Intrinsic Flaws of Element Enrichment Factors (EFs) in Environmental Geochemistry

CLEMENS REIMANN*,[†] AND
PATRICE DE CARITAT[‡]

*Geological Survey of Norway, N-7491 Trondheim, Norway,
and CRC LEME, Australian Geological Survey Organisation,
GPO Box 378, Canberra ACT 2601, Australia*

The popular concept of enrichment factors (EFs) as a means of identifying and quantifying human interference with global element cycles is evaluated. It is demonstrated that the concept of normalizing element concentrations to an average total crust value is of doubtful merit, for theoretical considerations alone. Serious flaws with EFs include the variable composition of the Earth's crust at any given point compared to the global average, the natural fractionation of elements during their transfer from the crust to the atmosphere through processes such as weathering and winnowing of fines, and the differential solubility of minerals in the weak chemical digestions generally used in environmental studies. Furthermore the impact of biogeochemical processes is neglected. A biomonitoring survey of atmospheric chemistry over a 1.5 million km^2 area in northern Europe is used to show that EFs are governed here by completely different processes than anthropogenic activities. As a simple means to assess the maximum possible interference of human activities with global element reservoirs, the mining interference factor (MIF = (total tonnage mined annually/total tonnage in upper 2 km of crust) × 100%) is introduced. The elements C ≫ Br > Cu > Sb ≫ Ag > Cd > Pb show the highest MIFs, while Ga, Cs, Ge, K, In, I, and Rb show very low MIFs. We recommend indiscriminate usage of EFs in the scientific literature be abandoned and more large-scale surveys be supported internationally to collect quality, statistically significant environmental data. Only thus can human interference with natural biogeochemical cycles be properly documented.

Introduction

Element enrichment factors (EFs) are widely used in environmental sciences to speculate on the origin of elements in air, atmospheric dust or precipitation. To calculate the EF for a given element, the measured concentration of that element in the sampling medium investigated is divided by the concentration of the same element in the Earth's crust, i.e.,

$$EF_{(El)} = conc(El)_{sample}/conc(El)_{crust}$$

where "El" is the element under consideration, "conc" is concentration (usually in mass/mass units, such as mg/kg),

---

* Corresponding author present address: Verbundplan GmbH, Parkring 12, A-1010 Wien, Austria; phone: +43 1536050; fax: +43 15360554748; e-mail: Reimannc@verbundplan.at.
† Geological Survey of Norway.
‡ CRC LEME, Australian Geological Survey Organization.

and the subscripts "sample" or "crust" indicate which medium the concentration refers to.

Concentrations of practically all naturally occurring elements in the Earth's crust, also known as Clarke values (*1*), can be found in refs *2*−*4* or have been compiled in ref *5*.

In a more advanced version of the above formula, these values are in addition normalized to a "conservative" element (*6*). "Conservative" or "reference" elements are those for which the concentration in the sample medium will practically exclusively be influenced by crustal sources. Most widely used for this purpose are Al, Fe, Li, Sc, Ti, and Zr, for which the interference factor (IF), where

$$IF = 100 * \text{total emissions}/(\text{continental} + \text{volcanic fluxes})$$

is very low (Al, Fe, Ti (*7*)) or which are simply assumed to be practically not emitted by human activities (Li, Sc, Zr). The resulting formula is

$$EF_{(crust)}El = (conc(El)_{sample}/conc(X)_{sample})/(conc(El)_{crust}/conc(X)_{crust})$$

where "X" is the chosen reference element (e.g., Al). Al (and Na for an oceanic source) have been used originally (*6*) for the purpose of comparing the chemical composition of atmospheric particulate material collected at the South Pole to the composition of the crust (or the ocean). These authors suggested that if this ratio is close to unity for any element this element may have a crustal (oceanic), and thus natural, source. They observed high EFs for the elements Zn, Cu, Sb, Se, Pb, and Br and attributed this to vapor-phase condensation or a high-temperature dispersion source (volcanism or anthropogenic emissions) because of their high volatility.

Since that time, EFs have increasingly been used to identify geogenic vs anthropogenic element sources in environmental sciences (e.g., refs *8*−*19*). When EFs are calculated, elements such as Ti, Al and Fe quite typically give very low values around 10 or less, while elements such as Cd, Se, Pb, Sb, Hg, Ag, Zn, As, Cu, Sn have EFs between 100 and 1000 (e.g., ref *20*). This is then often taken as proof of a major influence of anthropogenic activities on the concentration of these elements in the atmosphere at the sampling site. The cautioning words in the first publication using EFs (*6*) with regards to the multitude of possible reasons for high EFs have been forgotten or ignored in many of the subsequent publications using EFs. Given the local variations in geogenic element levels, as well as the different element "cocktails" emitted by different pollution sources, it is surprising that EFs always show the same elements as being highly enriched, regardless of where the samples were taken. Furthermore, not only is the sequence of elements similar but also the absolute EF values are also often practically the same. This fact is then explained by a large and chemically very comparable anthropogenic contamination level of the atmosphere by the "highly volatile" elements that top the EFs (e.g., ref *20*)—probably on a worldwide scale.

