F3, S5, S6, F6, and F8

F3: Depleted Matrix

Photos by John Kelley

Depleted Matrix (F3)

A layer at least 15 cm (6 in.) thick with a depleted matrix which has 60% or more chroma 2 or less starting within 10 in. of the surface.

- *Matrix values must be 4 or more.*
- *Redox. concentrations may or may not be required—see glossary*

S5: Sandy redox

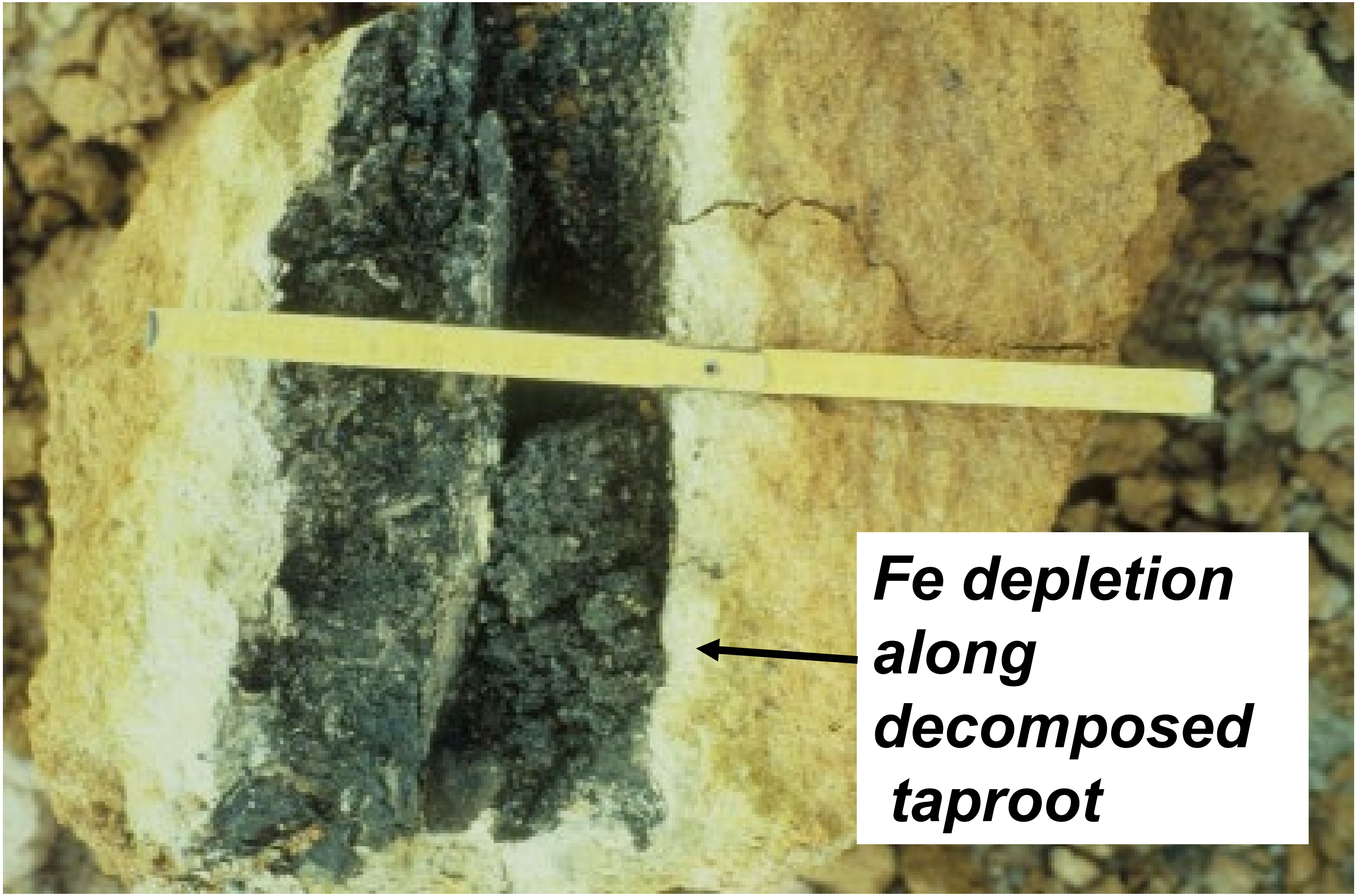
Most commonly used sandy soil indicator along hydric soil boundaries.

Photos by John Kelley

S5. Sandy redox

A layer starting at a depth ≤ 15 cm (6 in.) from the soil surface that is at least 10 cm (4 in.) thick and has a matrix with 60% or more chroma of 2 or less and 2% or more distinct or prominent redox concentrations occurring as soft masses and/or pore linings.

Value not specified, so matrix may be black or gray

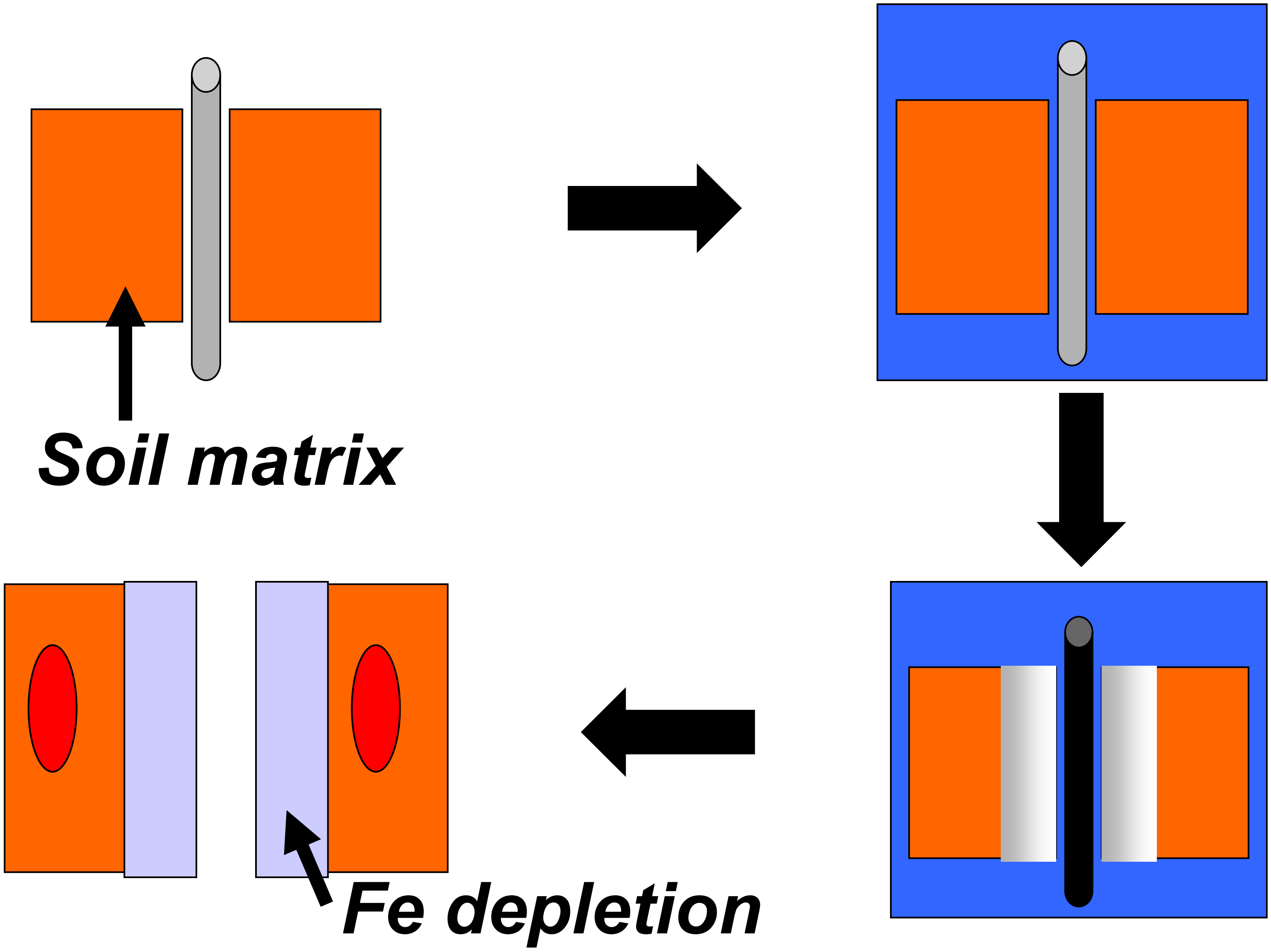

Fe depletion along decomposed taproot

Formation of Fe Depletions

Simplest model showing formation is one where

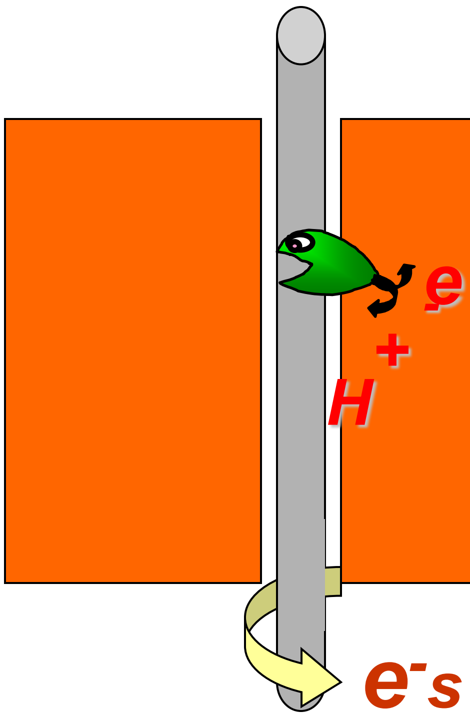
the depletions form around root channels.

