FORGING A BETTER SUPPLY CHAIN

Managing nonrenewable **MINERAL RESOURCES** will increasingly challenge the sustainability of the chemical enterprise

STEPHEN K. RITTER, C&EN WASHINGTON

SPREAD OUT ACROSS central Florida's Bone Valley, and buried some 30 to 50 feet below the surface of a mixed landscape of sand pine forests, citrus groves, and grass prairies, rests a vast deposit of phosphate rock waiting to be mined. To an approximation, some 540 million metric tons of the sedimentary material is here, laid down millions of years ago at the bottom of an ancient sea.

Michael R. Rahm, chief economist and market analyst at Mosaic, the world's leading producer of phosphate fertilizer, figures his company will dig up and process 12 million metric tons of Florida's phosphate rock this year and turn it into ammonium phosphate. That's enough fertilizer to supply half the U.S.'s needs or 10% of global needs.

Human society is now dependent on mineral fertilizers. Without them, there wouldn't be enough food for all 7 billion people on the planet. Rahm reckons the Florida phosphate deposits will last perhaps another 45 years before they run out. The availability of phosphate ultimately could determine how much human life Earth can support.

Of equal concern is society's dependence on metals, for everything from structural steel and power lines to vehicles and portable electronics. Scientists studying metal stocks suggest that, without a more disciplined effort at recycling, some metals could soon become scarce enough to inhibit global economic growth and limit our technological future.

The fates of phosphate and metals are just two of the dilemmas society faces in attempting to create a sustainable future in a resource-constrained world. Manufacturing industries and utility companies are already hard at work developing technologies to improve energy and fuel efficiency, reduce greenhouse gas emissions, prevent pollution, and conserve water. Those efforts are the low-hanging fruit for sustainability. But the meat and potatoes of global sustainability, for which the chemical enterprise bears much of the burden, is the harder task of managing the consumption of nonrenewable mineral resources.

Asked whether he thinks the world will soon run out of phosphate fertilizer, Rahm doesn't give a direct answer, but he doesn't seem too worried. He acknowledges the talk in academic circles about global peak phosphorus production, which might come as early as 2030. But he suggests the situation isn't as dire as it might seem. He has faith in economics and technology to keep phosphate supplies solid.

"There's more phosphate out there than is being described in some of the peak phosphorus studies," Rahm believes. "It all comes down to at what price," he contends.

"If the world needs more phosphate, markets will adjust to provide the incentive to address the scarcity issue," Rahm continues. "The markets will tell us we need capital to flow into this sector to develop some of the less useful resources that weren't viable a decade or two ago."

MOSAIC

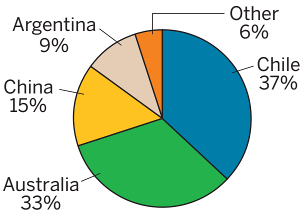
FERTILE DIGGING A drag line, large enough to park a Greyhound bus in, digs phosphate rock at Mosaic's mining and processing operations in Florida.

OF THE THREE major nutrients in fertilizers—nitrogen, phosphorus, and potassium—phosphorus is the least abundant and most complicated to process, Rahm says.

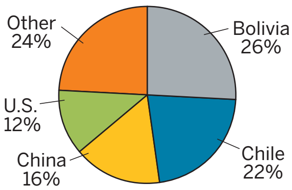
Mining phosphate is an intricate dance of stripping sandy soil off the phosphate, blasting the soft rock with water to form a slurry, and pumping the slurry to a processing plant where it is

