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Applied Geochemistry

journal homepage: www.elsevier.com/locate/apgeochem

Acidification of Earth: An assessment across mechanisms and scales

Karen C. Rice^{a,*}, Janet S. Herman^b

^aU.S. Geological Survey, University of Virginia, Charlottesville, P.O. Box 400123, VA 22904-4123, USA

^bDepartment of Environmental Sciences, University of Virginia, Charlottesville, P.O. Box 400123, VA 22904-4123, USA

ARTICLE INFO

Article history:

Received 5 April 2011

Accepted 1 September 2011

Available online xxx

Editorial handling by R. Fuge

ABSTRACT

In this review article, anthropogenic activities that cause acidification of Earth's air, waters, and soils are examined. Although there are many mechanisms of acidification, the focus is on the major ones, including emissions from combustion of fossil fuels and smelting of ores, mining of coal and metal ores, and application of nitrogen fertilizer to soils, by elucidating the underlying biogeochemical reactions as well as assessing the magnitude of the effects. These widespread activities have resulted in (1) increased CO₂ concentration in the atmosphere that acidifies the oceans; (2) acidic atmospheric deposition that acidifies soils and bodies of freshwater; (3) acid mine drainage that acidifies bodies of freshwater and groundwaters; and (4) nitrification that acidifies soils. Although natural geochemical reactions of mineral weathering and ion exchange work to buffer acidification, the slow reaction rates or the limited abundance of reactant phases are overwhelmed by the onslaught of anthropogenic acid loading. Relatively recent modifications of resource extraction and usage in some regions of the world have begun to ameliorate local acidification, but expanding use of resources in other regions is causing environmental acidification in previously unnoticed places. World maps of coal consumption, Cu mining and smelting, and N fertilizer application are presented to demonstrate the complex spatial heterogeneity of resource consumption as well as the overlap in acidifying potential derived from distinctly different phenomena. Projected population increase by country over the next four decades indicates areas with the highest potential for acidification, so enabling anticipation and planning to offset or mitigate the deleterious environmental effects associated with these global shifts in the consumption of energy, mineral, and food resources.

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1. Introduction

Natural sources of acidity in the environment range from volcanic emissions to drainage from newly exposed, sulfide-enriched igneous rocks to decomposing organic matter. A collection of reports on natural low-pH environments recently was published in this journal (Eppinger and Fuge, 2009). Natural acidic settings described by geochemists include those associated with oxidizing sulfide-rich mineral deposits of Cu (Verplanck et al., 2009), Zn, Pb and Ag (Graham and Kelley, 2009), and Fe (Kwong et al., 2009). Volcanic eruptions inject gaseous SO₂ and NO into the atmosphere, where subsequent oxidation to H₂SO₄ and HNO₃ supports aerosol formation (Pueschel, 1996) and causes acidification of local rainfall (Mather et al., 2004). Oxidation of natural organic matter, including petroleum (Borgund and Barth, 1994) and peat (Gorham et al., 1986), is well known to lower the pH of freshwater with organic acids. Unusually low-pH waters, however, are associated with parts of the landscape disturbed by human activities far more

commonly than deriving from natural processes in pristine settings (Langmuir, 1997; Drever, 1997).

In this review paper, the authors explore the nature and magnitude of acidification from human activities that exacerbate the oxidation and hydrolysis reactions of C, Fe, N and S. The objectives of this paper are to (1) describe and compare the mechanisms of anthropogenic acidification of Earth's atmosphere, waters and soils; (2) ensure that specialists in each of the disciplinary fields touched on in this paper are aware of other mechanisms of environmental acidification; and (3) demonstrate that it is the many overlapping sectors of human activity that cumulatively cause acidification of Earth. To the authors' knowledge, no attempt has been made to amass an assessment of all the major anthropogenic acidifying processes. Growing specialization of the sciences has tended to result in a lack of awareness of the useful information that exists in allied fields, limiting the success of comparative studies. This effort is presented to identify and quantify the most influential processes acidifying the environment across a range of spatial scales as a starting point for others to discuss and extend.

The major anthropogenic causes of acidification of the environment are (1) electric power generation, whereby the combustion of fossil fuels affects the atmosphere and the resultant acid is widely distributed to the oceans, freshwaters and soils; (2) resource

* Corresponding author. Tel.: +1 434 243 3429.

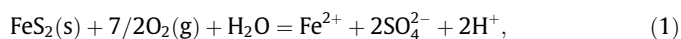
E-mail addresses: kcrice@usgs.gov (K.C. Rice), jherman@virginia.edu (J.S. Herman).

extraction, whereby the mining and processing of mineral and energy resources result in acid mine drainage into freshwaters and emissions from smelting contaminate the atmosphere and soils; and (3) food production, whereby the manufacture and application of N-based fertilizer affect the atmosphere through gaseous emissions as well as alter freshwaters and soils receiving runoff from agricultural fields. These alterations of Earth's environment all increase with expanding human population and resource consumption and have direct consequences for the present and future chemical quality of the atmosphere, waters, and soils that support human life.

1.1. Acidifying reactions

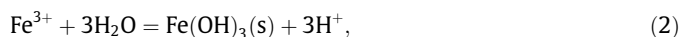
Biogeochemical reactions involving water in contact with the minerals of soil and bedrock and with the gases of the atmosphere result in solutes in aqueous solution, many of which subsequently undergo oxidation or hydrolysis (Hem, 1985). These two types of reactions are notable for their concomitant production of acidity. A typical oxidation reaction utilizes O_2 in the atmosphere or dissolved in water as the oxidizing agent, and the electron-transfer reaction occurs by adding H^+ to the aqueous environment (Stumm and Morgan, 1996). The abundant redox-sensitive elements C, Fe, N and S are intrinsic to human exploitation of energy, mineral and food resources, so oxidation of those elements is at the center of the analysis here.

In the aquatic environment, sulfide undergoing oxidation to sulfate generates acidity (Garrels and Christ, 1965). Exposure of pyrite-containing rocks to O_2 and water through human-induced disturbances associated with mining initiates oxidative weathering,



and the reaction equally describes the oxidative dissolution of marcasite and pyrrhotite.

Frequently the dissolution of a mineral solid in water is followed by hydrolysis of the aqueous cation (Baes and Mesmer, 1976). The cation coordinates with hydroxyl ions (OH^-), the source of which is the self-dissociation of water. Once OH^- is taken up by the cation, H^+ remains in solution, as in this hydrolysis leading to precipitation of an insoluble ferric oxyhydroxide solid phase

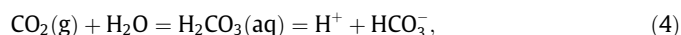


or to formation of aqueous complexes of Fe(III) depending upon local geochemical conditions. The details of aqueous speciation and its interaction with mineral solubility and solution pH have been quantitatively presented in textbooks (Butler, 1998) and in a host of computerized geochemical models such as WATEQF (Plummer et al., 1976).

The growth of organisms requires the fixation and reduction of C into biomass. Following death, oxidation proceeds in Earth-surface environments, ordinarily accelerated by microbial respiration

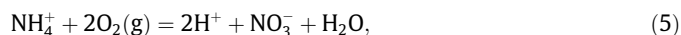


although alternate electron acceptors are utilized in O_2 -restricted environments (Stumm and Morgan, 1996). In aquatic systems, CO_2 gas dissolves, hydrates, and dissociates to form weak carbonic acid



which drives natural weathering reactions (Drever, 1997).

The representation of decaying biomass as C in Eq. (3) is over simplified, because a typical soil organic matter composition is closer to $C_{115}N_{10}S_{1.2}P_3$ (Walker and Adams, 1958). Ammonium (NH_4^+) is the initial N-containing product of microbial decomposition of biomass, and reduced N can follow two pathways: (1) volatilize as gaseous NH_3 and be oxidized in the atmosphere or (2) stay in the soil as NH_4^+ where it can undergo nitrification in the presence of O_2 in the reaction



which generates acidity (van Breemen et al., 1987).

Overall, acidification of the atmosphere, surface waters, and soils results from oxidation reactions, primarily of reduced (1) C compounds, through fossil-fuel burning and a host of other anthropogenic activities; (2) Fe compounds, associated with extraction of mineral and coal deposits; (3) N compounds, through fossil-fuel burning and production and application of N-based fertilizers; and (4) S compounds, associated with removal of mineral and coal deposits and the burning of fossil fuel. The nature and scales of effect of each means of human exacerbation of acidifying processes are summarized in Table 1. Although the complex inter-relations among these numerous processes and the receiving media prevent a neat separation into individual components of the Earth-surface environment, this paper is roughly organized along the hydrological

Table 1
The acidification processes exacerbated by human activities and their environmental effects.

