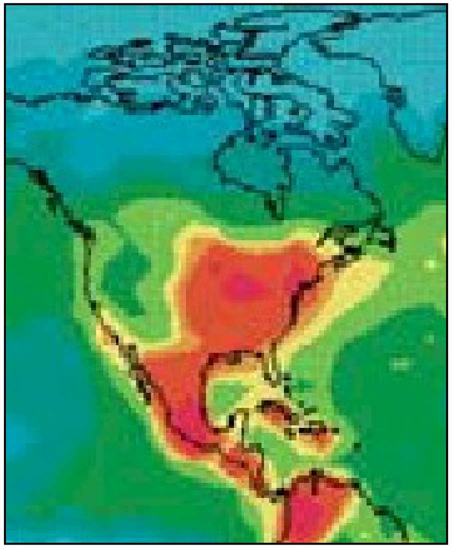
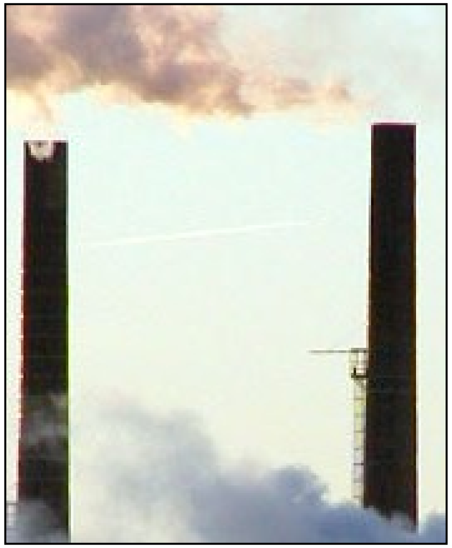
The general science of nitrogen acidification





Julian Aherne

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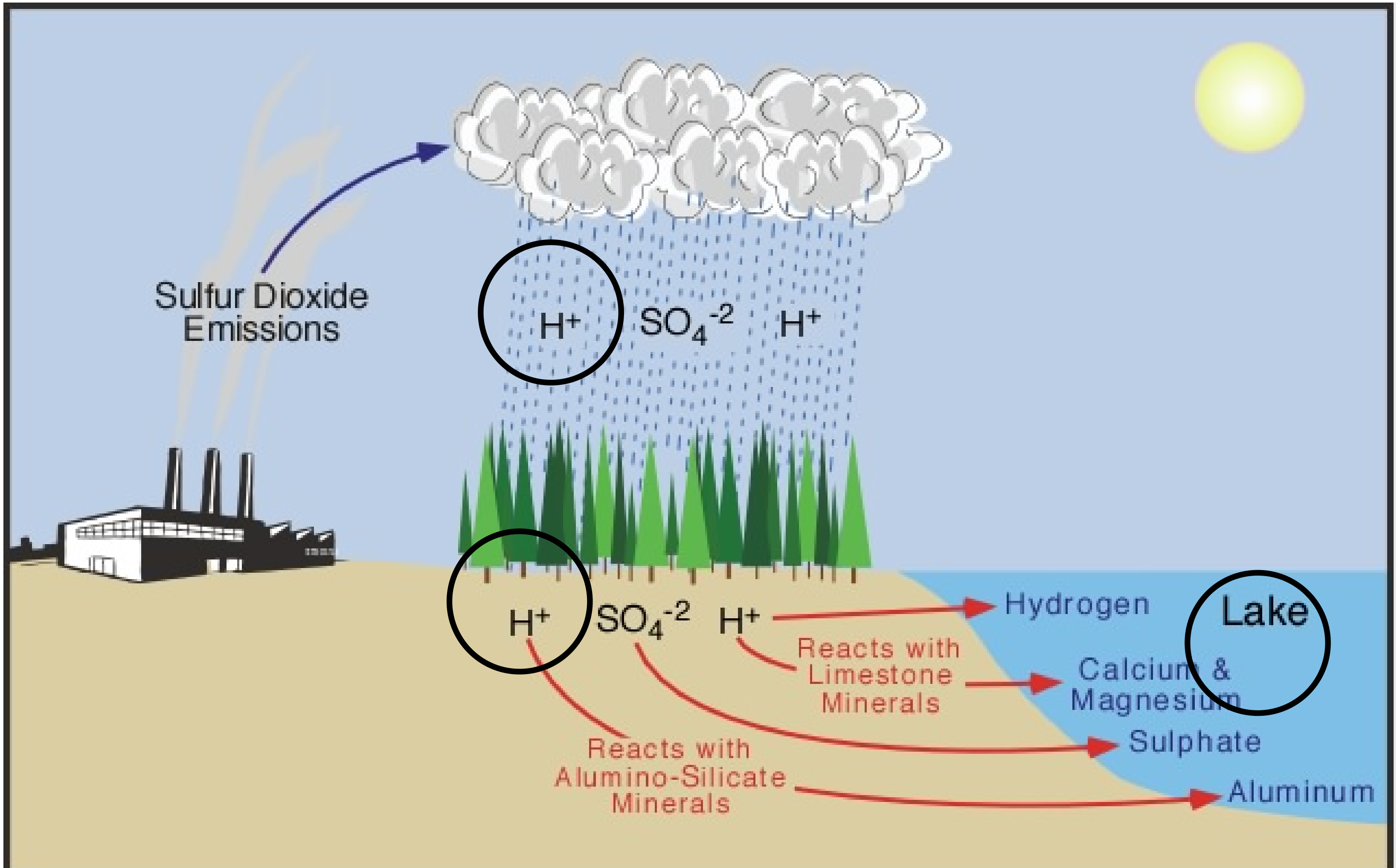
Key questions. what are the:

What is nitrogen acidification?

What are the environmental and depositional factors that influence nitrogen acidification?

How is nitrogen acidification measured/determined and what are some of the effects or manifestations of nitrogen acidification?

What are the unknowns regarding nitrogen acidification?



source: www.physicalgeography.net

What is acidification?

The process of becoming acid; the lowering of pH in soils or water, commonly associated with changes caused by external processes such as acid precipitation

natural sources

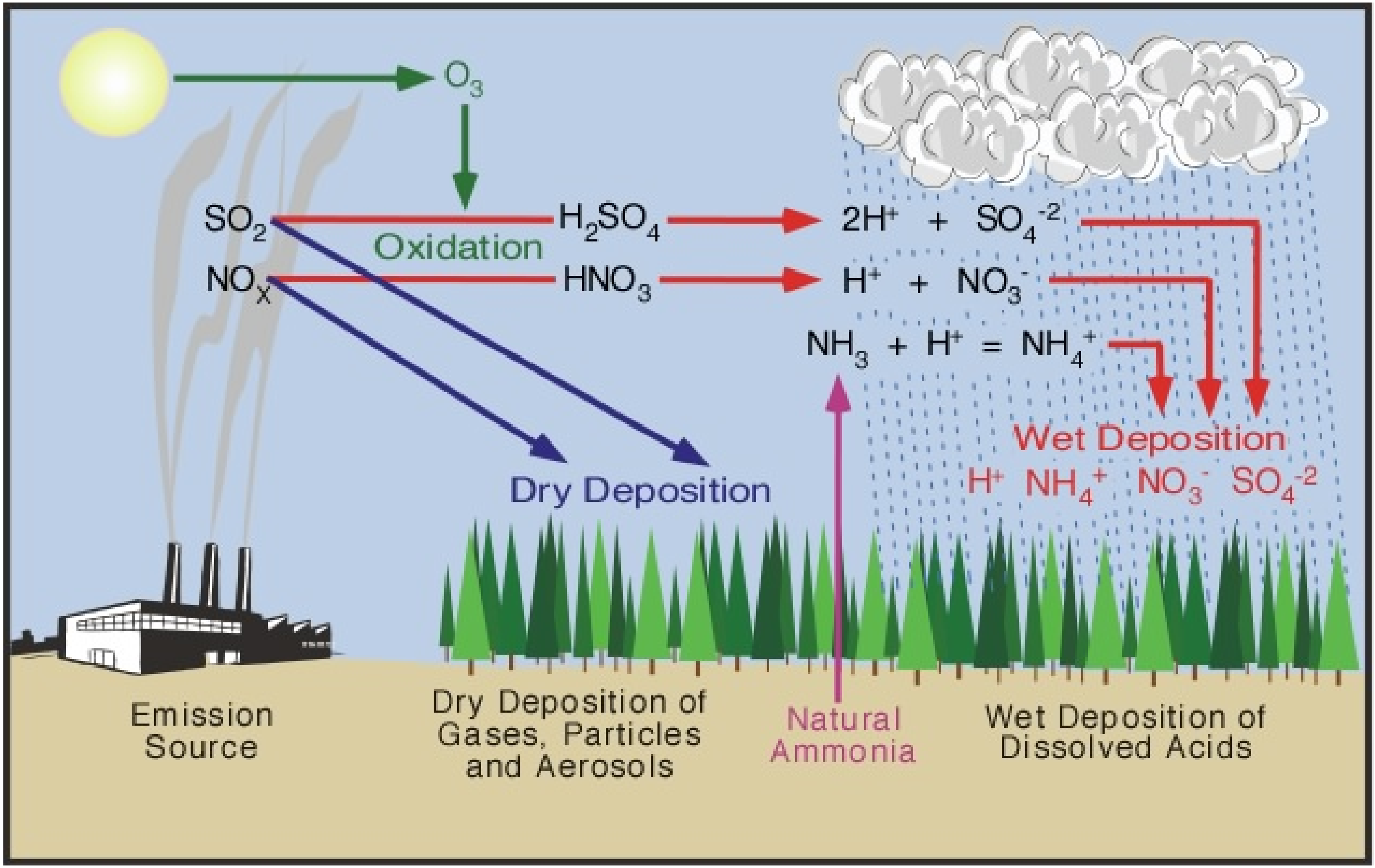
Observation d'une pluie acide, par M. Ducros, *pharmacien à Nîmes.*

En mai, ou au commencement de juin 1842, éclata sur notre ville un orage, pendant lequel se succédèrent de violents coups de tonnerre ; il tomba une quantité considérable de grêle : ce fut cet orage qui ravagea les bois et les vignes dans la direction de Nîmes à Saint-Geniez de Melgoin. La quantité de grêle qui tomba en peu de temps fut assez grande pour recouvrir le sol de la cour de la maison que j'habite ainsi que la terrasse qui la couronne d'une couche d'au moins 4 ou 5 centimètres. La grosseur des grêlons ne dépassait guère celle des plus petits pois ordinaires, et leur forme était ovoïde ; ils paraissaient formés de plusieurs couches dont la première moins diaphane que les autres.