For the last 20 years or so, plants have often been used to monitor general atmospheric pollution levels on a regional scale (e.g., ref *21*). Several plants, among them the terrestrial moss species *Hylocomium splendens* and *Pleurozium schreberi,* are widely accepted as giving a good reflection of atmospheric input of air pollutants (e.g., ref *22*). In some early and in more recent publications (e.g., *11*, *15*, *23*, *24*),
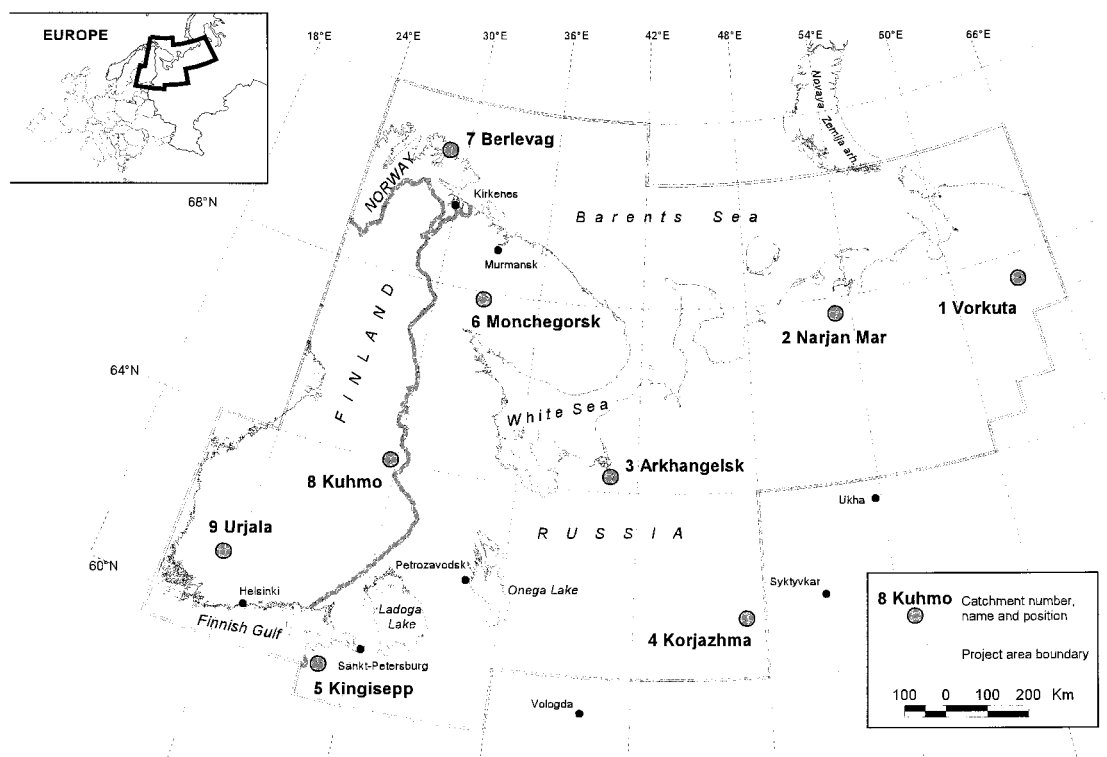
FIGURE 1. Location of the survey area in northern Europe and of the 8 catchments where moss was collected for this study. No moss could be collected in C6, Monchegorsk due to the high local levels of pollution. (Reprinted from *Environ. Pollut. V. 112*, Reimann et al., Copyright (2000), with permission from Elsevier Science.)

the concept of EFs has been used in connection with such plant data to discuss likely element sources.

Here, different published datasets on the composition of the Earth's crust and different rock types, in combination with world production figures (*5*), are used to discuss fundamental shortcomings of the concept of EFs as a means to differentiate between geogenic and anthropogenic element sources. Multielement moss analyses from a large area in northern Europe are then used to demonstrate the effects these shortcomings have in practice. Results based on leave/needle analyses from 7 further plant species (*Vaccinium myrtilus*, *Vaccinium vitis-idaea*, *Empetrum nigrum*, *Betula pubescens*, *Salix spp.*, *Pinus sylvestris* and *Picea abies*) from the same survey yield similar results.

Materials and Methods

A total of 140 duplicate samples of *Hylocomium splendens* and *Pleurozium schreberi* were collected in 8 catchments spread over a 1.5 million km² area. The area includes northwestern Russia from St. Petersburg to the northern end of the Urals Mountains, northern Norway and Finland (Figure 1). A minimum of 11 moss samples were collected from each of 8 catchments, that varied in size between 14 and 50 km². Table 1 summarizes the important information about the catchments visited (location, landscape, climate, vegetation zone, geology, likely sources of pollution, geochemical characteristics of the parent soil material). Note that no moss could be collected in C6 (Monchegorsk), which is in the immediate vicinity of the Monchegorsk nickel refinery, as almost all vegetation is destroyed here (e.g., ref *25*).

Sampling. All samples were collected in accordance with the methods used in the European moss monitoring project (*22*, *26*, *27*). Every effort, starting in the field, was made to collect samples of each species that are well comparable. Samples were collected wearing talcum-free polyethylene (PE) gloves. The gloves were analyzed for all trace elements used in this study, and all results were below detection limit.

Smoking during sample collection and handling was strictly prohibited. About 1 L of moss was collected at each site, as a composite sample from an area measuring at least 50 m × 50 m, and was cleaned of any other species and litter. The samples were placed in white, plastic-lined bags, which were identified with catchment and site numbers. Again, several empty bags were dissolved and analyzed for all elements considered here, and all values were below detection. The bags were opened in the evening at the field camp to allow the moss to air-dry. PE gloves were worn to open and close the bags. After arrival in the laboratory of the Geological Survey of Finland (GTK), all samples were dried to a constant weight at 40 °C.

Analyses. The dried samples were checked once more for any contamination by other plant species or litter in the laboratory. They were not washed. They were milled in a centrifugal mill to pass through a 1 mm sieve. Tests were run to prove that neither milling nor sieving contaminated the samples with any of the 38 elements on the analytical program. Sample material (0.5 g) was dissolved in 10 mL of concentrated nitric acid (Merck suprapure) in a microwave oven. The samples were then diluted to 50 mL with milli-Q water before being analyzed for 38 elements by ICP-MS, ICP-AES and cold vapor AAS-techniques. The procedure closely follows the US-EPA-standard 3051.

GTK's laboratory is accredited to meet the requirements of the EN-standard 45001 and ISO-guide 25. Analytical precision, as judged from frequent duplicate analyses, is generally better than 5%. A microwave digestion in concentrated nitric acid will completely dissolve all organic material and is, in environmental sciences, often viewed as a "total dissolution". Mineral particles (e.g., silicates), which might be incorporated in the moss, will, however, usually not dissolve completely.