Element oxidized	Means of human exacerbation	Environmental effect	Scale of effect	Nature of effect	Potential for natural amelioration	Trends in human exacerbation
S oxidation generates strong acid, H_2SO_4	Fossil-fuel combustion	Acidic atmospheric deposition	Regional	Acidified receiving waters (freshwater); acidified soils	Rate of bedrock weathering too slow to balance stress; depleted exchange capacity in soils	Western hemisphere emission controls implemented and emissions reduced; global fuel consumption increasing
S oxidation generates strong acid, H_2SO_4	Mining coal and base-metal sulfides; processing and smelting metal-sulfide ores	Acid mine drainage	Local	Acidified receiving waters (freshwater)	Bedrock weathering restricted to geochemically reactive substrate	Global materials and energy consumption increasing
Fe oxidation and hydrolysis releases free protons, H^+						
C oxidation generates weak acid, H_2CO_3	Fossil-fuel combustion; deforestation; cement manufacturing; biofuel development	Elevated CO_2 in atmosphere	Global	Acidification of oceans	Neutralization capacity of oceans inadequate	Global fuel consumption increasing; deforestation increasing
N oxidation generates strong acid, HNO_3	Fossil-fuel combustion; production and use of N fertilizers	Acidic atmospheric deposition	Regional	Acidified receiving waters (freshwater); acidified soils	Rate of bedrock weathering too slow to balance stress; depleted exchange capacity in soils	Global food production and consumption increasing; transportation sector increasing

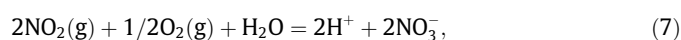
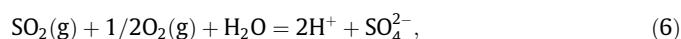
pathway of acidification of the atmosphere, followed by effects on surface waters, first the ocean and then freshwaters, and finally the effect on soils.

2. Acidification of the atmosphere

Combustion of fossil fuels and various industrial and agricultural emissions of reduced C, N, and S compounds support oxidation reactions and the resulting acidification of the atmosphere (Table 1). The largest source of CO₂ and SO₂ released to the atmosphere is from combustion of coal for generation of electric power (Energy Information Administration, 1998). Additionally, significant atmospheric emissions derive from combustion of natural gas and petroleum, refining of crude oil, smelting of ores, burning of forests, and manufacture of chemicals, pulp and paper, steel, Al, and cement, all of which have different spatial scales and location of effect. For example, in Canada, the largest portion of SO₂ emissions (>30%) derives from the base-metals smelting sector, whereas in the USA, 69% of total SO₂ emissions derive from electric power generation. The largest source of NO_x (NO plus NO₂) compounds released to the atmosphere is exhaust emissions from motor vehicles, aircraft, marine vessels, and other forms of transportation, but electric utilities and industrial combustion also contribute (USEPA, 1990). Here, the effect of the major processes acting to acidify the atmosphere are considered.

2.1. Emissions of S and N compounds and acidic atmospheric deposition

Water in equilibrium with an unpolluted atmosphere containing CO₂ and natural organic acids has a pH of about 5.66, which is slightly acidic. Atmospheric deposition with a pH of less than 5 is considered acidic atmospheric deposition, commonly referred to as acid rain (Drever, 1997). The primary cause of acid rain is emission of SO₂ and NO_x to the atmosphere during the combustion of fossil fuels. The S and N compounds undergo oxidation and hydration in the atmosphere in the reactions (Langmuir, 1997)



to form strong acids, H₂SO₄ and HNO₃, which return to Earth as H⁺, SO₄²⁻ and NO₃⁻ through “atmospheric deposition,” i.e., rain, snow, fog, cloud water, gases, as well as dry deposition. Schemenauer (1986) presents a summary of the pH of fog and cloud waters, measured at Earth’s surface and by aircraft at locations around the world, indicating that pH values range from 2.1 to 7.5. The higher pH values likely are influenced by the marine environment. Because cloud water/fog almost always has a lower pH than precipitation and is in contact with vegetation for greater lengths of time, it has the potential to do more harm to the terrestrial ecosystem than precipitation alone. One of the lowest fog–water pH values ever measured, 1.69, was in southern California (Schemenauer, 1986).

Deleterious effects of acid rain on plants, animals, and humans were observed as long ago as the middle of the 17th century in England, when the atmospheric transport of pollutants between England and France was recognized (Bricker and Rice, 1993). By increasing the height of chimneys, pollution was displaced downwind of the source of emissions. The average height of industrial smokestacks in the USA has tripled since 1950 (Patrick et al., 1981). Comparable height increases in most industrialized countries in the 20th century has transformed acid rain from a local urban problem into one of global scale. Indeed, monitoring of wet-deposition chemistry during the 1980s and 1990s at remote locations indicates that even Mt. Fuji, Japan (Dokiya et al., 1995),

the eastern shore of the Baltic Sea (Milukaite et al., 1995), and Torres del Paine National Park, Chile (Galloway et al., 1996) are affected by regional- to long-range transport of anthropogenic pollutants. Because the sources of atmospheric acids are widely distributed across the landscape, even the short atmospheric residence times of hours to days for the pollutants is adequate to support world-wide occurrence of acidic aerosols and compounds.

2.1.1. Decreasing emissions in the Western hemisphere

In the Western Hemisphere, unprecedented economic expansion followed the Second World War, resulting in strongly increasing SO₂ emissions (Fig. 1). In the USA, the Clean Air Act was passed by Congress in 1970 to reduce the adverse effects of acid rain, and amendments were passed in 1990. Similar mandates were passed in Canada and Europe (Warby et al., 2009; Monks et al., 2009), and an Air Quality Agreement between the USA and Canada was signed in 1991. Implemented SO₂ emissions reductions (Fig. 1) were followed by widespread declines in wet SO₄²⁻ deposition, resulting in improvements in surface-water quality across the USA, Canada and Europe (e.g., Stoddard et al., 1999; Skjelkvale et al., 2001; Kahl et al., 2004).

While the progress in decreasing SO₂ emissions is noteworthy, NO_x emissions in the USA continued to increase until 1990, when they peaked at 23.2 × 10⁶ metric tons and were slightly reduced by 2002 to 19.4 × 10⁶ metric tons (USEPA, 2002). Similarly, in Europe, NO_x emissions were the highest at the beginning of the 1990s (about 25 × 10⁶ metric tons NO₂) and although emissions declined by about 32% by 2005, the reductions in recent years have been small (Vestreng et al., 2009). In several European countries, NO_x emissions have increased again, mostly due to vehicular transport (Vestreng et al., 2009). In the USA in 2002, emissions of NH₃ were 3.8 × 10⁶ metric tons, a 2% reduction from 1990 (USEPA, 2002). Atmospheric deposition of NH₄⁺ in the USA, however, has remained more or less constant over the past 30 years (Driscoll et al., 2005).

2.1.2. Increasing emissions in developing countries

In contrast to trends of decreasing SO₂ emissions in industrialized countries, the rapid growth in population and industrialization of developing countries is tied to increasing emission of atmospheric pollutants. Emissions from Africa, Asia and Central and South America are projected to increase significantly by 2020 (Galloway, 1995). Asia’s emissions have been increasing and likely will continue to increase in the coming decades (Bhatti et al., 1992;

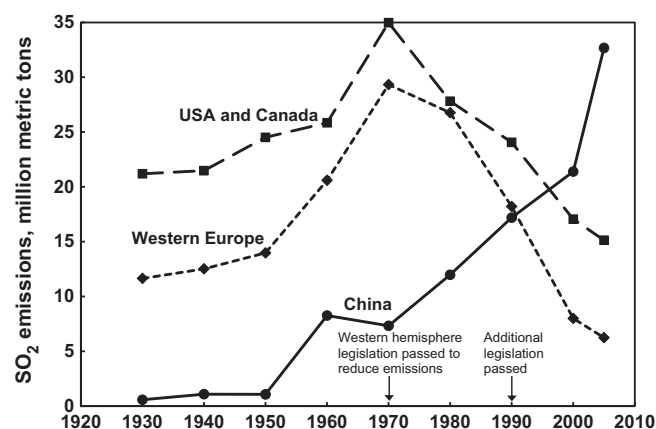


Fig. 1. Annual total SO₂ emissions, including all anthropogenic sources, estimated by Smith et al. (2011). Points represent the emissions estimate for the indicated year for the USA and Canada, Western Europe, and China, 1930–2005 (data from Smith et al., 2011). Lines are linear interpolations plotted in order to better illustrate trends.

Galloway, 1995; Seip et al., 1995; Klimont et al., 2001). During the 1990s, North America and Europe were the leaders in emissions of SO₂ and NO_x to the atmosphere, contributing about 70% of each species (Galloway, 1995). By 2000, China had surpassed the USA and Canada as the world's largest emitter of SO₂ (Fig. 1). By 2005, Asia's contribution to the global emissions of SO₂ and NO_x had increased to 50% and 35%, respectively (Klimont et al., 2009).

