Annu. Rev. Environ. Resour. 2004. 29:69–107
doi: 10.1146/annurev.energy.29.042203.104034

ELEMENTAL CYCLES: A Status Report on Human or Natural Dominance

R.J. Klee and T.E. Graedel
Center for Industrial Ecology, School of Forestry and Environmental Studies, Yale University, New Haven, Connecticut 06511; email: robert.klee@yale.edu, thomas.graedel@yale.edu

Key Words biogeochemical cycles, industrial ecology, mobilization, periodic table, trace elements

■ **Abstract** The modern technological society mobilizes and uses a very large number of materials. These substances are derived from rocks, sediments, and other natural repositories, and most undergo transformation prior to use. A large fraction of the materials is eventually returned to the environment. Natural processes do the same but not necessarily with the same suite of materials. For purposes of better understanding industrial development and potential environmental impact, it is important to know, even approximately, the elemental cycles of all materials potentially useful for modern technology. In this review, we examine and summarize cycle information for 77 of the first 92 elements in the periodic table. Mobilization calculations demonstrate that human activities likely dominate or strongly perturb the cycles of most of the elements other than the alkalis, alkali earths, and halogens. We propose that this pattern is ultimately related to the aqueous solubilities of the predominant chemical forms of the elements as they occur in nature: Human action dominates the cycles of the elements whose usual forms are highly insoluble, nature those that are highly soluble. Examples of the utility of anthropogenically dominated cycle determinations for resource supply analyses, environmental impact assessment, and public policy are presented and discussed. If the rapid rise in the use of materials by the technological society in the twentieth century continues into the next century, anthropogenic dominance of the cycling of a majority of the elements of the periodic table will only increase.

CONTENTS

INTRODUCTION

The characterization of cycles has a rich history in biogeochemistry. The obvious example, among many others, is the global carbon cycle. Knowledge of this cycle has evolved over several decades as new sources and sinks have been discovered, flows quantified, missing flows identified, and the relatively small but climatically important human influence monitored in detail. Two goals have driven this effort: (*a*) to establish a firm scientific understanding and (*b*) to do so with sufficient reliability and in enough detail that policy options related to human perturbations might be reasonably discussed. The utility of this approach has given rise to similar efforts related to other chemical cycles of nature, including nitrogen, sulfur, and phosphorus. The job is not yet complete, but good progress is being made.

In contrast to these vigorous efforts related to Earth's natural cycles, little effort has been expended on the cycles of materials dominated by human action, such as the engineering metals. There have been suggestions that human action has an effect on the global cycles of the crust-forming elements and metals—Bertine & Goldberg (1) discussed this issue from the perspective of rock weathering; Martin & Meybeck (2) for riverine systems; and Lantzy & Mackenzie (3) for the atmosphere—but those efforts made only a very preliminary attempt to quantify the human-initiated flow magnitudes. Perhaps the most noteworthy work in this area (but work that is now outdated) is the estimation of global metal flows from natural and anthropogenic sources by Nriagu, Pacyna, and their colleagues (see for example, References 4, 5). Clearly, if we have a good quantitative understanding of cycles dominated by human action, we will be much better able to assess the long-term availability of resources, the potential for accumulative toxicity to ecosystems, and the potential for "mining" the landfills and other nonvirgin resource reservoirs, among a host of other issues that currently cannot be reliably addressed.

Despite the potential utility of technological material cycles, there are surprisingly few available. In an effort to provide a status report, we have collected and summarized anthropogenically related cycle information. We have chosen, for tractability, to restrict our scope to the first 92 elements of the periodic table (or most of them). We thus do not treat aggregates, such as stone or sand, products synthesized wholly or virtually so by human technology [chlorofluorocarbons (CFCs), plastics, composites, and others], or renewables, such as forest products. The cycles of the elements themselves prove to be subjects of great breadth and interest, and serve as a guide toward approaches suitable for the groups of materials we have omitted.

Because there are so few complete, global, elemental cycles available, we have attempted here a preliminary calculation of the total global mobilization of 77 elements (all but the noble gases and short-lived radioactive elements) from both anthropogenic and natural processes. Accordingly, herein we attempt to address the following questions:

- How well do we know the cycles of the naturally occurring elements? Although both nature and humans sequester and/or mobilize essentially all of the elements, are all of the cycles of interest?
- Which of these cycles are dominated by human activity? Some cycles are without question dominated by nature, at least so far as total fluxes are concerned. Some are not. The degree of human dominance has thus far been addressed only in special cases, not universally.
- What are the implications of human dominance? Three areas might well be addressed in this connection: resource depletion, the functioning of natural systems, and biological toxicity.

COMPONENTS OF CYCLES

Cycles of technological and natural materials provide perspectives difficult to achieve by other techniques. A well-done analysis begins with an overview of the more important and less important inputs and outputs, identifies gaps in knowledge, and stimulates additional efforts to identify and quantify poorly known cycle elements (6). Unlike biogeochemical cycles, where some of the most important input and output processes may be unknown (such as the current scientific debate surrounding the forest, soil, and/or ocean sinks in the global carbon cycle), technological cycles, in principle, have no components that cannot be determined by studying the activities of industries, governments, and customers. In practice, however, issues of national sovereignty, corporate proprietary information, or absent measurement and monitoring systems to collect the desired information represent challenges to the analyst.

An overview of cycle analysis can be demonstrated with the aid of the two-reservoir model shown in Figure 1*a*. *Reservoirs* are compartments in which a material can be stored, and the amount of a particular material in a reservoir constitutes the *stock*. Reservoirs may be ensemble entities difficult to assess with great accuracy (e.g., an ocean) or small, easily quantifiable ones (e.g., a warehouse). Flows into and out of reservoirs are termed *fluxes*. An analysis treating fluxes into and out of only a single reservoir (a personal bank account or an organism, for example) is termed a *budget*. We refer to the reservoir or reservoirs within which nature stores the majority of a given element as *sequestration reservoirs*. Residence times in these reservoirs are typically long. Analogously, the reservoir or reservoirs into which this material is transferred, typically for much shorter periods of time, are termed *mobilization reservoirs*. Flows from the former are termed *mobilization flows*, and those from the latter *sequestration flows*. Because material that is transferred from a sequestration reservoir is eventually returned to it, the cycle of Figure 1*a* is termed *closed*. A somewhat more complicated anthropogenic system is pictured in Figure 1*b*. In this system, the first reservoir (Earth's crust) continually supplies material, and the fourth reservoir (the landfill)

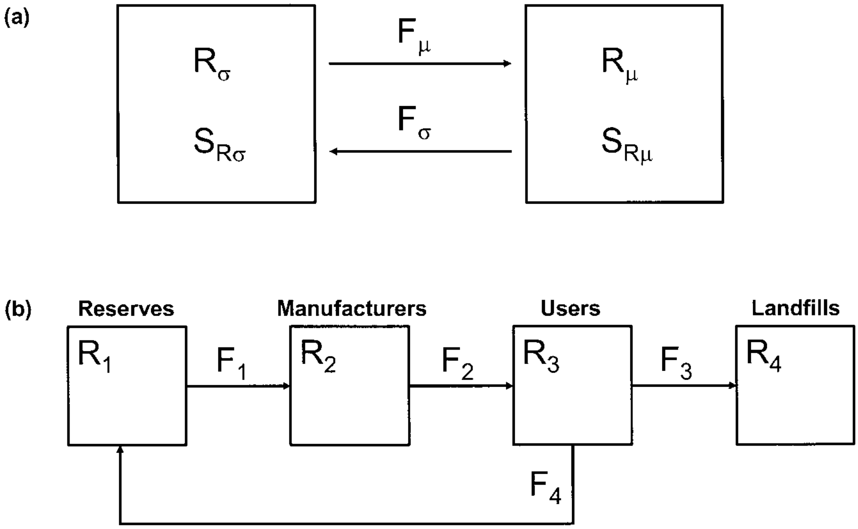

Figure 1 (*a*) A two-reservoir model of a closed cycle. The notation is R, reservoir; S, stock; F, flow; μ, mobilization; and σ, sequestration. (*b*) A four-reservoir model of an anthropogenic open cycle, where raw material resources are mobilized from geologic reserves, transformed during manufacturing and use, and then discarded to a landfill or recycled.

continually receives it. (The term *landfill* implies a generic final repository for anthropogenic material, which, in addition to actual landfills, would also include terrestrial sediments, ocean sediments, and seawater, among others.) As a result, even though the diagram contains cyclic elements, the cyclicity is not complete, and the cycle is not in balance. In the terminology of cycling, the landfill is an *accumulative* reservoir, and the system is *open*.

Cycle analysis becomes more complicated when the amount of time that a material spends in a specific reservoir (which need not be the same as the time spent in other reservoirs) is factored in. In Figure 1*b*, for example, we expect that material will flow rapidly through a manufacturing facility and much more slowly through the cycle of use. This characteristic is determined by dividing the pool size of a reservoir by the total flux from it; the result is the *turnover time*, which can be thought of as the time necessary to empty the reservoir if the sinks remained constant and the sources were removed. Cycle analyses can become much more intricate than suggested by the simple example above, particularly if nonlinearities and coupled cycles are involved (6). For the present purposes, however, the rudimentary approach of Figures 1*a* and 1*b* represents a level of sophistication that is quite sufficient to produce interesting and useful results.

SURVEY OF ELEMENTAL CYCLE INFORMATION

To derive an assessment of the current state of elemental cycle understanding, we searched for existing cycles or partial cycles that met the following criteria:

- Encompass at least several of the flows and/or stocks of the generic Figure 1*a*, not merely a single one, such as gaseous emissions;
- Use what appears to be reliable data, not conjectures; and
- Are directed to a geographical region, country, or the planet, not merely a localized system, such as a factory.

The complete results of our survey are shown in the Supplemental Table: Follow the Supplemental Material link from the Annual Reviews home page at http://www.annualreviews.org. In this Supplemental Table, we provide information on the major anthropogenic uses, the type of cycle analysis available in the literature (flows only, or stocks and flows; we found none dealing with stocks only), the year or years for which the cycle was developed, the geographical scope, and relevant citations for each of the elements. In some cases, the cycles include both anthropogenic and natural components. Where they do not, we provide a citation to the natural flows.

One unsurprising result from our survey is the number of elements for which little or no global cycle information is available (21 of 92, or slightly over 20%). Most of these elements are inert gases, rare earths, or actinides. Only two groups have tended to receive extensive study: (*a*) the grand nutrient and halogen cycles of nature [e.g., carbon (7), nitrogen (8), phosphorus (9), and chlorine (10)], of interest because of the degree to which those natural cycles are being perturbed by human action, and (*b*) the toxic metals, of interest because of their human health hazards [e.g., lead (11, 12), mercury (13, 14), cadmium (12, 15, 16), and arsenic (17, 18)]. There are pieces of information for many of the common engineering metals [e.g., iron (19), nickel (20), and copper (21, 22)], but few broad-scale cycles, and there is essentially no information for materials with comparatively low flows but critical uses (e.g., gallium, germanium, and indium). A few of the elements have extensive country-scale information but little on a broader scale [e.g., cobalt (23), silver (24), tungsten (25), and vanadium (26)].

Even where cycles have been characterized, they tend to lack a number of desirable attributes. Most deal only with flows, not with stocks. Most also were derived for only a single point in time; they are thus merely snapshots of transport between reservoirs. This characteristic effectively decouples flows from stocks, because the stocks in the various reservoirs cannot generally be measured and because the absence of flow information as a function of time prevents the stocks from being derived. Although some measures of geologic stocks vary over time according to the price of the resource, extraction technology, and new discoveries, geologists customarily estimate the *reserve base* (the quantity of identified resources regardless of their current economic viability) or *resources* (the total quantity of a resource thought to exist regardless of its location or concentration) (27).

A final inadequacy of nearly all the cycles is a lack of spatial distribution of the flows, the stocks, or both. The only exceptions are carbon, nitrogen, and sulfur, for which anthropogenic influences are treated as perturbations to the natural cycles. It is clear from even casual assessment that a signal characteristic of human materials use is the spatial transfer of materials from their geological source reservoirs (typically in remote areas) to human reception reservoirs (typically in urban and peri-urban areas). Very little quantitative information on such spatial transfers is thus far available.

ESTIMATING RELATIVE ANTHROPOGENIC DOMINANCE OF ELEMENTAL CYCLES

One item of particular interest for the elemental cycles is the degree to which they reflect anthropogenic activity. The relevant data are not the stocks, which nature always dominates, but the mobilization flows from the geological reservoirs. These flows are the F_μ flows of Figure 1*a*. If all relevant flows and their magnitudes are known, anthropogenic cycle dominance exists if

$$\sum F_\mu(a) > \sum F_\mu(n),$$

where a and n refer to anthropogenic and natural, respectively.

As stated above, there are only a handful of complete, global elemental cycles that incorporate both natural and anthropogenic mobilization flows (including carbon, nitrogen, sulfur, phosphorous, and mercury). For purposes of preliminary investigation (and to stimulate thought, debate, and further research), we have devised a system to approximate anthropogenic and natural mobilization flows for over 70 other elements on the basis of three anthropogenic mobilization factors and three natural mobilization factors. The former are (*a*) the amount of element mobilized through mining; (*b*) the amount of element mobilized through fossil-fuel combustion; and (*c*) the amount of element mobilized through human-initiated biomass burning (such as deforestation, biofuel burning, charcoal making, charcoal burning, and combustion of agricultural residues). The latter factors are (*a*) the amount of element mobilized through weathering of continental crust into rivers; (*b*) the amount of element mobilized through sea spray; and (*c*) the amount of element mobilized through net primary production. These mobilization factors are graphically depicted, using sample data for the mobilization of magnesium, in the cartoon in Figure 2.