TABLE 1: Location and General Characteristics of the 8 Catchments Where Moss Samples Were Collected[a] (Reprinted from *Environ. Pollut. V.112*, Reimann et al., Copyright (2000), with permission from Elsevier Science)

catchment no.	name	outlet coordinates	area (km²)	altitude (masl)	annual precipitation (mm)	vegetation	bedrock	industry, possible pollution sources	special geochemical characteristics of the C-horizon
Russia									
C1	Vorkuta	67°27'09'' N 63°49'38'' E	19.7	140—220	600	moss—lichen shrub tundra with birch and willow	sandstone, siltstone, argillite, coal seams	coal mining, town (200,000 inhab.)	high: As, Be, Cd, Sb, V
C2	Narijan-Mar	67°39'18'' N 53°03'39'' E	16.8	5—15	580	southern tundra with birch and shrub	clay, sandstone, siltstone and brown coal	local airport, small town, some scrap metal yards	low: Ag, Al, Ba, Ca, Cd, Cr, Cu, Mg, S, Sr, V, Zn
C3	Arkhangelsk	64°22'06'' N 40°37'55'' E	24.4	24—64	650	northern taiga with coniferous forest	sandstone, siltstone dolomite, limestone	major town, several large power plants, metal industry	high: B, Ba
C4	Korjazhma	61°18'39'' N 47°08'50'' E	40.3	40—80	780	middle taiga	siltstone, limestone, clay	large cardboard factory, pigment factory, railroad	low: Ag, As, Be, Bi, Cd, Co, Cr, Cu, Fe, K, P, Sb, Sc, Sr, V, Zn
C5	Kingisepp	59°24'15'' N 28°34'59'' E	36.6	10—60	710	southern taiga	marl, limestone, dolomite, siltstone, sandstone, clay	major phosphate producer, traffic, waste dump, agriculture	high: Ag, B
C6	Monchegorsk	67°48'29'' N 32°47'08'' E	13.6	150—400	391	northern taiga; almost completely destroyed vegetation cover	metagabbroid, tuff, gabbro, gabbronorite, labradorite-gabbro	Cu/Ni-smelter and refinery, traffic	high: Al, Ca, Cr, Cu, Na, Ni, V low: As, Sb
Norway									
C7	Berlevåg	70°51'32'' N 28°55'37'' E	46.7	20—320	850	Arctic tundra	sandstone, phyllite, siltstone	none	high: Al, As, Bi, Co, Cu, Fe, Li, Mg, Ni, P, Pb, Sb, Th, Zn
Finland									
C8	Kuhmo	64°03'17'' N 29°46'33'' E	36.0	170—270	750	mixed forest with spruce, pine and birch	leucocratic granite, granodiorite, mafic metavolcanite, tonalite, trondhjemite and migmatite	forestry	low: As, Be, Bi, S, Sr
C9	Urjala	61°06'58'' N 23°25'56'' E	40.1	100—140	650	mixed forest with spruce, pine and birch	granodiorites, tonalites, quartz, diorites, mica shist, mica gneiss	agriculture	high: Ag, As, K, Mo, S, Se, Th, Ti

[a] Due to the extreme level of pollution in C6, no moss is growing here.

TABLE 2. Average Al, Zr, Cd, Cu, Pb and Rb Concentrations in the Upper Crust (2, 3) and in Some Major Rock Types (28) and World Production Figures for 1995 (5)[a]

	upper continental crust		ref 28					ratio shale/crust		world production in 1000 t
	ref 2	ref 3	shale	sandstone	ultramafite	granite	limestone	ref 2	ref 3	
Al	77440	80400	91000	37000	20000	73000	4000	1.18	1.13	25093
Zr	237	190	160	250	30	200	20	0.68	0.84	471
Cd	0.102	0.098	0.25	<0.04	0.05	0.1	0.1	2.45	2.55	19
Cu	14.3	25	45	2	40	12	6	3.15	1.80	9988
Pb	17	20	22	10	0.05	20	5	1.29	1.10	2629
Rb	110	112	140	40	2	120	4	1.27	1.25	3
(Cd/Al)*10000	0.013	0.012	0.027	0.005	0.025	0.014	0.250			
(Cu/Al)*10000	1.85	3.11	4.9	0.5	20	1.6	15			
(Pb/Al)*10000	2.20	2.49	2.42	2.70	0.03	2.74	12.50			
(Rb/Al)*10000	14.2	13.9	15.4	10.8	1.0	16.4	10.0			
EF(Cd)		0.96	2.45	0.20	0.49	0.98	0.98			
EFc(Cd)al	1	0.93	2.09	0.41	1.90	1.04	19.0			
EF(Cu)		1.75	3.1	0.1	2.8	0.8	0.4			
EFc(Cu)al	1	1.68	2.68	0.29	10.8	0.89	8.12			
EF(Pb)		1.18	1.29	0.59	0.003	1.18	0.29			
EFc(Pb)al	1	1.13	1.10	1.23	0.01	1.25	5.69			
EF(Rb)		1.02	1.27	0.36	0.02	1.09	0.04			
EFc(Rb)al	1	0.98	1.08	0.76	0.07	1.16	0.70			

[a] Ratios of different elements (El) to Al and EFs calculated as EF = El(sample)/El(crust) and EFc(El)al = (El(sample)/Al(sample)/(El(crust)/Al(crust)) both based on crust as given by ref 2.

Results

Here, we focus on two widely used "reference" elements, Al and Zr, and four trace elements, Cd, Cu, Pb and Rb, for the calculation of EFs. Pb and Cd are two typical examples of highly volatile elements that always give very high EFs (e.g., 20). Cu is much less volatile, but as Pb it is produced and used in large quantities (Table 2)—one should expect high EFs for this element as well if EFs provide a direct means of differentiating between geogenic and anthropogenic element sources. Finally, Rb is an example of an element that has few uses in the human society and is not likely to be emitted in large quantities by man's activities.

Table 2 summarizes published results (2, 3) for the composition of the upper continental crust. Furthermore, compiled average concentrations for several important rock types (28) are also given. World production figures for 1995 (5) are added to give an idea of the human usage of the elements discussed. These figures provide at the same time an upper limit for possible emissions. With the exception of Pb, which was widely used as an additive to gasoline and thus released in huge quantities over large areas by vehicular traffic, one can assume that total annual emissions of any of these elements will be considerably less than 10% of the production figure.