LITHIUM

Versatile and abundant



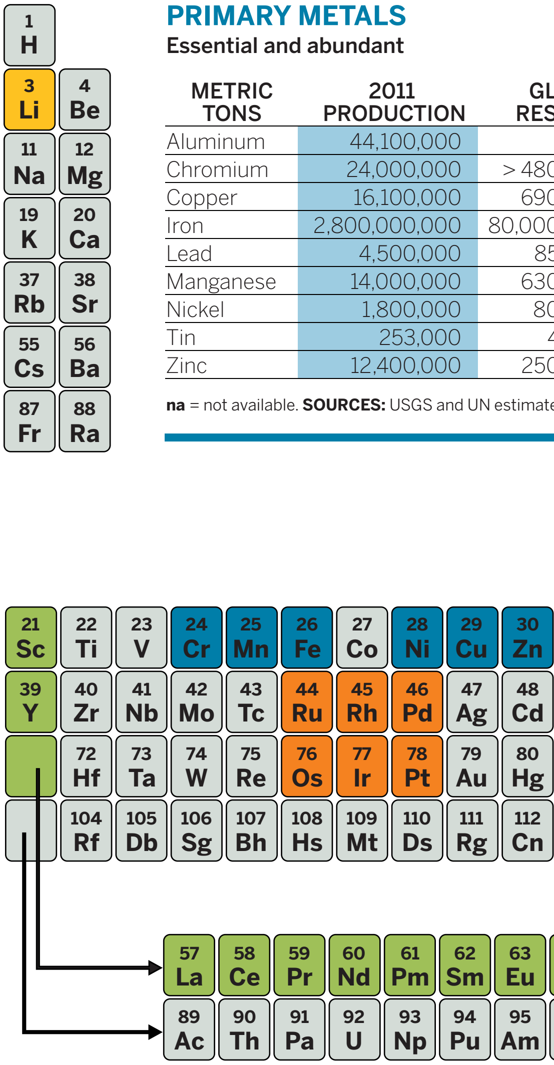
2011 production = 34,000 metric tons



Global resources = 34 million metric tons
Global reserves = 13 million metric tons

Uses: rechargeable batteries, ceramics and glass, lubricating greases
Recycle rate: < 1%
Substitutes: calcium, magnesium, mercury, zinc, aluminum, sodium, potassium

NOTE: Excludes small amount of U.S. production.
SOURCES: USGS and UN estimates



PRIMARY METALS

Essential and abundant

METRIC TONS	2011 PRODUCTION	GLOBAL RESERVES	GLOBAL RESOURCES	RECYCLE RATE
Aluminum	44,100,000	na	na, but extensive	40–70%
Chromium	24,000,000	> 480,000,000	> 12,000,000,000	90
Copper	16,100,000	690,000,000	> 3,000,000,000	50
Iron	2,800,000,000	80,000,000,000	> 230,000,000,000	70–90
Lead	4,500,000	85,000,000	> 1,500,000,000	70–90
Manganese	14,000,000	630,000,000	na, but extensive	55
Nickel	1,800,000	80,000,000	> 130,000,000	60
Tin	253,000	4,800,000	na, but extensive	75
Zinc	12,400,000	250,000,000	1,900,000,000	50

na = not available. **SOURCES:** USGS and UN estimates

INDIUM

Versatile but scarce

2011 refinery production: 640 metric tons
2011 consumption: 1,800 metric tons
Global reserves: 310,000 metric tons
Global resources: 570,000 metric tons
Uses: indium tin oxide coatings for flat-panel displays, solar cells, and LEDs
Recycle rate: < 1%
Substitutes: antimony, carbon nanotube coatings, graphene quantum dots, polymer thin films

SOURCES: USGS and UN estimates

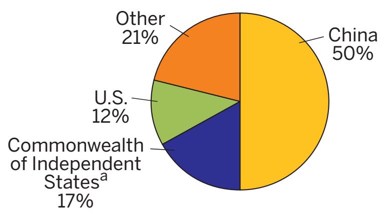
RARE EARTHS

Not rare but hard to come by

2011 production: 130,000 metric tons, 97% from China
Uses: magnets, catalysts, phosphors for flat-panel displays, metal alloys, ceramics
Recycle rate: < 1%
Substitutes: other metals that are generally less effective

Four examples:

METRIC TONS	GLOBAL RESERVES	GLOBAL RESOURCES	USE
Cerium	31,000,000	58,000,000	catalysts, polishing optical components
Lanthanum	15,000,000	27,000,000	hybrid-electric car batteries
Neodymium	12,000,000	22,000,000	magnets, lasers
Terbium	300,000	600,000	phosphor for compact fluorescent lightbulbs