Formation of Fe Depletions Along a Root Channel

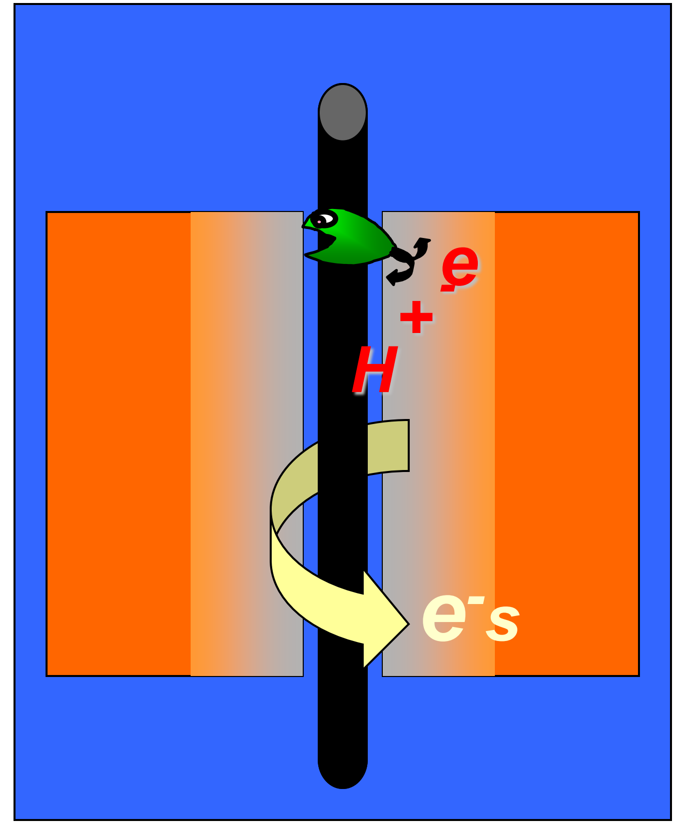


Fe depletions along channels

Dead root in channel



Channel fills with water

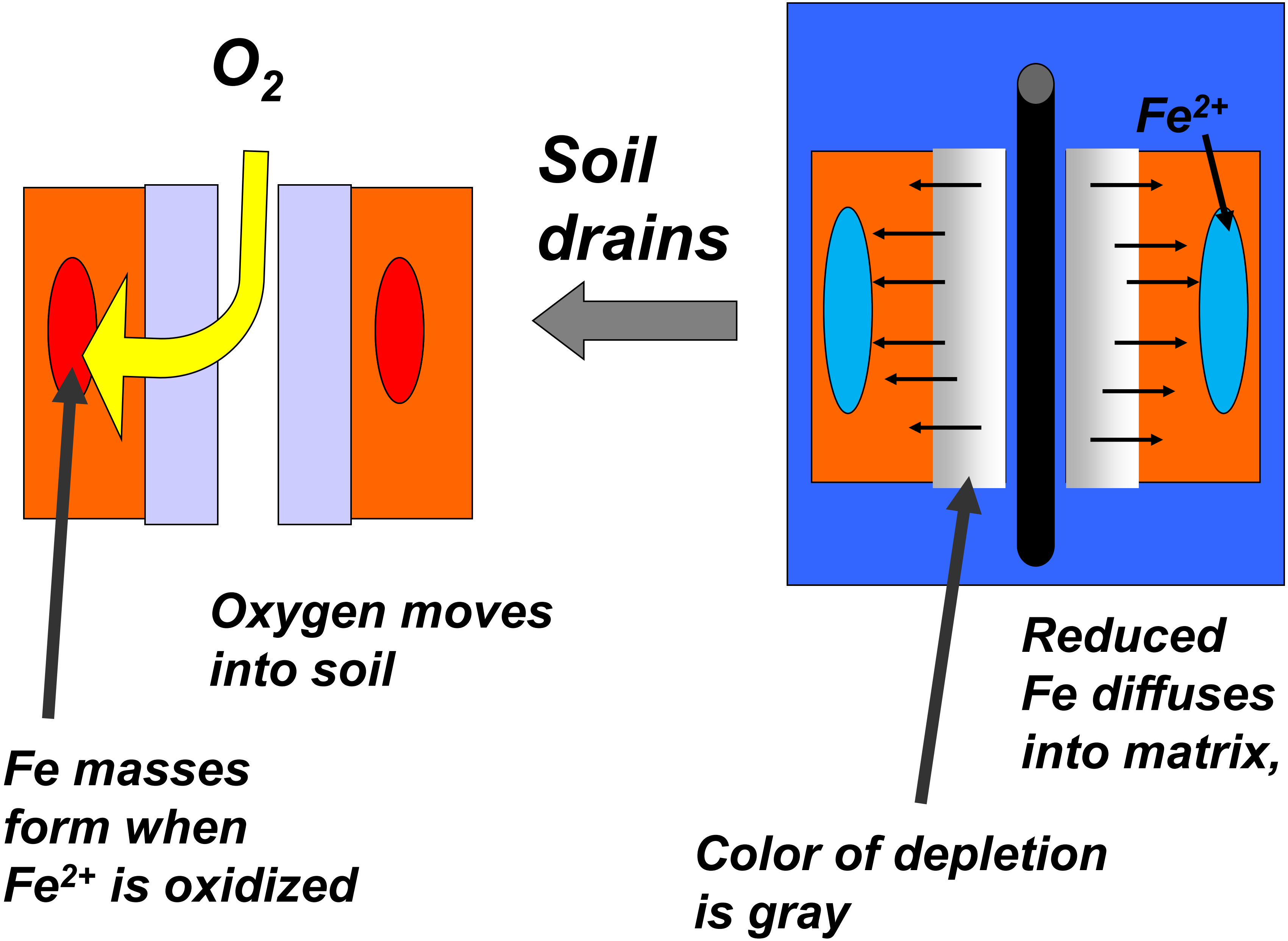


Soil matrix has brown color due to oxidized Fe

Bacteria eating root releasing e^-s to reduce O_2 to water

Bacteria eating root, but e^-s reduce Fe along channel

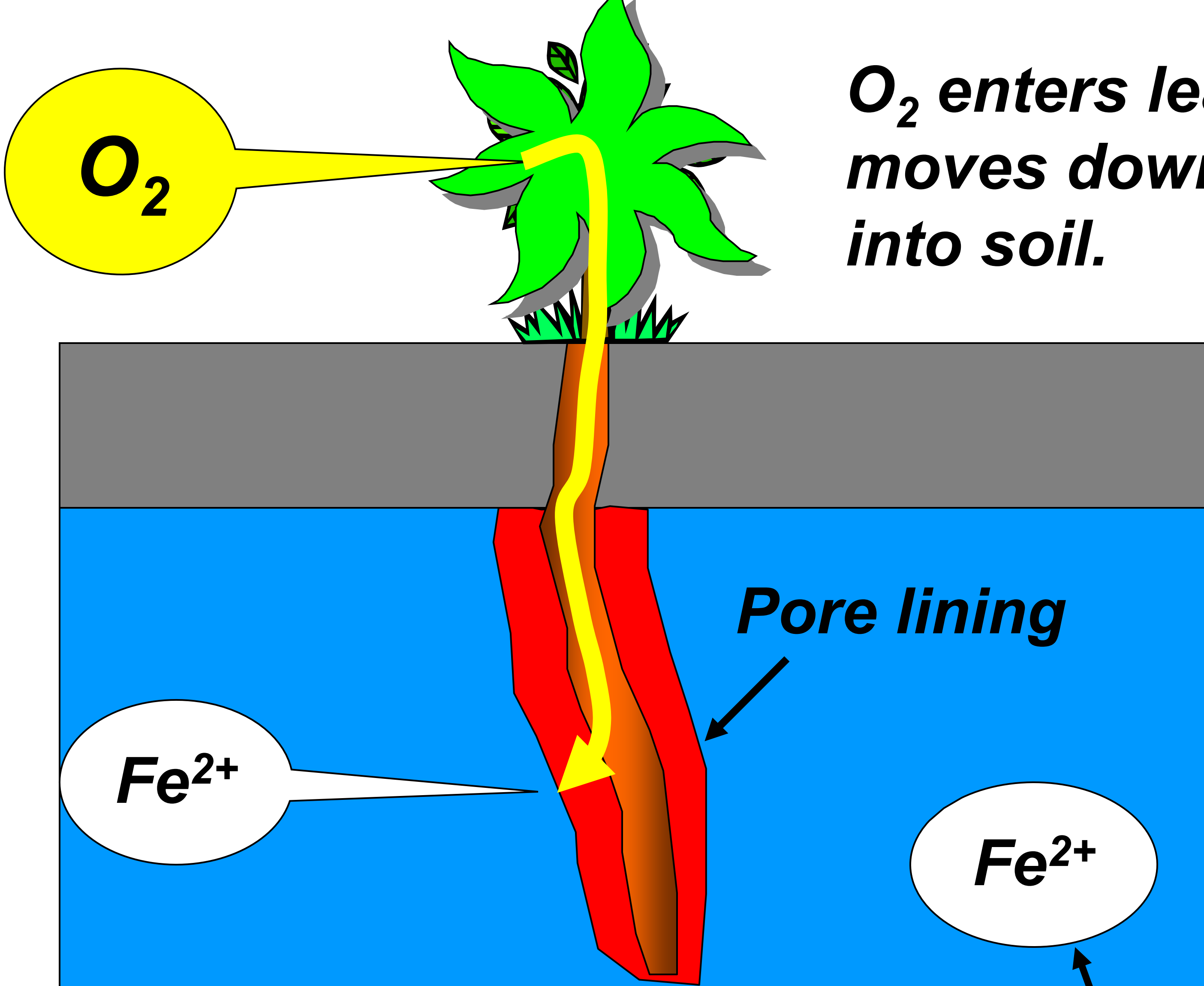
Soil along channel turns gray


O_2
Soil drains
Fe^{2+}
Oxygen moves into soil
Reduced Fe diffuses into matrix,
Fe masses form when Fe^{2+} is oxidized
Color of depletion is gray