The discrepancies between the two cited "upper crust" values are due to the fact that these are hypothetical concentrations based on assumed proportions of various crustal rock types, themselves assumed to have given, fixed compositions. Unfortunately, the earth is not made of simple, homogeneous blocks. Large crustal blocks can show widely different chemical composition, depending on the predominant rock type at surface (e.g., limestone in the calcareous Alps). If normalizing to Al (or Zr) is supposed to give realistic and directly comparable EFs at any one place in the world, then the ratio of any element to Al (or Zr) in all these different rock types should be more or less the same as the average crustal ratio. Table 2 shows that this clearly is not the case (for ease of comparison, the ratio El/Al was multiplied by 10000). Differences in this ratio between the different rock types cover up to 2.5 orders of magnitude! A mere change in the local surficial rock type can result in a different composition of the local dust and thus in considerably different EFs (Table 2). Therefore, the use of the "upper crust" average value can already introduce an uncertainty of the order of 100 to 1000 to any calculated EF.

It has been noted above that the sequence of calculated EFs is almost invariably Cd, Se > ... Pb > ... > Cu ≫ Fe, Al, Ti (20) regardless of where on earth samples are from, and, even more disturbingly, regardless of which sampling medium is chosen to represent "atmospheric composition" (urban dust, bulk precipitation or terrestrial moss). When studying the world production figures in Table 2, it is hard to see how EFs can really give an indication of the level of human interference with the atmosphere. It is indeed rather difficult to imagine how a higher enrichment of Cd in the atmosphere is possible compared to Pb and/or Cu due to anthropogenic interference with element cycles, when 138 times more Pb and 525 times more Cu are mined annually than Cd. Interference factors (IFs) of 1363, 1897 and 34,583 for Cu, Cd and Pb were calculated (7). In terms of the elemental boiling point as a measure of volatility (6), Cd is much more volatile than Pb or Cu (1040, 2022, 2835 °C), which would explain its high EFs—but this by no means indicates solely an anthropogenic origin.

It is not established, and actually quite unlikely, that element ratios remain constant during the biogeochemical cycle, as matter is transferred from the crust, via soils, to the biosphere and the atmosphere. Soil-forming processes involve differential movement, and thus fractionation, of elements within soil profiles. Upper soil horizons are usually rich in organic material compared to the deeper, minerogenic horizons. As early as 1937, it was realized that organic material can be substantially enriched in quite a number of elements (29)—not least all those that show notoriously high EFs in the atmosphere. Plants can actively change their chemical environment—they are very selective as to which elements they take up and which they do not. One can thus argue that the average composition of the crust is of limited relevance to the composition of natural dust in the Earth's lower atmosphere, since that dust contains a significant biogenic component.

Furthermore, all crustal values in the literature are ultimately based on "total" element concentrations as determined by methods such as X-ray fluorescence, neutron activation analyses or multiacid dissolution (including hydrofluoric and hydrochloric acid digestions). In contrast most data presented in environmental projects are obtained by weaker extractions, e.g., by aqua regia. Element recovery from aqua regia digestion is widely different from element to element, varying between >90% (e.g., Cd, Pb) and <1% (e.g.,

TABLE 3: Relative Solubility of Al, Cu and Pb in Mineral Soils (C-Horizon) from the Barents Project Area (Unpublished Data) and in the Catchments Discussed Here[a]

element	aqua regia, mg/kg	"total", mg/kg	available, %
Al	7470	58312	13
Zr	na	225	
Cd	0.04	<0.1	>40
Cu	13.2	14.8	89
Pb	3.4	12	28
Rb	na	56	

element		C1	C2	C3	C4	C5	C7	C8	C9
Al	% available	28	14	22	11	17	24	6	21
Cu	% available	80	48	94	32	94	100	98	99
Pb	% available	36	19	31	19	22	56	15	22

[a] Total concentrations: milled <2 mm fraction, Al, Zr: XRF, Cu, Pb, Rb: multiacid dissolution, ICP-MS, aqua regia data: aqua regia extraction on <2 mm fraction, ICP-MS. na: not analysed.

TABLE 4: Results of Moss Analyses from 8 Catchments in Northern Europe (for Location see Figure 1)[a,b]

element	method	DL	min.	max.	med.
Al	503P	15	88	2380	355
Zr	503M	0.01	0.068	1.81	0.369
Cd	503M	0.005	0.032	0.536	0.132
Cu	503M	0.02	2.5	17.5	4.9
Pb	503M	0.02	1.7	11.9	4.1
Rb	503M	0.01	1.3	48.0	12.7

element	median C1	C2	C3	C4	C5	C7	C8	C9	ratio max./ min.
Al	849	936	344	362	713	167	146	330	6.4
Zr	1.01	0.52	0.39	0.40	0.66	0.15	0.12	0.30	8.4
Cd	0.142	0.096	0.139	0.137	0.190	0.053	0.096	0.161	2.0
Cu	4.6	4.3	5.3	5.1	6.0	4.1	3.5	6.4	1.9
Pb	3.8	5.3	4.0	3.8	6.3	4.2	3.3	4.3	1.9
Rb	6.6	9.1	9.3	14.3	14.4	2.7	20.1	34.4	12.9

[a] 503: dissolution in concentrated HNO_3 in a microwave oven, "P" = ICP-AES, "M" = ICP-MS. DL = detection limit. Minimum (min.), maximum (max.) and median (med.) values for the whole data set and median concentrations for the 8 catchments. [b] All values in mg/kg dry weight.

Na, Si, Zr) (e.g., ref 30), because different elements are bound in different minerals. Some of these minerals weather (and dissolve) more easily than others, and thus release incorporated elements more readily to the environment. Others are very resistant to weathering (dissolution). The mineralogical composition of a sample thus determines to a large extent what the element concentrations in an aqua regia extraction can be. Table 3 shows such results for the C-horizons soils from the survey area. Not only is the relative solubility different from element to element but also it varies from location to location as a result of the changing local mineralogy of the soils.