Dans les premiers moments de l'orage, le hasard me fit porter à la bouche quelques grêlons que j'avais recueillis dans la main, et la saveur piquante particulière, que j'avais prise d'abord pour l'impression du froid sur la langue, me donna l'idée de vérifier si cette grêle ne contiendrait pas quelque principe particulier.

J'exposai alors sur ma terrasse un flacon en verre surmonté d'un entonnoir de même matière que j'avais d'abord bien lavés ; mon flacon plein fut bouché de son bouchon de verre, et après la fonte complète des grêlons, à la température ordinaire qui ne fut opérée que six ou sept heures après, le liquide était transparent, incolore, inodore. Un flacon qui, plein d'eau dis-

anthropogenic acidification

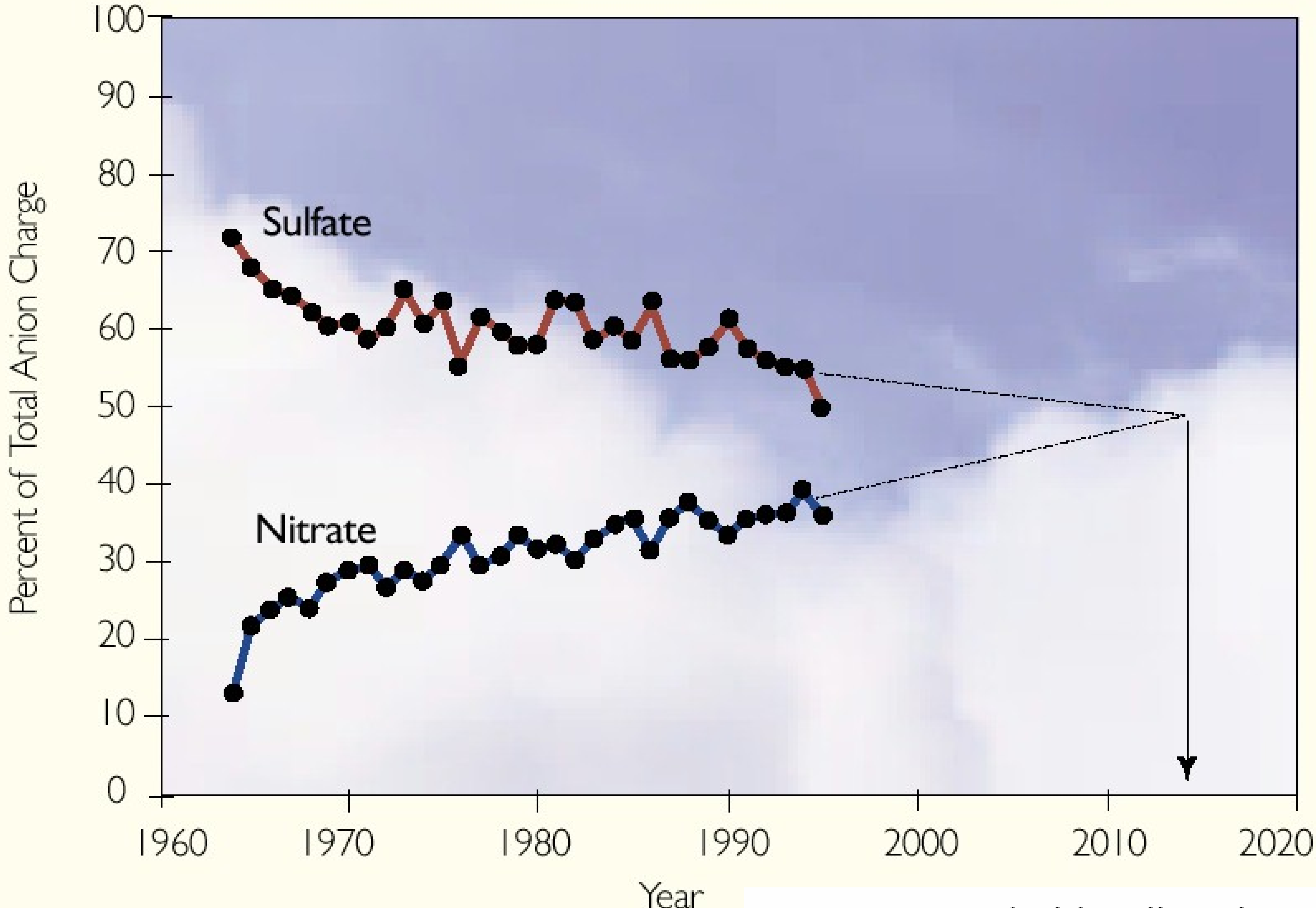


source: www.physicalgeography.net

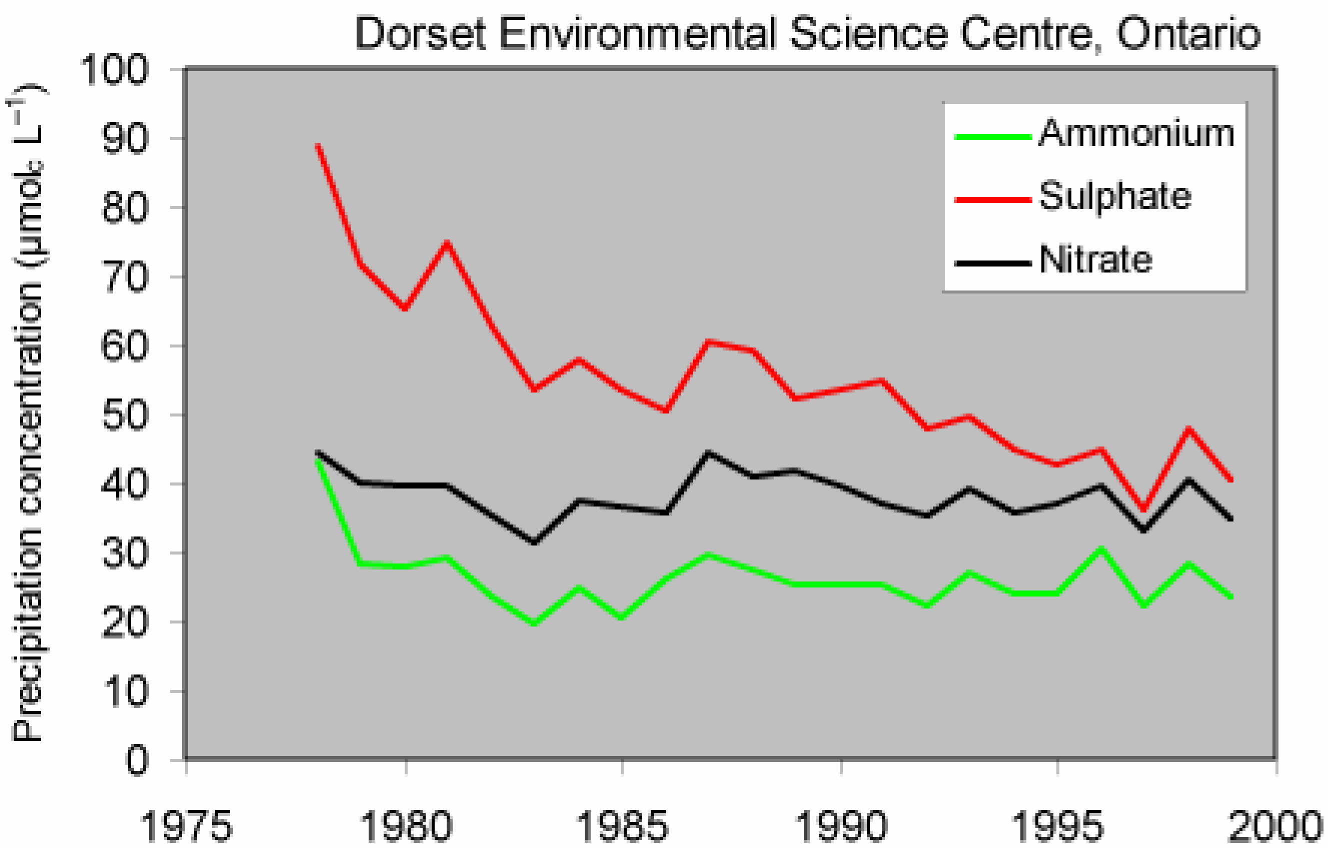
First mentioned in the scientific literature by Likens et al. (1972), who indicated that *nitric acid resulting from atmospheric transport of NO_x adds to the acidity of precipitation in the eastern US*

rain," he says. In industrialized areas of the United States, nitric acid has become an increasingly significant component of acid raid, says Gene Likens, director of the Institute of Ecosystem Studies in Millbrook, New York. "Our long-term studies at Hubbard Brook Experimental Forest—the longest continuous measurement of precipitation and stream-water chemistry in the world—clearly indicate that there is a major change under way," he says. In 1963, when the studies began, he says, sulfuric acid contributed about 70% of total acidity of rain, and nitric acid was about 15%. Currently sulfuric acid is about 50%, and nitric acid is about 40%. "We project that if the current trends continue, nitric acid will become the dominant acid in eastern North America by about 2012," Likens says. "And yet we've focused all of our regulations primarily on reducing sulfur."