Pore Linings Along Root Channels

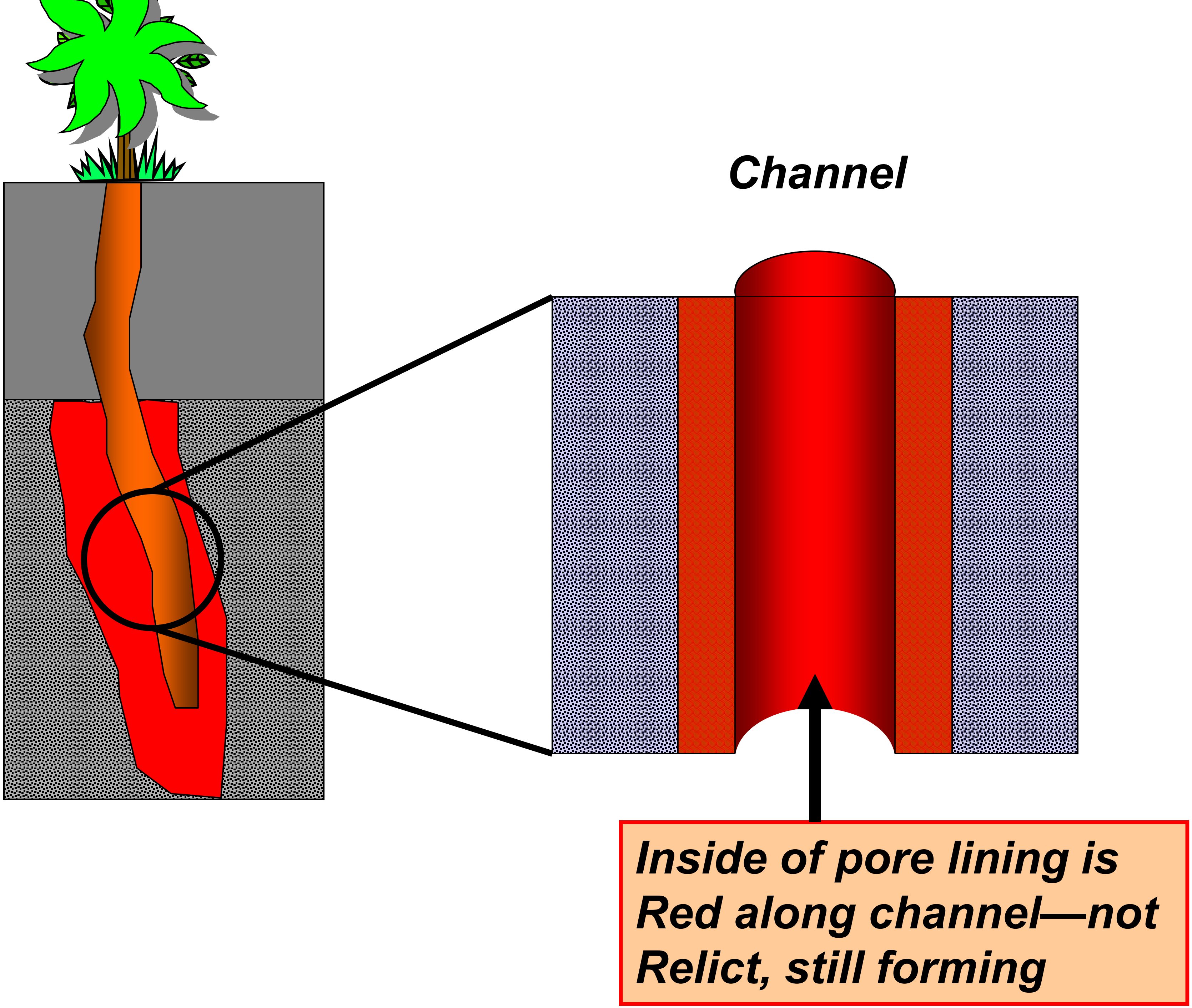
David Lindbo, NRCS

O$_2$ enters leaves, moves down root into soil.



Fe diffuses toward O$_2$ and oxidizes

Reduced soil


Channel
Inside of pore lining is
Red along channel—not
Relict, still forming

F3 and S5 Form the Same Way

Fe is reduced, dissolved, and moved.

It may oxidize in the matrix and form masses.

If saturated for long periods, it may diffuse to air-filled pores and re-oxidize as pore linings

S6: Stripped Matrix

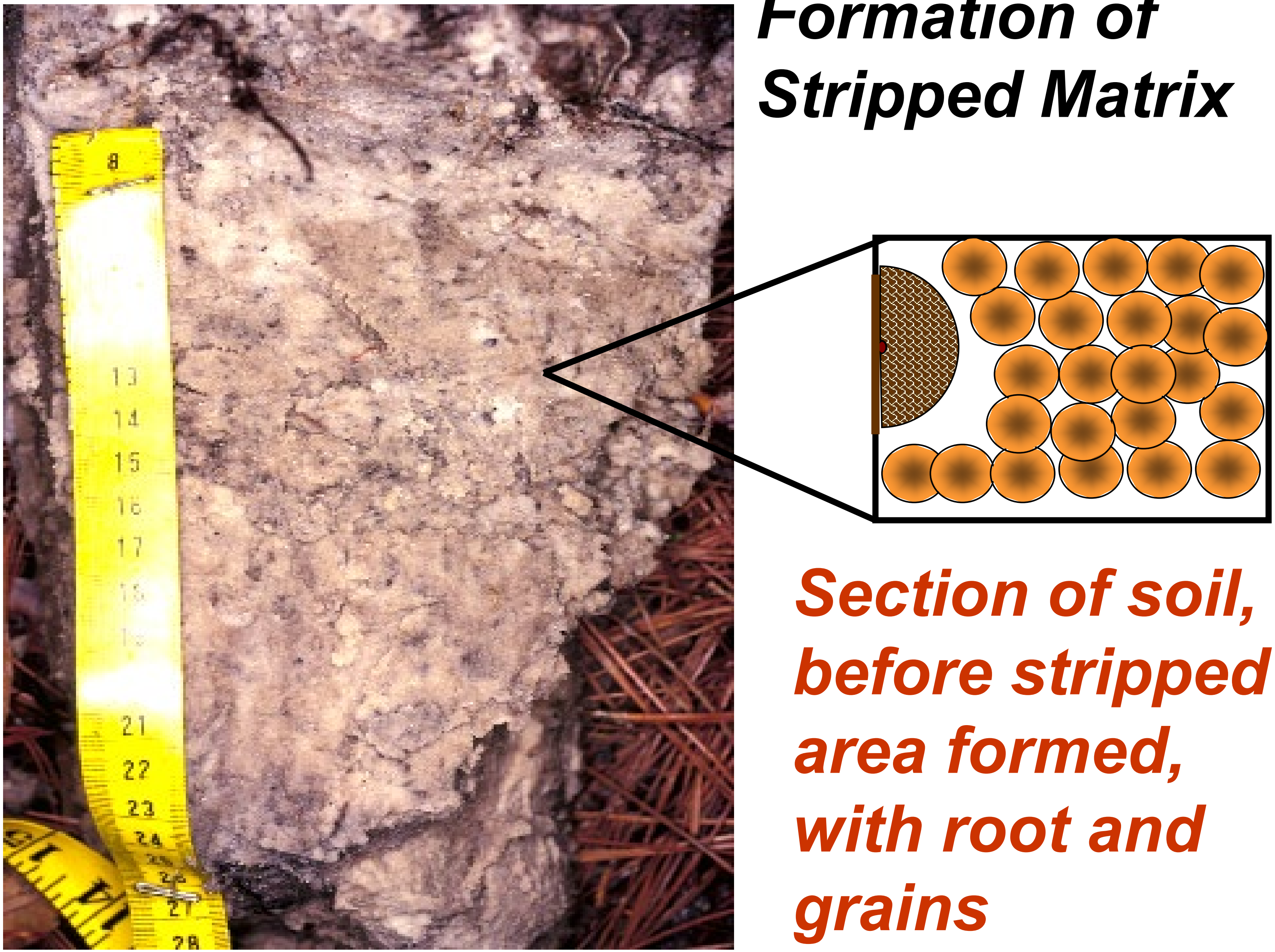
Photos by John Kelley

S6. Stripped Matrix

A layer starting within15 cm of the soil surface in which Fe/Mn oxides and / or organic matter have been stripped from the matrix (in places) exposing the primary base colors of the minerals. The stripped areas and translocated oxides and/or organic matter form a diffuse splotchy pattern of 2 or more colors.