Finally, the natural composition of atmospheric particulates will be largely determined by wind blown dust. Wind erosion is actually a grain size separation process, referred to as the "winnowing of fines", whereby finer fractions are preferentially being taken up to higher elevations and transported over greater distances. Geochemists are well aware that finer grain sizes, enriched in clay minerals, contain much higher metal values than the "average crust". Thus, wind erosion results in a further fractionation of the elements. As a first approximation of what must be expected to happen, one can compare the composition of the "upper crust" to that of average shale (as a proxy for a "clay minerals" enriched medium). The ratios shale/crust in Table 2 clearly show that this process will result in a relative enrichment of most metals in relation to Al, even though Al also shows higher values in finer-grained materials.

A Practical Example—Terrestrial Moss in the Barents Region

Table 4 summarizes the results of moss analysis for the elements discussed in this paper and gives the analytical method and the detection limit for each of these. EFs for Cd, Cu, Pb and Rb were calculated using the two "conservative" elements Al and Zr. The EFs are presented in Figure 2 in order to demonstrate the magnitude of their variability between sites in catchments and between catchments. The resulting average EFs calculated for the four trace elements using both reference elements differ by a factor of about 3 (Table 5).
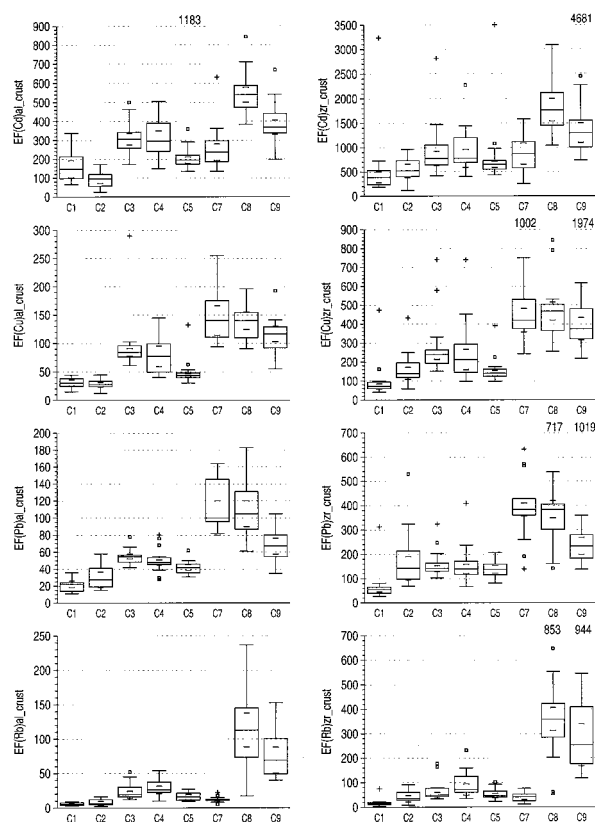
Cd gives by far the highest average EFs, followed by Cu, Pb, then Rb (which has the lowest boiling point of all the elements considered here, 961 °C). At first glance, this fits well with common interpretations about which elements are emitted by anthropogenic sources. What do, however, these values reflect in reality? Based on considerations of analytical

FIGURE 2. Boxplot comparison of the calculated EFs in the 8 catchments. Note that although the overall appearances are quite similar for Al (left) or Zr (right) used as the "reference" element, there are subtle differences in the sequence of EFs in the different catchments.

chemistry one can infer that the observed sequence of elements can just as well mirror the relative solubility of these elements in nitric acid and might have absolutely nothing to do with a differentiation between anthropogenic and geogenic element sources. To further complicate the issue, extractability of elements from natural soils will vary in space (see Table 3), depending on their local mineralogical composition. The much higher EFs obtained with reference

TABLE 5: Average EFs Relative to Crust as Observed for the Moss Samples—Al and Zr Used as the "Conservative" (Lithogenic) Element

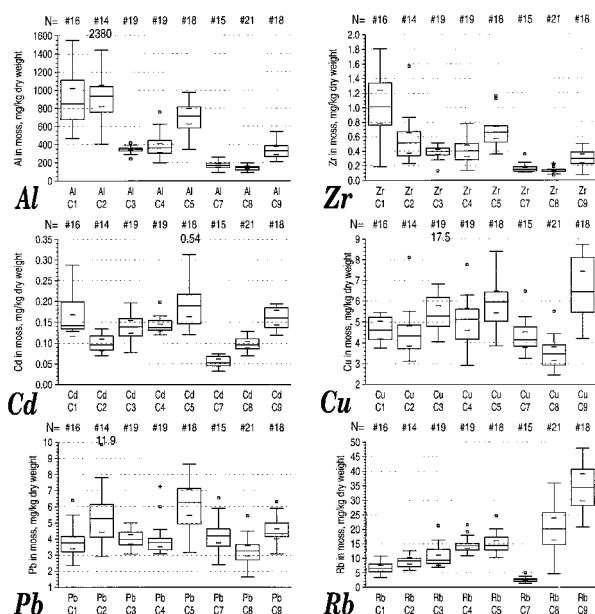| El	Cd	Cu	Pb	Rb
EFc(El)Al	289	75	53	25
EFc(El)Zr	831	221	156	74

FIGURE 3. Boxplot comparison of the "raw" moss composition data from the 8 catchments for the elements discussed here—note the large local variation for some elements.
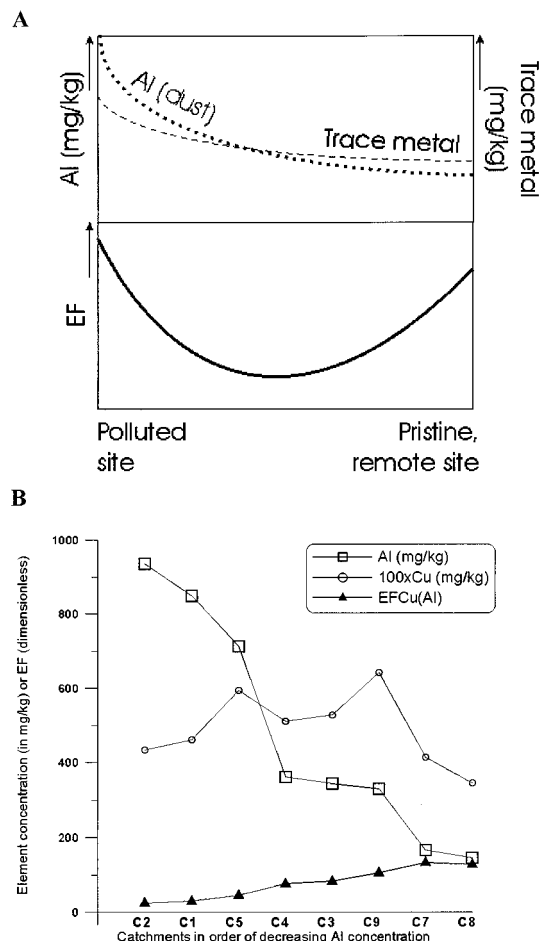