The Changing Chemistry of Acid Rain



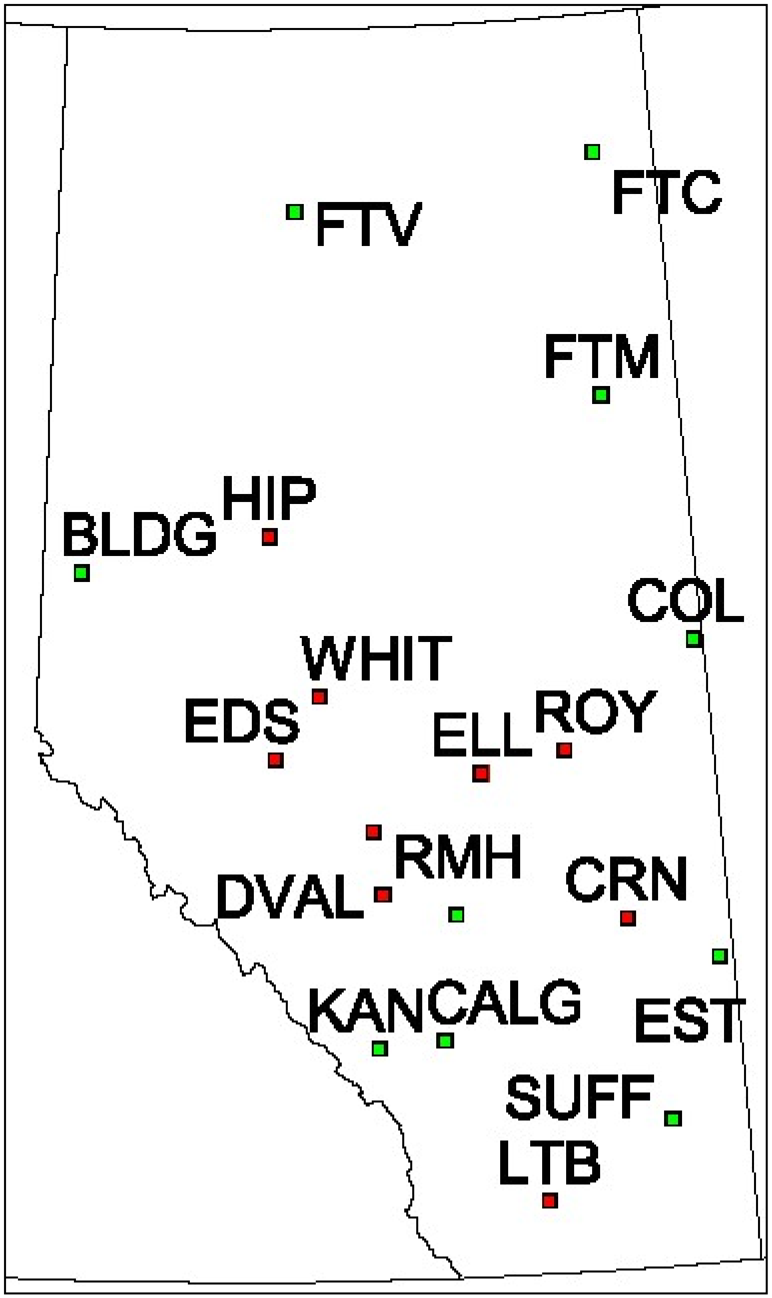
source: www.hubbardbrook.org/hbrf



Dorset Environmental Science Centre, Ontario
Precipitation concentration (µmolc L-1)
Ammonium
Sulphate
Nitrate
100
90
80
70
60
50
40
30
20
10
0
1975
1980
1985
1990
1995
2000

trends @ 8 wet deposition stations

	↓	↑	—
PPT	1	2	5
pH	1	1	6
SO_4^{2-}	6	–	2
NO_3^-	–	3	5
Cl^-	2	–	6
NH_4^+	–	4	4
Ca^{2+}	1	–	7
Mg^{2+}	4	–	4
Na^+	2	–	6
K^+	1	–	7