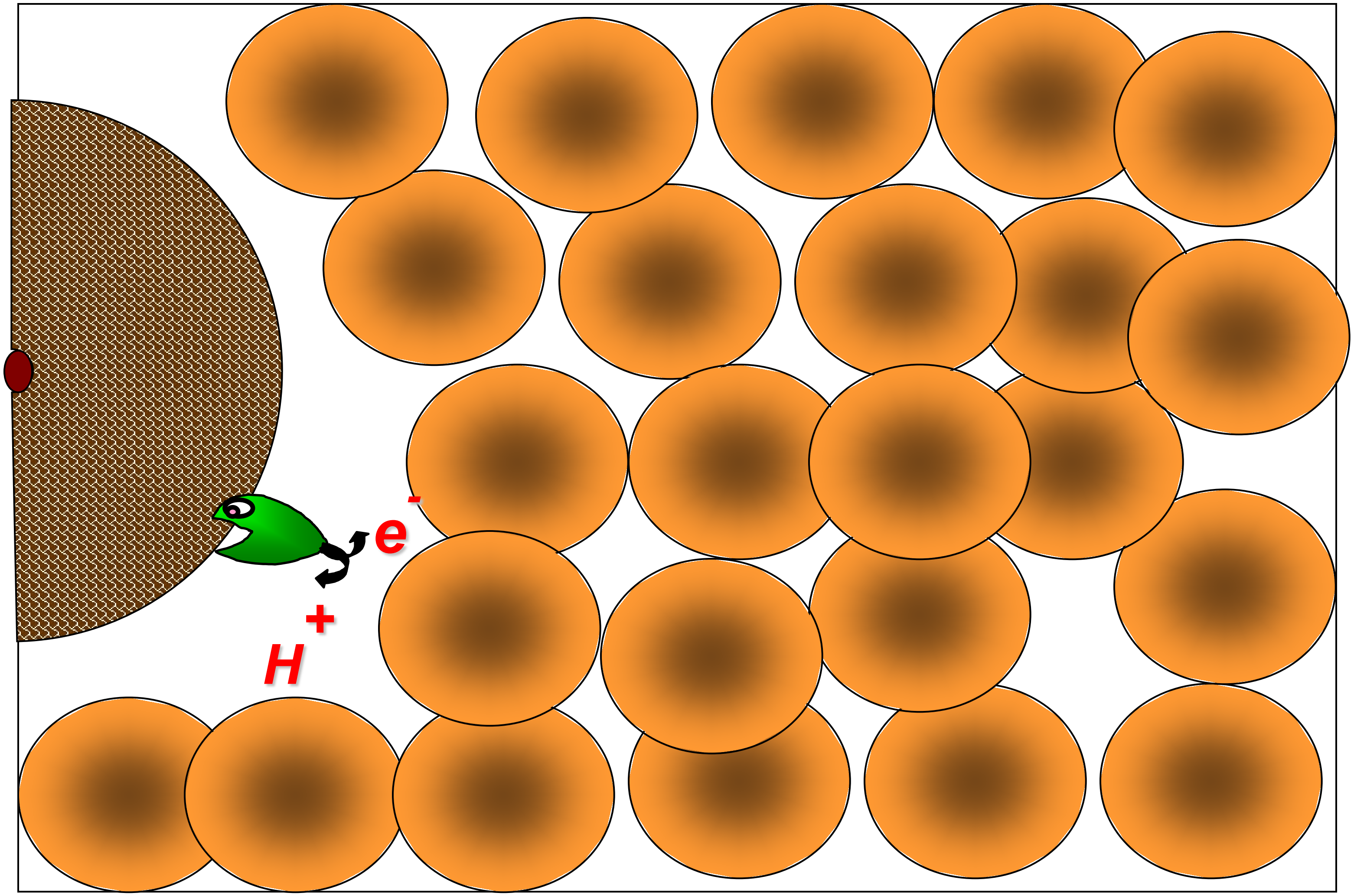
S6 is consists of Fe depletions which probably formed around dead roots