Asia's SO₂ emissions today are larger by a factor of 1.6 than the peak in USA emissions in 1973 of 29×10^6 metric tons SO₂ (Zhang et al., 2009). Klimont et al. (2009) estimate that SO₂ and NO_x emissions from Asia each will reach 60×10^6 metric tons by 2020, with higher emissions by 2030 if projected doubling of coal use in India materializes. Klimont et al. (2001) predicted that NH₃ emissions from East Asia (Japan, South and North Korea, China, Mongolia and Taiwan) will double by 2030. More recent estimates by the same group (Klimont, pers. comm., 2010) suggest a slightly lower increase of NH₃ emissions in this region in the same time period (factor of 1.7) and comparable growth rates are expected in other parts of Asia. About half of the SO₂ and NH₃ emitted by Asia originates in China (Zhang et al., 2009).

2.2. Other emissions to the atmosphere

A variety of industrial and manufacturing processes involve the combustion of fossil fuels, including steel and Fe production, municipal waste incineration, petrochemical synthesis, and metals refining (USEPA, 2010). Industrial processes constituted 15% of the fossil fuel combustion in the US in 2008 (USEPA, 2010). Although a thorough assessment of all such processes is beyond the scope of this review, several activities appropriate to a discussion of the acidification of the atmosphere or the surface waters and soils that receive atmospheric deposition are briefly discussed.

Deforestation, including clearing land for agriculture, development, or mining, and harvesting trees for use as a commodity, feedstock for power plants, or fuel, is a problem warranting international attention. To clear land for agriculture, the biomass generally is burned. Combustion of biomass is an important contributor to the global cycles of C, N and S species (Andreae et al., 1988) and, more specifically, a major source of NO_x to the atmosphere (Bobbink et al., 2010). About 90 million hectares (nearly the size of Venezuela) of forest were lost from Earth's surface from 1990 to 2000 (<http://www.un.org/esa/population/publications/pdewallchart/popenvdev.pdf>).

A major component of concrete, the most used human-made material in the world, is cement (C & EN, 2010). The 1.45×10^9 metric tons of annual global cement production account for about 5% of the anthropogenic CO₂ emissions (Worrell et al., 2001), as well as significant emissions of other acid-generating pollutants including SO₂ and NO_x (Horvath, 2004). Although for decades the USA was the largest manufacturer of cement (Flower and Sanjayan, 2007), China has recently claimed that position (Gregg et al., 2008), followed by India and the USA. In the USA in 1997, cement production released approximately 10.1×10^6 metric tons of C (Energy Information Administration, 1998). Cement production consumes about 3% of all energy usage in the USA (CandEN, 2010).

Concentrated Animal Feeding Operations (CAFOs), common in modern industrial agriculture, release significant quantities of NH₃ to the atmosphere and serve as a source of NH₃ runoff into surface waters (National Research Council, 2003). In fact, CAFOs may account for as much as 40% of the agricultural NH₃ emissions to the atmosphere (Aneja et al., 2006). Therefore, the consideration of the effect of N fertilizer usage in crop production discussed in this paper represents only one facet of the N loading and acidification of Earth's surface associated with food production.

3. Elevated atmospheric CO₂ and ocean acidification

The United Nations Population Division (2001) estimates that over 265×10^9 metric tons of C have been released to the atmosphere since 1751, with half of those emissions having occurred since the mid-1970s. The largest sources of CO₂ emissions are from fossil-fuel combustion (57%) and deforestation and biomass decay (17%). Globally, in 2008, approximately 30×10^9 metric tons of CO₂ were released to the atmosphere by the combustion of fossil fuels (USEPA, 2010). Atmospheric CO₂ levels have increased from pre-industrial levels of 280 parts per million as volume (ppmv) to nearly 384 ppmv, an increase of nearly 40% (Solomon et al., 2007).

About one third of the anthropogenic CO₂ released into the atmosphere in the past two centuries has been taken up by the ocean (Sabine et al., 2004), and the current annual rate of global oceanic uptake is estimated to be 2.2×10^9 metric tons C (Mikaloff Fletcher et al., 2006). As the ocean surface absorbs CO₂, pH is lowered according to Eq. (4) (Orr et al., 2005). The recently increased concentration of CO₂ in the atmosphere and the oceans has already resulted in the ocean becoming more acidic, with an average decrease of 0.1 pH units (Doney et al., 2009). Projections of global CO₂ emissions and resultant future atmospheric CO₂ concentrations lead to a prediction of an additional decrease in ocean pH of 0.1–0.35 units by the end of this century (IPCC, 2007), and longer-term predictions are even more severe (Caldeira and Wickett, 2003). Although still an alkaline solution, ocean pH decreasing from a value of 8.2 to 8.1 is a change causing significant scientific and societal concern (National Research Council, 2010). Thermodynamic expectations from a lowered pH include undersaturation with respect to aragonite and calcite and, therefore, an effect on the growth of calcifying organisms (Orr et al., 2005; Millero, 2007). Laboratory studies indicate that the current level of lowered ocean pH would noticeably affect carbonate biomineralization (Riebesell et al., 2000), and field studies are now beginning to document an effect (de Moel et al., 2009). In addition to the direct destabilization of calcitic and aragonitic organisms, dependent organisms may be compromised indirectly when, for instance, carbonate reef dissolves (Silverman et al., 2009).

Other human activities are affecting seawater chemistry and the ocean's acid-base balance, but not nearly to the extent of anthropogenic atmospheric CO₂-driven acidification (Doney, 2010). Acidic atmospheric deposition, which contains H₂SO₄ and HNO₃ derived from fossil fuel combustion (Eqs. (6) and (7)), falls on the coastal and open oceans, and input of nutrients by surface-water runoff, which includes NH₃ that subsequently generates HNO₃ upon nitrification (Eq. (5)), provide a net acidic input to the oceans. Although these effects of strong acids on surface ocean chemistry may be important locally and regionally, it amounts to only a few percent of the global ocean acidification driven by rising atmospheric CO₂ concentration (Doney et al., 2007).

In 2008, China led the world in total emissions of CO₂ (6.53×10^9 metric tons) (Energy Information Administration, 2008), reflective of that nation's position as the world's largest energy consumer (<http://www.iea.org/>), largely from coal combustion (Fig. 2). Yet, China's per capita CO₂ emission rate, 4.91 metric tons, is only 26% the rate of per capita emission in the USA (19.18 metric tons) (http://www.ucsusa.org/global_warming/science_and_impacts/science/each-countrys-share-of-co2.html). An even greater contrast can be made between India and Japan with comparable national emissions of 1.50 and 1.21×10^9 metric tons, respectively, yet India's per capita emission rate is 1.31 metric tons to Japan's 9.54 metric tons. The current distribution of CO₂ emissions is destined to shift as the more populous nations become more industrialized. If India were to modestly increase its per capita CO₂ emission to match the current level in China, the total emission would jump to

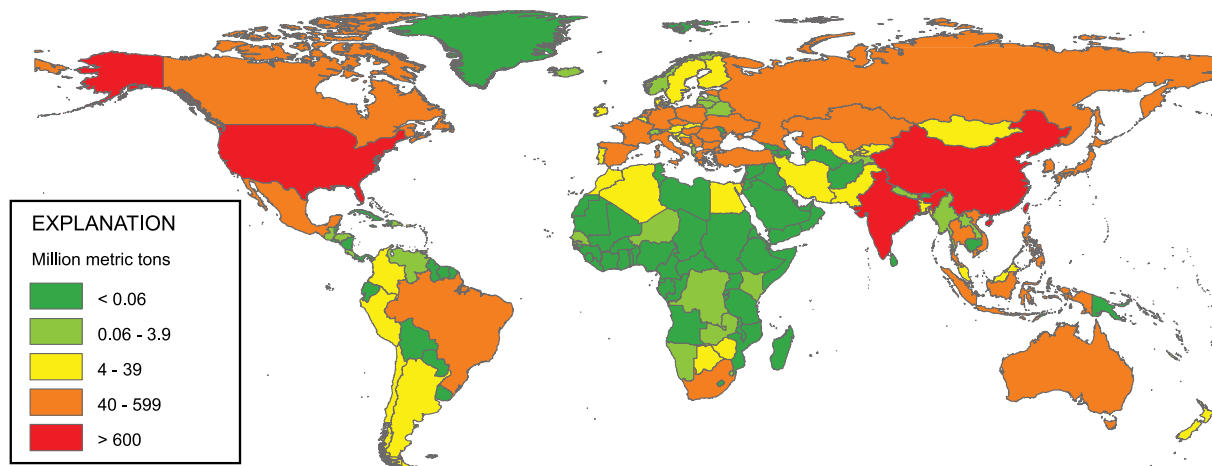
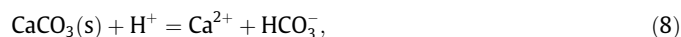


Fig. 2. Coal consumption by country in 2009 (<http://www.eia.gov/cfapps/ipdbproject/iedindex3.cfm?tid=1&pid=1&aid=2&cid=regions&syid=2009&eyid=2009&unit=TST>). The values defining the five brackets of amount of coal consumed were selected so as to identify the top 3 consuming countries (red), the next 15 (orange), next 30 (yellow), next 50 (light green), and the rest (dark green). Countries with no reported data are shown as white. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

5.76×10^9 metric tons per year without any population increase. With outputs on the order of 6×10^9 metric tons per year from each of China and the USA, reduced emissions from industrialized countries such as Germany ($\sim 800 \times 10^6$ metric tons), Canada ($\sim 600 \times 10^6$ metric tons), and the United Kingdom ($\sim 600 \times 10^6$ metric tons) are going to have minimal effect on atmospheric loading of CO_2 and ocean acidification.