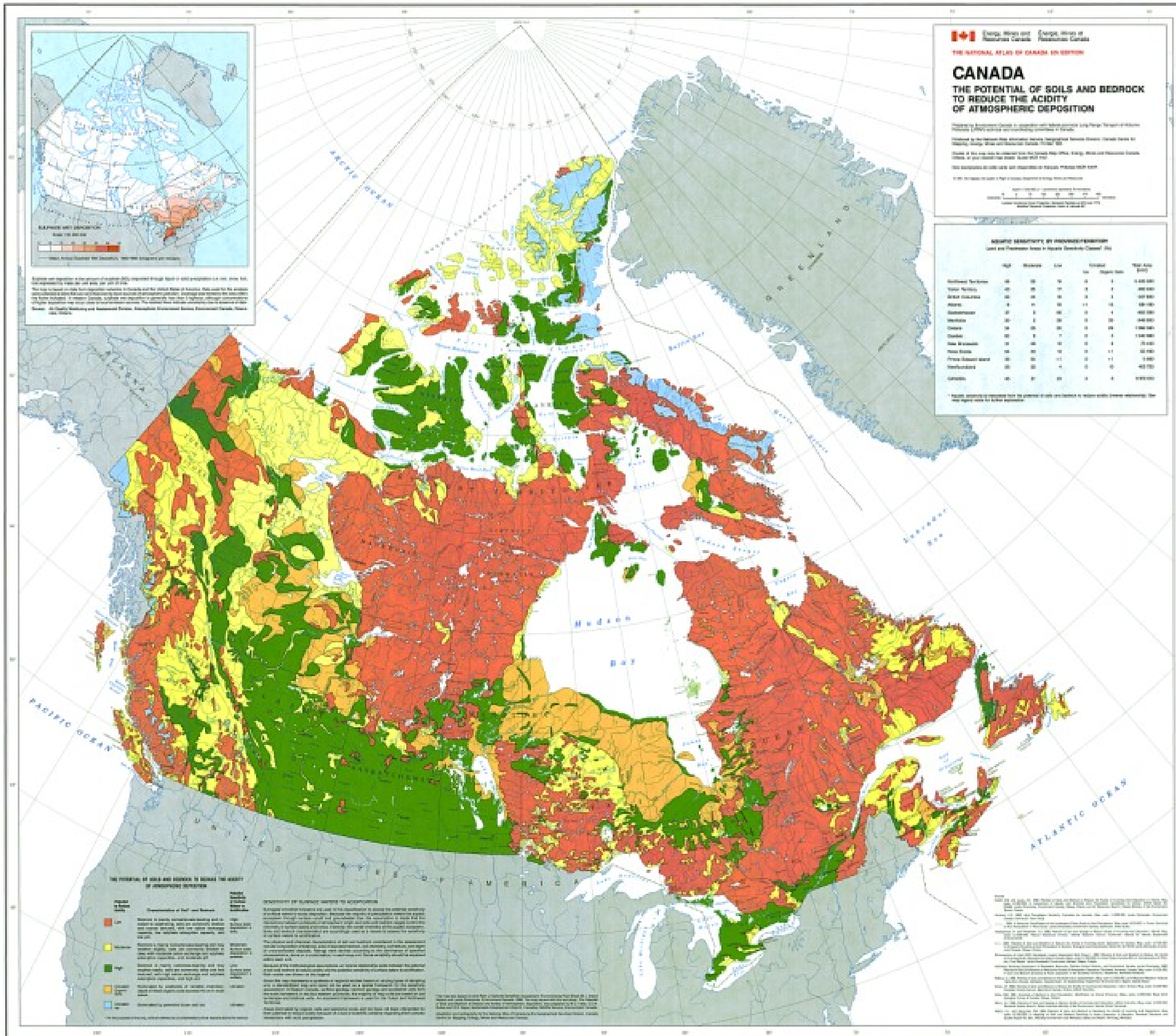


source: www.initrogen.org

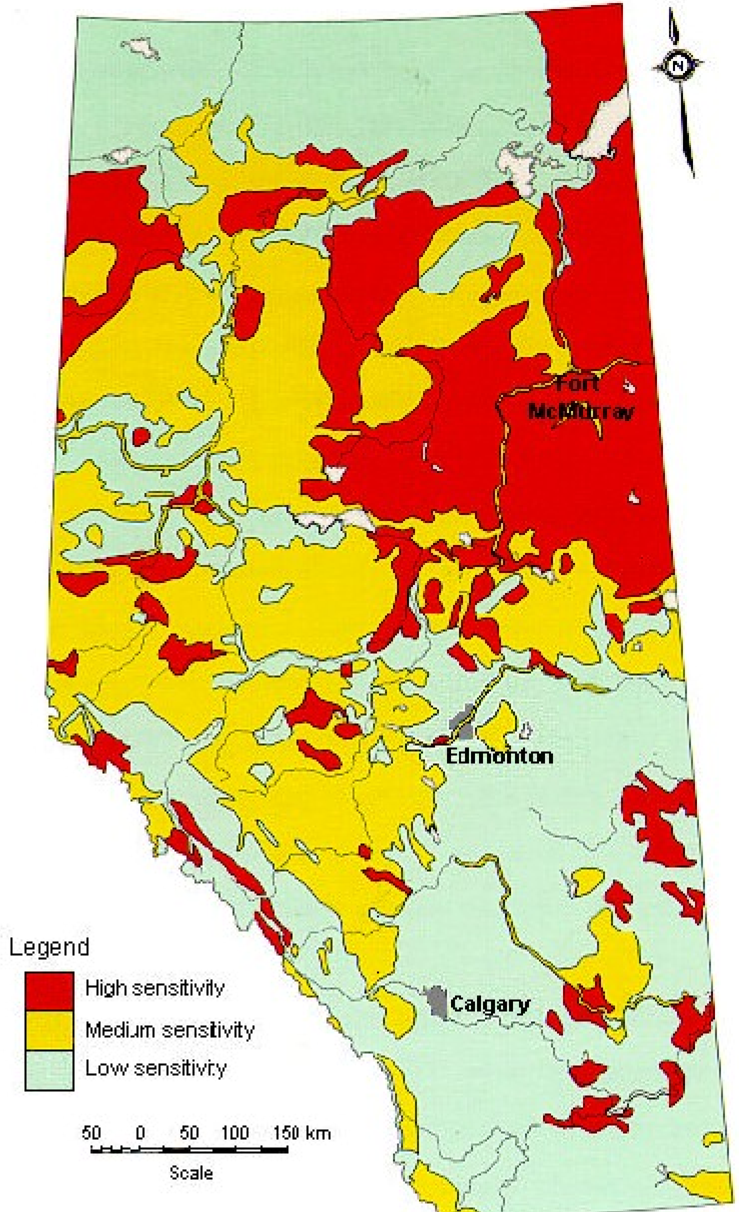
"The acidity of soil is [thus] determined by the relationship between the amounts of the basic cations and the acid aluminium species on the exchange complex. Process that would tend to acidify a soil include those that remove basic cations, such as leaching of bases in association with an acid anion"

"Capacity refers to the storage of base cations on the ion-exchange complex or in weatherable minerals"

source: Reuss and Johnson (1986)

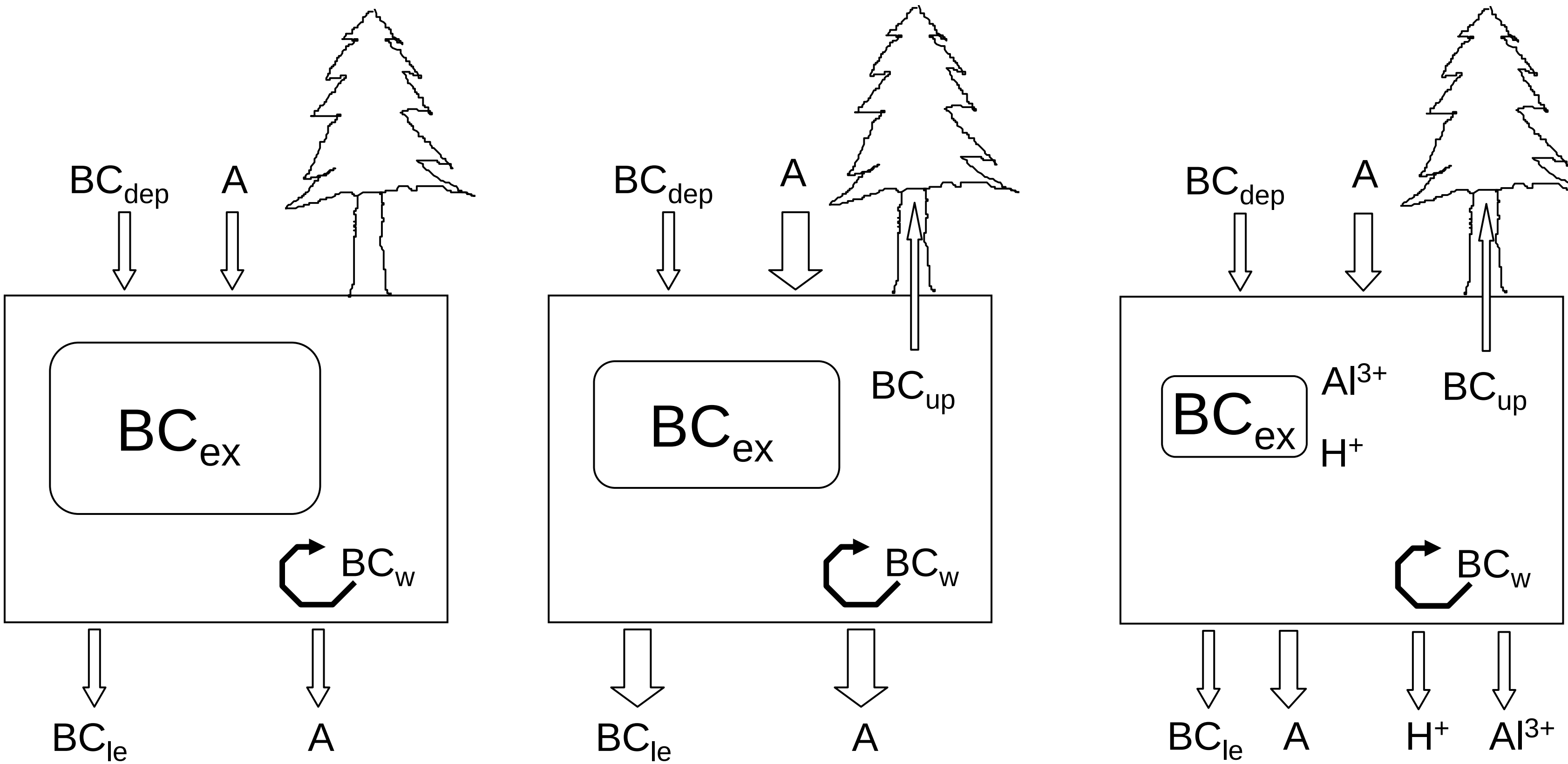


Source: atlas.nrcan.gc.ca



source: Holowaychuk and Fessenden (1987)