Formation of Stripped Matrix

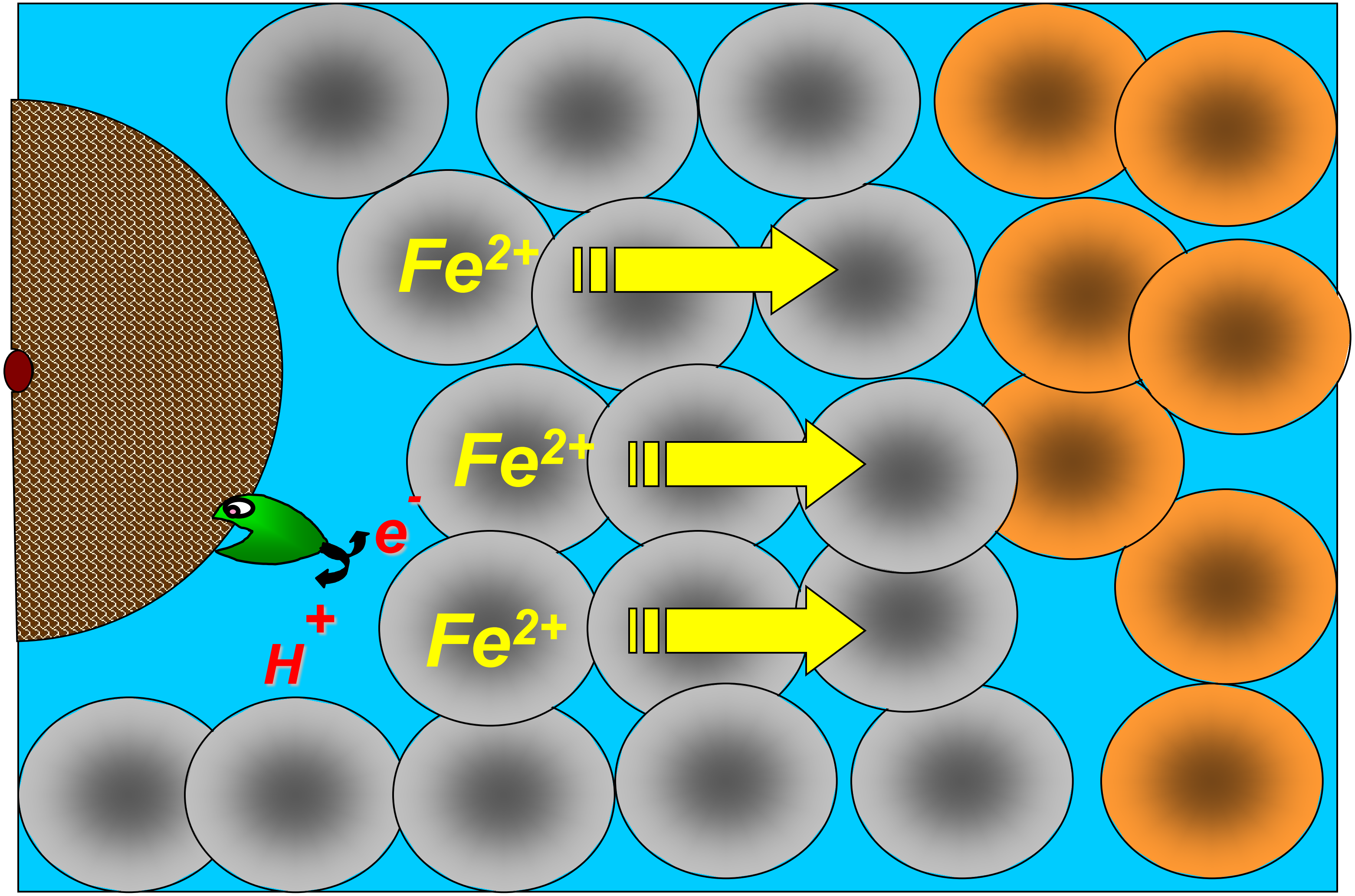


Section of soil, before stripped area formed, with root and grains

Fe-coated sand surrounds channel. Color unchanged when soil is aerobic

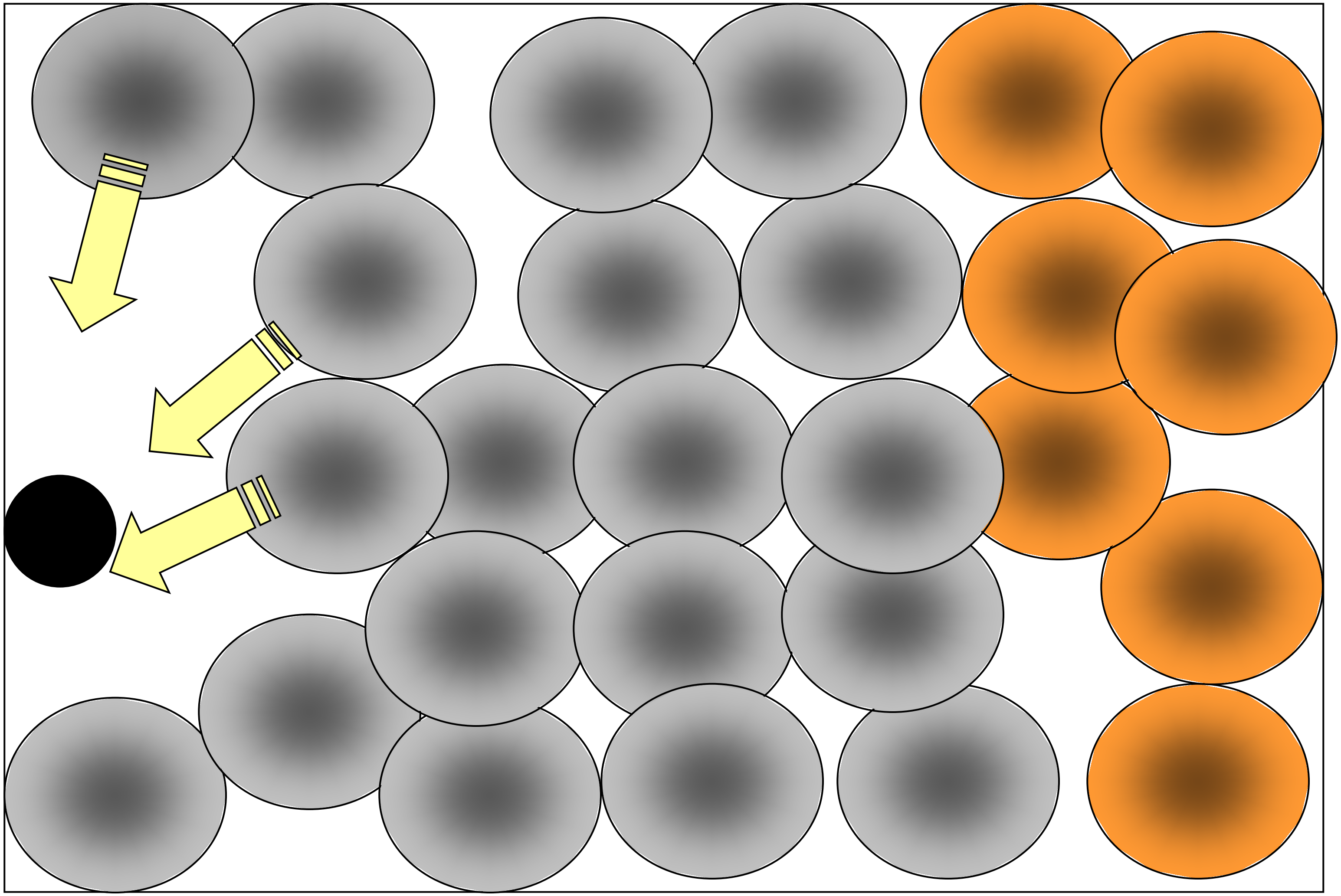


Bacteria decompose root, release electrons that reduce Fe. Soil turns gray near channel.

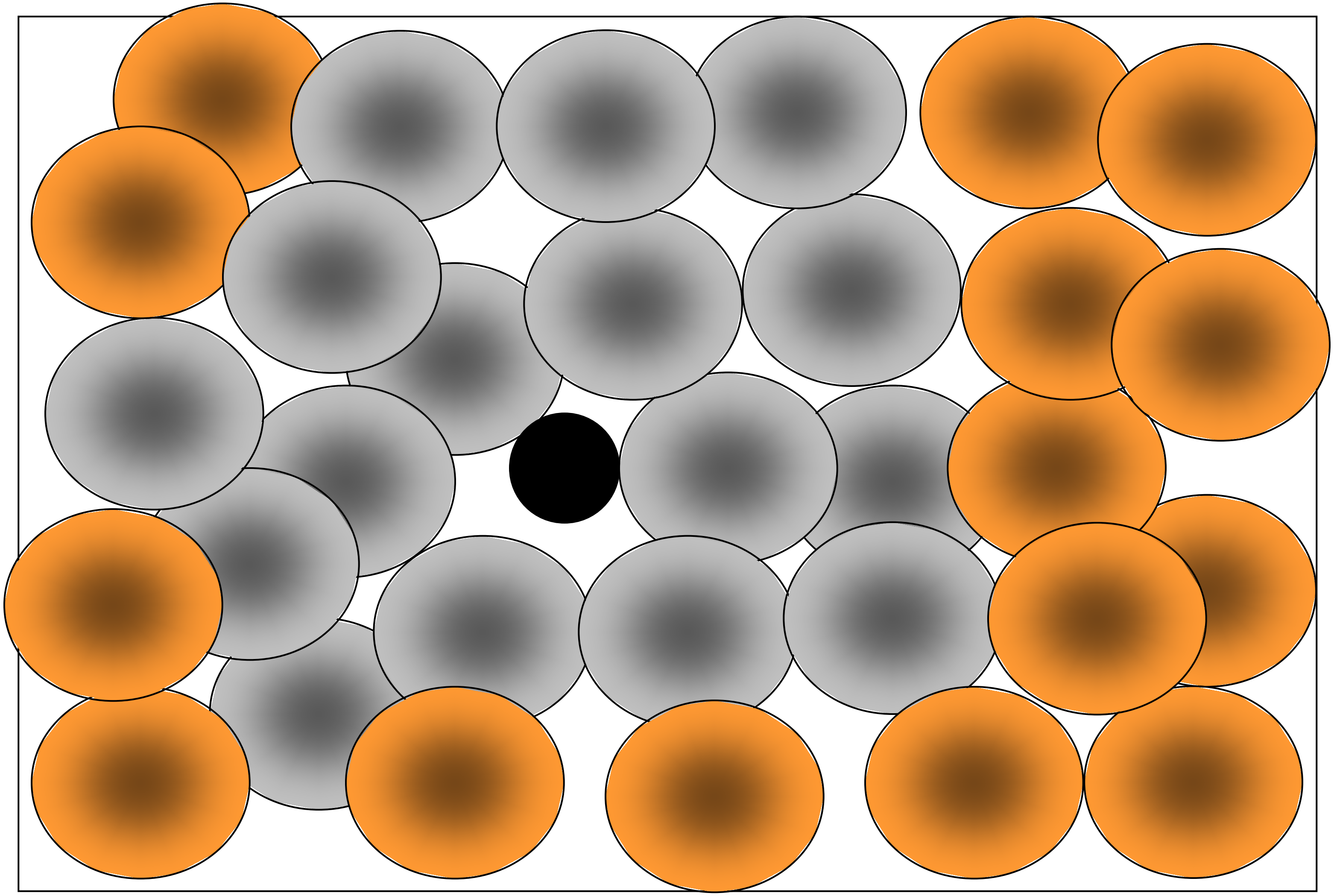


Anaerobic Conditions

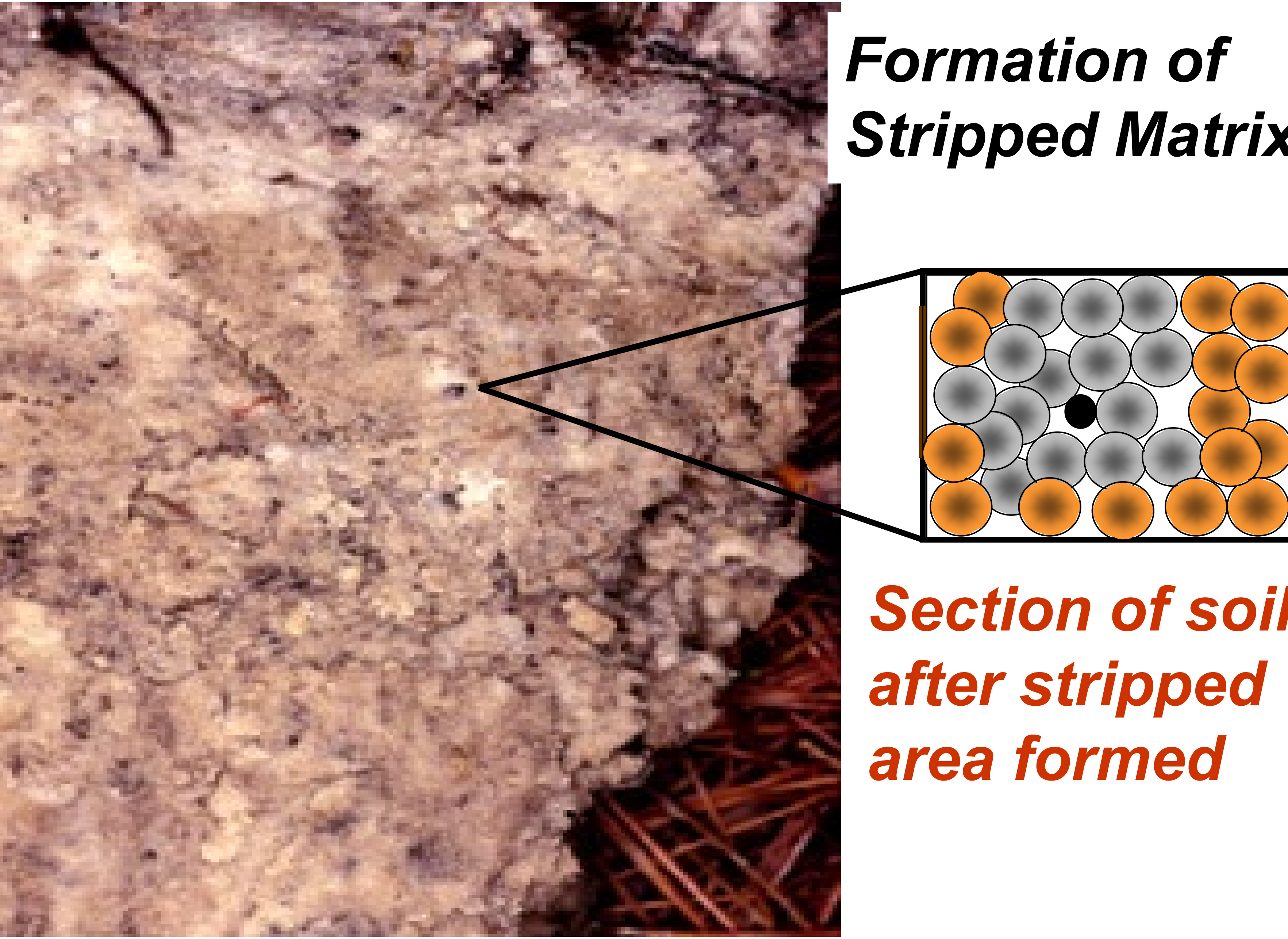
Once decomposed, root shrinks, grains fall into channel