3.1. Neutralizing reactions important in the oceans

The overall control of pH in the oceans has long been linked to the equilibria involving CO_2 and CaCO_3 as influenced by temperature and pressure and moderated by biological uptake (Holland, 1978; Millero, 2007). Solid CaCO_3 reacts with H^+



and the source of protons is H_2CO_3 (Eq. (4)). The slight supersaturation typical of surface seawater with respect to aragonite, a CaCO_3 polymorph composing the shells, tests, or skeletons of many marine organisms, is moderated by biological activity (Holland, 1978). In response to ocean acidification, calcite (e.g., foraminifera) and aragonite (e.g., corals, mollusks) dissolution will be favored (i.e., Eq. (8) shifts to the right), thereby preventing the growth of new skeletal parts or dissolving marine organisms or their structural substrate directly (Doney, 2010). The strong inverse temperature dependence of CO_2 solubility has resulted in the polar oceans acidifying more rapidly than mid-latitude waters (Fabry et al., 2009). Recent reports of seasonal undersaturation with respect to aragonite in polar surface waters have focused particular concern about ecosystem stability in oceans undergoing acidification (Bates et al., 2009).

4. Acidification of freshwaters

In the hydrological cycle, atmospheric water is delivered to the land surface, supplying rivers and lakes as well as groundwater (Winter et al., 1998). Delivery of acid and incompletely oxidized compounds of S and N by atmospheric deposition has a deleterious effect on the quality of Earth's freshwaters (Gorham, 1989). Anthropogenic activities have degraded freshwaters (Table 1); notably, acid mine drainage (AMD) has presented problems in coal and metal mining regions of the world. Although a survey of surface waters in the USA in 1991 revealed that 25% of acidic lakes and streams were dominated by natural organic acids, the role of human disturbance

was clear: 26% of acidic streams came about from AMD and 47% of acidic streams and 75% of acidic lakes were deemed to be affected primarily by acidic atmospheric deposition (Baker et al., 1991). Direct runoff of N from fertilized crop fields resulting from precipitation or irrigation can recharge groundwater and contribute to groundwater contamination, or discharge to streams or lakes and cause surface-water acidification (Rabalais, 2002).

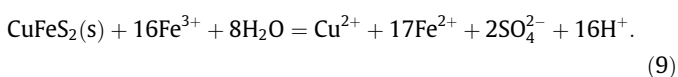
4.1. Acid mine drainage

Oxidation of reduced Fe and S by dissolved O_2 in surface waters generates intensely acidified waters in local settings. The production of acid is so commonly a result of the exploitation of metallic ores and coal that the term AMD is readily known to many lay readers, is included in mineral resources textbooks (Craig et al., 2001), and has been the subject of extensive scientific study (Blowes et al., 2003). AMD typically refers to water of pH 2–4.5 with significant concentrations of dissolved SO_4^{2-} , Fe, and other metals (Bates and Jackson, 1984; Langmuir, 1997). In the 1960s, over 16,900 km of streams in the coal-mining regions of the Appalachian Mountains were compromised by acidity (Appalachian Regional Commission, 1969). The total effect of AMD on water quality has been and continues to be profound and without universally uncomplicated remediation techniques (Evangelou and Zhang, 1995).

The common thread to the generation of acid waters from the weathering of sulfide minerals is exposure to O_2 -containing air and water. Pyrite (FeS_2), the most abundant metal-sulfide mineral in Earth's crust (Klein and Hurlbut, 1999), oxidation (Eq. (1)) occurs through stepwise reactions that proceed at differing rates and are catalyzed by bacteria to differing degrees (Singer and Stumm, 1970; Moses et al., 1987). The formation of "yellowboy," a mix of Fe(III) oxyhydroxide solids, including goethite, ferrihydrite, and amorphous material (Jambor and Dutrizac, 1998), releases acidity (Eq. (2)). Although oxidative weathering and the production of acid rock drainage does occur naturally (e.g., Verplanck et al., 2009), any disturbance of pyritic bedrock greatly accelerates acid generation. Mining, the first operation in the commercial exploitation of a mineral or energy resource (Lottermoser, 2007), involves breaking solid rock that frequently contains sulfide minerals into increasingly smaller sizes, thereby exposing extensive fresh surfaces of sulfide minerals. Subsequent steps in the recovery of the desired resource include mineral processing to separate and concentrate the ore of interest and, in the case of metals, smelting; each of these steps produces acid-causing wastes (Lottermoser, 2007).

4.1.1. Metal ores

The economic importance of metallic ore deposits is central to the development of industrialized societies, and the processes and products of local mineralization are many (Park and MacDiarmid, 1975). Metals are often exploited from sulfide mineral deposits where, in addition to pyrite, the ore minerals are subject to the same oxidative weathering reactions that produce acidity. These minerals may be part of the bulk mineralization of the country rock, or they may constitute the ore body itself (Rose and Burt, 1979). The value of the metallic ore can be so great as to make moving mountains of Earth worthwhile in order to reach and remove the ore. The Bingham Canyon porphyry Cu deposit in Utah, USA, has yielded 16.42×10^6 metric tons Cu, obtained by moving approximately 9.2 km^3 of Earth (<http://www.kennecott.com/visitors-center/amazing-facts/>). Sulfide minerals comprise the ore, notably chalcopyrite (CuFeS_2) and chalcocite (Cu_2S), as well as gangue, primarily FeS_2 , throughout the hydrothermally altered granite of the region. Kimball et al. (2010) point to the great potential for acid generation in chalcopyrite oxidation by ferric iron



Sulfide mineralization in a porphyry Cu deposit is finely disseminated throughout felsic igneous country rock. The dispersed character of the sulfide mineralization (Singer et al., 2008) requires that vast volumes of rock be blasted and crushed in order to recover the ore. In open-pit mining operations, waste rock is heaped into massive benches of unconsolidated waste and impounded into expansive tailings ponds, both of which are subject to oxidation and acidification. The disseminated porphyry deposit is the leading source of Cu worldwide, with numerous deposits of nearly the scale of Bingham Canyon throughout the American Cordillera. Annual mine production (Fig. 3a) in the USA was last reported for the year 2008 as 1.31×10^6 metric tons Cu (USGS, 2009). The largest open-pit Cu mine in the world, Chuquibambilla, Chile, produced 5.6×10^6 metric tons Cu in 2008 (USGS, 2009). Using global annual total mine production of Cu metal of 15.7×10^6 metric tons (USGS, 2009), a rough calculation of S released, assuming a 2:1 molar ratio of S:Cu as in Eq. (9) for chalcopyrite, amounts to 15.8×10^6 metric tons of S. An estimate of acid-generating potential amounts to 4.0×10^6 metric tons of H^+ assuming all Cu comes from chalcopyrite (Eq. (9)). This amount of acid generation is a minimum calculation given that it is driven by the reported production of Cu metal without any consideration of the oxidation of the commonly co-occurring gangue mineral pyrite.

Abandoned open-pit mines have left behind one of the most noxious legacies of AMD known (Alpers and Blowes, 1994). When mining ceases and dewatering pumps are turned off, groundwater moves back into the mine. This oxygenated water comes into contact with pyrite-containing bedrock and produces an acid-rich solution (Eqs. (1) and (2)). Berkeley Pit near Butte, Montana, USA, is an abandoned open-pit Cu mine that at its highest stand contained $\sim 215 \times 10^9$ L of acidic, saline, metalliferous water (Davis and Ashenberg, 1989). Although pH varies with depth, season, and year, the 15-a median pH = 2.63 at the surface (Pellicori et al., 2005) has changed little since 2003 when a plant began treating influent water from flooded mine shafts in an effort to divert water and lower the lake level. Semi-annual monitoring shows pH ranging from 2.37 to 2.93 in the lake (Duaiame and Tucci, 2009). Even though none of the water in the flooded mine shafts (pH range 3.13–8.26), the underlying aquifer (pH range 4.01–7.32), or nearby surface streams (for example, median pH of a spring = 3.10) are as noxious as the acidic, metal-rich water in Berkeley Pit Lake (Pellicori et al., 2005), they are sufficiently contaminated to be

included in the USEPA clean-up effort for this mine site (Duaiame and Tucci, 2009).