Soil acidification



Impacts: plant nutrients are leached out and toxic metals are freed

Acid-base relationship of the natural nitrogen cycle

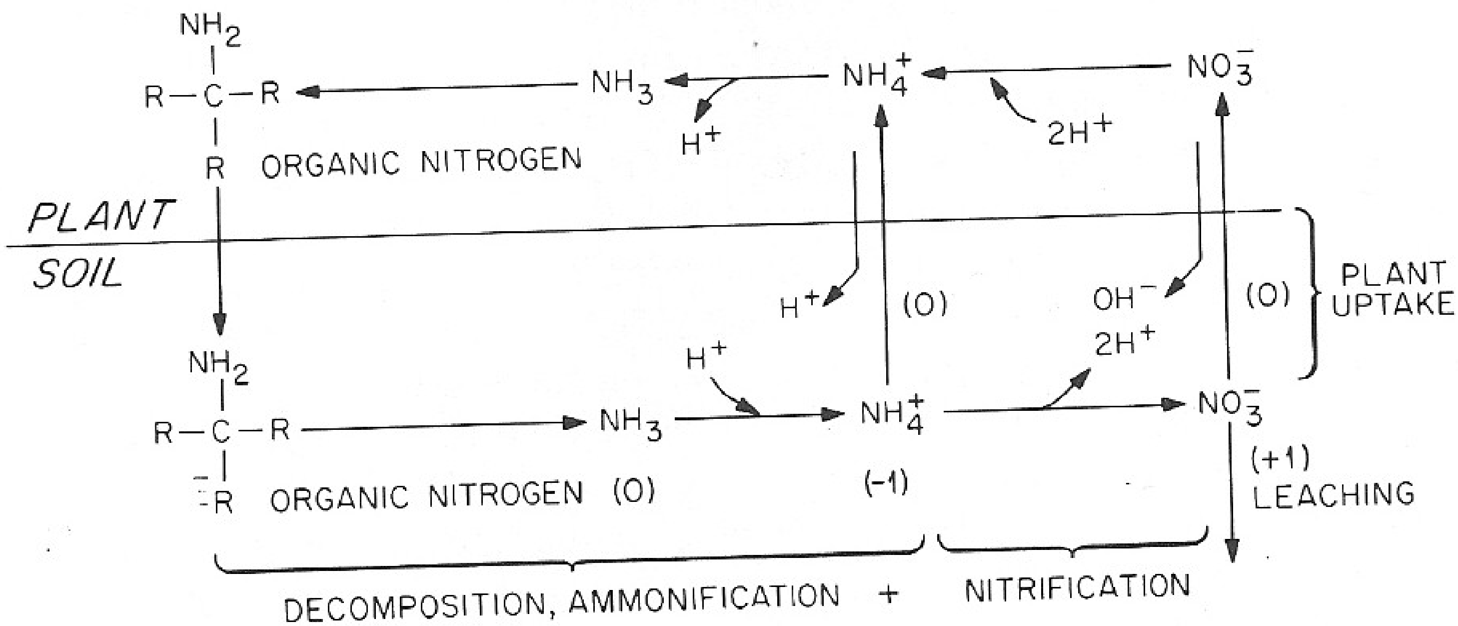
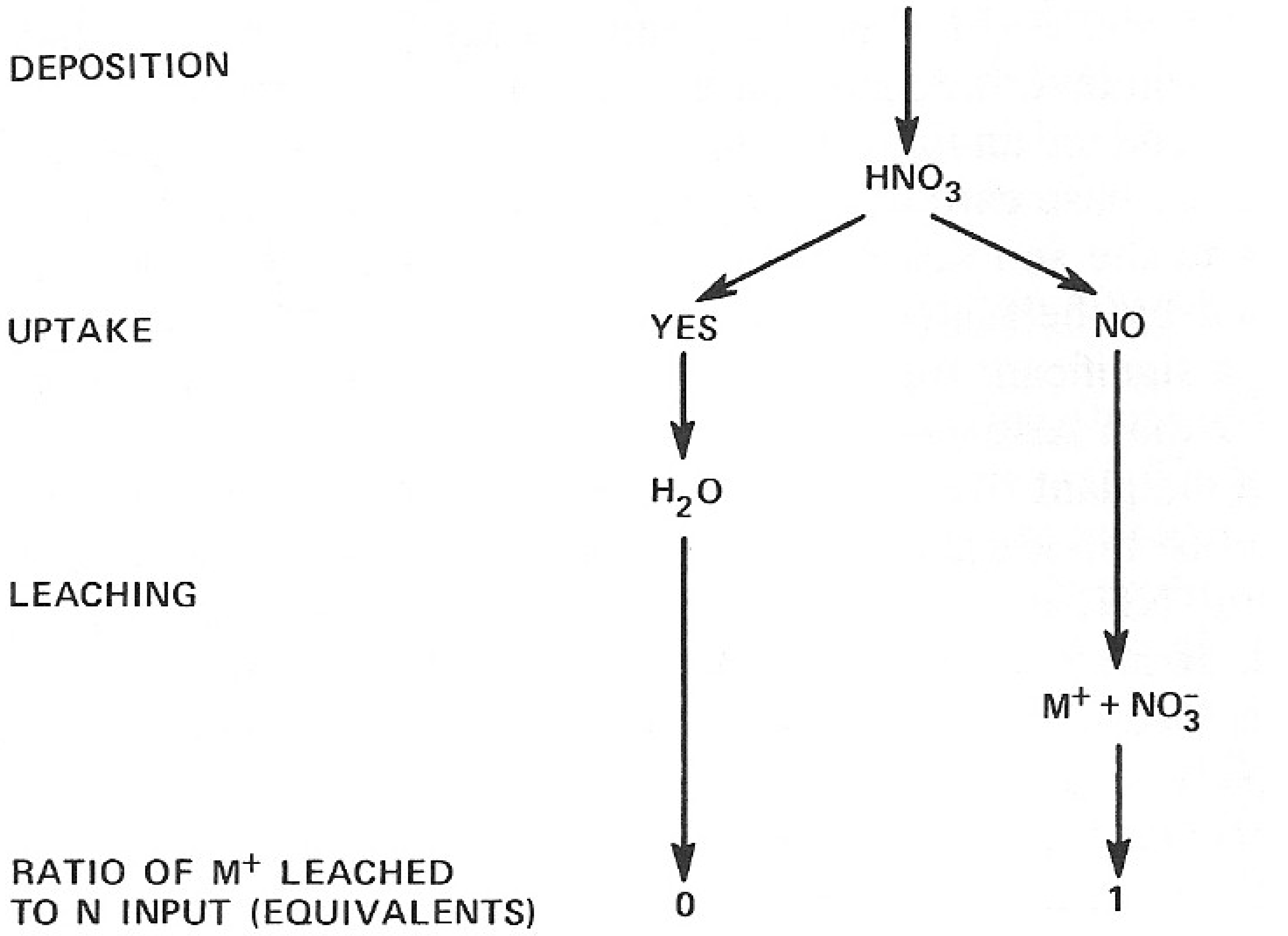


Figure 4.1. Acid–base relationships of the nitrogen cycle. Numbers in parentheses refer to the net production (+) or consumption (−) of H^+ ions in the soil system starting with soil organic nitrogen.

"The net H+ production of the natural nitrogen cycle is zero if (1) no nitrate leaching occurs and (2) no external inputs of nitrogen (e.g., atmospheric) occur"

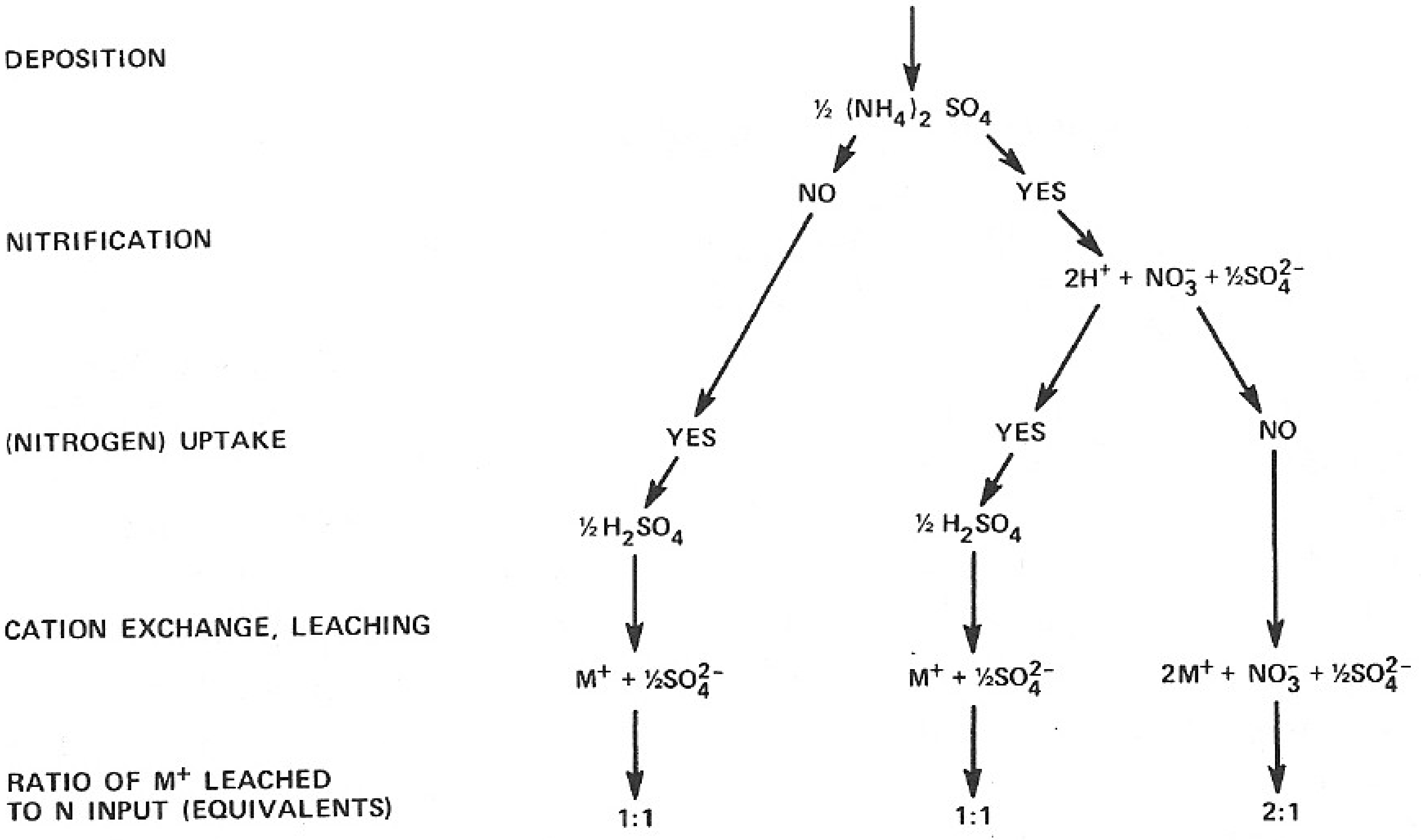
source: Reuss and Johnson (1986)