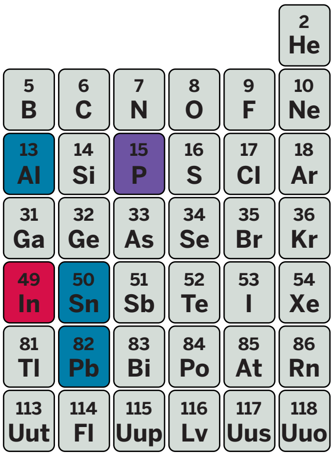
Global reserves = 110 million metric tons

a Includes Russia and other former Soviet republics. **SOURCES:** USGS and UN estimates

converted first to phosphoric acid and then to ammonium phosphate. The water is recycled and all the leftovers are handled in a way designed to minimize environmental disruptions: Sand and clay are returned to the mine site for land reclamation, and calcium-based detritus—which carries trace amounts of radioactive radium—is stacked in large piles out of harm's way.

"When it comes to sustainability with phosphate, it starts with reserves available in the ground," Rahm says. "But it extends to efficiency in processing the ore in the production plant and efficacy down on the farm to grow the food that the world needs."

Mosaic used to recover about 90% of the phosphorus in phosphate rock, the same as most phosphate producers globally, Rahm says. "As the quality of the ore in Florida has gone down, our efficiency at recovering phosphorus has gone up," he notes. Thanks to better engineering, the company now manages to recover up to 97% of the phosphorus. In addition, commercial farmers today use GPS-guided tractors to disperse fertilizers optimized for variable application rates in different areas of a field based



FUTURE OF METALS AND MINERALS The U.S. Geological Survey (USGS) keeps track of the mineral resources available in Earth's crust and estimates economically recoverable quantities. These data, used as economic indicators, are based on information from national governments and private industry. The values change over time on the basis of new information on the quality of known deposits and the discovery of new deposits. Production values are the marketable amount of a material produced per year. Reserves are the amount of material that can be economically produced within the next few years at current prices and with current technologies, whereas resources are a rough estimate of the total amount of material that might be economically feasible to produce with price increases or advances in technology. Because some areas of Earth still haven't been fully explored, such as Antarctica and deep-ocean floors, USGS reserve and resource values are considered lower limits. In 2011, a United Nations Environment Programme panel began issuing additional estimates on metals. Taken together, the USGS and UN data provide a snapshot of how much of each element is potentially available and how well society is doing at managing these resources.

PLATINUM-GROUP METALS

High value with moderate recycle rates

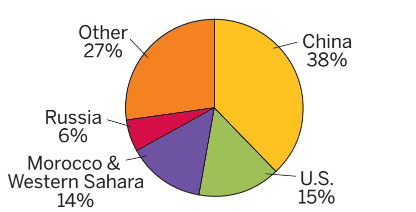
METRIC TONS	GLOBAL RESERVES	GLOBAL RESOURCES	RECYCLE RATE
Ruthenium	41,000	76,000	5–15%
Rhodium	29,000	53,000	50–60
Palladium	260,000	480,000	60–70
Osmium	80,000	140,000	< 1
Iridium	20,000	30,000	20–30
Platinum	1,600,000	2,900,000	60–70

Key reserves: South Africa (95%), Russia (1.7%), U.S. (1.4%)
Uses: automobile catalytic converters, organic synthesis catalysts, electronics, investment tools
Substitutes: other platinum-group metals, other metals that are generally less effective

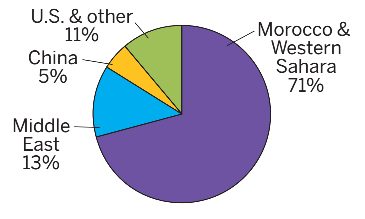
SOURCE: UN estimates

PHOSPHATE ROCK

Essential and becoming scarce



2011 production = 191 million metric tons



Global reserves = 71 billion metric tons
Global resources = 300 billion metric tons

Uses: fertilizer, phosphorus for industrial chemicals
Recycle rate: none, except as animal manure and sewage sludge for fertilizer
Substitutes: none

SOURCE: USGS estimates

on soil testing. This technology allows farmers to increase yields using the same amount of fertilizer, Rahm explains.