Active mining and mineral processing facilities dispose of pulverized waste rock in tailings ponds and waste heaps near the mine. The timescale of acid generation from pyrite oxidation in mine wastes depends upon factors including degree of water saturation, hydrological transport rates, and mineral grain size; nevertheless, predictive modeling studies indicate that acid generation typically continues for hundreds of years (Ritchie, 1994). Finely crushed waste rock left over from ore beneficiation is typically pumped in slurry to a tailings pond. This surface-water impoundment provides favorable conditions for sulfide mineral oxidation and acid generation. Tailings impoundments, with acidic, metal-rich water, may contaminate the surrounding aquatic environment by infiltration to groundwater and subsequent downgradient flow or by uncontrolled overflow to downstream surface water. The downstream transport of acid and metals has affected rivers (Rampe and Runnells, 1989; Keith et al., 2001) and lakes (Lee et al., 2008; Suchanek et al., 2009) in many locations around the world.

The local acidification of freshwaters as a result of mining metallic ores is only part of the legacy of metals exploitation. The subsequent smelting (Fig. 3b) and refining of ores typically releases SO_2 in the flue gases as well as fine particulates of metal sulfide minerals, leading to strong acid and metal contaminating waters and soils in the nearby region (Nriagu et al., 1998). While industrialized countries have dramatically improved smelter emissions since the 1970s (Keller et al., 1999), severe degradation of water and soil quality continues in developing countries, notably in Eastern Europe (see papers in a special issue of this journal edited by Fuge et al., 1996).

4.1.2. Coal

The effect of AMD in the coal-mining areas of the eastern USA has been profound (Herlihy et al., 1990). Historically, AMD was the single largest water-pollution problem in the Appalachian Mountains where surface streams, especially in Pennsylvania, West Virginia and Ohio, were severely degraded (Appalachian Regional Commission, 1969). Anthracite mining of the early 1900s left major rivers in the metamorphic terrain of eastern Pennsylvania with pH as low as 4 (Raymond and Oh, 2009) and small streams draining mined areas with pH values frequently below 3 (Rose and Cravotta, 1998). The historical shift in exploitation from finite deposits of anthracite located narrowly in the easternmost provinces of the Appalachian Mountains to the larger deposits of bituminous coal of widespread occurrence further expanded the area of degraded water quality, leaving AMD an integral part of the history of the 11 Appalachian states (Biesecker and George, 1966).

The transformation of a region hobbled by AMD comes about by reduction in mine production, improvements in mining and restoration regulations, and natural neutralization by water-rock interactions. In the Appalachian coal region, sedimentary sequences that include extensive limestone and dolomite are critically important to the environmental amelioration of acid drainage (Raymond and Oh, 2009). Acid released from sulfide oxidation comes into contact with rocks and minerals of bedrock and soil and is to some degree neutralized (Jambor et al., 2007), a fact that has been used in both passive and active remediation strategies (Skousen et al., 1998). Calcite, the predominant mineral in limestone, dissolves in contact with AMD (Eq. (8)) releasing bicarbonate alkalinity and neutralizing the pH of the acidic drainage. The extent to which the drainage is neutralized depends upon availability of carbonate minerals within the sedimentary sequence, the extent of reactive surface areas (White and Peterson, 1990), and rate of mineral dissolution (Plummer et al., 1978; Herman and White, 1985). There are a few cases where gangue minerals in the tailings provide

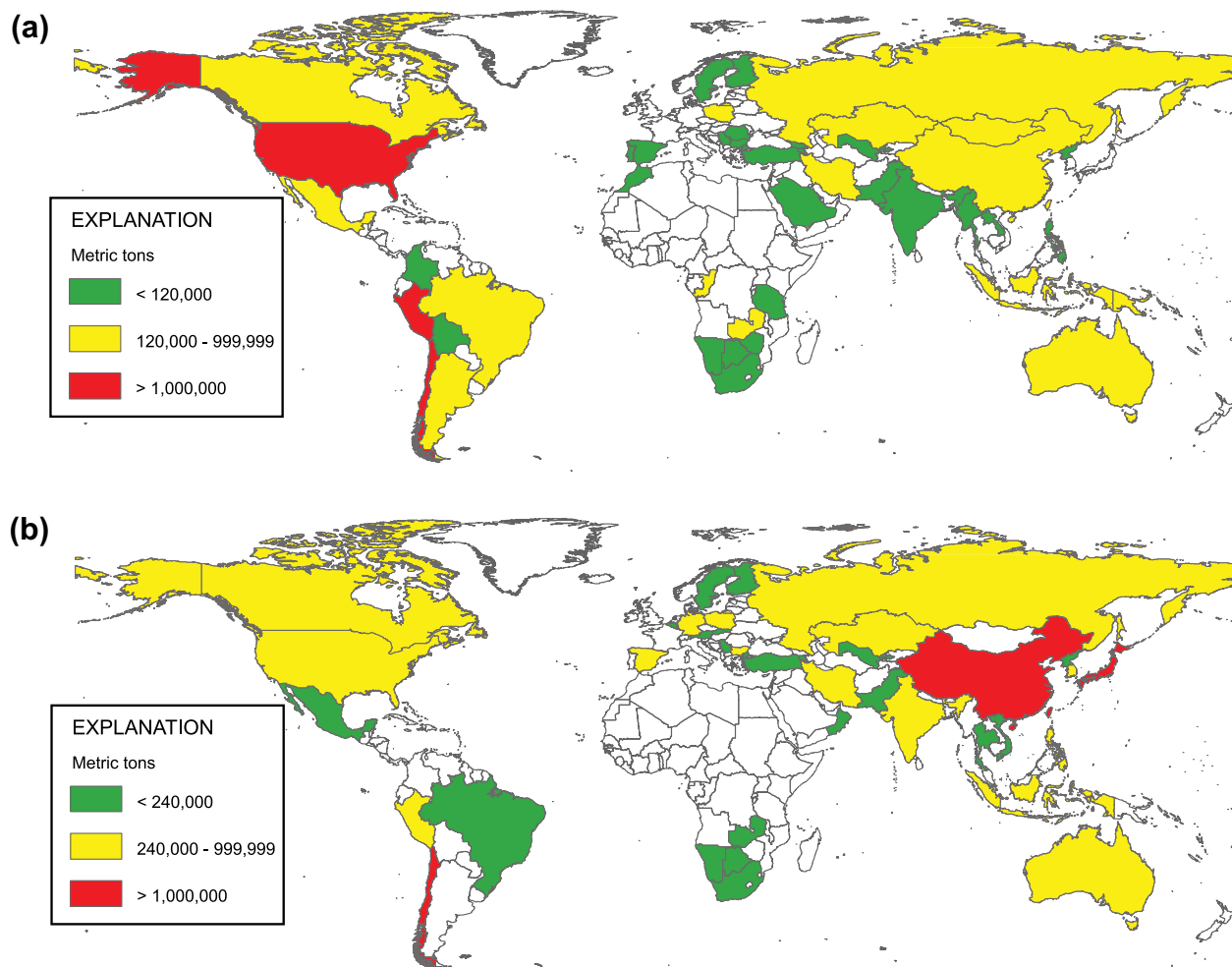


Fig. 3. Copper production by country in 2008 from (a) mines (http://www.indexmundi.com/en/commodities/minerals/copper/copper_t20.html), and (b) smelters (http://www.indexmundi.com/en/commodities/minerals/copper/copper_t21.html). The values defining the three brackets of amount of Cu produced were selected so as to identify the top 3 consuming countries (red), the next 15 (yellow), and the rest (dark green). Countries with no reported data are shown as white. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

adequate neutralizing capacity and the resultant drainage has circumneutral pH (Chappell and Craw, 2002). In another setting with underlying limestone, however, natural *in situ* neutralization was limited owing to the precipitation of oxidized Fe cements preventing further calcite dissolution (Germain et al., 1994).

Hydrological processes play a role in the generation and mitigation of acid drainage. Many former mines become flooded following cessation of pumping during mining. Initially oxygenated water rapidly oxidizes pyrite associated with the interbedded sedimentary rocks (Eq. (1)). Subsequently, O₂-depleted static water in flooded mines dramatically slows the rate of continuing pyrite oxidation and, therefore, acid generation (McDonough et al., 2005), resulting in improved quality of discharge water. Cravotta (2008) assessed 140 abandoned coal mines in Pennsylvania and found pH to range from 2.7 to 7.3, depending upon hydrological factors, such as residence time and dilution, as well as geochemical factors, such as reactivity of wall rock. Overburden, in contrast, remains unsaturated and is subject to continuing infiltration of water and contact with the O₂-containing atmosphere, so the generation of acidity continues and acidic effluent can reach a pH as low as 1 (Gerke et al., 1998). Similar reactions, slowed by O₂ diffusion through water-filled pore spaces, occur in tailings impoundments such that they can also be a continuing source of strong acid (Wunderly et al., 1996).