FIGURE 4. (A) Schematic illustration of how high EFs can arise in clean, dust-free, Al-poor environments, as well as around extremely polluted sites (note that the two Y-axes of the top diagram are not necessarily to scale). (B) Actual trend of decreasing Al concentration in moss in the catchments studied here, while EFCu(Al) increases steadily with little correlation to the actual Cu concentration trend.

to Zr are a direct result of the much lower solubility of zircon (the main Zr-bearing mineral) in comparison to most Al-minerals. One reason that Cd and Cu give so high EFs is that they are, in most cases, hosted in minerals that almost completely dissolve in aqua regia (see availability of Cu in Table 3).

When studying EFs and their variation in space (as shown in the 8 different catchments) it becomes clear that the calculated EFs have little to do with environmental pollution. Figure 3 shows boxplots of the original analytical data from the 8 catchments. Large differences in the concentration of Al and Zr in moss can be observed between the different catchments; most likely reflecting differences in the local dust levels and composition. C7 and C8, the two most pristine and remote catchments, show very low values for both Al and Zr.

Cd concentrations are very low in the moss from C7 and C8. Nevertheless, EFs show that C8 has the highest EFs of all catchments for Cd (Figure 2). These high EFs are not an indication of contamination but rather result from the low dust levels and thus Al and Zr concentrations in these catchments. The highest observed EFs have thus nothing to do with anthropogenic interference with natural element levels but are on the contrary an indication of a very clean atmosphere with especially low dust and thus Al levels. This phenomenon is schematically illustrated in Figure 4A. One could of course also argue that the high EFs for Cd reflect long range transboundary air pollution. If Cd has been transported into a "pristine" area where local dust is sparse, then the observed high EFs would be the expected result. The critical question is what is the appropriate value to use in preparing ratios or what are the local background values. It is highly unlikely that "average crust" represents the local background.

Cu shows relatively little contrast in the raw data, but C8 has the lowest values, followed by C7, while C9 and C5, the southernmost catchments (closest to civilisation), have the highest concentrations (Figure 3). When the EFs are plotted, a dramatically different picture emerges: C7 and C8 show the highest EFs followed by C9, while C5 shows a very low EF. Again this is an artifact of the low local dust levels and Al (Zr) concentrations; it does not reflect an anthropogenic addition of Cu to natural element levels (Figure 4B). It must be mentioned that it is very tempting to argue that the high EFs in C7 reflect the proximity of the Russian Cu/Ni-industry on the Kola Peninsula (250 km upwind). When neglecting the raw data—as too often done nowadays—this interpretation would definitely be possible from observation of the EF patterns shown in Figure 2. The raw data as well as the regional geochemical maps for moss and humus (25) show, however, that no significant amount of Cu from the Kola industry reaches C7.

Pb is another interesting example: the raw data show that there is little variation in the Pb levels in moss from these 8 catchments, with C8 having the lowest concentrations. The rather low contrast between the catchments is a surprise considering their location in relation to possible Pb sources. C5, which is close to St. Petersburg, a city with heavy traffic, has not only the highest Pb levels but also a very high local variation. The observed pattern may suggest that moss takes up Pb from other sources as well as the atmosphere. One likely source would actually be organic soil dust, which in

element	world production, t/y	mass in upper-most 2 km crust, t	relative use, MIF (%)
Ga	20	2.36E+16	8.5E−14
Cs	30	5.35E+15	5.6E−13
Ge	53	2.20E+15	2.4E−12
K	20400000	3.37E+19	6.1E−11
In	230	7.87E+13	2.9E−10
Ta	18300	1.73E+15	1.1E−09
I	13757	1.26E+15	1.1E−09
Rb	3000	1.23E+14	2.4E−09
Ca	1541000000	6.06E+19	2.5E−09
B	494000	1.73E+16	2.9E−09
Y	1150	3.77E+13	3.0E−09
Tl	30	8.20E+11	3.7E−09
Te	284	7.00E+12	4.1E−09
Be	327	3.77E+12	8.7E−09
Al	25093000	1.25E+17	2.0E−08
V	32300	1.54E+14	2.1E−08
Li	9,553	2.83E+13	3.4E−08
Ti	2378000	6.31E+15	3.8E−08
Co	18000	3.77E+13	4.8E−08
Na	53000000	3.71E+16	1.4E−07
Zr	471000	3.19E+14	1.5E−07
F	1960000	8.27E+14	2.4E−07
Ba	2900000	9.20E+14	3.2E−07
Mn	8200000	1.13E+15	7.3E−07
Fe	568128000	6.80E+16	8.4E−07
As	30453	2.67E+12	1.1E−06
Ni	1013000	8.80E+13	1.2E−06
U	32700	2.67E+12	1.2E−06
Se	2310	1.89E+11	1.2E−06
W	22800	1.57E+12	1.4E−06
P	18200000	1.19E+15	1.5E−06
Cr	3770000	1.98E+14	1.9E−06
Bi	3100	1.34E+11	2.3E−06
Hg	2,900	6.29E+10	4.6E−06
Au	2000	3.93E+10	5.1E−06
S	56000000	1.09E+15	5.1E−06
Sn	189000	3.62E+12	5.2E−06
Cl	40000000	7.40E+14	5.4E−06
Zn	6791000	1.02E+14	6.7E−06
Mo	119,000	1.73E+12	6.9E−06
Pb	2629000	2.33E+13	1.1E−05
Cd	19000	1.57E+11	1.2E−05
Ag	13500	1.10E+11	1.2E−05
Sb	119000	4.72E+11	2.5E−05
Cu	9988000	3.93E+13	2.5E−05
Br	432250	1.57E+12	2.7E−05
C	9613816020	3.13E+15	3.1E−04

[a] The MIF shows the amount mined annually in % of the reservoir in the uppermost 2 km of crust, based on 1995 figures. Data used are taken from ref *5*. For ease of comparison the elements are sorted in increasing order of the MIF.

contrast to minerogenic dust is enriched in elements such as Pb, Ag, As, Cd, and Sb (*31*). When studying the resulting EFs, C7 and C8, the two "cleanest" catchments, show the highest values. Again, this is due to the low values in Al and Zr there and not to contamination.