Stripped Matrix is an Fe Depletion



Formation of Stripped Matrix

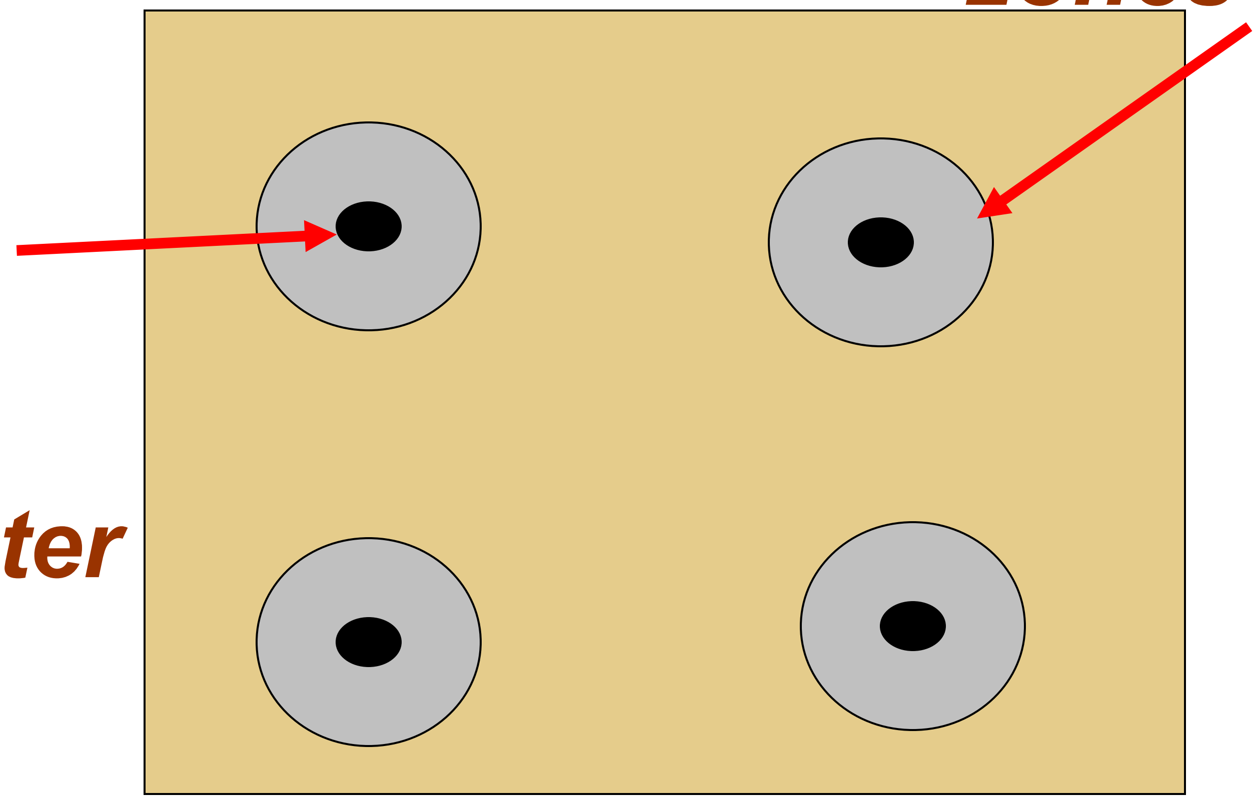


Section of soil, after stripped area formed

Formation of Stripped Zones

1. Roots grow into soil

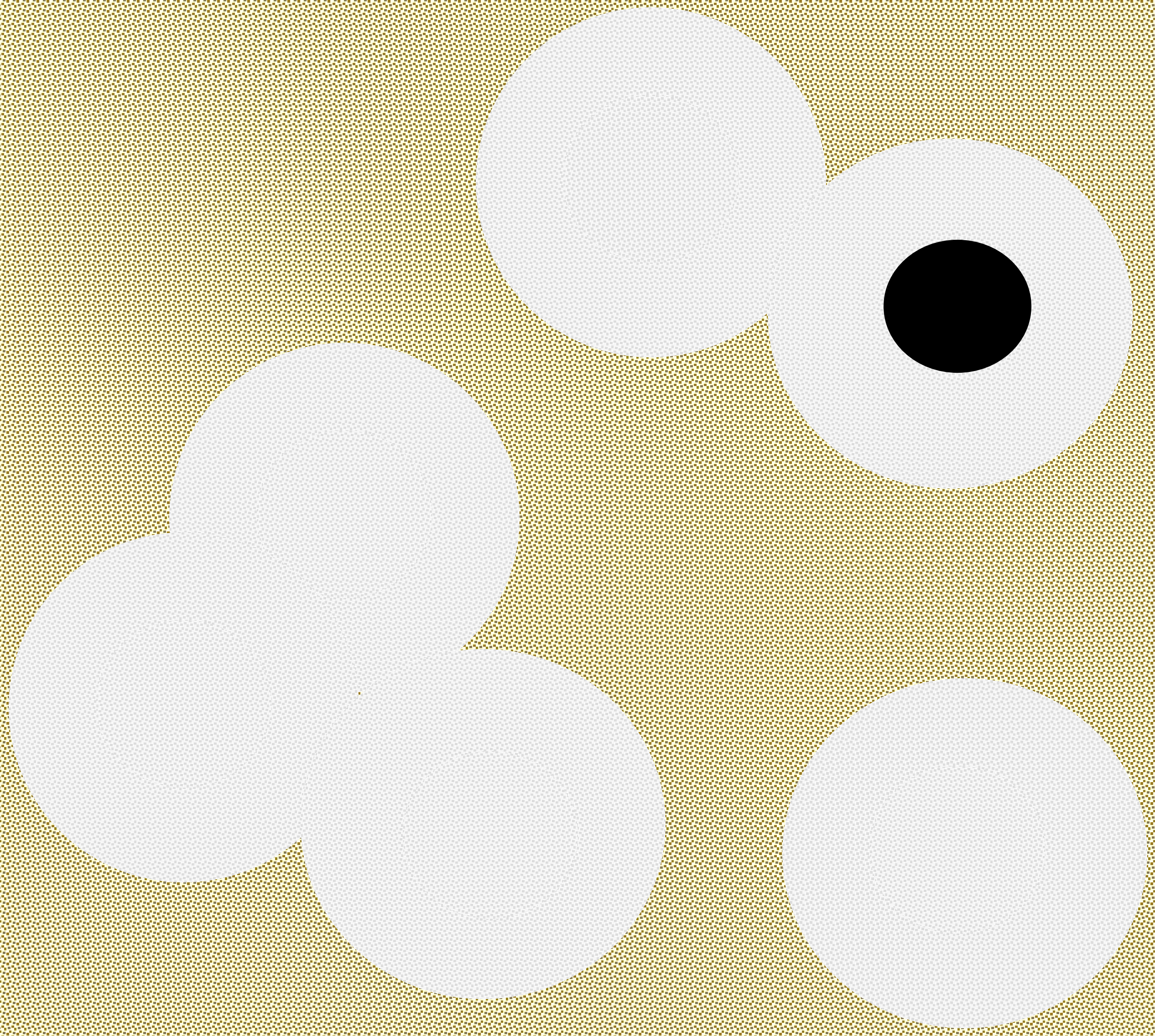
5. Depleted zones remain



2. Water table rises

3. Roots die

4. Fe is reduced and moves



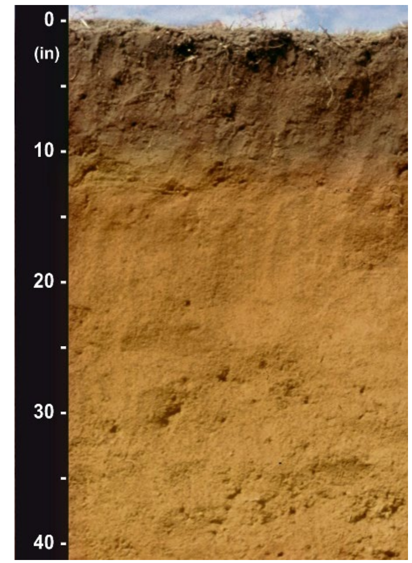
Why Did S6 Form and Not S5?