4.2. Acidic atmospheric deposition

Acidic atmospheric deposition is the transfer of strong acids from the atmosphere to the surface of Earth. Much of the knowledge about the effects of acidic atmospheric deposition is based on small catchment studies, settings that are subject to successful monitoring of stream discharge and wet precipitation such that input–output mass balances of major ions can be calculated. Through forested catchment studies in the 1960s, it was recognized that the transport of acidic pollutants across national boundaries was having an effect on lakes and streams in Scandinavia, where the link among acid rain, surface-water acidification, and loss of fisheries was documented (Gorham, 1989). Through catchment studies at the Hubbard Brook Experimental Forest in the USA, Birkenes in southern Norway, and many other research sites, it was learned that some catchments are base-cation poor, and, therefore, acid sensitive, in contrast to well-buffered catchments, which have abundant base cations and a greater ability to buffer acidic inputs. Base-poor catchments acidify within years, whereas their well-buffered counterparts may never acidify from deposition of strong acids (Driscoll et al., 2001).

Acidification of surface waters by acidic atmospheric deposition has been observed in most industrialized parts of the world. Examples include Great Britain, the Nordic countries, and northern,

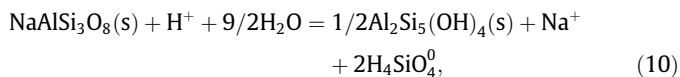
central, and eastern Europe (Evans et al., 2001); southeastern Canada (Jeffries, 1991); and eastern USA (Cronan and Schofield, 1979; Driscoll, 1991; Bricker and Rice, 1989). Despite two decades of decreased acidic atmospheric deposition in Germany, stream-water SO_4^{2-} concentration has decreased only slightly, and pH has not increased (Alewell et al., 2001).

Emissions of SO_2 and NO_x in industrialized countries have been and will continue to be reduced, but not eliminated, region by region. Meanwhile, other parts of the world will continue to contribute to acidic atmospheric deposition, at a magnitude even larger than occurred during the 20th century (Fig. 1). Thus, there is a “wave” of acidic atmospheric deposition-induced acidification moving across the landscape, leaving behind a “wake” of ecological damage that can linger for 2–6 decades (e.g., Cosby et al., 1985; Alewell et al., 2000), even centuries (Blake et al., 1999). Acidic atmospheric deposition is a common regional problem and will continue to be until Earth’s fossil-fuel resources have been depleted or until humankind develops alternate methods to produce sufficient energy for its “energy hungry” population.

4.3. Neutralizing reactions important in freshwaters

Some inorganic solutes as well as various organic species in natural waters are capable of buffering the solution against pH change, and their presence is widely used to indicate the susceptibility of a water body to acidification (Hemond, 1990). A quantitative measure of the ability of water to neutralize strong acid is the acid-neutralizing capacity (ANC), which is more or less equivalent to alkalinity (Drever, 1997). Strictly the sum of all the titratable bases minus the strong acids, ANC also can be expressed as the sum of base cations minus strong acid anions (Morel, 1983). Water bodies are considered to be “acidic” when $\text{ANC} \leq 0 \mu\text{eq/L}$. For example, a stream draining a base-poor catchment that receives acidic atmospheric deposition might have an $\text{ANC} < 0 \mu\text{eq/L}$, because the sum of the strong acid anion equivalents from the acidic deposition is greater than the sum of the base cation equivalents derived from bedrock weathering.

The minerals of soils and bedrock react to take up protons from the aquatic environment, typically releasing base cations to solution in the process. The possibilities for acid neutralization by water–rock interactions are nearly endless because most minerals dissolve in acid (Langmuir, 1997). The chemical composition of the bedrock underlying an area largely determines its surface-drainage chemistry (Walling and Webb, 1975; Johnson and Reynolds, 1977; Velbel, 1985) as well as the degree to which the area can ameliorate anthropogenically produced acids (Newton et al., 1987; Bricker and Rice, 1989). The classic weathering reaction for feldspar to form clay



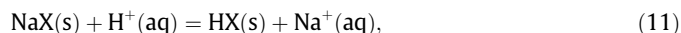
consumes protons and supports pedogenesis (van Breemen et al., 1983). Feldspar is a primary mineral constituent in granite, the predominant rock type underlying terrestrial settings (Grotzinger et al., 2007). Numerous bulk rock types demonstrate capacity to neutralize acid (Craw, 2000; Skousen et al., 2002; Jambor et al., 2007). The rates of reaction become critical to anticipating the short-term amelioration of acid drainage, and silicates are widely reported as slow to react (Lasaga, 1984; Sherlock et al., 1995). The rates of incongruent dissolution of individual aluminosilicate minerals have been studied in the context of soil formation (Schnoor, 1990; White et al., 1996), and those rates are inadequate to ameliorate acid loading at the current pace generated by humans.

The dissolution of calcite (Eq. (8)) is a faster neutralization reaction (Plummer et al., 1978) that provides significant natural

buffering capacity where it is present. Carbonate sedimentary rocks underlie 20% of the land surface (LaMoreaux, 1995), and calcite also is present as veins and cements in metamorphic and igneous rocks. Calcite has been used in localized and regional environmental neutralization efforts (Hedrin et al., 1994; Driscoll et al., 1996). Liming, the application of any base-rich material (e.g., ground limestone, soda ash) to surface waters, sediments, or soils with the intention of neutralizing the acidity, is the most commonly used technique for mitigating acidic surface waters (Olem, 1991). The results of application of the buffering material to the receptor are immediately observable, however, they are not permanent once the buffering capacity is exceeded and as long as the acidic input continues.

5. Acidification of soils

Natural processes such as organic matter accumulation and oxidation; N and S oxidation during the decomposition of plant residues; plant uptake of cations; and the deposition of weak carbonic acid all act to acidify soils (Brady and Weil, 2002). Under natural conditions, soils acidify very slowly, over hundreds to millions of years, with the acidification rate dependent upon the chemistry of the parent material and annual rainfall. About 30% of Earth’s ice-free land is covered by naturally acidic soils (Guo et al., 2010). Chemical indications that a soil is acidifying are a decrease in pH, a decrease in base saturation, a decrease in exchangeable Ca^{2+} , and increased mobilization of Al^{3+} (Warby et al., 2009). The dissolved H^+ ions in an acidified soil displace the base cations Na^+ , K^+ , Ca^{2+} , and Mg^{2+} from the soil exchange complex, as in



where X represents a mole of exchange sites of negative charge and the reaction proceeds by aqueous protons moving onto a mineral-surface site and releasing Na^+ to solution (Sparks, 1995). Subsequently, the base cations are leached from the soil. When natural weathering reactions (Eq. (10)) that ordinarily release base cations are slower than the rate at which protons are added through deposition or *in situ* oxidation, the soil is gradually leached of base cations, i.e., acidified (Brady and Weil, 2002). Acid sulfate soils may arise from parent material containing pyrite, such as coastal marsh deposits or sedimentary rocks associated with coal seams, exposed to oxygen and undergoing pyrite oxidation (Eq. (1)) that releases strong acid and residual sulfate (Brady and Weil, 2002). The preponderance of human-induced acidification over natural soil acidification is well documented for many soils covering a large range of ANC (van Breemen et al., 1984). Anthropogenic acidification of soils has occurred from both acidic atmospheric deposition and application of N-based fertilizer (Table 1).

The depletion of base cations from soils is clear indication that a soil is acidifying. As long ago as the 1970s, Overrein (1972) documented leaching of Ca^{2+} by acidic atmospheric deposition from different types of soils in southern Norway. Soil Ca^{2+} depletion has been studied at more than 70 acid-sensitive sites in the eastern USA. The consensus from these studies is that acidic atmospheric deposition has accelerated the loss of large amounts (in some cases 50%) of Ca^{2+} from the soils (e.g., Bailey et al., 1996, 2005; Johnson et al., 1994; Lawrence et al., 1999; Likens et al., 1996). The natural soil acidification process has been accelerated by high levels of acidic atmospheric deposition in soils in Russia (Lawrence et al., 2005) and in the United Kingdom (Blake et al., 1999).

The decrease in SO_2 emissions in some areas (Fig. 1) has caused particulate emissions from industrial sources to decrease, which has decreased atmospheric Ca^{2+} and Mg^{2+} input to forest soils (Hedin et al., 1994). Research on acid-sensitive soils in forested catchments in Germany (Wesselink et al., 1995; Alewell et al., 2000), the

United Kingdom (Blake et al., 1999), and the northeastern USA (Warby et al., 2009) indicates that soils are continuing to acidify, despite reductions in acidic atmospheric deposition. Alewell et al. (2000) suggest that for many central-European soils, desorption of stored SO_4^{2-} from acidic atmospheric deposition will continue for 30–50 years under current conditions. In the low mountain ranges of Germany, Alewell et al. (2001) report that the net loss of base cations has increased in nine catchments, indicating continued soil acidification, despite two decades of reduced acidic atmospheric deposition.