Nitric acid



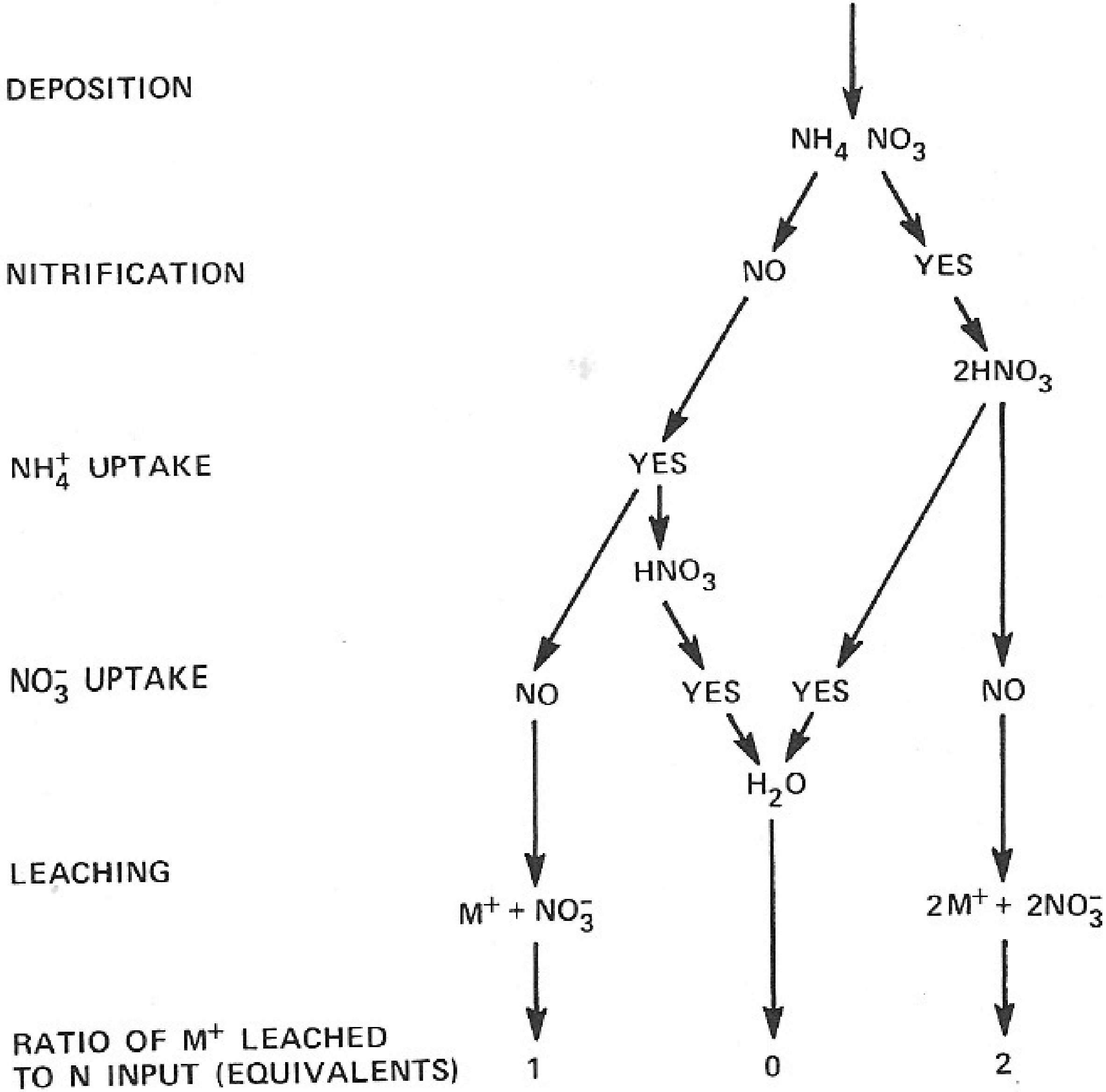
source: Reuss and Johnson (1986)

Ammonium sulphate



source: Reuss and Johnson (1986)

Ammonium nitrate



source: Reuss and Johnson (1986)

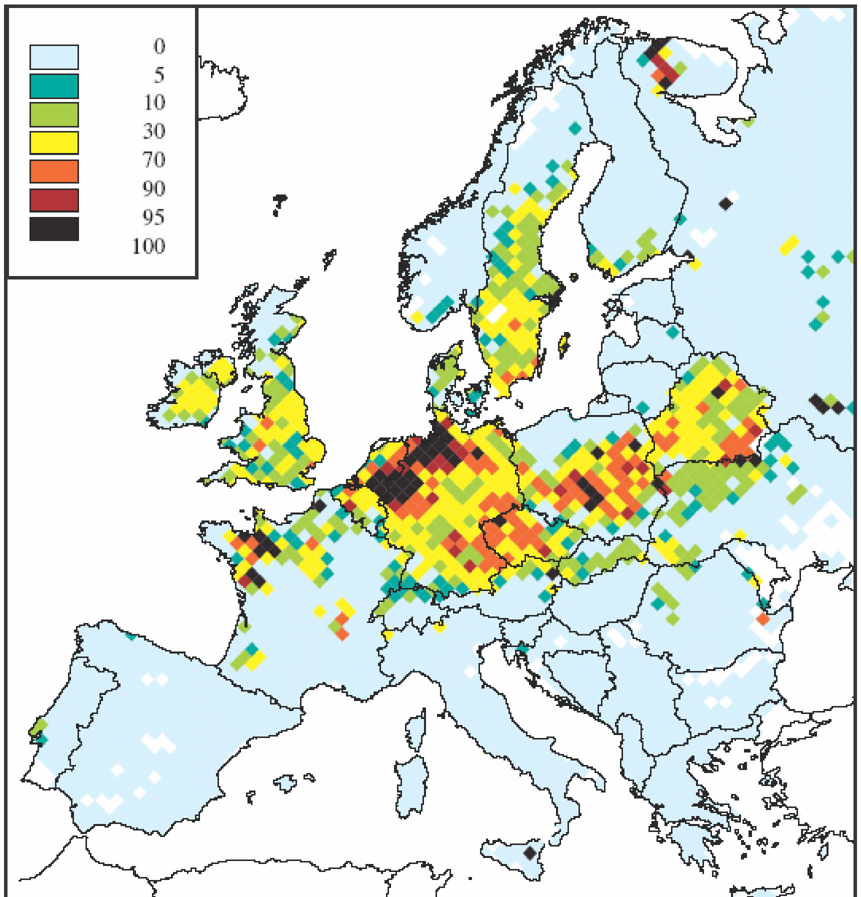
"The potential of nitrogen to acidify the soil through base leaching depends entirely on the fraction of the nitrogen that is leached in the form of NO_3^- and is virtually independent of the form in which the nitrogen enters the soil. In general, nitrogen-rich systems will be subject to NO_3^- leaching, and this leaching will be accelerated by additional atmospheric nitrogen inputs. Nitrogen-limited systems will not be subject to substantial acidification by accelerated NO_3^- leaching"

source: Reuss and Johnson (1986)

"Nitrogen inputs may cause acidification of nitrogen-limited systems through an entirely different mechanism, even though all additional nitrogen is taken up and no leaching occurs. This would occur as a result of increased growth and consequent increases in demands for Ca^{2+}, K^{+} and Mg^{2+} from the soil"

source: Reuss and Johnson (1986)

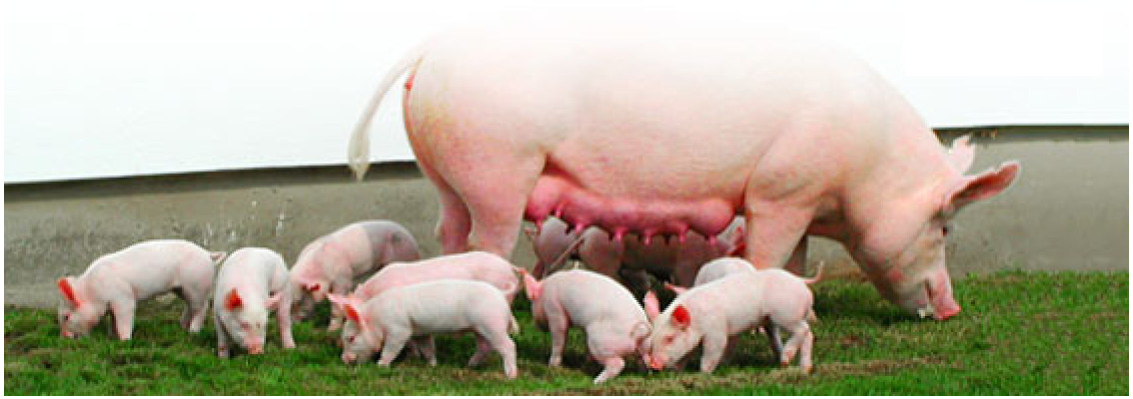
Acid deposition to forests 2020



Percentage of forest area with acid deposition above critical loads, using ecosystem-specific deposition, Average of calculations for 1997, 1999, 2000 & 2003 meteorologies