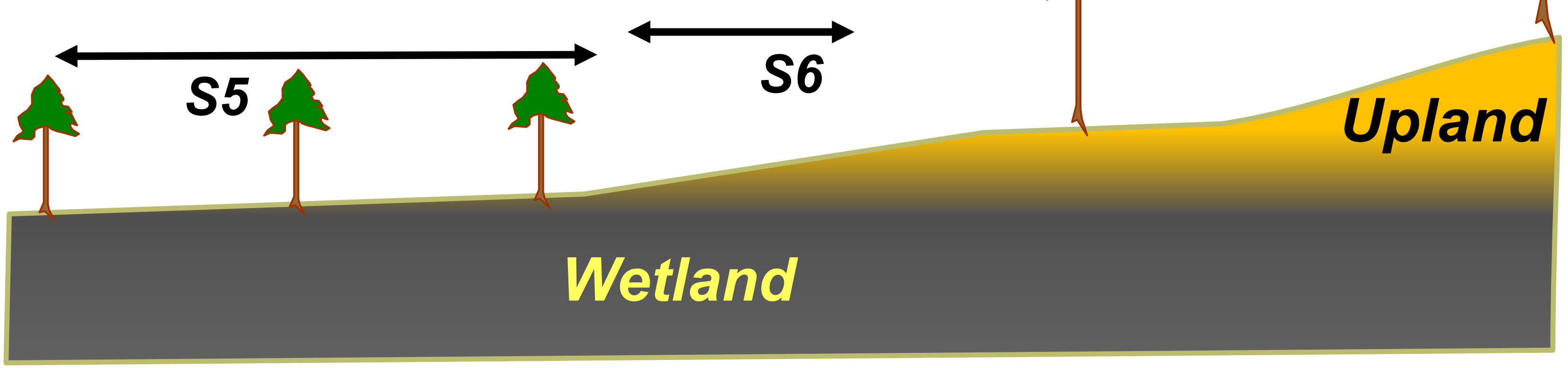
- ***S6 may form where saturation is short, and/or possibly on a slope***
- ***S6 may also form in soils with little reducible Fe.***
- ***S5 may occur at lower elevations than S6, where saturation is longer***

Possible Landscape Relationships (Sands)

Thick A

Thin A





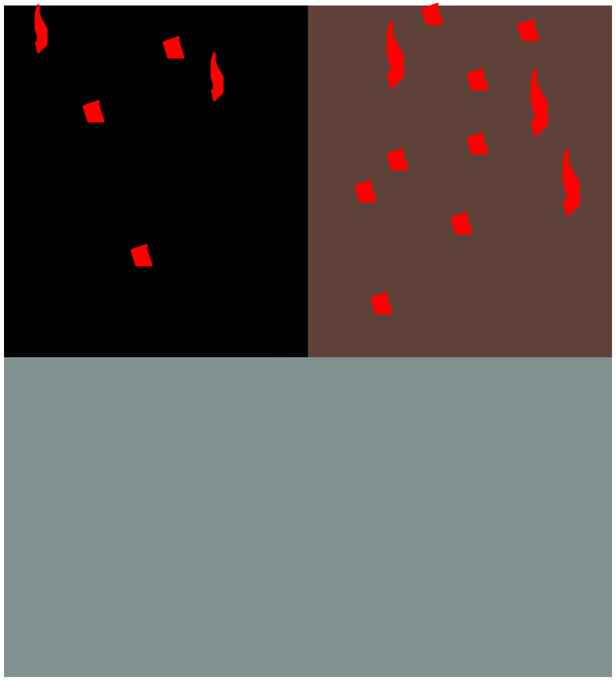
F6. Redox Dark Surface

A layer at least 4 in. thick entirely within the upper 12 in. that has:

a. matrix value 3 or less and chroma 1 or less and 2% or more distinct or prominent redox concentrations, or

b. matrix value 3 or less and chroma 2 or less and 5% or more redox concentrations.

- **Chroma 1 with 2%**



- **Chroma 2 with 5%**

Redox Dark Surface (F6)

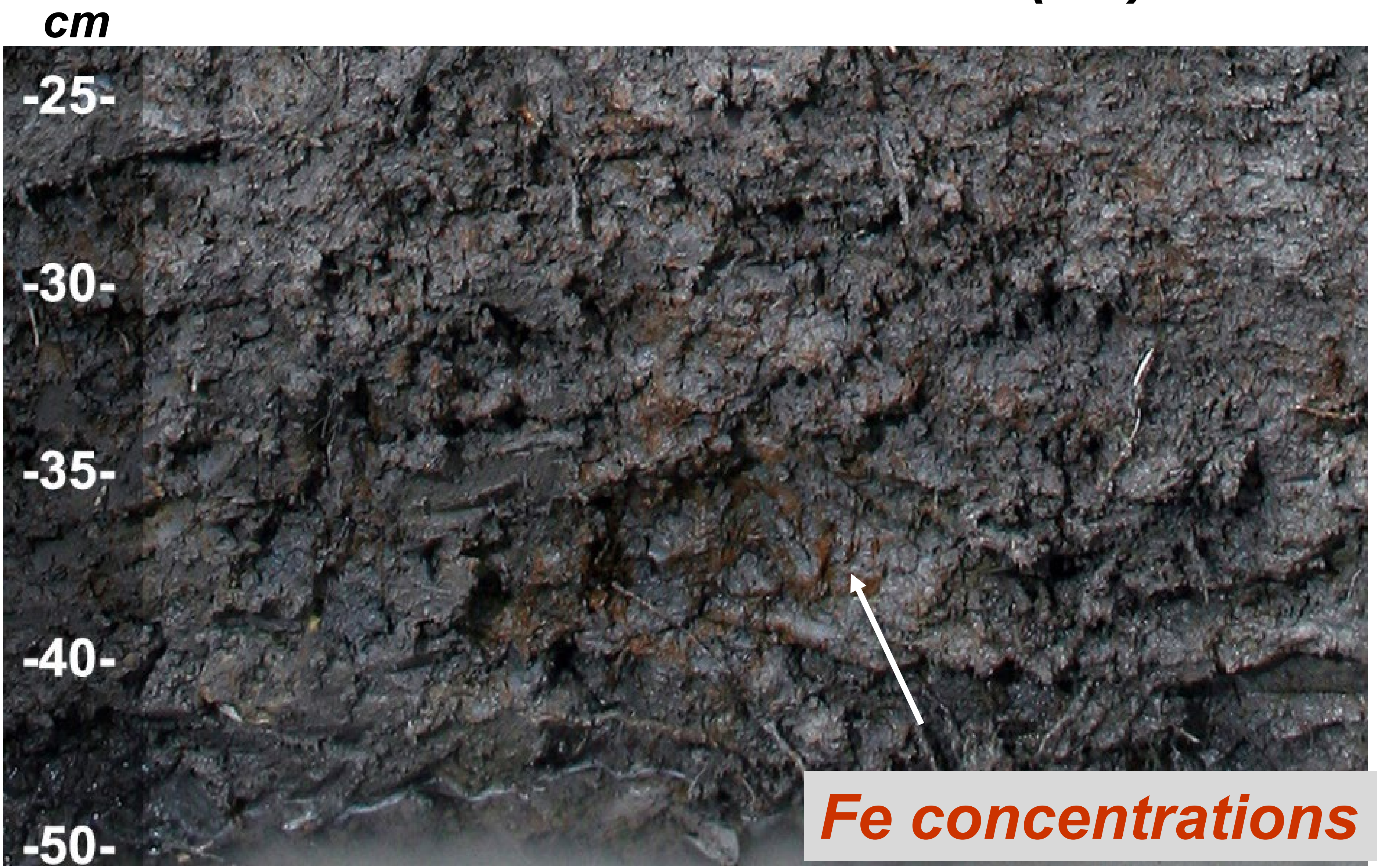
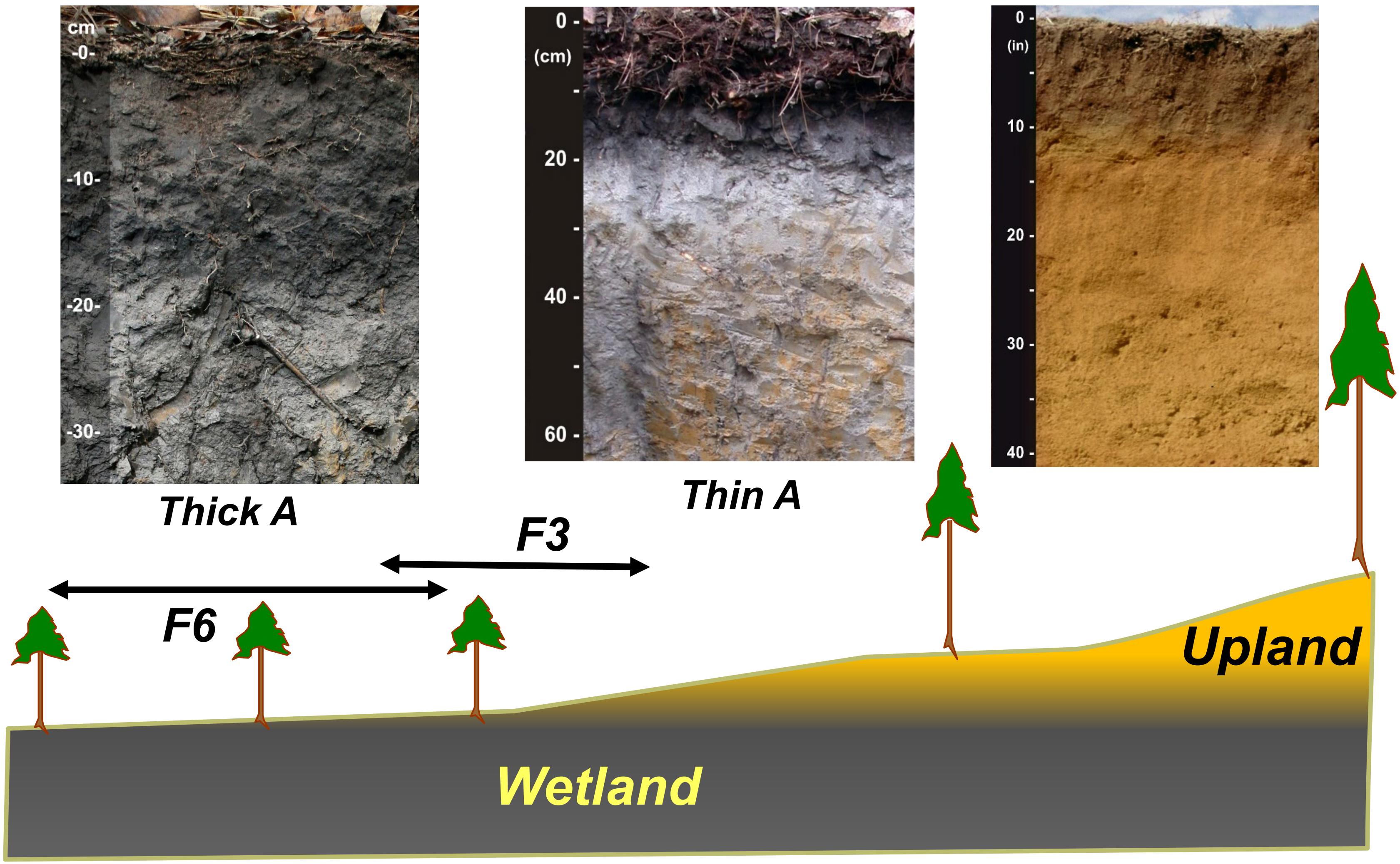