5.1. Fertilizer use for crop production

For pre-industrial agriculture in temperate regions of the world, N was usually the yield-limiting crop nutrient. The Haber–Bosch process removed that limitation: it is a N-fixation reaction that converts abundant but biologically unreactive N_2 from the atmosphere into a reactive form, NH_3 , making industrial-scale production of NH_3 -based fertilizer possible. Crops produced using such fertilizer currently sustain about 40% of Earth's population (Smil, 2002; Galloway et al., 2008). Urea, $(\text{NH}_2)_2\text{CO}$, the major N compound in fertilizer, gives off NH_3 in the presence of water. NH_3 emissions to the atmosphere emanate primarily from fertilized soil and livestock waste, with additional contributions from motor vehicles and industrial processes. Ammonia emissions then are deposited as NH_4^+ through wet and dry deposition. Oxidation of NH_4^+ in soils and surface waters generates acidity during nitrification (Eq. (5); van Breemen et al., 1982).

In food production, some of the applied N fertilizer not taken up by plants remains in the soil. The effect on the terrestrial ecosystems of N applied as fertilizer is the same as N delivered by acidic atmospheric deposition: depletion of base cations resulting in soil acidification (Matson et al., 2002). In the case of acidification of soils by application of N-based fertilizer, Guo et al. (2010) report that soil pH has statistically significantly declined 0.13–0.80 units over two decades in Chinese crop lands at the national scale. Even soils with relatively high (5–10%) CaCO_3 content had statistically significant pH declines. In China, acidification of soils by acidic atmospheric deposition pales in comparison to that by agricultural activities, which is 10–100 times greater (Guo et al., 2010).

Despite large uncertainty in the rate of N accumulation in environmental reservoirs (Galloway et al., 2004; Gruber and Galloway,

2008), it is clear that during the mid-1960s the anthropogenic contribution of N to the environment surpassed the natural terrestrial contribution (Galloway and Cowling, 2002). Connected to the purposeful application of N in the food production process, Galloway and Cowling (2002) point out a number of ways that N is “leaked” to the environment. Gruber and Galloway (2008) estimate that N fertilizer is added globally at a rate of 100×10^6 metric tons N a^{-1} . Although very difficult to quantify, Smil (2002) estimates that the overall loss of applied N fertilizer to crops is 50%. Nitrogen-use efficiencies lower than 10% in China have been reported (Guo, et al., 2010). This large amount of human-applied N (Fig. 4) is lost to the atmosphere, soils, and to Earth's surface waters and groundwaters (Smil, 2002). In the USA in 2002, 78% (3×10^6 metric tons) of NH_3 emissions came from fertilizer and livestock emissions (USEPA, 2002).

Just as acidic atmospheric deposition is a growing problem in developing countries, so too, is the over-application of N fertilizer in food production. Agricultural production has increased dramatically in China since 1975 as a result of increased application of N fertilizer; in some areas, yields of grain have doubled (Vitousek et al., 2009). Between 1981 and 2007, China nearly tripled its use of N fertilizer (Guo et al., 2010). Northern China currently has the highest N fertilizer inputs to crops in the world (Vitousek et al., 2009). For example, Northern China applies $588 \text{ kg ha}^{-1} \text{ a}^{-1}$ N to crops, compared to $93 \text{ kg ha}^{-1} \text{ a}^{-1}$ in the Midwestern USA, and $7 \text{ kg ha}^{-1} \text{ a}^{-1}$ in Western Kenya (Vitousek et al., 2009). Ju et al. (2009) report that rates of loss of N increase with increased application of N for important grain crops and indicate that over fertilization is a serious problem in agriculturally intensive regions of China.

Rapidly expanding non-food crops support biofuel production, and their growth is a fertilizer-intensive endeavor. Currently, most of the world's biofuels are produced from sugar cane in Brazil and corn in the USA (Galloway et al., 2008). Nitrogen fertilizer use averages 100 and $160 \text{ kg N ha}^{-1} \text{ a}^{-1}$ on Brazilian sugar cane and USA corn, respectively (Galloway et al., 2008). Collectively, Brazilian sugar cane (7 million ha) and USA corn (29 million ha) receive more than 5×10^6 metric tons N a^{-1} . Nitrogen uptake in sugar-cane plant tissues is low, about 30%, while the other 70% of applied N fertilizer escapes to the environment (Galloway et al., 2008). The USA has increased its production of corn-based biofuel nearly 4-fold since 2000. By 2016, the sugar cane growing area of Brazil is expected to double (Galloway et al., 2008).

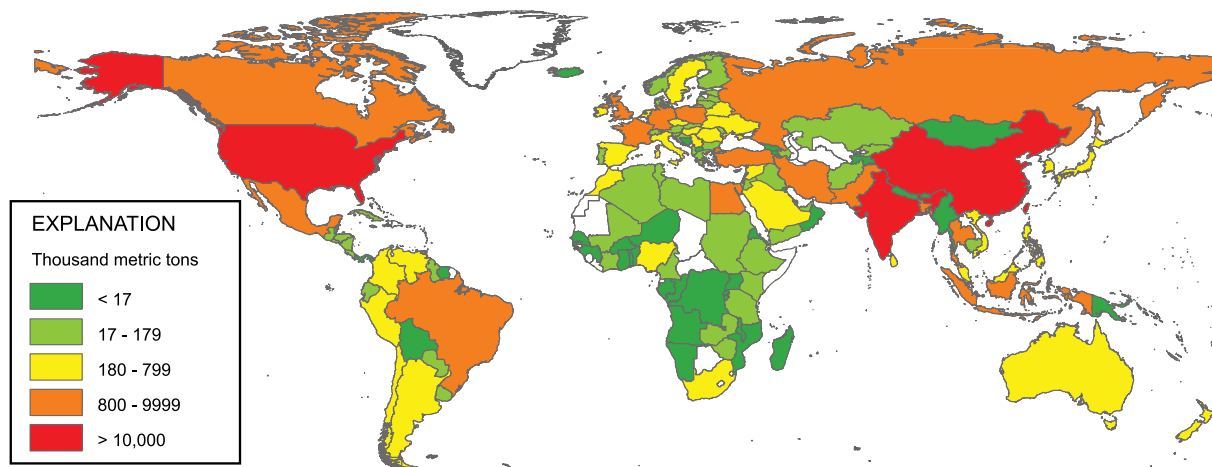


Fig. 4. Nitrogen fertilizer application by country in 2008 expressed as mass of N (<http://faostat.fao.org/site/575/DesktopDefault.aspx?PageID=575#ancor>). The values defining the five brackets of amount of nutrient consumed were selected so as to identify the top 3 consuming countries (red), the next 15 (orange), next 30 (yellow), next 50 (light green), and the rest (dark green). Countries with no reported data are shown as white. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

5.2. Neutralizing reactions important in soils

Ion-exchange reactions on clay minerals and particulate organic matter in soils can take up protons and release cations to aqueous solutions (Eq. (11)). The rates of ion-exchange reactions are rapid (Amacher, 1991; Sposito, 1994); however, an increase in H^+ concentration in soil, brought about by the various activities discussed in this paper, cause soils to acidify, resulting in widespread ecological effects (Robarge and Johnson, 1992; Lee, 1998). Natural weathering reactions (Eq. (10)) replenish the supply of secondary minerals that act as ion-exchange substrates and the base cations that initially occupy exchange sites, but at an insufficient rate to keep up with a soil receiving significant acidic atmospheric deposition or N fertilizer application.

6. Global aggregate effect

The anthropogenic cycle of acidification of Earth starts with a variety of emissions to the atmosphere that may be deposited to Earth's surface as acids. Increased global atmospheric concentration of CO_2 from the combustion of fossil fuels generates weak acid causing acidification of the ocean, and strong acids generated in the oxidation of N and S compounds cause acidification of freshwaters and of soils. Direct acidification of freshwaters also occurs by mining activities in which oxidation of Fe and S compounds generate strong acids. Application of N-based fertilizers to agricultural fields leads to some of the N volatilizing to the atmosphere where oxidation and deposition ensues and some of the N remaining in the soil for *in situ* oxidation. These broadly stated reactions (Table 1) apply to many more human activities than those explored in this paper. Acknowledgement of a number of important processes that received scant attention in this paper, including animal agriculture, deforestation, cement manufacturing, transportation, and petrochemical production to name just a few, serves to remind the reader that the assessment of the extent of acidification of Earth presented here likely is an underestimate.