First and foremost, the simplified method used herein to estimate the relative anthropogenic dominance of elemental cycles has been designed for standardized comparison across the breadth of the periodic table. Therefore, the calculations derived in this review will not necessarily exactly match (nor even measure) the exact same fluxes of existing biogeochemical cycle analyses [such as the work of

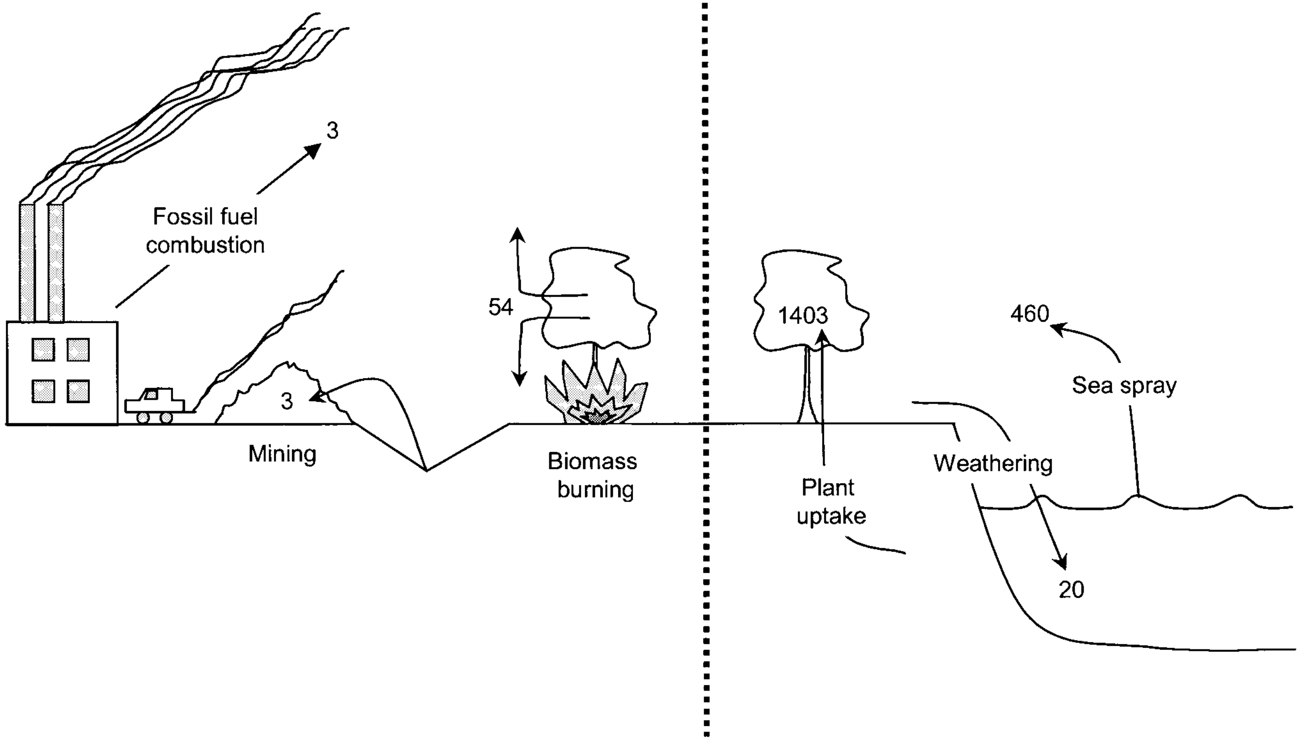

Figure 2 (*left*) Cartoon depicting anthropogenic mobilization (mining, fossil-fuel combustion, and biomass burning) and (*right*) natural mobilization (crustal weathering, sea spray, and plant primary production). Sample data (calculated in this review) on the relative anthropogenic and natural mobilization of magnesium is provided in terragrams per year.

Schlesinger (28), among others]. For instance, gaseous volcanic emissions are not included in this analysis; they are sporadic, poorly quantified, and almost certainly not dominant for the timescales we address [for example, for aluminum and iron, gaseous volcanic mobilization appears to be less than 10% of natural mobilization (3)]. Submarine hydrothermal emissions are also not included. As with gaseous volcanic emissions, they are currently poorly quantified on a global scale for the breadth of elements addressed herein. Mobilization of material through sea-spray processes is also poorly quantified, but it is included here because it is a perpetual and significant movement of material. Most of it, but not all, quickly returns to the sea surface, so this mobilization is more transient and involves less change over time than the other processes. Sea-spray mobilization is important for only a handful of elements (e.g., sodium, chlorine, bromine, sulfur, and a few others), but these deserve at least a preliminary estimate. We also make the logical assumption that nature mobilizes the majority of hydrogen and oxygen (obviously through the hydrologic cycle).

Definitions of mobilization are open to considerable discussion, largely because different definitions serve different uses. Our aim is to reflect the average rate at which the state of a material is transformed from passive (e.g., in rock or soil) to potentially interactive (e.g., in industrial products or in vegetation), with a focus on the pedosphere (where humans literally and figuratively leave their footprints) and the near-surface ocean. Although measuring the amount of these potentially interactive elements that are actually bioavailable but not yet bioincorporated would also be important and interesting, such detailed analysis is not currently possible for the breadth of elements we address in this analysis. We do not address very short-term processes, such as the uptake of carbon by plant photosynthesis during the day and its release by respiration at night. Our inclusion of sea spray might be contested on this basis but seems worth including because of its importance for addressing the cycles of a few elements. Overall, as a rough approximation, we believe that this method would capture over 80% of the actual total mobilization.

This method borrows from the work of Park & Schlesinger (29) on the geochemical cycle of boron, although with a key distinction. We do not partition the mobilization of material into the different recipient reservoirs (the atmosphere, oceans, or land) as is done by Park & Schlesinger. Therefore, the entire mass that has been mobilized is counted as mobilized with our method, regardless of the final destination of the element. For instance, our biomass burning mobilization estimates consider the entire bulk of combusted plant matter as mobilized for the purpose of our calculations. Unlike recent analyses that estimate the gaseous flux of various elements into the atmosphere (see, for example, References 29, 30), we do not differentiate between the amount of the plant matter that becomes a gas or an airborne particulate or that is left behind as ash. Park & Schlesinger's added level of detail would be an improvement for future analyses and would begin to more closely link human perturbation with sensitive natural processes, but this would only be possible with intimate knowledge of the behavior of each individual element. Our method sacrifices this detail to enable a broad comparison of a large number of elements. Also, we believe that our method is an improvement over that of Azar et al. (31), which limited natural mobilization to only weathering and volcanic processes (disregarding the considerable mobilization for a small number of elements from sea spray and biological production).

Table 1 provides the basic concentration factors used in the calculation of anthropogenic and natural mobilization. Specifically, the average elemental compositions of coal, petroleum, continental crust, seawater, and dry plant matter are given. Table 2 uses the basic concentration factors in Table 1, annual mine production statistics from Reference 55 (unless otherwise noted), and values for the annual consumption of fossil fuels (4741 Tg/yr coal, 3268 Tg/yr petroleum) (32), biomass burning (8600 Tg/yr) (30), suspended sediment flow in rivers (1500 Tg/yr) (33), sea-salt aerosol formation (3800 Tg/yr, see derivation below), and net primary production (224,500 Tg/yr) (34).

Sea-spray estimations for the suite of elements are computed using the method employed by Park & Schlesinger (29), except for chlorine, sodium, sulfur, and nitrogen, which have independently calculated values from Graedel & Keene (10) (for chlorine and sodium) and Schlesinger (28) (for sulfur and nitrogen). Specifically, the annual production of sea-salt aerosols has been estimated at 10×10^{15} g/yr (35) to 11.7×10^{15} g/yr (36). The average seawater salinity is 0.035% (29). Multiplying the estimated production of aerosols by the average seawater salinity and by the average concentration of each element in Table 1 [from Stumm & Morgan (37)], we yield two estimates of sea-spray flux. A third estimate is obtained using a similar calculation that takes the calculated sea-spray flux of chlorine estimated by Graedel & Keene (10) (6000 Tg/yr) and multiplies this value by the "chlorinity ratio" of each element in seawater—that is the ratio of the average concentration of each element in seawater to the concentration of chlorine in seawater, again from Table 1. We use the mean of these three estimates in the final estimate of sea-spray flux in Table 2.

Although the magnitudes of the mobilization flows may be known only approximately, such information is often sufficiently quantitative to permit us to explore the relationship between anthropogenic and natural mobilizations. The final three columns of Table 2 offer summary statistics on total element mobilization from its geological reservoirs, the ratio of anthropogenic to natural mobilization, and the percent of total flow of the element that is attributable to anthropogenic activity.

These summary statistics are used to create Figure 3, which depicts the logarithm of anthropogenic mobilization divided by natural mobilization for all of the elemental mobilization flows calculated herein. The elements where human activity dominates mobilization are on the left-hand (positive) side of the graph, and the elements for which nature dominates mobilization are on the right-hand (negative) side of the graph. Of the 77 elements depicted in this graph, human activities dominate 54 elements, and nature dominates 23 elements. Recall that nature also dominates the mobilization of hydrogen and oxygen, although these are not included in Figure 3. Figure 4*a–f* displays this information in more detail, showing bar graphs of the various elements and their relative mobilization from

TABLE 1 Concentration factors used in mobilization calculations

Element		Average concentration in coal in g/Mg[a]	Average concentration in petroleum in g/Mg[b]	Average concentration in crust in g/Mg[c]	Average concentration in seawater in g/Mg[d]	Average concentration in dry plant matter in g/Mg[e]
2	He	—	—	0.003[f]	0.00001	—
3	Li	20	—	22	0.2	—
4	Be	2.0	0.0004[g]	3.1		—
5	B	50	0.2[h]	17	4.5	58
6	C	890,000[i]	855,000[i]	3,240	28	478,000[k]
7	N	5,850[i]	10,500[j]	83	150	25,000
9	F	150	—	611	1.3	—
11	Na	400[l]	12	25,670	10,770	1,100
12	Mg	700[l]	0.1[g]	13,510	1,290	6,250
13	Al	11,000[l]	0.5[g]	77,440	0.002	500[m]
14	Si	—	—	303,480	2.2	—
15	P	150	—	665	0.1	2,250
16	S	13,500[i]	10,300[j]	953	905	2,000
17	Cl	1,000	10	640	19,354	550
19	K	1,000[l]	4.9	28,650	399	32,500
20	Ca	2,300[l]	5.0[g]	29,450	412	30,000
21	Sc	4.0	0.004	7.0	—	—
22	Ti	600	0.1	3,117	—	1.0[m]
23	V	40	279	53	0.003	1.6[m]
24	Cr	20	2.7[n]	35	0.0003	0.2[m]
25	Mn	70	0.6	527	0.0002	138
26	Fe	7,500[l]	20	30,890	0.002	175
27	Co	5.0	3.4	12	0.00005	15
28	Ni	20	66	19	0.001	3.0[m]
29	Cu	15	0.4[n]	14	0.001	10
30	Zn	50	0.8[n]	52	0.8	45
31	Ga	5.0	0.2	14	—	—
32	Ge	5.0	0.001[g]	1.4	—	—
33	As	10	0.2[n]	2.0	0.004	0.2[m]
34	Se	1.0	0.5	0.08	—	0.2[m]
35	Br	20	0.6	1.6	67	—
37	Rb	15	—	110	0.1	—
38	Sr	200	0.1[g]	316	8	—
39	Y	15	0.001[g]	21	—	—

(*Continued*)

TABLE 1 (*Continued*)

Element		Average concentration in coal in g/Mg[a]	Average concentration in petroleum in g/Mg[b]	Average concentration in crust in g/Mg[c]	Average concentration in seawater in g/Mg[d]	Average concentration in dry plant matter in g/Mg[e]
40	Zr	50	—	237	—	—
41	Nb	5.0	—	26	—	—
42	Mo	3.0	7.9	1.4	0.01	2.8
44	Ru	0.1[o]	—	0.001	—	—
45	Rh	0.1[o]	—	0.0006	—	—
46	Pd	0.1[o]	—	0.004	—	—
47	Ag	0.1	0.0001[g]	0.055	0.00004	0.06[m]
48	Cd	0.5	0.002[n]	0.102	0.0001	0.6[m]
49	In	0.1[o]	—	0.06	—	—
50	Sn	2.0	0.01[g]	2.5	0.00001	0.3[m]
51	Sb	1.0	0.1	0.3	0.0002	0.06[m]
52	Te	0.1[o]	—	0.005	—	—
53	I	5.0	1.4	1.4	0.1	—
55	Cs	1.0	—	5.8	0.0004	—
56	Ba	200	0.1[g]	668	0.02	—
57	La	10	0.005[g]	32	—	—
58	Ce	20	0.01[g]	66	—	—
59	Pr	3.0	—	6.3	—	—
60	Nd	10	—	26	—	—
62	Sm	2.0	—	4.7	—	0.01[m]
63	Eu	0.5	—	1.0	—	—
64	Gd	1.0	—	2.8	—	—
65	Tb	0.2	—	0.5	—	—
66	Dy	3.0	—	2.9	—	—
67	Ho	1.0	—	0.6	—	—
68	Er	1.0	0.001[g]	2.1	—	—
69	Tm	0.1[o]	—	0.3	—	—
70	Yb	1.0	—	1.5	—	—
71	Lu	0.2	—	0.3	—	—
72	Hf	1.0	—	5.8	—	—
73	Ta	0.2	—	1.5	—	—
74	W	1.0	—	1.4	0.0001	—
75	Re	0.1[o]	—	0.0004	—	—

(*Continued*)

TABLE 1 (*Continued*)

Element		Average concentration in coal in g/Mg[a]	Average concentration in petroleum in g/Mg[b]	Average concentration in crust in g/Mg[c]	Average concentration in seawater in g/Mg[d]	Average concentration in dry plant matter in g/Mg[e]
76	Os	0.1[o]	—	0.00005	—	—
77	Ir	0.1[o]	—	0.00005	—	—
78	Pt	0.1[o]	—	0.0004	—	—
79	Au	0.01[o]	—	0.003	0.000004	—
80	Hg	0.1	7.7	0.06	0.00003	0.02[m]
81	Tl	0.1[o]	—	0.8	—	—
82	Pb	40	0.3[g]	17	0.00004	2.7[m]
83	Bi	0.1[o]	—	0.1	—	—
90	Th	4.0	—	10	0.00001	—
92	U	2.0	0.02	2.5	0.003	—

[a] From Reference 45 unless otherwise noted.

[b] From Reference 46 unless otherwise noted.

[c] From Reference 47 unless otherwise noted.

[d] From Reference 37 unless otherwise noted.

[e] From Reference 48.

[f] From Reference 53.

[g] From Reference 50.

[h] From Reference 29.

[i] Major element concentrations derived from empirical formulas of bituminous ($C_{137}H_{97}O_9NS$) and anthracite ($C_{240}H_{90}O_4NS$) coal.

[j] From Reference 51.

[k] Average plant carbon concentration estimated from the Biomass Feedstock Composition and Properties Database (54).

[l] From Reference 49, on the basis of mean concentration in U.S. coal.

[n] From Reference 52.

[m] From Reference 3.

[n] From Reference 52.