ABOUT 95% OF PHOSPHATE rock globally is converted into ammonium phosphate for fertilizer and animal feed supplements. The other 5% is refined to elemental phosphorus, which in turn ends up in all other phosphorus-bearing chemicals, such as pesticides, detergents, and medicines.

Monsanto's subsidiary P4 Production, for example, operates a phosphate mine and the U.S.'s only elemental phosphorus plant in Idaho. The company processes phosphate in a high-temperature kiln to make P_4, which in turn is used to make phosphorus trichloride as a starting material for its Roundup-brand glyphosate herbicide.

Monsanto's reserves of phosphate will last "for many decades," states Sheldon Alver, P4 Production's manager. Long term, more phosphate reserves are likely to be found in the western U.S., he says. Even so, Monsanto has a team dedicated to continuous process optimization to improve phosphorus yield, he adds, both in the mining and downstream manufacturing processes.

Alver notes that farmers could look to other sources for phosphorus. For example, they are already supplementing mineral fertilizers with phosphorus-containing animal manure and sewage sludge. But there isn't enough of those materials to replace all the phosphate currently being used, let alone what will be needed as the world's population grows.

Scientists and engineers also have been studying how to chemically recover phosphorus from urine. Collecting, storing, and extracting the nutrient from urine could be a stinky, logistical mess, but one that could be viable in the future as the world population continues to concentrate in large cities.

In another possibility, John W. McGrath of Queen's University Belfast is leading a research team exploring an approach that might be easier and more palatable: Let phosphorus-loving microbes extract phosphorus from wastewater.

A variety of microbes in wastewater treatment plants accumulate phosphorus and store it as polyphosphate, a natural biopolymer built from PO_3^{2-} units, McGrath notes, at up to 20% of the dry weight of the microorganism. Phosphorus is also removed from wastewater by prescribed chemical precipitation. These processes help prevent eutrophication—that is, overstimulated growth of algae that can deplete oxygen and suffocate streams and lakes. But the current treatments aren't efficient enough for significant phosphorus recovery.

McGrath's team initially developed a pH shock treatment that doubles microbial phosphorus uptake when pH is suddenly lowered from just above 7.0—the norm in wastewater treatment facilities—to below 6.5. "It's similar to jumping into the sea on a winter's day," McGrath explains. "The first thing you do is take a sharp breath. When we shock the microorganisms, their response is to take in phosphorus."

The pH shock treatment led to a related physiological shock treatment that removes up to 90% of phosphorus from waste streams, a level that could be commercially useful. McGrath regrets that, to protect the idea, he can't yet disclose the exact process, but his team is now scaling it up.

McGrath believes developing a biotech process to recover phosphorus could become essential for a sustainable planet. "No alternative to phosphorus exists—we urgently need to find ways of recovering and reusing phosphorus," he argues. "It's a pollutant we can't live without."

"Technology is just beginning to scratch the surface of methods to recover phosphorus in these alternative sources," Monsanto's Alver observes. "It hasn't been that long ago when market analysts thought we had hit peak natural gas, and now fracking technology has unlocked natural gas reserves beyond all expectations. Phosphorus could easily follow a similar pattern."

For example, Florida start-up company JDC Phosphate is developing a commercial-scale process that relies on high heat in a rotary kiln reactor to convert phosphate rock into phosphoric acid, rather than using an aqueous acid treatment as Mosaic does. The technology enables the use of lower grade phosphate rock that isn't amenable to acid treatment. The method can even be used on some of the piles of old phosphate mining waste—there's some 700 million metric tons of it sitting in Florida—to glean phosphorus left behind.

Overall, JDC Phosphate's approach could nearly double phosphate production from a region like Florida's Bone Valley, Rahm says. "Perhaps there's another 1 billion metric tons of phosphate to dig up in Florida," he

DEMANDING AMERICANS

The Mineral Information Institute annually estimates the amount of new minerals each person in the U.S. requires to enjoy all the products and services they use each year, deriving the values from U.S. Geological Survey, Energy Information Administration, and National Mining Association data. The institute also calculates the amount of mineral resources each person will require over a lifetime. The total adds up to 32,052 lb of stuff per person per year for 2010, and a total of 2.96 million lb per person over a lifetime, assuming a life expectancy of 77.9 years. Listed here are a few of those key mineral resources.