The wide range of spatial scales and the large magnitude of numerous anthropogenic effects lead to the conclusion that Earth's atmosphere, waters, and soils are being significantly acidified by human actions in addition to any natural acidification processes documented previously (Eppinger and Fuge, 2009). The extent of

anthropogenic effect is truly global, considering that three-quarters of Earth's surface is covered by oceans, which are steadily acidifying because of continuing anthropogenic emissions of CO_2 . In an effort to convey a sense of global distribution and magnitude of acidifying processes, several maps of current (Figs. 2–4) and future (Fig. 5) terrestrial conditions are developed. All maps depict total national resource or population data, although the reader will understand that the per capita consumption of resources varies among countries with different technological development or economic status. Further, the extent of consumption is expressed as the aggregated total national consumption, even though the actual site of consumption varies spatially by population density and location of industrial processes.

Magnitude of coal consumption gives an indication of the countries grappling with potentially severe acidic atmospheric deposition at some location within their borders as well as pointing out the relative contribution to ocean acidification by various nations (Fig. 2). Of 213 countries with reported data for 2009, the three largest coal-consuming countries were China (3.15×10^{12} metric tons), the USA (908×10^9 metric tons), and India (622×10^9 metric tons). All other countries consumed less than 227×10^9 metric tons each during 2009. Because the coal consumption data do not correlate directly to the magnitude of C (Eq. (3)), S (Eq. (6)), or N (Eq. (7)) oxidation, conclusions cannot be reached about the detailed balance of weak- and strong-acid effects. Further, by using data that do not include contributions of acidifying agents from the transportation sector, the map (Fig. 2) underestimates the severity of acidic atmospheric deposition arising from the combustion of fossil fuels. Nonetheless, localities that burn the most coal, despite the ameliorating effects afforded by scrubbers in some smokestacks, are having a disproportionate acidifying effect on Earth's air, water, and soils downwind of those localities.

An indication of the extent of environmental acidification derived from the mining (Fig. 3a) and smelting (Fig. 3b) of metal sulfide ores can be inferred from current Cu production statistics. Copper consumption is global, however, the distribution of Cu ore deposits is highly heterogeneous, being specific to certain geological settings. The location of acid production is tied to both the site of mining where wastes rich in reduced Fe and S phases undergo oxidation (Eq. (1)) and the site of smelting where reduced S phases in furnace emissions undergo oxidation (Eq. (6)). The magnitude of mine (Fig. 3a) and smelter (Fig. 3b) production of

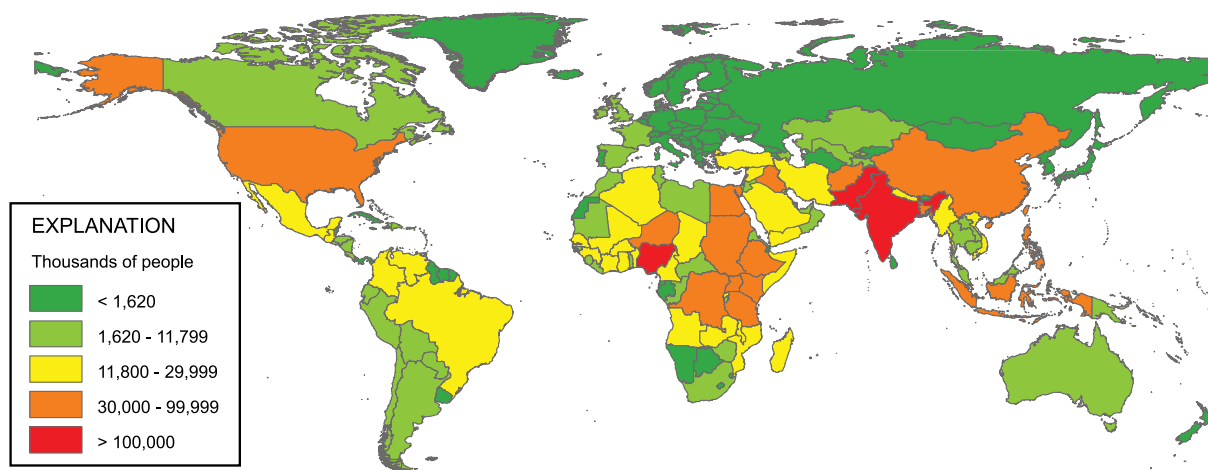


Fig. 5. Change in the number of people by country projected for the period 2010–2050. The United Nations Population Division publication World Population Prospects: The 2008 Revision (<http://esa.un.org/unpd/wpp2008/index.htm>) was used with the medium variant selection for fertility, mortality, and international migration (<http://esa.un.org/UNPP/>) to obtain the projected population change. The values defining the five brackets of increase in number of people were selected so as to identify the top 3 increasing countries (red), the next 15 (orange), next 30 (yellow), next 50 (light green), and the rest, some of which were actually decreasing in projected population (dark green). The aggregated magnitude of increased numbers of people are depicted here by nation, recognizing that population growth varies greatly by region within countries. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Cu metal is, therefore, proportional to the amount of acid generated. As demand for Cu increases, only the countries with significant ore deposits, already the major producers, will respond with increased mine production and will bear the greatest burden of relatively local and sometimes extreme environmental acidification. Smelting operations, in contrast, may become more widely distributed than at present but will be limited to locations with available energy resources. The atmospheric emissions from smelting, although in the past contributing to a more widespread effect than mining activities, have come increasingly under successful control at the stack.

The amount of N fertilizer applied for crop production gives an indication of areas where soil acidification (Eq. (5)) may be occurring or may occur in the future (Fig. 4). Of the 155 countries with reported data for 2008, the 3 countries with the highest applications of N fertilizer were China (33.2×10^6 metric tons N), India (14.9×10^6 metric tons N), and the USA (11.0×10^6 metric tons N). All other countries consumed less than 2.8×10^6 metric tons of N each during 2008. It is anticipated that a future trend toward increasing consumption of N fertilizer will be driven directly by an increase in population.

All the acid-generating activities described in this paper (Table 1) have increased in recent history with the growth of human population. Resource consumption is fundamentally driven by the number of human consumers. The United Nations monitors global population and publishes projections for growth under various assumptions of fertility, mortality, and international migration, and their data and projections have been used to quantify the change in population by country from 2010 to 2050 (Fig. 5). Although populations of some countries will decrease or stabilize, the vast majority of countries will increase in number of citizens. The greatest pressure of population increase will be in already populous, large countries (e.g., USA, India) and in small, rapidly growing countries (e.g., Pakistan, Nigeria).

We default to population increases as indicative of increases in energy consumption, resource extraction, and food production, thereby leading to greater acidification of Earth, yet population is not the only driving factor. A nation's people utilize resources in proportion to their wealth and to their level of technological development. For example, the main driver of energy demand throughout the world is the rate of growth in gross domestic product (GDP) (World Energy Outlook, 2008). As of 2010, China was ranked 3rd and India was ranked 5th in the world for GDP (<https://www.cia.gov/library/publications/the-world-factbook/rankorder/2001rank.html>). China and India are home to 19% and 17% of the world's population, respectively (<https://www.cia.gov/library/publications/the-world-factbook/geos/xx.html>). Together they hold nearly 40% of the world's population and a large fraction of global GDP, so it is no surprise that World Energy Outlook (2008) predicts that China and India will account for 51% of world energy demand from 2006 to 2030.

A recent article in National Geographic (Kolbert, 2011) uses an equation for the human effect upon Earth's environment as being a multiplicative result of population, affluence and technology, and this strikes the present authors as being the most comprehensive approach to take. Seeking to predict future conditions, another recent analysis in Time (Zakaria, 2011) uses an "index of prosperity," a large part of which is based in material wealth, to look at the broad international picture of shifting national fortunes. The authors see these topics as intimately related to their analysis. Because sociopolitics are the driver of the index of prosperity, which directly results in a geochemical response, major environmental changes in the near future will be controlled by the increase in numbers of and wealth of consumers.

The locations of greatest projected population change (Fig. 5), however, are often different from those countries currently

consuming large amounts of natural resources as a result of being either wealthy or populous (Figs. 2–4). In comparing the current consumption of coal (Fig. 2), production of Cu (Fig. 3), and application of N fertilizer (Fig. 4) with the projected population change (Fig. 5), it is noted that currently low-consuming regions in Africa and the Middle East are predicted to experience a tremendous population growth with its attendant demand for energy, mineral, and food resources. It may be that regions of Earth not currently burdened with environmental acidification soon will be contributing significantly to Earth's acid load. Now might be the time of opportunity to anticipate the coming shifts in population and resource consumption and plan for amelioration of acidifying processes from the outset.

Acknowledgments

Discussions with James N. Galloway and Howard E. Epstein contributed to our understanding of nitrogen biogeochemistry. We thank Zbigniew Klimont for generously providing an early review of the acidic atmospheric deposition section. Thoughtful reviews of the manuscript by Martin B. Goldhaber, Alan T. Herlihy, George M. Hornberger, William L. Lasseter, Jr., and an anonymous reviewer guided our preparation of the final document. We thank Amy K. Gilmer for her expert preparation of the maps. We thank Ron Fuge for his patience and encouragement throughout the development of this paper.

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