[o] Maximum concentration (element concentration at or below detection limit).

anthropogenic and natural processes. These diagrams are organized according to the total calculated mobilization flow. For ease of graphing, we only include those elements whose total mobilization is greater than 0.01 Tg/year; therefore only 56 of the 77 elements from Table 2 are depicted. As is apparent from these figures, nature generally dominates the high total flow elements (Figure 4*a–c*), whereas human activities generally dominate the low total flow elements (Figure 4*d–f*). This relationship is graphically displayed in Figure 4*g*, which shows the anthropogenic dominance of elements with low total mobilization.

An important caveat with respect to our dominance determinations is that they apply only to flows, not to impacts. The environmental impact of CFCs is very

TABLE 2 Calculation of mobilization rates and dominance

Element		Anthropogenic mobilization				Natural mobilization				Mobilization summary		
		From mining in Gg/year[a]	From fossil fuels in Gg/year[b]	From biomass burning in Gg/year[c]	Total in Tg/year	From crustal weathering in Gg/year[d]	From seaspray in Gg/year[e]	From plant primary production in Gg/year[f]	Total in Tg/year	Total in Tg/year	Anthro-pogenic vs. natural ratio	Anthro-pogenic as % of total
2	He	19	—	—	0.02	0.005	0.002	—	0.00001	0.02	2,879	100
3	Li	5.6[g]	95	—	0.1	33	62	—	0.10	0.2	1.1	51
4	Be	0.3	9.5	—	0.01	4.7	—	—	0.005	0.01	2.1	68
5	B	1,360	238	495	2.1	26	1,604	12,909	15	17	0.1	13
6	C	—	7,013,630	4,110,800	11,124	4,860	9,991	107,311,000	107,326	118,450	0.1	9
7	N	109,000	100,000[h]	215,000	424	125	30,000[h]	5,612,500	5643	6,067	0.1	7
9	F	2,320	711	—	3.0	917	463	—	1.4	4.4	2.2	69
11	Na	90,771	1,937	9,460	102	38,505	390,0000[i]	246,950	4,185	4,288	0.02	2
12	Mg	3,458	3,319	53,750	61	20,265	459,891	1,403,125	1,883	1,944	0.03	3
13	Al	24,000	52,153	4,300	80	116,160	0.8	112,250	228	309	0.4	26
14	Si	100,500	—	—	101	455,220	795	—	456	557	0.2	18
15	P	12,000[h]	711	19,350	32	998[h]	22	505,125	506	538	0.06	6
16	S	57,200	97,664	17,200	172	1,430	144,000[h]	449,000	594	766	0.3	22
17	Cl	129,812	4,772	4,730	139	960	6,000,000[i]	123,475	6,124	6,264	0.02	2
19	K	21,002	4,757	279,500	305	42,975	142,245	7,296,250	7,481	7,787	0.04	4
20	Ca	54,000[g]	10,921	258,000	323	44,175	146,915	6,735,000	6,926	7,249	0.05	4
21	Sc	0.3[j]	19	—	0.02	11	—	—	0.01	0.03	1.8	65
22	Ti	2,817	2,845	8.6	5.7	4,676	—	225	4.9	11	1.2	54
23	V	43	1,102	14	1.2	80	0.9	359	0.4	1.6	2.6	72
24	Cr	14,400	103	2.0	15	53	0.1	52	0.1	15	139	99
25	Mn	7,280	334	1,183	8.8	791	0.08	30,869	32	40	0.3	22
26	Fe	725,000[g]	35,622	1,505	762	46,335	0.6	39,288	86	848	8.9	90
27	Co	33	35	126	0.2	17	0.02	3,278	3.3	3.5	0.1	6

(*Continued*)

TABLE 2 (*Continued*)

Element		Anthropogenic mobilization				Natural mobilization				Mobilization summary		
		From mining in Gg/year[a]	From fossil fuels in Gg/year[b]	From biomass burning in Gg/year[c]	Total in Tg/year	From crustal weathering in Gg/year[d]	From seaspray in Gg/year[e]	From plant primary production in Gg/year[f]	Total in Tg/year	Total in Tg/year	Anthro-pogenic vs. natural ratio	Anthro-pogenic as % of total
28	Ni	1,250	311	26	1.6	28	0.5	673.5	0.7	2.3	2.3	69
29	Cu	13,200	72	86	13	21	0.2	2,245	2.3	16	5.9	85
30	Zn	8,730	240	387	9.4	78	293	10,103	10	20	0.9	47
31	Ga	0.1	24	—	0.02	21	—	—	0.02	0.05	1.2	54
32	Ge	0.1	24	—	0.02	2.1	—	—	0.002	0.03	11	92
33	As	34	48	1.7	0.08	3.0	1.3	45	0.05	0.1	1.7	63
34	Se	1.4	6.2	1.7	0.01	0.1	—	45	0.05	0.05	0.2	17
35	Br	542	97	—	0.6	2.4	23,993	—	24	25	0.03	3
37	Rb	0.001	71	—	0.07	165	43	—	0.2	0.3	0.3	25
38	Sr	520	949	—	1	474	2816	—	3.3	4.8	0.4	31
39	Y	1.9	71	—	0.07	31	—	—	0.03	0.1	2.4	70
40	Zr	1,040	237	—	1	356	—	—	0.4	1.6	3.6	78
41	Nb	33	24	—	0.1	39	—	—	0.04	0.1	1.4	59
42	Mo	129	40	24	0.2	2.1	3.4	617	0.6	0.8	0.3	24
44	Ru	0.01[k]	0.5	—	0.0005	0.002	—	—	0.000002	0.0005	325	100
45	Rh	0.03[l]	0.5	—	0.0005	0.001	—	—	0.000001	0.001	555	100
46	Pd	0.2	0.5	—	0.0006	0.01	—	—	0.00001	0.001	108	99
47	Ag	18	0.5	0.5	0.02	0.1	0.02	13	0.01	0.03	1.4	58
48	Cd	20	2.4	5.2	0.03	0.2	0.04	135	0.1	0.16	0.2	17
49	In	0.3	0.5	—	0.0008	0.1	—	—	0.0001	0.001	8.8	90
50	Sn	238	10	2.6	0.3	3.8	0.004	67	0.07	0.3	3.5	78
51	Sb	118	5.2	0.5	0.1	0.5	0.09	13	0.01	0.1	8.8	90
52	Te	0.1	0.5	—	0.0006	0.008	—	—	0.000008	0.0006	80	99

53	I	19	28	—	0.05	2.1	23	—	0.02	0.07	1.9	66
55	Cs	100	4.7	—	0.1	8.7	0.1	—	0.009	0.1	12	92
56	Ba	3,060	949	—	4	1002	8	—	1.0	5.0	4.0	80
57	La	20[j]	47	—	0.1	48	—	—	0.05	0.1	1.4	58
58	Ce	33[j]	95	—	0.1	99	—	—	0.1	0.2	1.3	56
59	Pr	0.3[j]	14	—	0.01	9.5	—	—	0.01	0.02	1.5	61
60	Nd	11[j]	47	—	0.06	39	—	—	0.04	0.10	1.5	60
62	Sm	0.3[j]	9.5	0.05	0.01	7.1	—	1.2	0.01	0.02	1.2	54
63	Eu	0.3[j]	2.4	—	0.003	1.4	—	—	0.001	0.004	1.9	65
64	Gd	0.3[j]	4.7	—	0.005	4.2	—	—	0.004	0.01	1.2	55
65	Tb	0.3[j]	0.9	—	0.001	0.8	—	—	0.001	0.002	1.7	63
66	Dy	0.3[j]	14	—	0.01	4.4	—	—	0.004	0.02	3.3	77
67	Ho	0.3[j]	4.7	—	0.005	0.9	—	—	0.001	0.006	5.5	85
68	Er	0.3[j]	4.7	—	0.005	3.2	—	—	0.003	0.01	1.6	62
69	Tm	0.3[j]	0.5	—	0.001	0.5	—	—	0.0005	0.001	1.8	64
70	Yb	0.3[j]	4.7	—	0.005	2.3	—	—	0.002	0.01	2.3	69
71	Lu	0.3[j]	0.9	—	0.001	0.4	—	—	0.000	0.002	3.2	76
72	Hf	21[m]	4.7	—	0.03	8.7	—	—	0.01	0.03	2.9	75
73	Ta	0.8	0.9	—	0.002	2.3	—	—	0.002	0.004	0.8	44
74	W	37	4.7	—	0.04	2.1	0.03	—	0.002	0.04	20	95
75	Re	0.03	0.5	—	0.001	0.001	—	—	0.000001	0.001	838	100
76	Os	0.0002[n]	0.5	—	0.0005	0.0001	—	—	0.0000001	0.0005	6323	100
77	Ir	0.004[k]	0.5	—	0.0005	0.0001	—	—	0.0000001	0.0005	6373	100
78	Pt	0.2	0.5	—	0.001	0.001	—	—	0.000001	0.001	1049	100
79	Au	2.6	0.05	—	0.003	0.004	0.001	—	0.000005	0.003	504	100
80	Hg	1.4	26	37	0.06	0.08	0.01	3.4	0.003	0.07	18.5	95
81	Tl	0.02	0.5	—	0.0005	1.1	—	—	0.001	0.002	0.4	30

(*Continued*)

TABLE 2 (*Continued*)

Element		Anthropogenic mobilization				Natural mobilization				Mobilization summary		
		From mining in Gg/year[a]	From fossil fuels in Gg/year[b]	From biomass burning in Gg/year[c]	Total in Tg/year	From crustal weathering in Gg/year[d]	From seaspray in Gg/year[e]	From plant primary production in Gg/year[f]	Total in Tg/year	Total in Tg/year	Anthro-pogenic vs. natural ratio	Anthro-pogenic as % of total
82	Pb	3,100	191	23	3.3	26	0.01	606	0.6	3.9	5.2	84
83	Bi	5.9	0.5	—	0.01	0.2	—	—	0.0002	0.01	34	97
90	Th	1.5[o]	19	—	0.02	15	0.003	—	0.02	0.04	1.3	57
92	U	35[g]	10	—	0.04	3.8	1.1	—	0.005	0.05	9.2	90

[a] From Reference 55 unless otherwise noted. Some elemental values were calculated from their common mineral ore compounds.

[b] Assuming worldwide consumption of 4741 Tg/yr (32) and concentration factors from Table 1.

[c] Assuming worldwide biomass burning of 8600 Tg/yr (30) and concentration factors from Table 1.

[d] Assuming suspended sediment flux of 1500 Tg/yr (33) and concentration factors from Table 1.

[e] Assuming 2×10^{11} Mg/yr seawater becomes sea spray, using the method from Park & Schlesinger (29).

[f] Assuming worldwide net primary production of 224,500 Tg/yr (34).

[g] Reference 27.

[h] Independently calculated values (28).

[i] Independently calculated values (10).

[j] Rare-earth mining estimated using average ratio of rare-earth elements in common mineral ores (56) and bulk rare-earth mining statistics (55).

[k] Reference 57.

[l] Reference 58.

[m] Hafnium mining estimated from average ration between zirconium and hafnium in common mineral ores of 50:1 (55).

[n] Estimate from Christie & Challis (59).

[o] Estimate from Roskill (60), using thorium content of total monzanite produced for its rare-earth element content (thorium is an unwanted by-product).

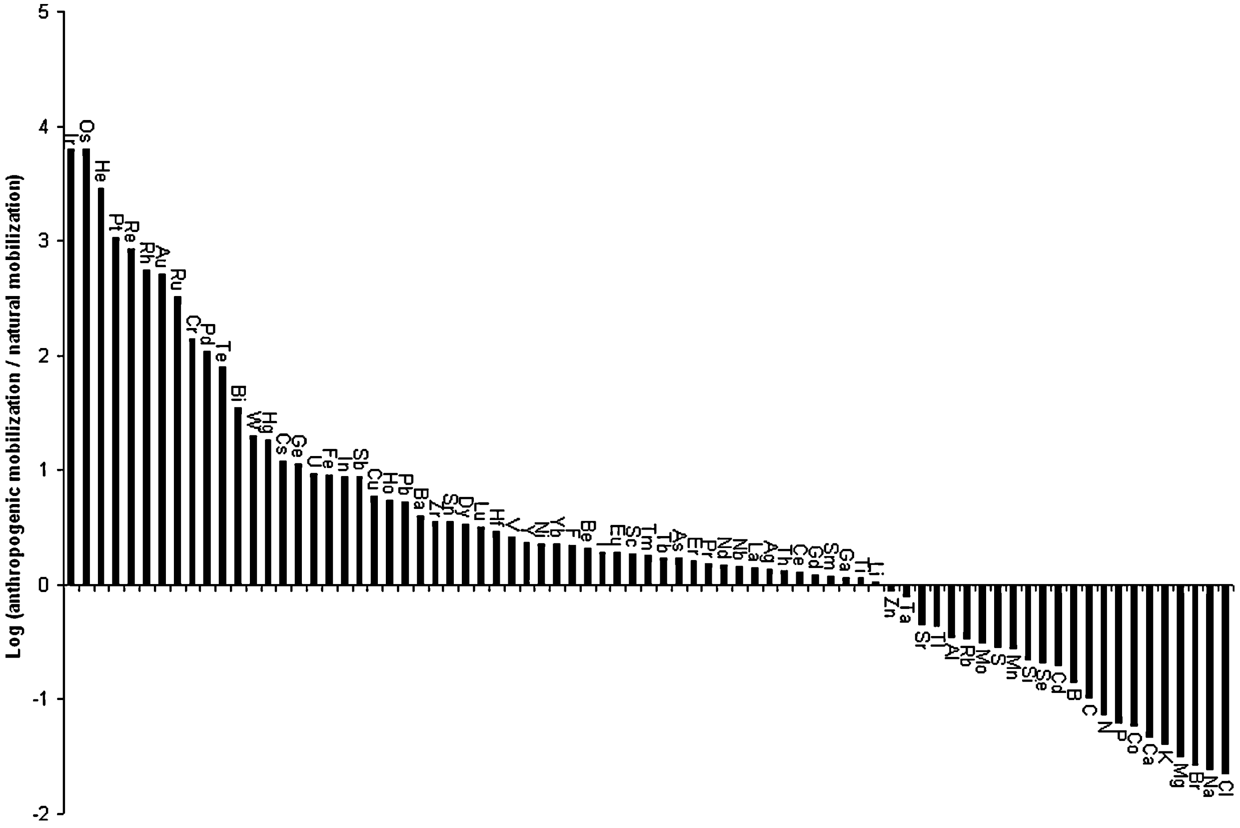

Figure 3 Graphic comparison of the ratio of anthropogenic and natural mobilization flows. Human activities mobilize more of each element on the left side of the diagram; natural processes mobilize more of each element on the right side of the diagram.

