Acid Rain Watershed Interactions Revisited

Until recently, the scientific consensus has been that acid-rain-watershed interactions are those of processes which predominate in deep, well-drained mineral soil and the waters derived from them. In such watersheds alkaline minerals dissolve to naturally impart alkalinity to surface waters and normally acid components in rain would be neutralized. Furthermore, the sulfate of the sulfuric acid component of acid rain can be retained in the watershed by reaction with iron and aluminum oxide residues left behind by the dissolving of silicate minerals. These processes effectively minimize the impact of acid rain on the acidity of runoff. The situation is different in the watersheds of acid lakes and streams. The hydrologically most important landscape elements in such watersheds receiving acid rain in North America and Europe are highly acidic, organic rich soil and their associated vegetation. These materials are poor in alkaline minerals, metal oxide residues and runoff is poor in alkalinity; thus the acidity of such waters was asserted to be from acid rain, the consensus being that but small additions of acid can easily acidify runoff from such materials. The more water received from such landscape units the more "sensitive" the watershed was believed to be to acidification by acid rain.

In 1983 Krug and Frink published an article, "Acid Rain on Acid Soils: A New Perspective," in Science offered a competing hypothesis. They said that highly acidic, organic-rich soils and their acid-loving and acid-producing vegetation naturally produce acid runoff and is resistant to further acidification by acid rain. The organic matter of organic-rich soils (peats and humus) is made up of organic acids that dissolve to acidify water. Adding acid reduces the amount of organic acids dissolving thereby resisting (buffering) against further acidification by the acid additions of acid rain.

Recently, on 22 November 2007, Monteith et al. published an article, "Dissolved Organic Carbon Trends Resulting from Changes in Atmospheric Deposition Chemistry," in Nature. This article is the first, clear, large-scale validation of the organic acid buffering hypothesis: that changes in surface water acidity induced by acid rain are offset by changes in organic acidity, the latter as measured by dissolved organic carbon (DOC). Regionally, the study shows that for most acid-sensitive waters, the greater the change in acid rain the greater the change in DOC. Also, the more sensitive the system the greater the change in DOC. Thus this study shows that declining surface water acidity resulting from decreasing acid rain is being partially offset by increasing organic acidity resulting in increasing DOC in most, but not all, acid-sensitive waters: some waters show a decrease in DOC.

Both types of DOC response can be explained by the more recent and comprehensive organic buffering hypothesis (Krug and Isaacson, 1984; Krug et al., 1985; Krug, 1991) which considers the interaction of acid rain with the three major kinds of watershed organic matter: biomass and litter, organic acids of peat and humus, and organomineral complexes of mineral soil. Unlike with the organic acids of peats and humus, acid rain here is consumed by increasing DOC though the dissolving of the other two kinds of organic matter by acid rain. Nevertheless, while the more comprehensive hypothesis more comprehensively explains the data, Monteith et al. (2007) show that acid-rain-organic-acid-interaction to be the predominant one for the watersheds of acidsensitive regions of Europe and North America. Edward C. Krug

References

Krug, E.C. and C.R. Frink. 1983. Acid rain on acid soil: a new perspective. Science 221:520-525.

Krug, E.C. and P.J. Isaacson. 1984. Comparison of water and dilute acid treatment on organic and inorganic chemistry of leachate from organic-rich horizons of an acid forest soil. **Soil Sci**. *137*:370-378.

Krug, E.C., P.J. Isaacson, and C.R. Frink. 1985. Appraisal of some current hypotheses describing acidification of watersheds. **J. Air Pollut. Control Assoc**. *35*:109-114. Krug, E.C. 1991. Review of acid-deposition-catchment interaction and comments on future research needs. **J. Hydrol**. *128*:1-27.

Monteith, D.T., J.L. Stoddard, C.D. Evans, H.A. de Wit, M. Forsius, T. Hogasen, A. Wilander, B.L. Skjelkvale, D.S. Jeffries, J. Vuorenmaa, B. Keller, J. Kopacek, and J. Vesely. 2007. Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. **Nature** *450*:537-540.