		PER CAPITA REQUIREMENTS	
RESOURCE	USE	ANNUAL	LIFETIME
Cement	Roads, sidewalks, buildings	496 lb	38,638 lb
Iron ore	Steel to make buildings, vehicles	357 lb	27,810 lb
Sand, stone, and gravel	Building and roadway construction	14,108 lb	1.1 million lb
Salt	Food, agriculture, roadway deicing	421 lb	32,796 lb
Copper	Wiring, plumbing	12 lb	935 lb
Soda ash	Glass, detergents	36 lb	2,804 lb
Bauxite	Aluminum to make cans, power lines, airplanes	65 lb	5,064 lb
Phosphate rock	Fertilizer	217 lb	16,904 lb
Clays	Tile, dinnerware, bricks, paper	164 lb	12,776 lb
Other minerals & metals		378 lb	41,832 lb
Petroleum		951 gal	73,884 gal
Coal		6,792 lb	592,097 lb
Natural gas		80,905 cu ft	6.3 million cu ft
Uranium		0.25 lb	19.5 lb

"Metal shortages are going to push us to become more innovative designers. And more efficient recyclers."

notes. Yet, there will be a time when Earth's phosphate supply simply runs out. U.S. Geological Survey (USGS) data suggest that time is at least another 370 years away. But exactly how soon is hard to predict, Rahm admits.

JUST AS USING UP phosphate could lead to food shortages, using up metals could lead to shortages that hamper global economic growth and inhibit technological advances. The sustainability challenge for metals will come from managing current metal stocks as mining deposits dwindle and as more people desire to have a smartphone in their hand while also having a continuous supply of nuts and bolts for basic housing, transportation, and energy needs.

According to Yale University industrial ecologist Thomas E. Graedel, modern society is fully dependent on just a few of the 60-plus metals in the periodic table: aluminum, manganese, iron, copper, and lead. We also rely heavily on chromium, nickel, zinc, and tin, he notes. Together, these nine metals are key components of structural steel in buildings; planes, trains, and automobiles; batteries; power transmission lines; metal corrosion inhibitors; and all manner of portable electronics and appliances.

Graedel leads a United Nations Environment Programme panel charged with determining whether society needs to be concerned about the long-term supply of only a few metals or many metals. In some cases, such as copper, the amount of metal in use aboveground is about equal to the amount still in the ground, Graedel states. Although "dependency metals" like copper are being used at high rates, they also are being recycled at high rates—all more than 50%.

But these metals are typically tied up in long-term applications. And as people in developing regions come to enjoy the same lifestyle as those in industrialized nations during the coming decades, the amount of these metals in use will be up to 10 times greater, he notes, constraining availability of even the most abundant metals.

What's more, the past 20 years has sparked an explosion of new uses for a greater variety of metals in applications from which they aren't yet easily recycled, Graedel says. This is the case for scarce metals such as the main-group element indium used in flat-screen computer monitors, solar cells, and light-emitting diodes. It's also the case for abundant metals such as the alkali metal lithium used in rechargeable batteries for cell phones, cordless tools, and hybrid electric vehicles, as well as for rare-earth metals used as catalysts, in magnets for wind turbines, and as phosphors in flat-panel displays.

"We have learned how to develop state-of-the-art technologies by using an ever-wider range of metals with special properties in very diverse, complex combinations," Graedel says. "Without them, performance would suffer—we would have slower computers, fuzzier medical images, and heavier and slower aircraft, for example. But in doing so, we make their recovery and reuse very difficult.

"As the planet's mineral deposits become less able to respond to demand," Graedel continues, "whether for reasons of low mineral content, environmental challenges, or geopolitical decisions, we limit our technological future by using these resources once and then discarding them."

The energy and environmental cost of processing metals is critical when considering when and whether recovery and reuse is feasible, adds UN panel contributor Christian Hagelüken of Umicore Precious Metals Refining, one of the world's leading precious-metal recyclers, in Hoboken, Belgium.