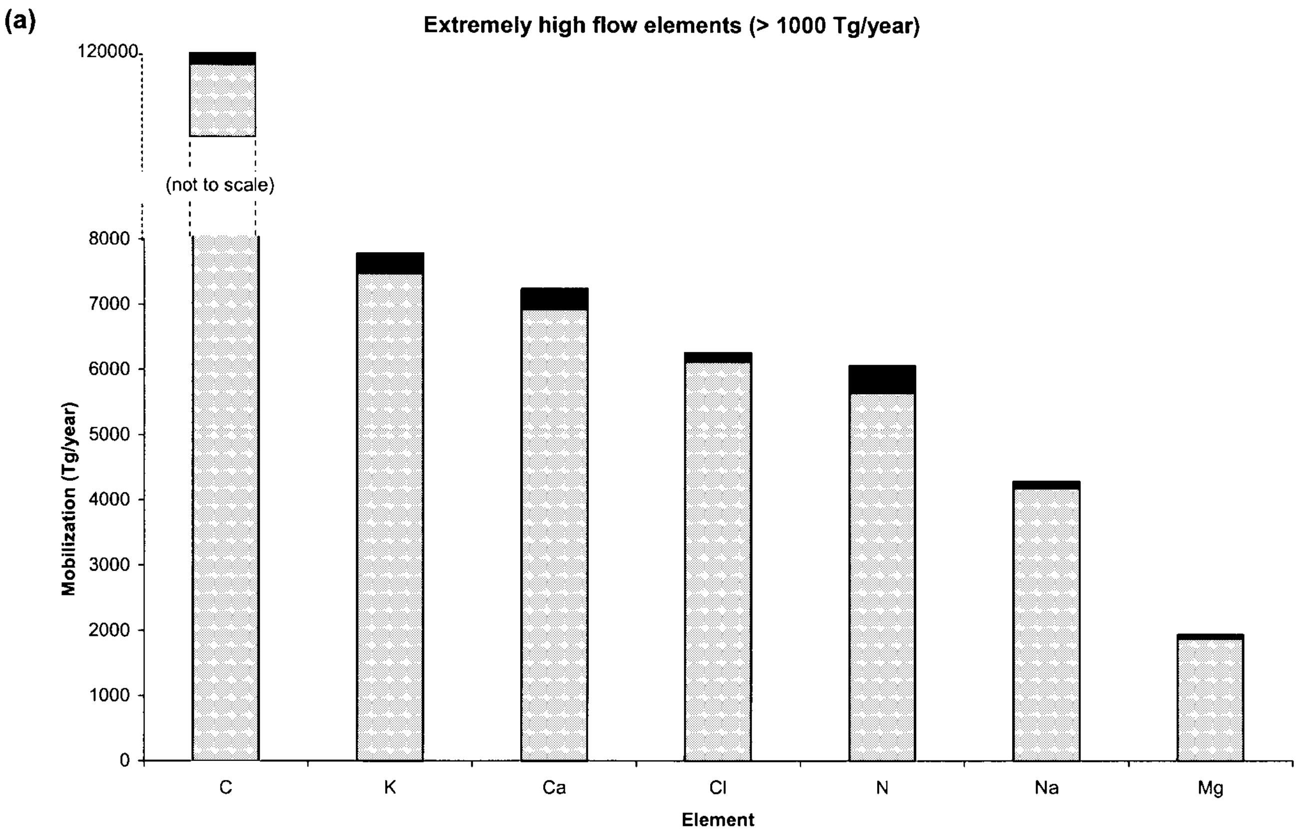

Figure 4 Charts depicting anthropogenic (*black* regions) and natural (*gray* regions) mobilization of selected elements, organized according to descending magnitude of total mobilization. Elements with total mobilization below 0.01 Tg/year are not shown.

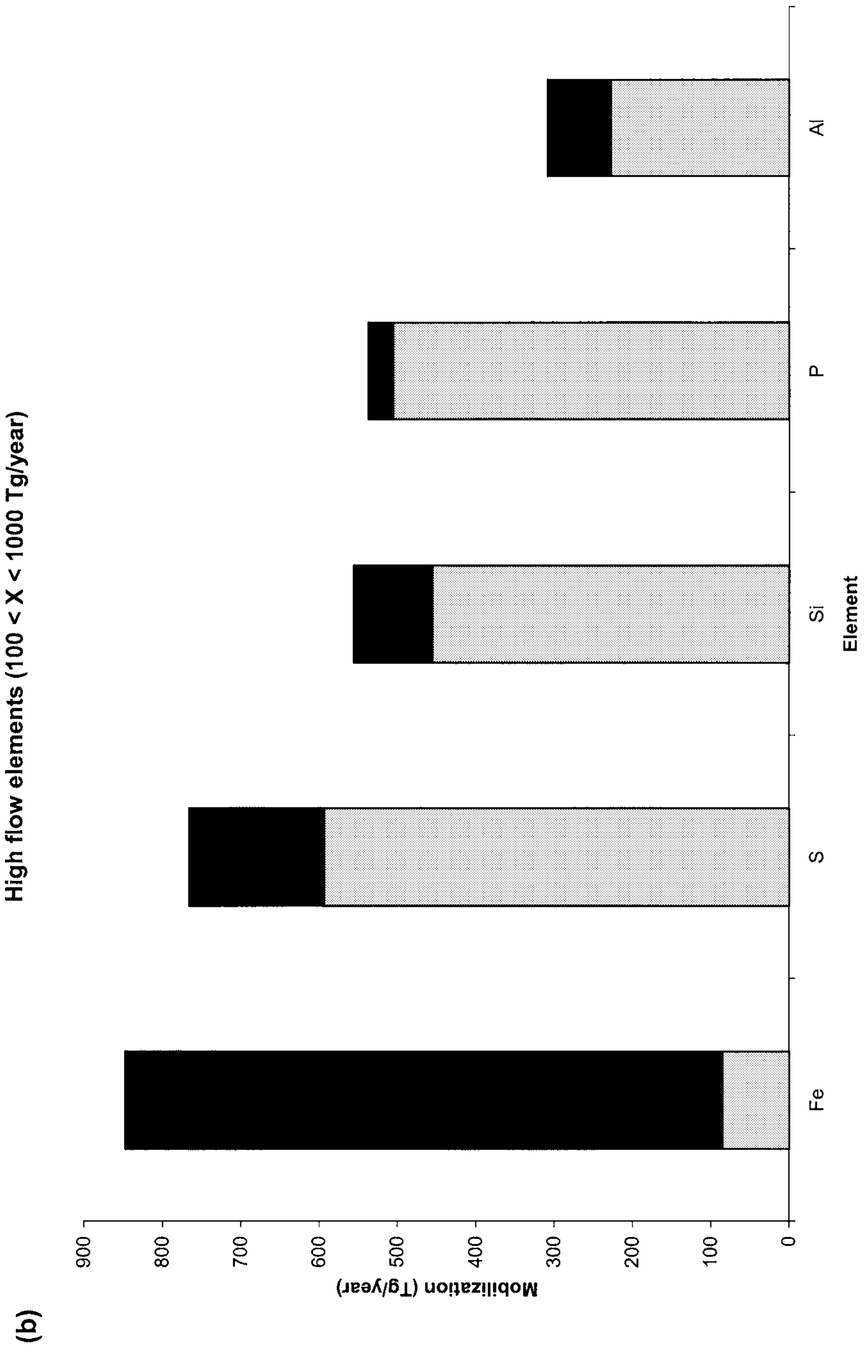

Figure 4 *(Continued)*

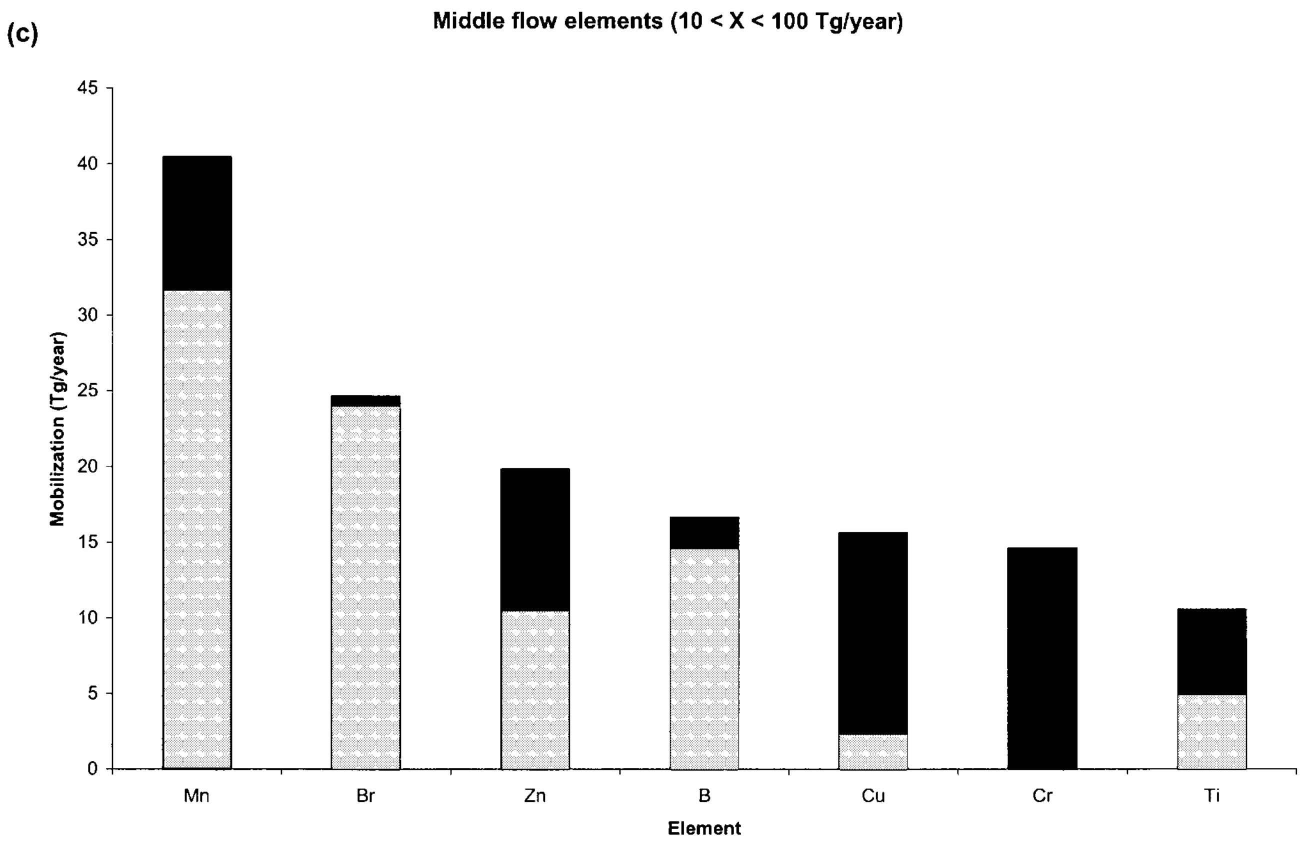

Figure 4 (*Continued*)

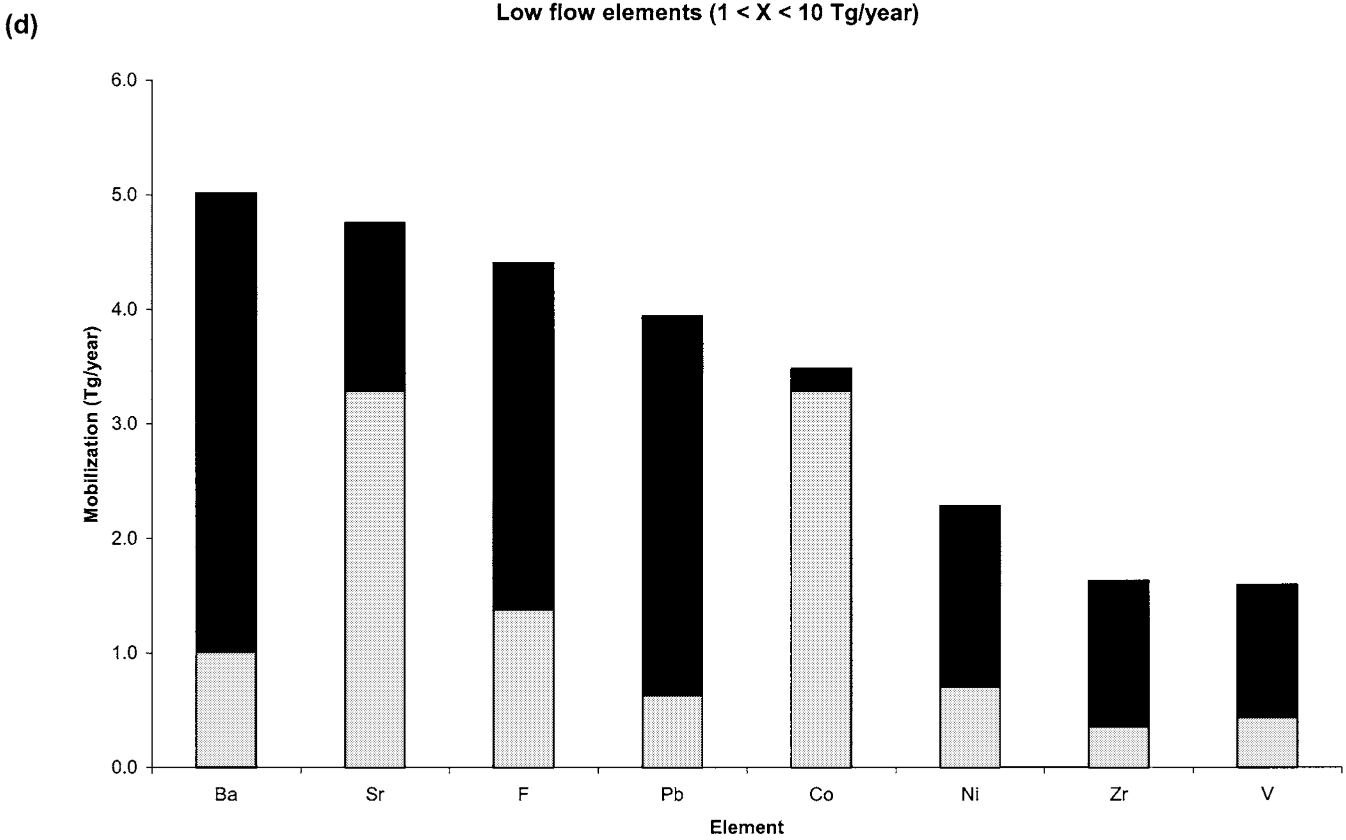

Figure 4 (*Continued*)