Photo by John Kelley

Possible Landscape Relationships (Loams)

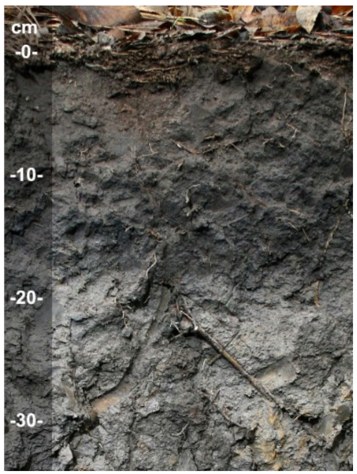


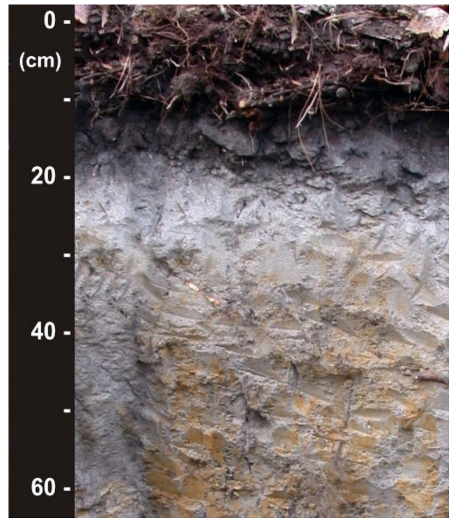
F8: Redox Depressions

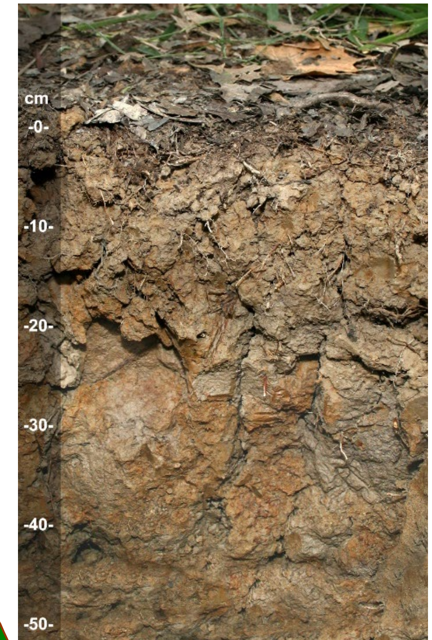
F8. Redox Depressions

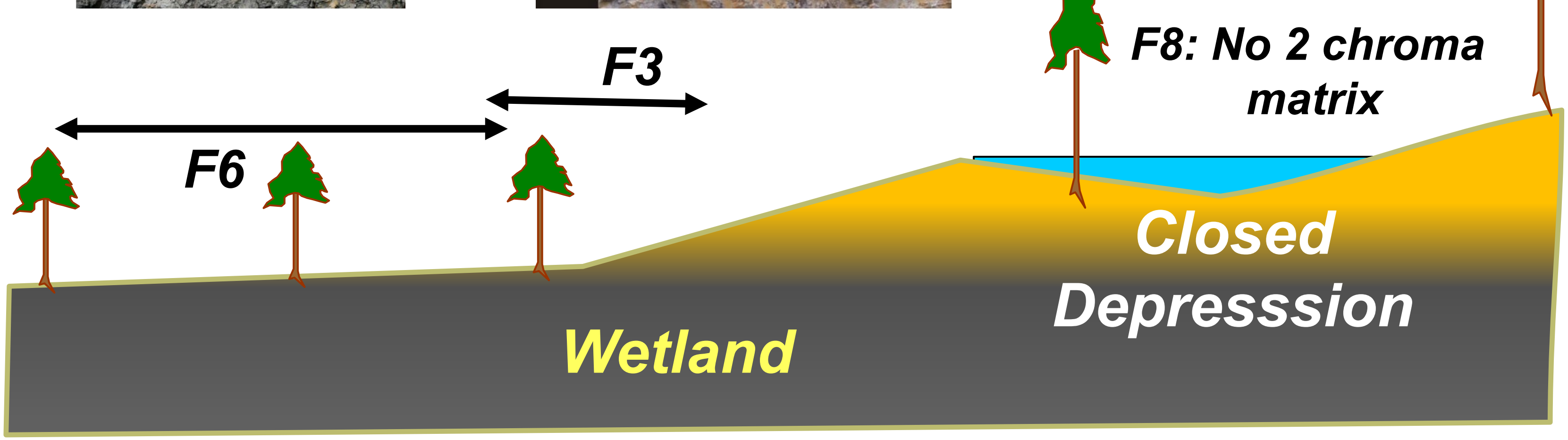
In closed depressions subject to ponding, 5% or more redox conc. in a layer 2 cm or more thick entirely within upper 15 cm.

Possible Landscape Relationships (Loams)









Relation of 40 year Hydrology to Field Indicators

Field Indicator	Hydric soil field indicator	Years wetland hydrology met (% of years)	Average duration of saturation (days yr^{-1})	Average duration of ponding (days yr^{-1})
A1	*Organic soil*	*100*	*228*	*139*
A2	*Org. Surf.*	"	*178*	*67*
S7	*Dark Surf.*	"	*115*	*3*
F3, S5?	*Depl. Matrix*	*95*	*40*	*ND*
F8, S6?	*Redox Depr.*	*87*	*29*	*ND*
None	*--*	*6*	*5*	*ND*

Catena 73 (2008) 153–165

Summary-1

1. ***Redoximorphic features are used to identify soils that are saturated and reduced.***

2. ***The features need four conditions to form: organic matter, active bacteria, saturation, and stagnant water.***

Summary-2

3. Redoximorphic features show where oxidation and reduction of Fe occur in horizons.

4. The features frequently are related to where roots grow.

Summary-3

5. Field indicators F3 and S5 are similar and occur near the hydric soil boundary.

6. Field indicator F6 has carbon accumulating and may be found in wetter locations than F3.

Summary-4

7. Field indicator S6 is formed from Fe depletions developing along root channels. It may be upslope from indicator S5 and saturated for shorter periods.

8. Field indicator F8 is formed during short saturation periods in closed depressions.

The End

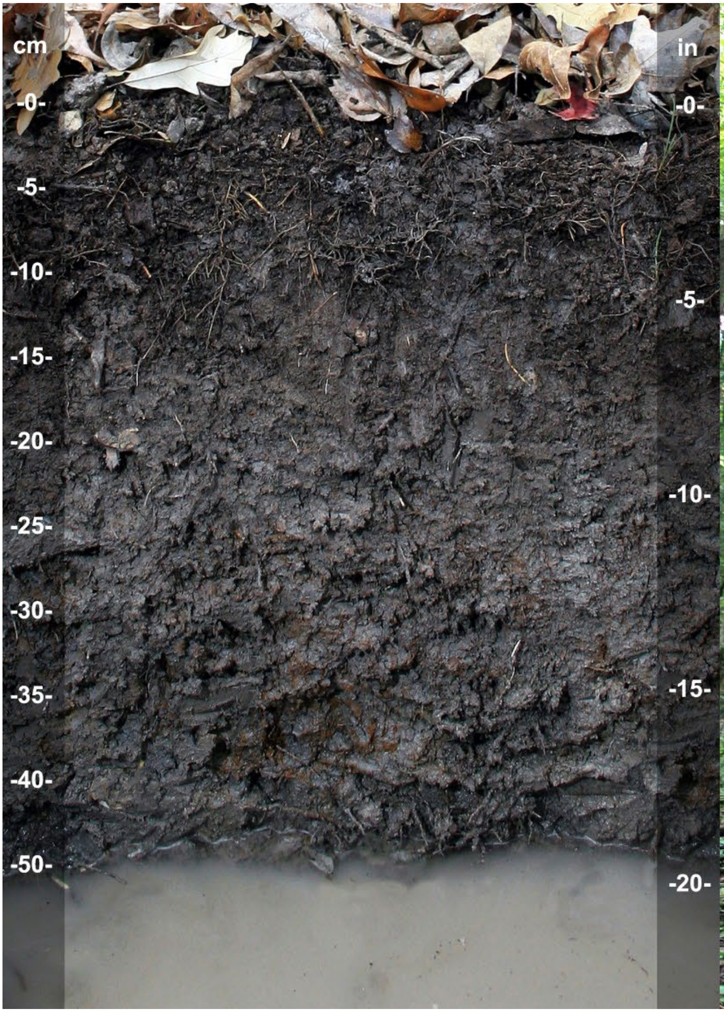


Photo by John Kelley