Mining will continue to be important to meet metal demands from growing uses and new product uses, and to cover unavoidable life-cycle losses, Hagelüken says. But recycling to keep metals "in the loop" is usually less energy-intensive than mining and generates less of an environmental burden, in particular when it comes to greenhouse gas emissions and water consumption, he notes.

The reasoning is simple, Hagelüken explains. To mine gold in South Africa, one of the big producers in the world, "you have to go nearly 2 miles deep underground and extract an ore with an average gold content of 5 g per ton," he says. "In a computer motherboard, there is about 200 g of gold per ton of material—and it's already at the surface. The same is true for many other metals, but in different magnitudes."

The chemical, petroleum, pharmaceutical, and automotive industries have already set the standard for recycling platinum-group metals, which include important catalyst metals such as rhodium, palladium, and platinum, Hagelüken says. But even here there are wide variations: 70 to 90% of platinum-group metals in industrial catalysts are recycled because companies treat them as assets in a closed loop.

However, only about 50% of the metals in automobile catalytic converters are recycled as a consequence of poor end-of-life-cycle management, he says. Further down the ladder, only about 10% of the platinum-group metals in electronic goods are recycled because of their low concentration in billions of devices that aren't designed for easy metal recycling—they are designed to be thrown away, and their afterlife is hard to trace.

THE SITUATION IS WORSE for most other metals, Graedel, Hagelüken, and their colleagues contend, with a small amount of recycling taking place for indium and virtually no recycling yet taking place for lithium and rare earths.

"We limit our technological future by using resources once and then discarding them."

Lithium is relatively abundant, and batteries are easily recycled, Graedel points out. Thus, lithium battery manufacturers are gearing up to significantly expand recycling efforts, he notes.

Indium doesn't have that luxury, Graedel adds. Indium is relatively abundant in Earth's crust, but it's dispersed at a low concentration and typically coproduced with other metals, such as zinc. Because indium is used in small amounts in products that are hard to recycle, such as an indium tin oxide layer in a semiconductor, global supplies of indium are expected to become tighter, and substitutes will be necessary, he predicts, possibly at a higher cost.

For rare earths, such as cerium used in catalysts and for polishing glass lenses and neodymium used in magnets, China has about 50% of known global resources but currently controls 97% of production from the most economically accessible deposits, according to USGS statistics. There are no substitutes for most uses of rare earths that don't compromise performance, Graedel asserts, and inroads to rare-earth metal recycling are just getting started. Geopolitical control of rare earths could create problems should China choose not to share and reserves of rare earths don't materialize elsewhere around the globe.

Graedel, Hagelüken, and their colleagues believe avoiding supply-chain issues and ensuring a sustainable future for metals requires shifting thinking about end-of-life processing of industrial and consumer products away from "waste management" to "resource management," a step that will hinge on recycling.

For example, the UN panel recommends boosting global metal recycling by encouraging product design that makes disassembly and material separation easier. It notes that developing countries need help building a recycling infrastructure as their use of mobile phones, televisions, home appliances, and automobiles grows.

In industrialized countries, the biggest problem is collecting materials for recycling, Graedel argues. Metal recycling needs to focus more on "urban mining," he says. Society needs to recognize that old buildings are chock-full of unused pipes, structural steel, and wiring. Countless old mobile phones and their chargers, USB cables, defunct laptops, and outdated video game consoles and their power cords all end up squirreled away in drawers and closets never to be recycled.

"Metal shortages are going to push us to become more innovative designers," Graedel states. "And more efficient recyclers."

Liberal estimates being made by some mining experts are that Earth has enough mineral resources to last 10,000 years before we run out of options. Those estimates include going ever deeper in Earth's crust, mining the bottoms of oceans, and sifting seawater. The estimates also assume that the cost of extracting and processing the materials is no object and overlook any environmental or geopolitical concerns.

Even with enhanced technologies to extract Earth's waning resources, Monsanto's Alver sums up what might be sustainability's greatest need: prudence. "Prudence argues that natural resources be used sparingly and as efficiently as possible." ■