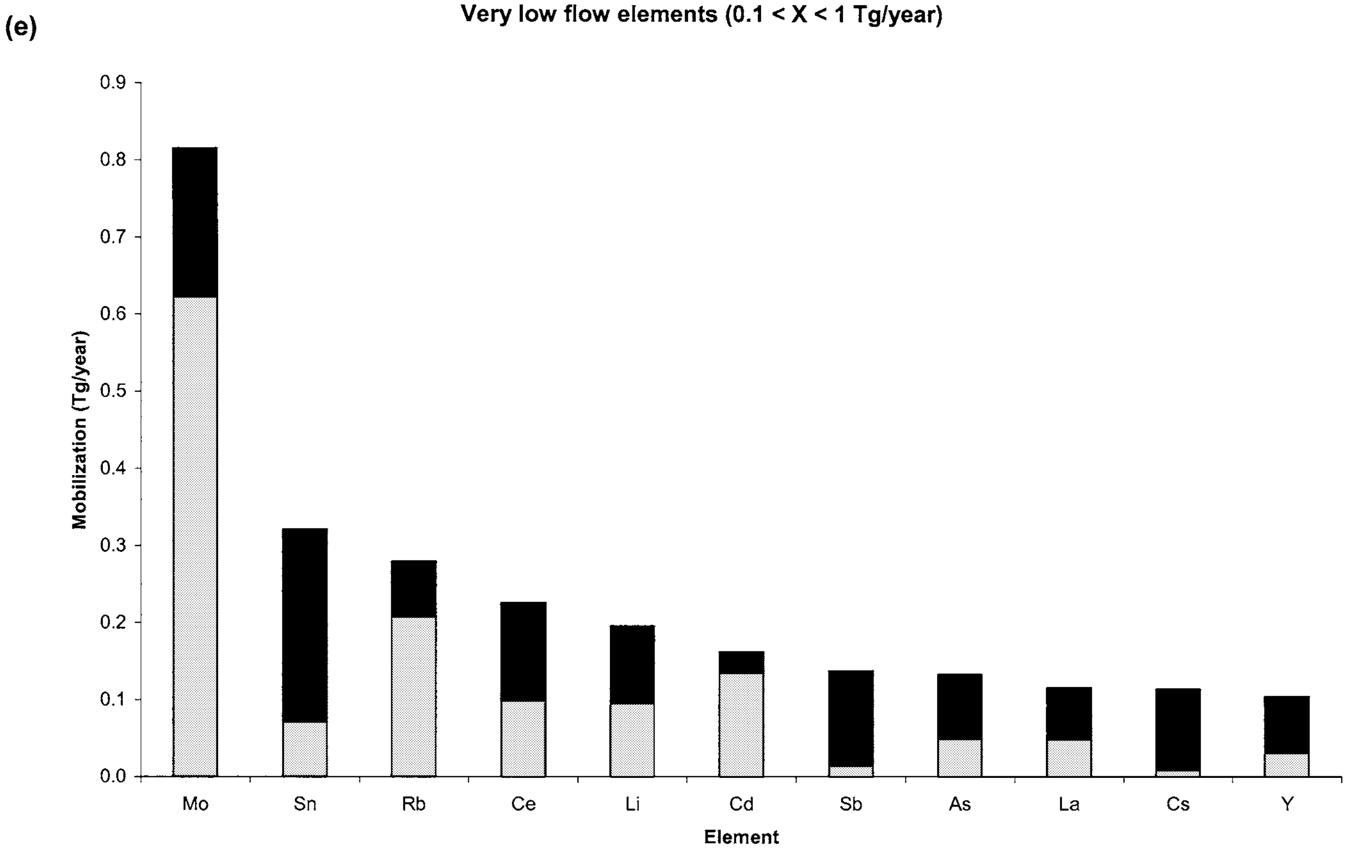

Figure 4 (*Continued*)

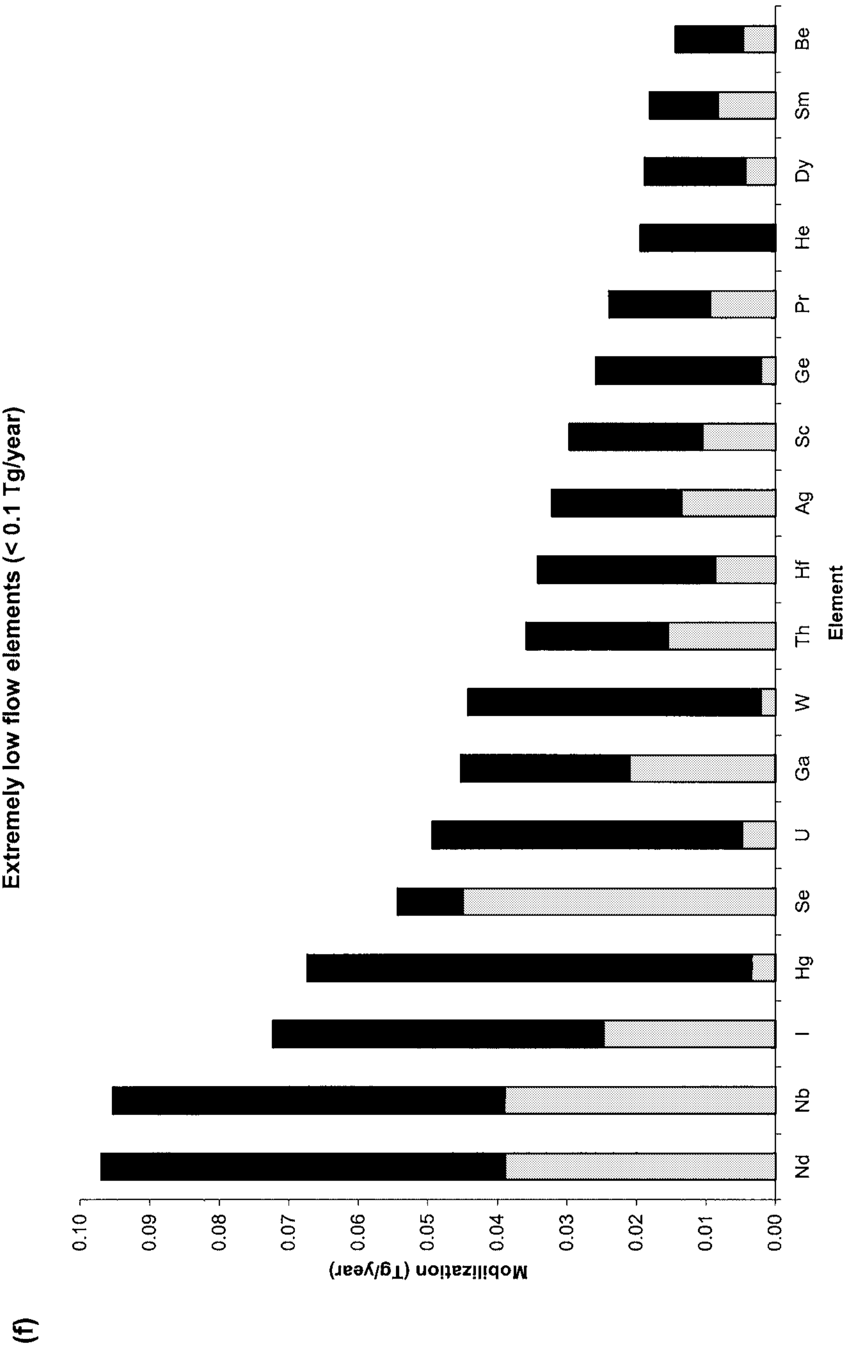

Figure 4 *(Continued)*

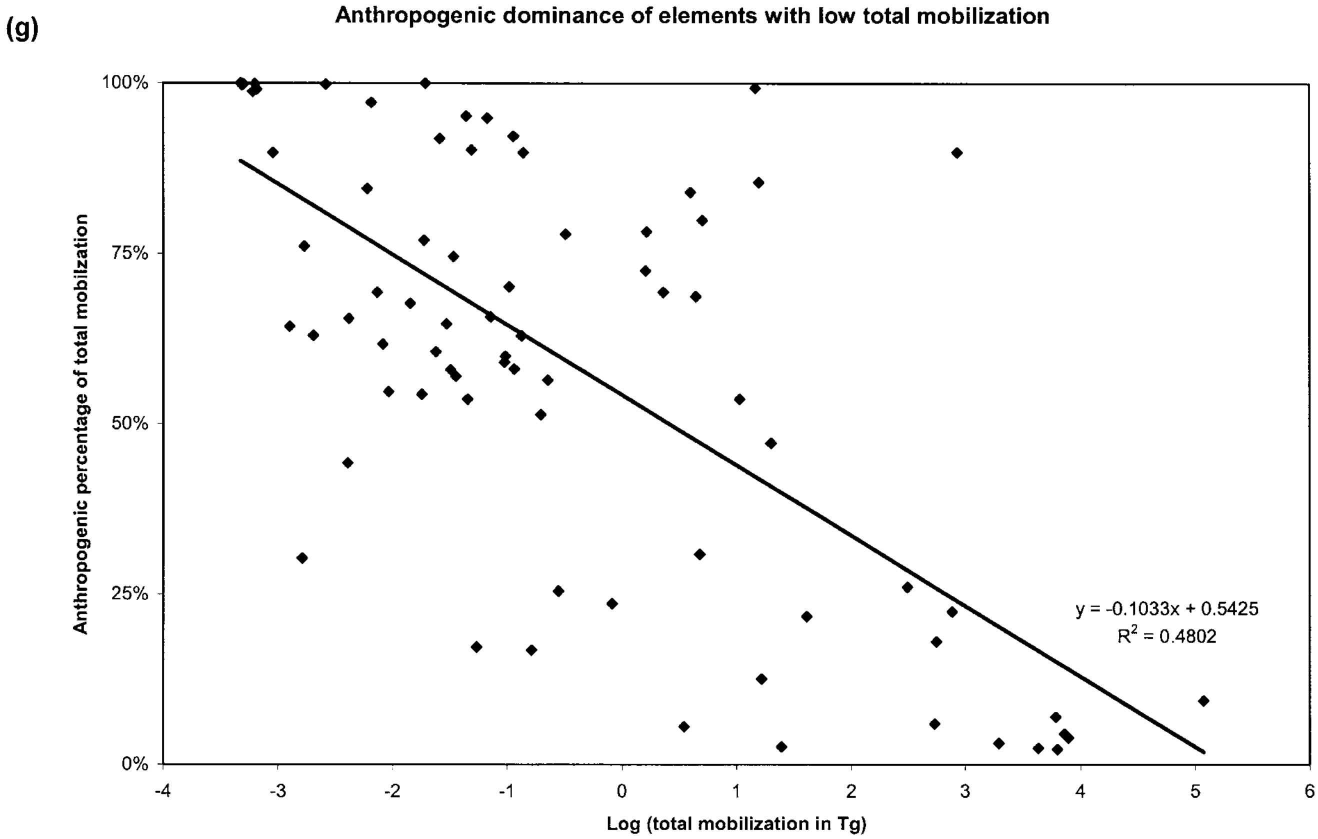

Figure 4 (*Continued*)

great, for example, but the CFC flows are only tiny parts of the flows of carbon and the halogens. In many cases, environmental impacts are better studied using cycles of particular molecules rather than those of the elements that make up the molecules. For tractability, however, this paper restricts itself to the elements.

Again we stress that the precise ratio calculated herein is simply an initial measure until more detailed determinations are undertaken. Acknowledging the large uncertainties in our method for estimating anthropogenic and natural mobilization in elemental cycles, it may be more useful to group our estimates of anthropogenic influence on elemental mobilization on a three-level scale: unperturbed ($<$15%), perturbed (15% to 50%), and dominant ($>$50%). In some cases, these evaluations can be quite accurate; in others, the information is sketchy at best. In Figure 5, indications of the degree of anthropogenic dominance are shown on a periodic table. Figure 5 demonstrates dramatically the dominance of nature for many of the elements in Groups IA, IIB, and VIIA of the periodic table, and of human action for most of the elements in Groups IB, IIIB, IVB, VB, VIB, and VIIIB. Groups IIB, IIIA, IVA, VA, and VIIB show mixed dominance. However, it is clear from this figure that humanity places a considerable footprint on the entire periodic table.

We propose that the reason for this pattern of dominance is related principally to the solubility in water of the predominant natural forms of the elements. Calcium carbonate is relatively water soluble, for example, and nature dominates the calcium cycle. The oxides and sulfides of copper are very poorly soluble in water, and human action dominates the copper cycle. The way the elements are used reflects their water solubility. Those that are water soluble include the nutrients transported to and taken in by plants and animals, whereas the water-insoluble structural metals provide humans with long-lasting structures. This potential correlation is demonstrated in Figure 6 by plotting the anthropogenic cycle dominance against the aqueous solubility of common naturally occurring compounds for a selection of elements.

The outliers of Figure 5—manganese, cobalt, zinc, cadmium, selenium, and molybdenum—do not follow the proposed pattern of human dominance of most of the metals and heavier elements. As the underlying data show (see Table 2), the natural mobilization from plant uptake during primary production tilts the mobilization dominance of these elements toward nature. Closer inspection of Table 2 shows that plant uptake also accounts for considerable mobilizations of iron, arsenic, tin, antimony, and lead, even though human activity still dominates total mobilization.