Conclusions

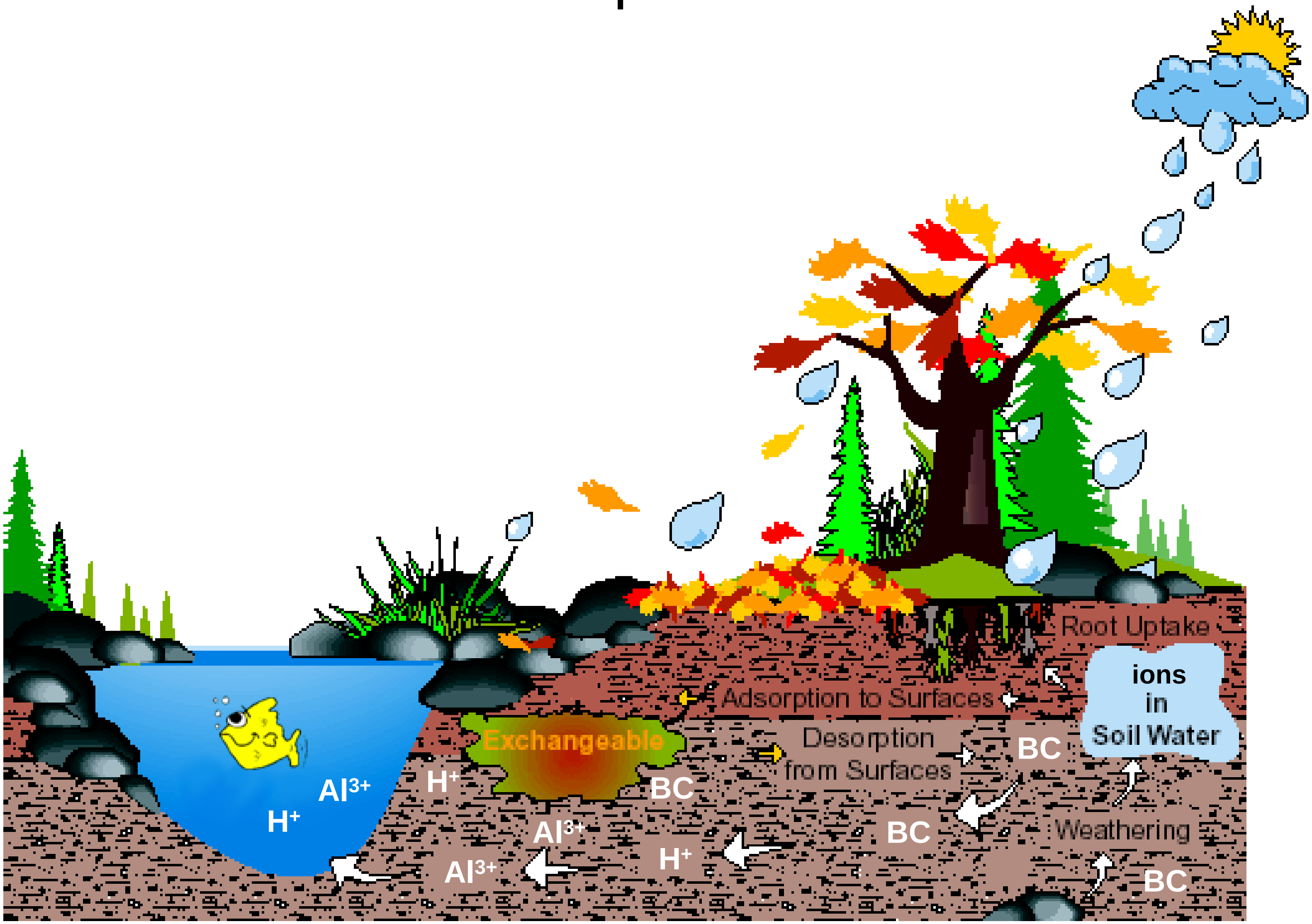
- With decreasing pollution, also impacts are expected to decline in the future.
- However, problems will not be entirely resolved:
  - PM remains serious (~5 months life expectancy loss in 2020)
  - Ozone:
    - Remains a significant cause for premature deaths (Several 1000 cases in 2020)
    - Vegetation damage:
      Wide-spread violations of AOT40 critical level will prevail
  - Acidification: Will not disappear, mainly due to NH_3
  - Eutrophication remains unresolved

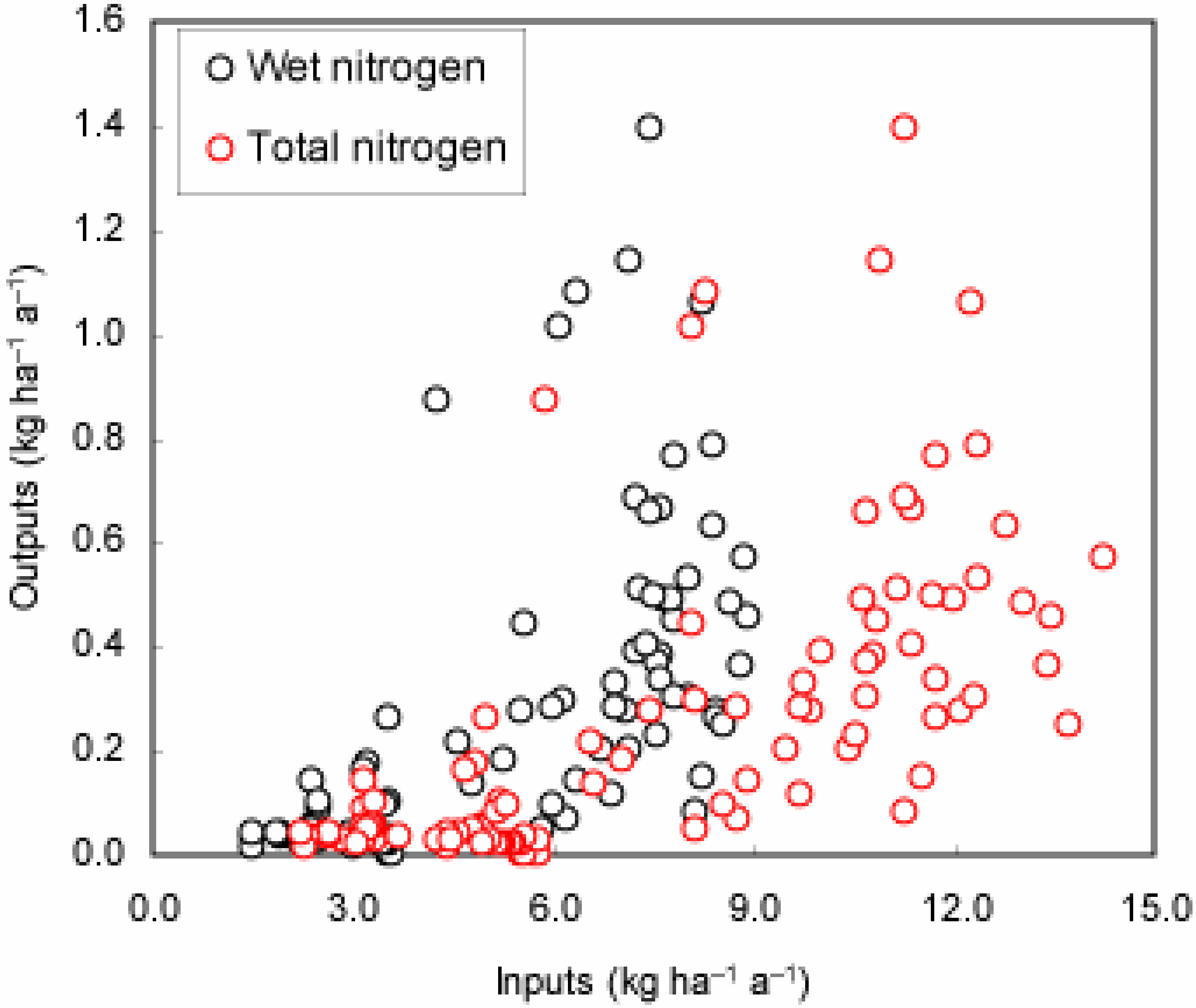


source: www.initrogen.org

The quality of surface water depends to a large extent on the characteristics of the surrounding land. Surface water that is surrounded by soil that does not weather easily usually has limited buffering capacity.

acidification of soils: impacts on freshwaters

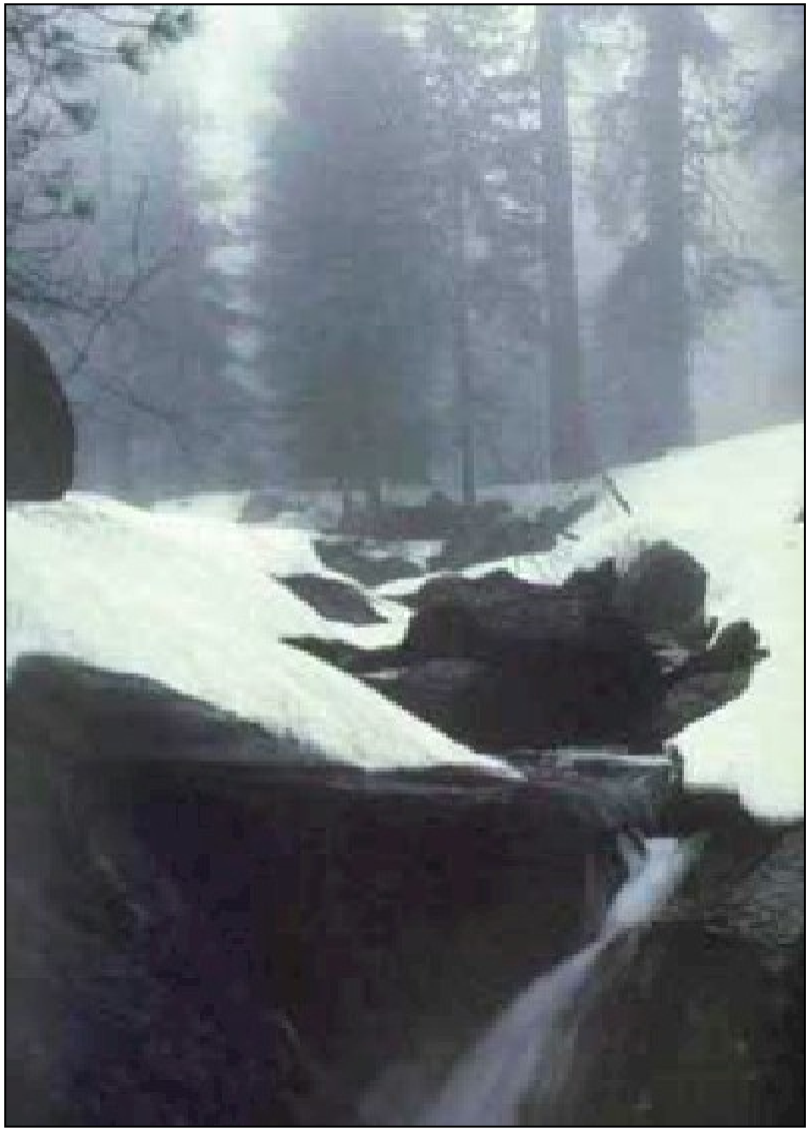




Wet nitrogen
Total nitrogen
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Outputs (kg ha⁻¹ a⁻¹)
0.0
3.0
6.0
9.0
12.0
15.0
Inputs (kg ha⁻¹ a⁻¹)