Rubidium (Rb) is not emitted in any notable amount by human activities. In fact, when calculating the mining interference factor (MIF)

$$\text{MIF} = (\text{total tonnage mined annually}/ \text{total tonnage in upper 2 km of crust}) \times 100 \ (\%)$$

Rb gives one of the lowest values of more than 40 elements (Table 6—note that ref *32* used a graph plotting Clarke values against world production to define a measure of "technophilness" of the elements, giving quite comparable results). Still, in C8 and C9 extremely high EFs are obtained for Rb (Fig. 2)! EF values up to 853 (C8) and 944 (C9) (and not "2 or 3" as so often stated in the literature as their typical level of uncertainty) can thus be obtained without any human impact on element fluxes. In contrast C1 and C5, which have

considerable human impact and thus high dust levels, give very low EFs because the "reference" elements Al and Zr are high here.

Discussion

These above arguments and data indicate that EFs do not provide a simple technique to differentiate between anthropogenic and geogenic element sources or to recognize and quantify anthropogenic interference relative to natural element fluxes. Instead, they reflect the relative solubility of the different elements, which, not surprisingly, results in easily soluble elements such as Cd and Cu showing generally very high EFs. The highest EFs are reached when an element, such as Zr, that is bound in insoluble minerals is used as the "conservative" reference element. EFs are furthermore governed by the mineralogy of atmospheric dust at any one point in space. Natural geochemical differences such as large tracts of land with different underlying lithologies can easily alter EFs by a factor of 100 (e.g., limestone vs shale areas). In the biogeochemical cycle from crust to soils, elements undergo natural chemical fractionation, which can severely disturb EFs based on "average crust composition" without the need to call upon human interference. Winnowing of fines is a physical fractionation process that will result in a natural enrichment of many heavy metals relative to Al and other "conservative" elements in atmospheric dust—again without the need for anthropogenic interference. Low dust levels will generally result in much lower Al (and Zr) values compared to other elements. It is also not sufficiently realized that there are different kinds of dust at the earth surface. There is "geogenic" or better "minerogenic" dust originating from the deeper soil horizons or rock weathering, that is high in certain elements typical for crustal materials (e.g., Al, Fe, Li, Sc, Ti, and Zr). However, there is also "biogenic" or "organic" dust, originating from plant materials or the O-horizon of soils. This "dust" is high in a quite different suite of elements e.g., Pb, As, Bi, Cd, Sb, and Zn (*31*). The nature of the dust alone can result in very high EFs at the cleanest locations. It should be noted that when approaching a major local anthropogenic pollution source, EFs will of course start to increase due to unusually high concentrations of the pollutants and thus indicate the presence of this source by very high values (Figure 4).

Comparing EFs based on moss analyses from 8 catchments spread over a large area in northern Europe shows that the resulting figures can be seriously influenced by other factors than human interference with element cycles. The findings presented here demonstrate that routinely applying established methods can result in misleading interpretations. Instead of using EFs one is better advised to study the raw data. The major advantage of using raw data is that they are not affected by an interfering second element that may show locally high or low values for a multitude of different reasons. Results presented here for the elements Cd, Cu, Pb and Rb clearly demonstrate that EFs should not be used when working with data from biomonitoring (note that not only moss but also leaves/needles of 8 different species were tested for his study and yielded similar results). The discussed problems and findings should discourage the indiscriminate use of EFs in environmental sciences in general.

If the EFs cannot be used, what is then the best approach to establishing a human impact on local element levels? The answer is simple: raw data, collected over a large enough area to reach background levels or to allow meaningful comparisons. Preferably such data should be collected from several different compartments of the ecosystem to begin to better understand the interactions between atmosphere, biosphere, hydrosphere and pedosphere—and the human interference with element cycles on both local and regional scales. Very few such data sets exist (e.g., ref *25*). Where such

data have been collected, they show that human interference can be massive—but mostly on a local scale, declining fast with distance from emission sources. A noteworthy exception may be Pb, which has been and is still used in some countries as an antiknock additive to gasoline, resulting in large amounts of Pb being spread over very large areas. Not recognizing the important difference between local point-sources and mobile sources may have resulted in many misconceptions about global element cycles in today's environmental literature.

Currently it is often argued that more than enough data have been collected and that we need to go a step ahead in the interpretation of these data. The simple example presented here on the shortcomings of EFs demonstrates that more quality raw data are needed: there exists in fact all too little knowledge about element sources and cycles to reliably establish geogenic versus anthropogenic element fluxes. This is mostly due to the fact that there are no internally comparable, statistically significant data sets covering large enough areas. Data presented so far (e.g., ref 7) were highly speculative and based on very scarce real world data (note that the authors (7) were very well aware of these limitations) and have been used subsequently to develop ill-conceived notions that have been applied indiscriminately, damaging scientific advancement during the last 20 years. The only quantification concerning element cycles that can presently be established with relatively high confidence is the mining interference factor (MIF) (Table 6). This factor, however, does not give a true impression of anthropogenic input to the atmosphere because most of the mined material is not released to the atmosphere (with the exception of C) and because the MIF cannot accommodate releases of trace metals by burning of fossil fuel. It may, however, provide a good first approximation of which elements are likely to show substantial human interference with global fluxes. Note that even for the most used elements, the percentage of amount mined annually to the reservoir in the uppermost 2 km of crust is very low. It is also worth keeping in mind that the bulk of the mined mass is of course not released to the atmosphere, with noteworthy exceptions, e.g., C, H, N, S (burning of fossil fuels, roasting of sulfide ores) or Pb (gasoline) and As (pesticides—e.g., ref 33)!