CYCLES OVER SPACE AND TIME

Only since the industrial revolution (i.e., since about 1750) have human beings conducted technological activities on a scale broad enough to be noticeable in planetary materials' cycles. As shown in Figure 7*a*, virtually the entire historical production of copper and zinc, for example, occurred within the years 1800–2000, and some 90% occurred within the twentieth century alone. Trends in coal

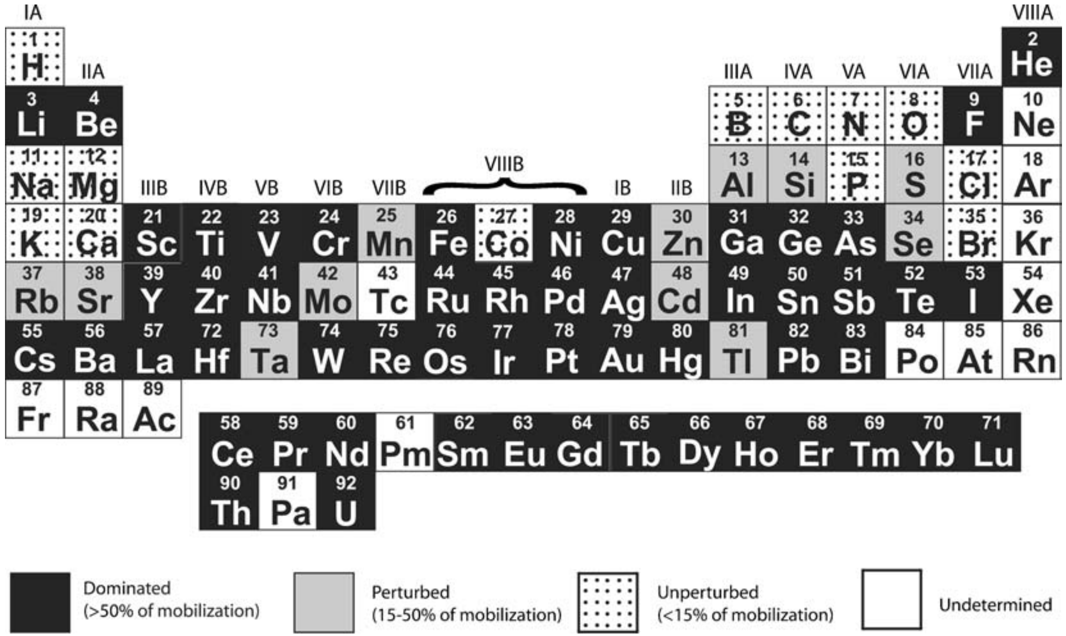

Figure 5 A periodic chart of the relative anthropogenic dominance of the mobilization flows of the elements. Unfilled boxes indicate elements for which dominance is undetermined.

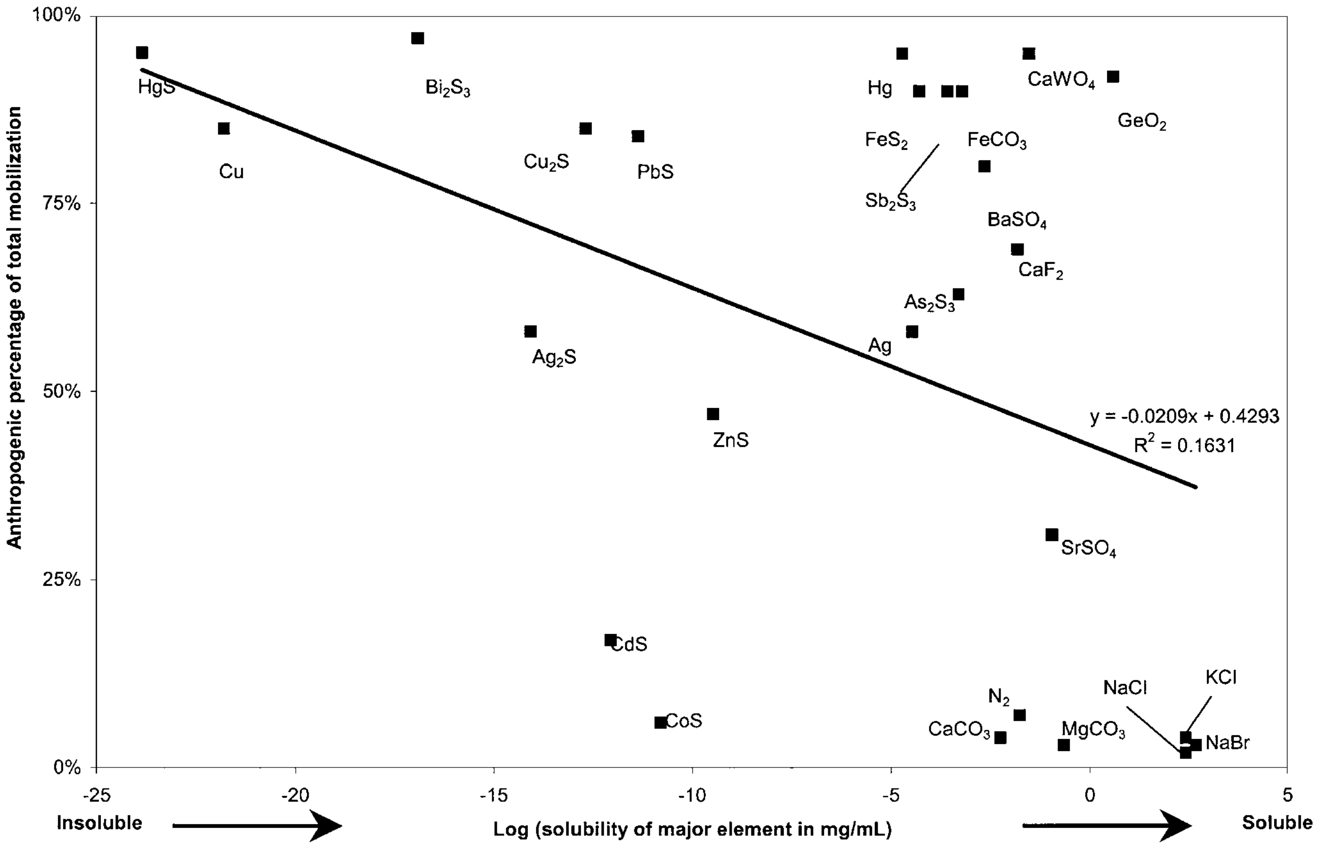

Figure 6 Plot of the degree of anthropogenic cycle dominance for selected elements versus the logarithm of the aqueous solubility of common chemical forms of the element in nature. Aqueous solubility data from References 61–64.

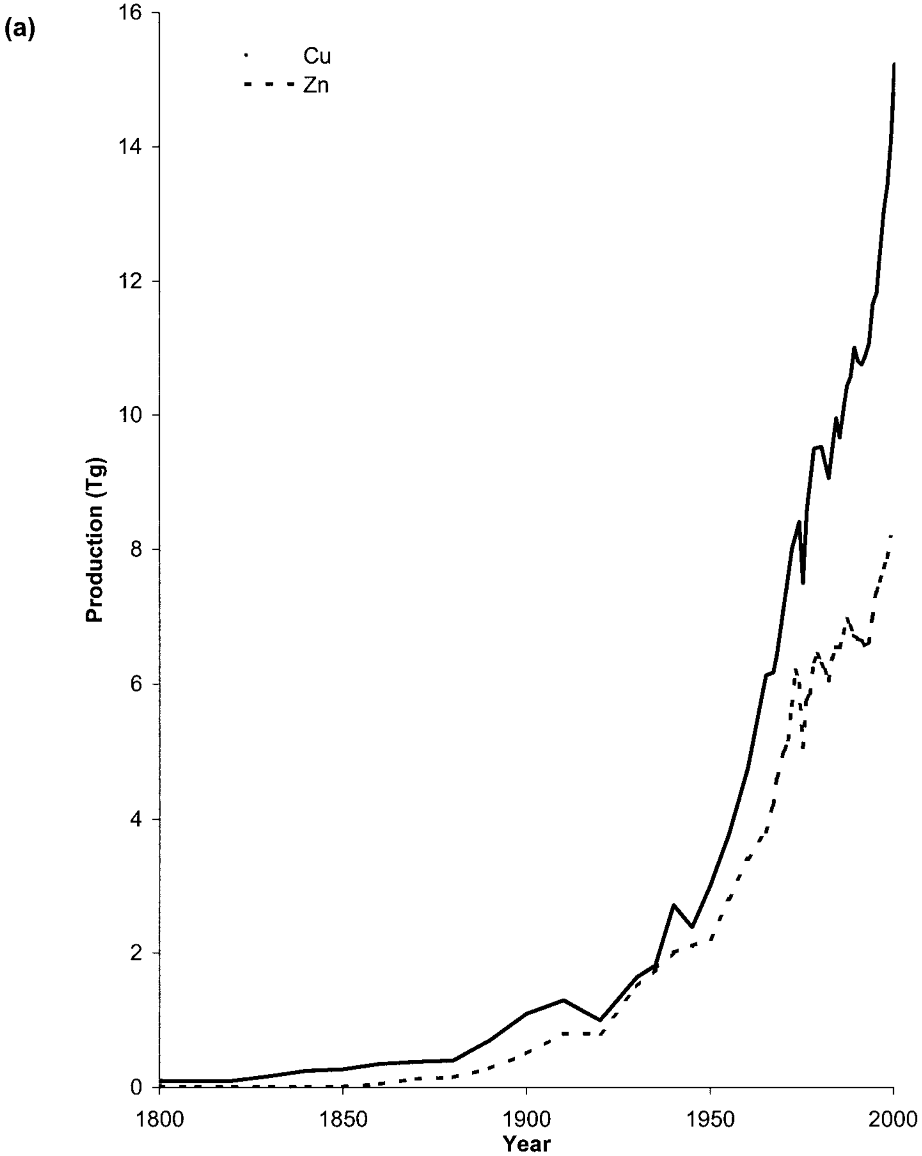

Figure 7 Trends in material production (i.e., mining and extraction statistics) from 1800 to 2000 for (*a*) copper and zinc (adapted from References 65–68); and (*b*) coal and oil (adapted from References 69–70).

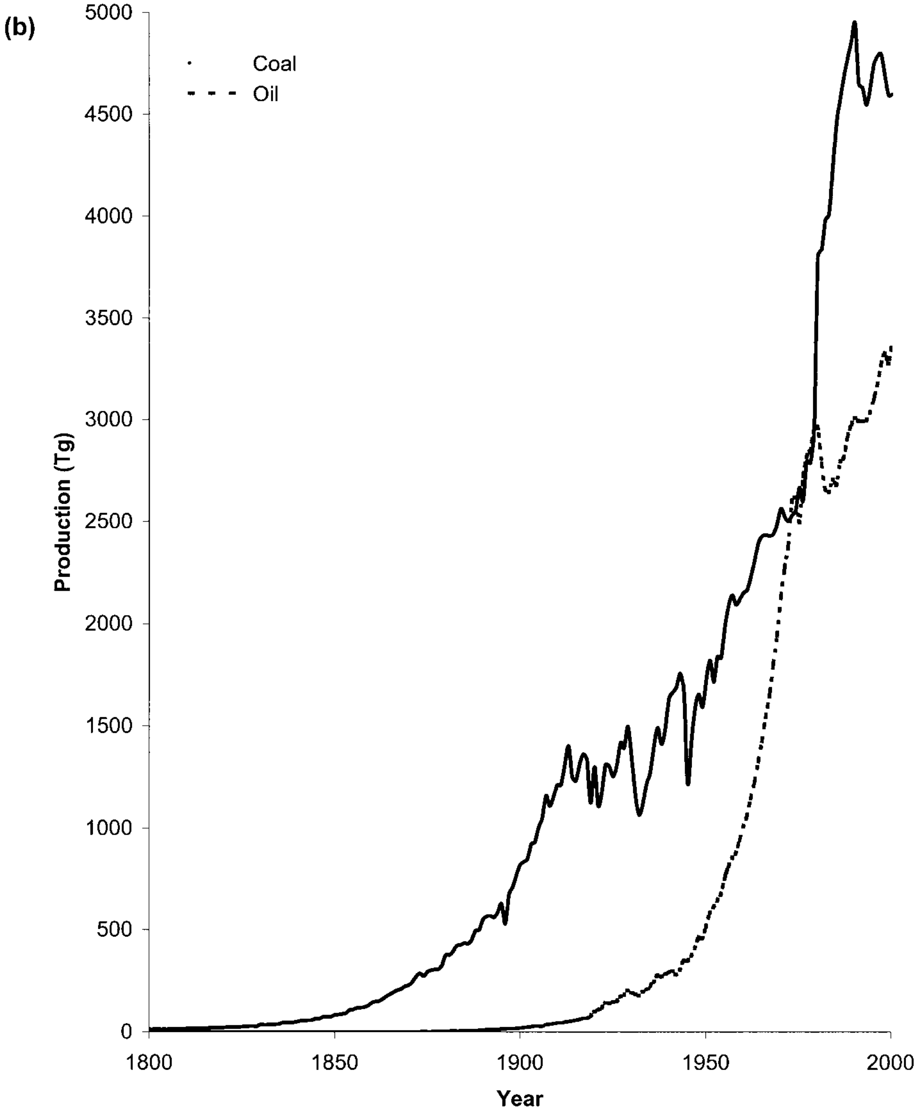

Figure 7 (*Continued*)

and crude oil production, shown in Figure 7*b*, are similar. Accordingly, relatively accessible commercial and industrial information should, in principle, be sufficient to prepare at least an approximate analysis of human influence.

Such cycles are potentially of great value to environmental scientists and to resource specialists. Cycles developed by Socolow & Thomas and the United States Interagency Working Group on Industrial Ecololgy, Material and Energy Flows (11, 38) for lead in the United States for 1970 and 1993 (Figure 8*a* and *b*, respectively) suggest the benefits that may accrue from technological cycle analysis. As shown in Figure 8, there are some very interesting differences between the cycles for the two years, including the following:

- Total lead consumption in 1993 was about 17% higher than in 1970.
- The 1993 lead recycling percentage is much higher: 64% vs 37%.
- Mine production in 1993 was down by 40% relative to 1970 because of recycling.
- The loss of lead to gasoline exhaust emissions was about 30% of total emissions in 1970; by 1993, there was none.
- Lead paint use was down by more than 30% in 1993 vs 1970 (one cannot tell exactly how much because the category includes lead in glass, which has increased with high rates of computer screen manufacture).

Note how environmental and human health issues (including the hazards from lead releases to the environment, especially from auto emissions; the hazards of using leaded paints in indoor situations, where paint chips may be ingested by children; and the efforts to recycle batteries) drove these changes. Also note that neither of these cycles attempted to quantify any of the reservoir contents, so they are partial (though very illuminating) assessments.

Although the lead-cycling work in Figure 8 is a significant step forward, the fact that it is limited to only two years, and to only anthropogenic flows, prevents the preparation of a time-integrated, comprehensive cycle. It also prevents the analyst from deriving information about pool size for the various reservoirs. In theory, integrated industrial materials cycles should be relatively straightforward to construct, once the cycle for a single year is available to serve as guidance. As seen in Figure 8, the first part of those cycles—the extractions from the natural reservoirs—are reasonably well quantified. However, the uses and fates of the materials over time are not well quantified. Additionally, the uptake of lead from soil by plants, about 15% of the total mobilization (Table 2), is not included. Such integrated cycles are likely to be of great value, but they will require substantial effort to construct with any accuracy. However, the lead-cycling work is still very useful because of the strong human dominance of the lead cycle.