Nitrate leaching is extremely variable:

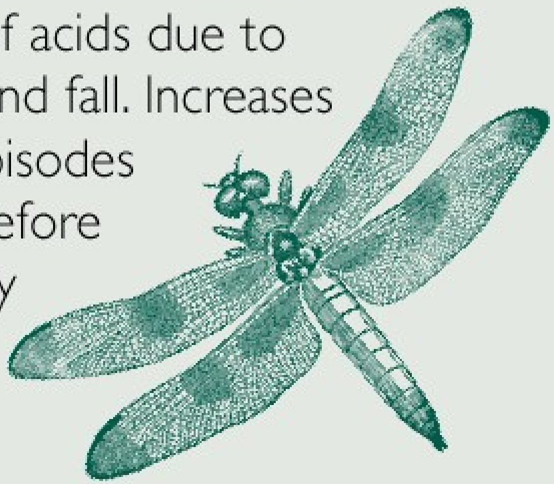
- bare rock
- thin soils
- wetlands
- slope
- soil temperature
- soil moisture
- rain-on-snow
- spring melt



source: nadp.sws.uiuc.edu

Seasonal and episodic acidification

Seasonal acidification is the seasonal increase in acidity and the corresponding decrease in pH and ANC in streams and lakes. Episodic acidification is caused by the sudden pulse of acids due to spring snowmelt and large rain events in the spring and fall. Increases in nitrate are important to the occurrence of acid episodes and tend to occur when trees are dormant and therefore using less nitrogen. Short-term increases in the acidity of surface waters can reach levels that are lethal to fish and other aquatic organisms.



source: www.hubbardbrook.org/hbrf

Increased nitrate (NO_3) concentrations in streamwaters draining forested catchments are reportedly an early indicator of nitrogen (N) saturation. Nitrate concentrations in streams draining 16 forested catchments in south central Ontario were monitored over a 16-year period, during which time N bulk deposition was relatively constant (~9 kg ha^{-1} yr^{-1}). Mean annual NO_3 concentrations in streams were both highly variable among catchments and among years, although patterns of annual concentration were similar among many catchments. Coherence analysis identified two stream groupings. Shallow soils, moderate slopes, low NO_3 concentration, and a large wetland component characterized the first group. The second group had primarily upland characteristics including deeper soils, steeper slopes, higher NO_3 concentrations, and a much smaller wetland component. Patterns in NO_3 concentration in wetland-influenced streams appeared to be related to summer drought and cumulative frost depth, whereas NO_3 concentrations in upland-draining streams appeared to be related to both mean annual air temperature and summer drought. Because a number of different climate parameters as well as the physical character of the catchments apparently influence NO_3 export, NO_3 concentrations in streams are not a good indicator of N saturation in this region.

Climate Effects on Stream Nitrate Concentrations at 16 Forested Catchments in South Central Ontario

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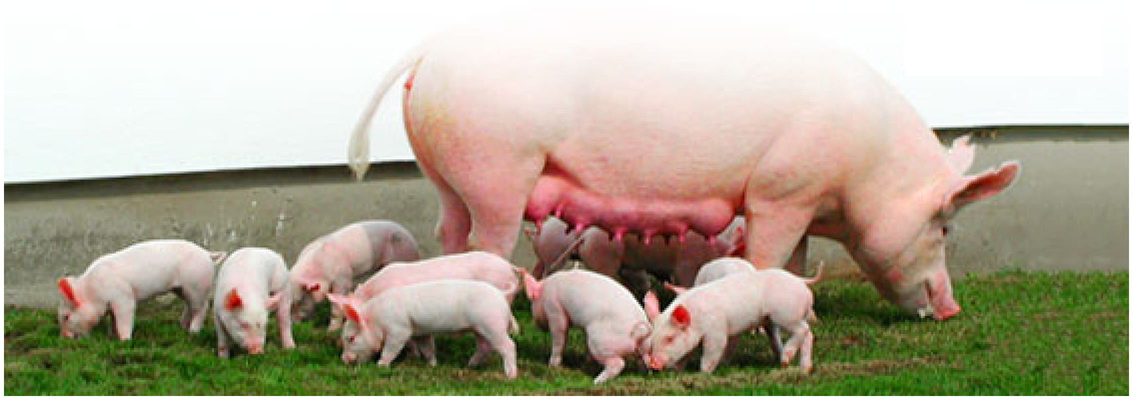


source: www.initrogen.org

Research Needs

The greatest remaining challenge in the study of N saturation of forests is to understand the mechanisms by which large amounts of N are incorporated into forest soils, and to develop a method for predicting N retention capacity.

Nitrogen Excess in North American Ecosystems: Predisposing Factors, Ecosystem Responses, and Management Strategies

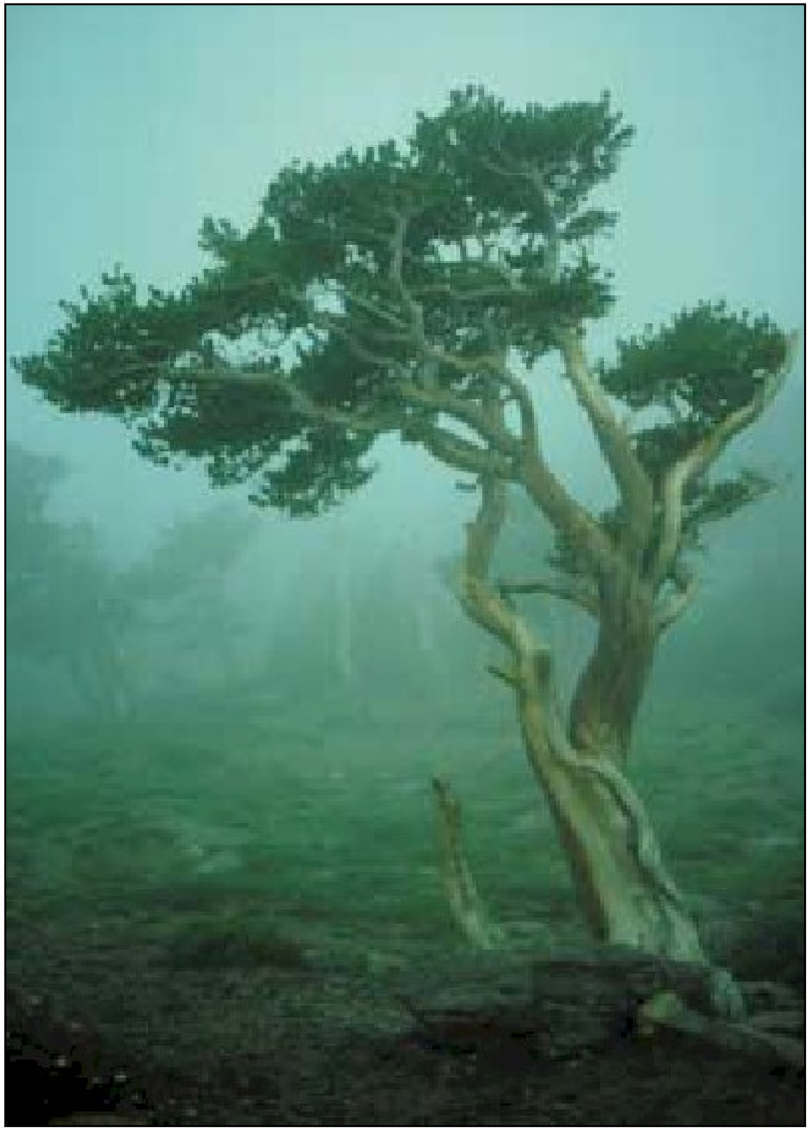
Mark E. Fenn; Mark A. Poth; John D. Aber; Jill S. Baron; Bernard T. Bormann; Dale W. Johnson; A. Dennis Lemly; Steven G. McNulty; Douglas F. Ryan; Robert Stottlemyer

Ecological Applications, Vol. 8, No. 3. (Aug., 1998), pp. 706-733.

Conclusions

- nitrate important contributor to acid precipitation
- nitrogen can contribute to the acidification of sensitive soils but impacts depend on the ‘state of the system’
- nitrate leaching to surface waters is highly variable; however, nitrate is recognised as an important driver in acid episodes
- it would be nice to be able to predict nitrogen retention capacities

If it's true that saturated soil immediately passes additional nitrogen, rather than denitrifying it, that could be bad news for the near future, says Howarth, with all that excess nitrogen flowing straight to groundwater, rivers, streams, and seas. However, he says, we have a very poor understanding of what is actually happening. "If the nitrogen is accumulating in soil, it could be a temporary phenomenon until it saturates the ability to store it. Then we have a much bigger problem," he says. "If it is being denitrified, on the other hand, that's more of a steady-state process, and it can probably continue to do that."



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