We can conclude that while presently "data collecting" projects are unfashionable, a pillar of research in environmental sciences is based on doubtful concepts that do not accommodate the reality of the biogeochemical cycle. We recommend the indiscriminate usage of EFs be abandoned by environmental scientists.

Acknowledgments

Literature Cited

(1) Clarke, F. W. *The data of geochemistry*; U.S. Geol. Surv. Bull. 770, 1924.

(2) Wedepohl, K. H. *Geochim. Cosmochim. Acta* **1995**, *59*, 1217−1232.

(3) Taylor, S. R.; McLennan, S. M. *Rev. Geophys.* **1995**, *33*, 241−265.

(4) *CRC Handbook of Chemistry and Physics 1996−1997*, 77th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, USA, 1997.

(5) Reimann, C.; Caritat, P. de *Chemical Elements in the Environment − Factsheets for the Geochemist and Environmental Scientist*; Springer-Verlag: Berlin, 1998.

(6) Zoller, W. H.; Gladney, E. S.; Duce, R. A. *Science* **1974**, *183*, 199−201.

(7) Lantzy, R. J.; Mackenzie, F. T. *Geochim. Cosmochim. Acta* **1979**, *43*, 511−525.

(8) Cawse, P. A. *A survey of atmospheric trace elements in the U.K.: results for 1976*; U.K. Atomic Energy Research Establishment Report AERE-R8869; 1977.

(9) Maenhaut, W.; Zoller, W. H., Duce, R. A.; Hoffman, G. L. *J. Geophys. Res.* **1979**, *84*, 2421−2431.

(10) Adams, F.; Van Craen, M.; Van Espen, P.; Andreussi, D. *Atmos. Environ.* **1980**, *14*, 879−893.

(11) Puckett, K. J.; Finegan, E. J. *Can. J. Bot.* **1980**, *58*, 2073−2089.

(12) Prodi, F.; Levizzani, V.; Santachiara, G.; Carboni, G.; Ventura, A.; Ravasini, G. J. *Aerosol Sci. 23, Suppl. 1* 1992, 5957−5960.

(13) Dongarra, G.; Ottonello, D.; Sabatino, G.; Triscari, M. *Environ. Geol.* **1995**, *26*, 139−146.

(14) Shotyk, W. *Environ. Rev.* **1996**, *4*, 149−183.

(15) Bargagli, R. *Trace Elements in Terrestrial Plants*; Springer-Verlag: Berlin, 1998.

(16) Biegalski, S. R.; Landsberger, S.; Hoff, R. M. *J. Air Water Manag. Assoc.* **1998**, *48*, 227−237.

(17) Weiss, D.; Shotyk, W.; Appleby, P. G.; Kramers, J. D.; Cheburkin, A. K. *Environ. Sci. Technol.* **1999**, *33*, 1340−1352.

(18) Chabas, A.; Lefevre, R. A. *Atmos. Environ.* **2000**, *34*, 225−238.

(19) Halstead, M. J. R.; Cunninghame, R. G.; Hunter, K. A. *Atmos. Environ.* **2000**, *34*, 665−676.

(20) Heinrichs, H.; Brumsack, H.-J. *Anreicherung von umweltrelevanten Metallen in atmosphärisch transportierten Schwebstäuben aus Ballungsgebieten;* Matschullat, J., Tobschall, H. J., Voigt, H.-J., Ed,; Springer: Berlin, 1997 (in German).

(21) Wittig, R. *General aspects of biomonitoring heavy metals by plants*; Markert, B., Ed.; VCH Verlagsgesellschaft: Weinheim, 1993; pp 3−22.

(22) Rühling, Å. Ed. Atmospheric heavy metal deposition in Europe − estimations based on moss analysis; Nord, 1994: 9.

(23) Varrica, D.; Aiuppa, A.; Dongarra, G. *Environ. Pollut.* **2000**, *108*, 153−162.

(24) Gerdol, R.; Bragazza, L.; Marchesini, R.; Alber, R.; Bonetti, L.; Lorenzoni, G.; Achilli, M.; Buffoni, A.; De Marco, N.; Franchi, M.; Pison, S.; Giaquinta, S.; Palmieri, F.; Spezzano, P. *Environ. Pollut.* **2000**, *108*, 201−208.

(25) Reimann, C.; Äyräs, M.; Chekushin, V. A.; Bogatyrev, I.; Boyd, R.; Caritat, P. de; Dutter, R., Finne, T. E.; Halleraker, J. H.; Jæger, Ø.; Kashulina, G.; Niskavaara, H.; Lehto, O.; Pavlov, V.; Räisänen, M. L.; Strand, T.; Volden, T. *Environmental Geochemical Atlas of the Central Barents Region;* NGU-GTK−CKE special publication; Geological Survey of Norway: Trondheim, Norway, 1998.

(26) Äyräs, M.; Reimann, C. *Joint ecogeochemical mapping and monitoring in the scale of 1: 1 mill. in the West Murmansk Region and contiguous areas of Finland and Norway − 1994−1996. Field Manual*; Nor. Geol. Unders. Rep. 95.111; 1995.

(27) Gegorauskiene, V.; Salminen, R.; Reimann, C.; Chekushin V. *Field Manual for Barents Ecogeochemistry project*; Report S/44/0000/2/2000; Geological Survey of Finland: Espoo, 2000.

(28) *Geochemical Atlas of Finland. Part 2: Till*; Koljonen, T., Ed.; Geological Survey of Finland: Espoo, 1992.

(29) Goldschmidt, V. M. *J. Chem. Soc., London* **1937**, 655−673.

(30) Ruppert, H. *Mitt. Österr. Geol. Ges.* **1991**, *83*, 243−265 (in German).

(31) Reimann, C.; Kashulina, G.; Caritat, P. de; Niskavaara, H. *Appl. Geochem.* **2001** (in press).

(32) Perel'man, A. I. *Geochemistry*; Vysshaya Shkola: Moscow, 1979 (in Russian).

(33) Matschullat, J. *Sci. Tot. Environ.* **2000**, *249*, 297−312.