Another type of cycle analysis with the potential to produce extremely useful results is the spatially resolved cycle. In such a cycle, the extraction, use, and deposition of the subject material are specified within a discrete spatial scale. Several possible uses for such a cycle are (*a*) potential environmental impacts to sensitive

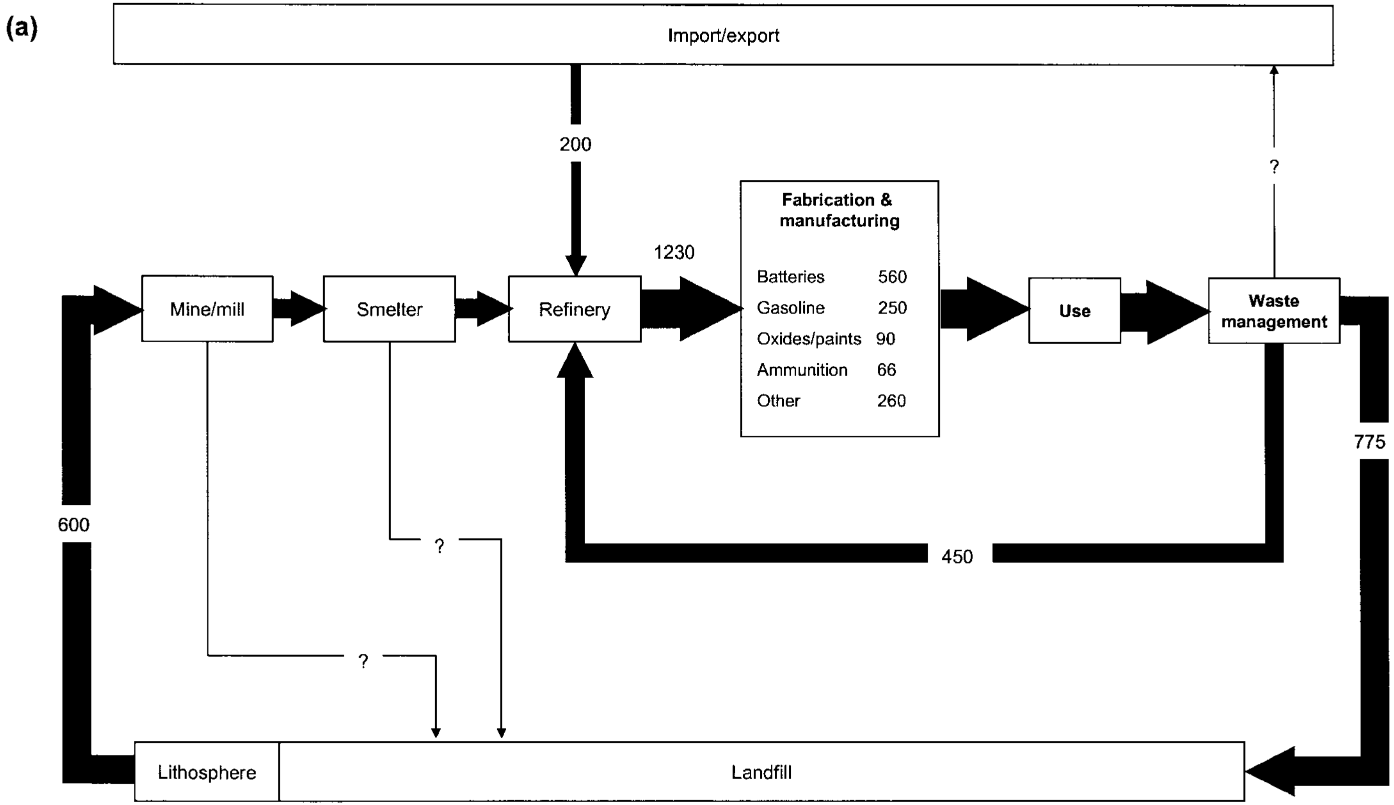

Figure 8 The flows of lead through the U.S. economy in (*a*) 1970 and (*b*) 1993 (in metric tons of lead content per year). Adapted from Reference 38.

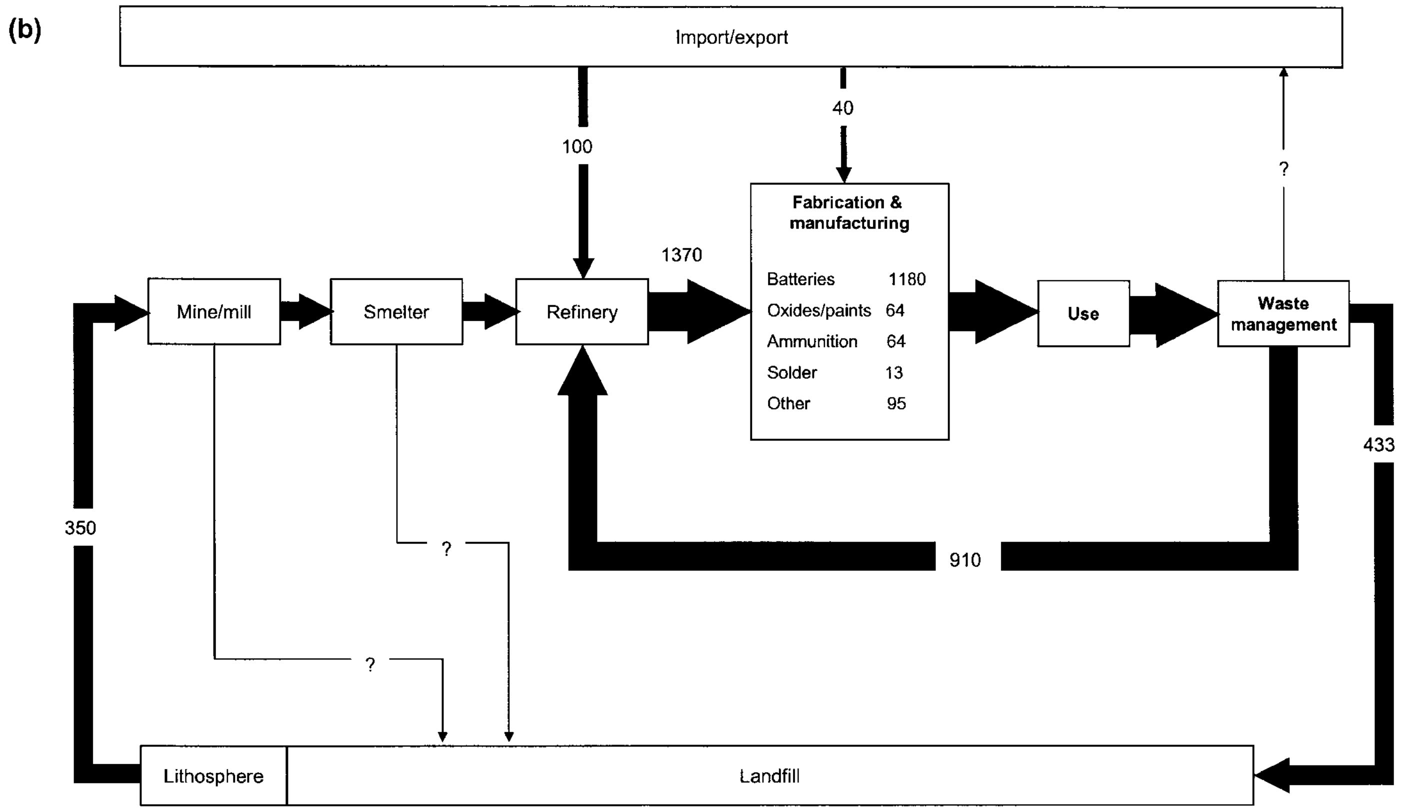

Figure 8 (*Continued*)

ecosystems could be better anticipated; (*b*) reservoirs of materials in use or deposited in specific locations could be of use in future recycling activities; and (*c*) the economics of materials use could be followed in more detail. To our knowledge, no comprehensive spatially resolved industrial cycles have been produced. The closest to that goal may be the cycle for the emissions of carbon dioxide derived by Andres et al. (39). In that work, the emissions (i.e., the source term) were presented globally on a $1^\circ \times 1^\circ$ grid. Because all emissions were to the atmosphere, where carbon dioxide is well mixed and essentially unreactive, the work dealt with sources that were spatially resolved and sinks that were not. Benkovitz et al. (40) developed gridded emissions for sulfur and nitrogen. Comprehensive spatially resolved cycles for copper or zinc, for example, present a more difficult challenge. Spatially diverse reservoirs (e.g., rural mine tailings piles, urban apartment buildings, or suburban landfills), transformations (e.g., refining, milling, or alloying), and alternative uses (e.g., automobile parts, electronics, or plumbing fixtures) need to be considered, and these stocks and flows are not yet very well characterized. However, a spatially discrete determination of stocks of copper in Cape Town, South Africa (41), showed that because of high population densities in poor areas, the copper per square kilometer in those areas was higher than in the wealthy areas. This nonintuitive result hints at the potential value of spatially discrete cycles.

THE PRACTICAL UTILITY OF CYCLES

An example of an industrial materials cycle analysis that demonstrated its usefulness is one for silver in the United States. Kimbrough and coworkers (42) began this cycle study after observing unexpectedly high levels of silver in the sediments of San Francisco Bay. Its origins were not understood until a detailed analysis showed that 15% of the silver supply to the region was being used for X-ray photography in doctor and dentist offices. Individually, these users employed too little silver to justify economic recovery, and so any silver lost to the photographic fluids was being sent to sewage treatment plants and ultimately into the Bay. Once this source was determined, new regulations were written to require pickup and recycling of developing fluids.

The second part of this story was supplied by Ortiz, a student at Harvard, (43) who studied the flow of silver in photographic applications in more detail. His analysis, reproduced in Figure 9, contained a startling result: About 20% of the silver used in photography (i.e., 10% of the total silver flow) was retained on X-ray films in the medical offices. Over time, those offices became rich lodes of silver. Furthermore, modern technology was on the verge of offering a way to make that silver available, namely scanning the X-ray films into some form of digital storage so that the films themselves were no longer needed. As of this writing, neither the value of the silver nor the information transfer technology has reached the point where the silver in the film is being mined, but the potential is obvious.

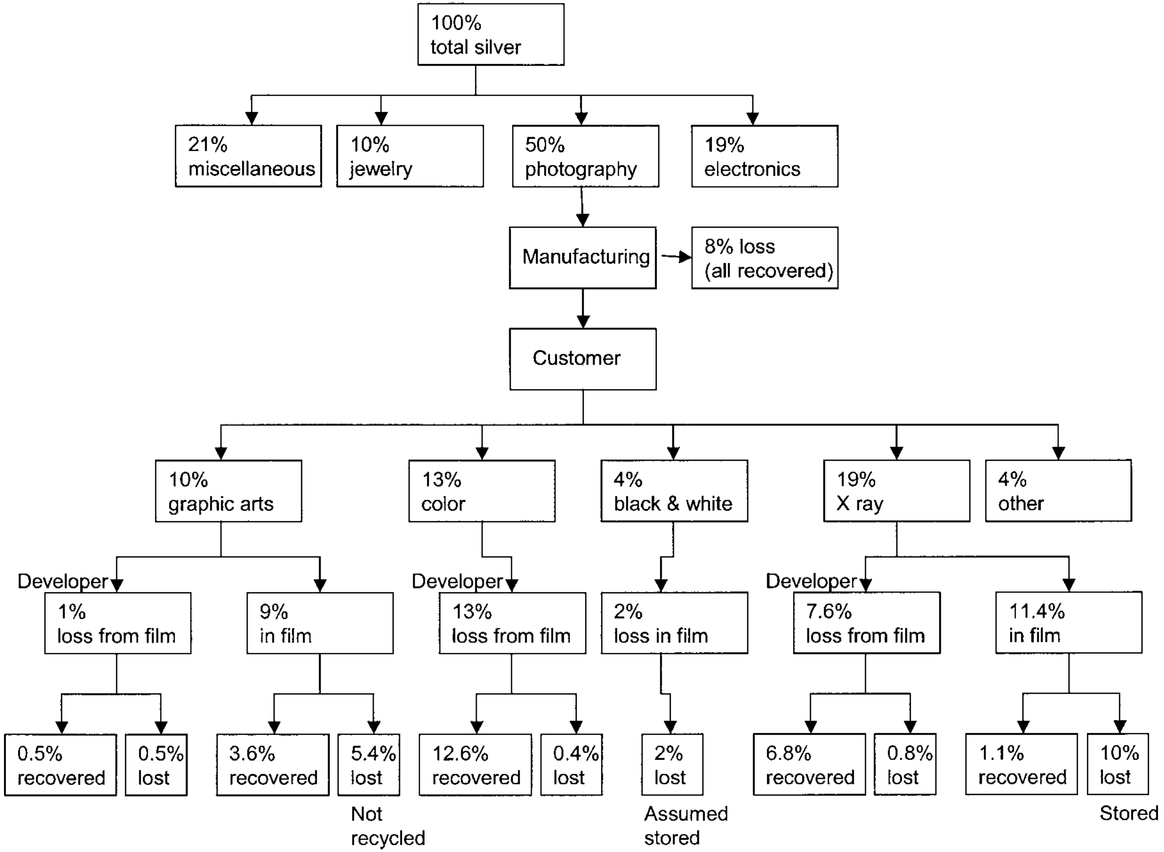

Figure 9 A cycle for the use of silver in photographic applications in the United States. All percentages are the amount of total silver consumed, for example, X rays use 19% of total silver. Adapted from (43).

As with the lead example above, this silver analysis has utility because human mobilization of silver exceeds natural mobilization (Table 2) and because most natural mobilization is by vegetation, which does not tend to generate fluxes of silver to surface waters. In contrast, a similar analysis for aluminum, with only about 25% of the mobilization being anthropogenic, is much more problematic and much less useful.

DISCUSSION

The results and conclusions of this paper rest in large part on our definition of mobilization. Most people would probably not contest our inclusion of mining, fossil-fuel combustion, weathering, or sea spray. Mobilization by plants, however, takes up from the soil elements that are already to some extent nonpassive in that they are periodically recycled. The same reservation may apply to mobilization by biomass burning. In each case, however, the elements involved in such processes are much more available for interaction with humans and the environment than was the situation before the mobilization processes occurred; this is the basis for their inclusion in our methodology. In any case, because the flux from each process is broken out in Table 2, individuals can apply whatever mix of mobilization processes they deem appropriate for their purposes.

Few existing elemental cycles are well enough established to justify decision making on the basis of the perspectives in this review. It is worth contemplating the uses to which such cycles could be put, however, when they are sufficiently validated. Resource analysts will find these cycles useful for coupling information on reserves vis-à-vis resources held in in-use reservoirs, stockpiles, the environment, and landfills, which could hypothetically be the mines of the future. Environmental scientists could use such information to examine sources and flows of hazardous materials to ecosystems, historical environmental impacts in space and time, and potential future inputs and outputs to natural reservoirs. These data will be useful to begin the process of actually measuring our progress toward environmental sustainability, when we can measure whether or not the extraction of nonrenewable resources exceeds the ability to find renewable substitutes and whether or not the flows of materials from the technological society will overwhelm the natural assimilative capacity of the environment (44).

At the industrial facility level, analysis of elemental cycling also has a role to play. Managers find that tracking product or process constituent flows within a facility can help to identify portions of materials that were purchased but discarded, avoidable burdens on waste-treatment or air-handling systems, and potential regulatory and liability concerns. The result is more efficient operation as well as an improved interaction with government agencies and with the environment.

Finally, accurate cycles have roles to play in the environmental policy arena. They can identify opportunities for the avoidance or minimization of resource imports, for national stockpile determinations, and for modifications in policy to balance technology and the environment as we make the journey toward environmental sustainability. Furthermore, our findings are not likely to be stable over time, as indicated by the dramatic trends in material consumption shown in Figure 7. Although natural mobilization rates likely remain relatively constant over time, anthropogenic mobilization has clearly increased over the past century, and if trends continue, it will continue to increase in this century. Environmental policy directed toward increasing the cycling of technological materials once extracted from natural reservoirs and promoting renewable energy sources can play a role in controlling future anthropogenic mobilization rates, thereby reducing the anthropogenic footprint on the periodic table of elements.

As the examples above demonstrate, the characterization and analysis of cycles for the materials used in our technological society provide substantial insight into the flows of resources, the ways in which industry utilizes materials, and the magnitude of interaction of those materials with the environment. The present state of cycles is, however, insufficient for firm guidance in many of these areas. Much more effort is needed to characterize and validate detailed cycles on regional, national, and global scales to take full advantage of the opportunities that these tools can provide.

ACKNOWLEDGMENTS

This research was funded by the U.S. National Science Foundation under grant BES-9818788. R.J.K. thanks the Environmental Research and Education Foundation for graduate student support.

The *Annual Review of Environment and Resources* is online at
http://environ.annualreviews.org

LITERATURE CITED

1. Bertine KK, Goldberg ED. 1971. Fossil fuel combustion and the major sedimentary cycle. *Science* 173:233–35
2. Martin JM, Meybeck M. 1979. Elemental mass-balance of material carried by major world rivers. *Mar. Chem.* 7:173–206
3. Lantzy RJ, Mackenzie FT. 1979. Atmospheric trace metals: global cycles and assessment of man's impact. *Geochim. Cosmochim. Acta* 43:511–25
4. Nriagu JO, Pacyna JM. 1988. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. *Nature* 333:134–39
5. Pacyna JM, Scholtz MT, Li YF. 1995. Global budget of trace metal sources. *Environ. Rev.* 3:145–59
6. Rodhe H. 1992. Modeling biogeochemical cycles. In *Global Biogeochemical Cycles*, ed. SS Butcher, RJ Charlson, GH Orians, GV Wolfe, pp. 55–72. London: Academic
7. IPCC Working Group I. 2001. *Climate Change 2001 Summary for Policymakers: The Scientific Basis*. http://www.ipcc.ch/pub/spm22-01.pdf
8. Ayres RU, Schlesinger WH, Socolow RH. 1994. Human impacts on the carbon and nitrogen cycles. See Ref. 71, pp. 121–55

9. Smil V. 2000. Phosphorous in the environment: natural flows and human interferences. *Annu. Rev. Energy Environ.* 25:53–88
10. Graedel TE, Keene WC. 1996. The budget and cycle of Earth's natural chlorine. *Pure Appl. Chem.* 68:1689–97
11. Socolow RH, Thomas V. 1997. The industrial ecology of lead and electric vehicles. *J. Ind. Ecol.* 1(1):13–36
12. Thomas V, Spiro T. 1994. Emissions and exposure to metals: cadmium and lead. See Ref. 71, pp. 297–318
13. Mason RP, Fitzgerald WF, Morel F. M. 1994. The biogeochemical cycling of elemental mercury: Anthropogenic influences. *Geochim. Cosmochim. Acta* 58: 3191–98
14. Jasinski SM. 1995. The materials flow of mercury in the United States. *Resourc. Conserv. Recycl.* 15:145–79
15. Brunner PH, Rechberger H. 2001. Anthropogenic metabolism and environmental legacies. In *Encyclopedia of Global Environmental Change.* Vol. III: *Causes and Consequences of Global Environmental Change*, ed. T. Munn, pp. 54–72, Chichester, UK: Wiley
16. Llewleyn TO. 1994. *Cadmium* (*materials flow*). *US Bureau Mines Inf. Circ. 9380*, Washington, DC: US Dep. Inter. 17 pp.
17. Ayres RU, Ayres LW. 1996. *Industrial Ecology: Toward Closing the Materials Cycle*. Cheltenham, UK: Elgar. 379 pp.
18. Loebenstein JR. 1999. *The material flow of arsenic in the United States*. *US Bureau Mines Inf. Circ. 9382*, Washington, DC: US Dep. Inter. 12 pp.
19. Baccini P, Brunner PH. 1991. *Metabolism of the Anthroposphere*. Berlin: Springer-Verlag. 157 pp.
20. Nriagu JO. 1980. Global cycle and properties of nickel. In *Nickel in the Environment*, ed. JO Nriagu, pp. 1–26. New York: Wiley
21. Graedel TE, Bertram M, Fuse K, Gordon RB, Lifset R, et al. 2002. The characterization of technological copper cycles. *Ecol. Econ.* 42:9–26
22. Spatari S, Bertram M, Fuse K, Graedel TE, Rechberger H. 2002. The contemporary European copper cycle: 1 year stocks and flows. *Ecol. Econ.* 42:27–42
23. Shedd KB. 1993. *The materials flows of cobalt in the United States*. *US Bureau Mines Inf. Circ. 9350*. Washington, DC: US Dep. Inter. 26 pp.
24. Kimbrough DE, Wong PW, Biscoe J, Kim J. 1996. A critical review of photographic and radiographic silver recycling. *J. Solid Waste Technol. Manag.* 23:197–207
25. Smith GR. 1994. *Materials flow of tungsten in the United States. US Bureau Mines Inf. Circ. 9388*. Washington, DC: US Dep. Inter. 23 pp.
26. Hilliard HE. 1994. *The materials flow of vanadium in the United States*. *US Bureau Mines Inf. Circ. 9409*. Washington, DC: US Dep. Inter. 18 pp.
27. Kesler SE. 1994. *Mineral Resources, Economics, and the Environment*. New York: Macmillan. 391 pp.
28. Schlesinger WH. 1997. *Biogeochemistry: An Analysis of Global Change*. San Diego: Academic. 588 pp.
29. Park H, Schlesinger WH. 2002. The global biogeochemical cycle of boron. *Glob. Biogeochem. Cycles* 16:1072;10.1029/2001GB001766
30. Andreae MO, Merlet P. 2001. Emission of trace gasses and aerosols from biomass burning. *Glob. Biogeochem. Cycles* 15:955–66
31. Azar C, Holmberg J, Lindgren K. 1996. Socio-ecological indicators for sustainability. *Ecol. Econ.* 18:89–112
32. US Dep. Energy-Energy Inf. Adm. (DOE-EIA). 2000. *International Energy Annual 2000*. http://www.eia.doe.gov/emeu/iea/wec.html
33. Nriagu JO. 1990. Human influence on the global cycling of trace metals. *Paleogeogr. Palaeoclimatol. Palaeoecol.* 82:113–20
34. Vitousek PM, Ehrlich PR, Ehrlich AH, Matson PA. 1986. Human appropriation of

the products of photosynthesis. *BioScience* 36:368–73

35. Möller D. 1990. The Na/Cl ratio in rainwater and the seasalt chloride cycle. *Tellus B.* 42:254–62
36. Gong SL, Barrie LA, Prospero JM, Savoie DL, Ayers GP, et al. 1997. Modeling seasalt aerosols in the atmosphere. *J. Geophys. Res.* 61:3819–30
37. Stumm W, Morgan JJ. 1981. *Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters*. New York: Wiley. 780 pp.
38. US Interag. Work. Group Ind. Ecol. Mater. Energy Flows. 1998. *Materials*. Washington, DC: Counc. Environ. Qual. 29 pp.
39. Andres RJ, Marland G, Fung I, Matthews E. 1996. A 1° × 1° distribution of carbon dioxide emissions from fossil fuel combustion and cement manufacture, 1950–1990. *Glob. Biogeochem. Cycles* 10:419–29
40. Benkovitz CM, Scholtz MT, Pacyna J, Tarasón L, Dignon J, et al. 1996. Global gridded inventories of anthropogenic emissions of sulfur and nitrogen. *J. Geophys. Res.* 101:29,239–53
41. van Beers R, Graedel TE. 2003. The magnitude and spatial distribution of in-use copper stocks in Cape Town, South Africa. *S. Afr. J. Sci.* 99:61–69
42. Kimbrough DE, Wong PW, Biscoe J, Kim J. 1996. A critical review of photographic and radiographic silver recycling. *J. Solid Waste Technol. Manag.* 23:197–207
43. Ortiz L. 1995. *Uses of silver in the United States*. MS thesis. JF Kennedy Sch. Gov. Harvard Univ.
44. Graedel TE, Klee RJ. 2002. Getting serious about sustainability. *Environ. Sci. Technol.* 36:523–29
45. Clarke LB, Sloss LL. 1992. *Trace Elements—Emissions from Coal Combustion and Gasification.* London: Int. Energy Agency Coal Research. 111 pp.
46. Filby RH, Shah KR. 1975. Neutron activation methods for trace elements in crude oils. In *The Role of Trace Metals in Petroleum*, ed. TF Yen, pp. 89–110. Ann Arbor, MI: Ann Arbor Sci.
47. Wedepohl KH. 1995. The composition of the continental crust. *Geochim. Cosmochim. Acta* 59:1217–32
48. Hewitt EJ, Smith TA. 1974. *Plant Mineral Nutrition*. New York: Wiley
49. Finkelman R. 1999. Trace elements in coal: Environmental and health significance. *Biol. Trace Elem. Res.* 67:197–204
50. Bertine KK, Goldberg ED. 1971. Fossil fuel combustion and the major sedimentary cycle. *Science* 173:233–35
51. Kinghorn RRF. 1983. *An Introduction to the Physics and Chemistry of Petroleum*. Chichester, UK: Wiley. 420 pp.
52. Stigter JB, de Haan HPM, Guicherit R, Dekkers CPA, Daane ML. 2000. Determination of cadmium, zinc, copper, chromium and arsenic in crude oil cargoes. *Environ. Pollut.* 107:451–64
53. Graedel TE. 1978. *Chemical Compounds in the Atmosphere*. New York: Academic
54. Biomass Feedstock Composition and Properties Database. Accessed Jan. 11, 2002. http://www.ott.doe.gov/biofuels/properties_database.html#biomass
55. US Geol. Surv. 2002. *Mineral Commodity Summary*. Reston, VA: Miner. Inf. Cent. http://minerals.usgs.gov/minerals/pubs/mcs/
56. Molycorp, Inc. 1992. *Cerium: A Guide to its Role in Chemical Technology*. Mountain Pass, CA: Molycorp. www.molycorp.com/cerium_ book.pdf
57. Johnson Matthey, PLC. 2002. *Platinum 2002*. London: Johnson Matthey, PLC. http://www.platinum.matthey.com/publications/pdf2002/Pt_ 2002. pdf
58. Johnson Matthey. 2002. *Platinum Today—Market Data*. London: Johnson Matthey, http://www.platinum.matthey.com/data/rh_92-02.pdf
59. Christie J, Challis A. 1994. *Mineral Commodity Report 5—Platinum Group Metals*. Wellington, NZ: NZ Minist. Econ. Dev. Crown Miner. http://www.med.govt.

nz/crown_minerals/minerals/docs/comreports/report05_pgm.pdf

60. Roskill Consult. Group. 1985. *The Economics of Thorium*. London: Roskill Inf. Serv. http://www.roskill.co.uk/thorium.html
61. Stephen H, Stephen T, eds. 1963. *Solubilities of Inorganic and Organic Compounds.* Vol. I: *Binary Systems*, pp. 5–79. New York: Pergamon
62. Linke WF. 1965. *Solubilities of Inorganic and Metal-Organic Compounds.* Vol. I & II. Washington, DC: Am. Chem. Soc. 1914 pp. 4th ed.
63. Weast RC, Astle MJ, eds. 1980. *CRC Handbook of Chemistry and Physics*. Boca Raton, FL: CRC Press. 2454 pp. 61st ed.
64. Lide DR, ed. 2000. *CRC Handbook of Chemistry and Physics*. Boca Raton, FL: CRC Press. 2540 pp. 81st ed.
65. Craig J. 1998. *Scarcity and abundance* Presented at Workshop Mater. Flows, Natl. Acad. Eng. Washington, DC
66. World Bureau Stat. 1996. *Metal Statistics*. Ware, UK: World Bureau Metal Stat.
67. Int. Copper Study Group. 2001. *Focus on Copper*. http://www.icsg.org
68. Int. Zinc Assoc. Accessed Sept. 7, 2001. *Zinc Production and Consumption: Annual World Totals 1970–1999*, http://www.zincworld.org/zwo_org/zwo00-index.htm
69. Etemad B, Luciani J. 1991. *World Energy Production 1800–1985*. Geneva: Libr. Droz. 272 pp.
70. US Dep. Energy—Energy Inf. Adm. 2000. *International Energy Annual—2000*. http://www.eia.doe.gov/emeu/iea/contents.html
71. Socolow R, Andrews C, Berkhout F, Thomas V, eds. 1994. *Industrial Ecology and Global Change.* Cambridge, UK: Cambridge Univ. Press

Annual Review of Environment and Resources
Volume 29, 2004

CONTENTS

I. EARTH'S LIFE SUPPORT SYSTEMS

II. HUMAN USE OF ENVIRONMENT AND RESOURCES

III. MANAGEMENT AND HUMAN DIMENSIONS

INDEXES

ERRATA

An online log of corrections to *Annual Review of Environment and Resources* chapters may be found at http://environ.annualreviews.org