Biological Cycles for Toxic Elements in the Environment

J. M. Wood

Toxic substances in the environment can be categorized as (i) naturally occurring toxic elements and compounds and (ii) toxic compounds that are synthesized industrially. The danger associated with naturally occurring toxic elements and compounds depends on their distribution in the environment. Under natural conditions their distribution remains relatively constant, largely because of natural biological processes that effect both their degradation and synthesis, and they do not pose serious public health problems. When used in industrial processes, however, they may reenter the environment and disrupt the natural action of organisms in such a way that the balance between degradation can no longer be maintained. Industrial effluents containing mercury, for example, may enter aqueous systems where the mercury is converted by natural biological processes to the poisonous neurotoxin methylmercury. Because the methylmercury is produced at a rate faster than other organisms can accomplish its degradation, it may accumulate in fish used for consumption by human beings and so pose a threat to public health. We must, therefore, become aware of the circumstances that lead to an increase in the rate of synthesis or release of toxic compounds compared to the rate of their degradation or removal.

The natural poisons are undoubtedly the most difficult to study because certain amounts are always present in the environment. Also, a small disturbance in an ecosystem can bring about a natural increase in the rate of synthesis of these compounds. Technically, therefore, it is simpler to monitor the amounts of toxic compounds that are synthesized industrially. Some of these compounds persist in the environment because there are no biological systems capable of actively transporting or degrading them. Such compounds are easily monitored. The maximum amount of these compounds that can accumulate in the environment is related to their solubility in water or lipids, or both (*1*). Although we cannot expect the occurrence of rapid mutations of microorganisms in nature, such as would enable them to synthesize enzymes capable of transporting and degrading many new synthetic compounds, such an approach is possible in the laboratory because mutation frequency for microorganisms can be increased enormously by using large doses of physical and chemical mutagens under controlled conditions. This laboratory approach to biodegradation could be useful in providing microorganisms active in the dispersal and metabolism of persistent compounds.

In this article I describe some of the chemical and biochemical transformations of toxic elements in the environment, placing special emphasis on the role played by microorganisms. I also show that our present knowledge of the biological cycles of toxic elements enables us to predict the behavior of other toxic elements in the environment.

Microbial Interconversions of Toxic Elements

From the standpoint of environmental pollution, toxic elements can be considered (i) noncritical, (ii) toxic and relatively accessible, or (iii) toxic, but very insoluble or very rare. Using these general criteria one can determine which elements are most likely to pollute the environment (Table 1). Toxic elements move through the environment under natural conditions by way of the "geocycle" from which the elements become available to plants and animals (Fig. 1). Man's activities provide new sources of toxic elements that influence the "geocycle" and consequently the availability of these elements to biological processes. Compare, for example, the movement and metabolism of mercury with that of cadmium. The low vapor pressure of elemental mercury allows its global dispersal, and the natural synthesis of stable alkylmercury compounds aids in the bioaccumulation of mercury. Cadmium alkyls are not stable in aqueous systems, and so the movement of cadmium depends on the solubility of cadmium salts. The metabolic activity of microorganisms plays a significant part in the mobility of toxic elements in the environment. Microorganisms are exceedingly versatile in the way they metabolize natural substances, and it can be said that if they do not degrade a particular compound, then it is unlikely that higher organisms will have the capacity to do so. Therefore, a study of microbial interconversions of toxic compounds can contribute substantially to environmental science. Microorganisms can be grouped according to their oxygen requirements: (i) aerobes, or those that degrade compounds oxidatively; (ii) anaerobes, or those that degrade compounds reductively; and (iii) facultative anaerobes, or those that degrade compounds both oxidatively and reductively. Organisms in any of these groups may also hydrolyze, dehydrate, or hydrate compounds. The availability of alternative pathways for the metabolism of toxic compounds facilitates the removal of these compounds from the environment. When confronted with a toxic substance, microorganisms frequently adapt to detoxify it. However, the detoxification of a substance by microorganisms can yield a product that is either more or less toxic to higher organisms. Let us therefore consider what is known about biological cycles for toxic elements.

Heavy Metals

By means of oxidative and reductive reactions catalyzed by enzymes, microorganisms can convert inorganic compounds into mixtures of compounds that are in equilibrium with respect to the formal oxidation states of the element in question. For example, with cobalt the following equilibriums exist

$$Co^{3+} + e \rightleftharpoons Co^{2+} + e \rightleftharpoons Co^{1+}$$

The basic chemistry of these three cobalt species is very different. The species Co^{3+} has a large affinity for electrons, but Co^{1+}, for example, is one of the best nucleophiles known in chemistry. Thus, because of their difference in chemical reactivity these cobalt species cannot be considered as a group.

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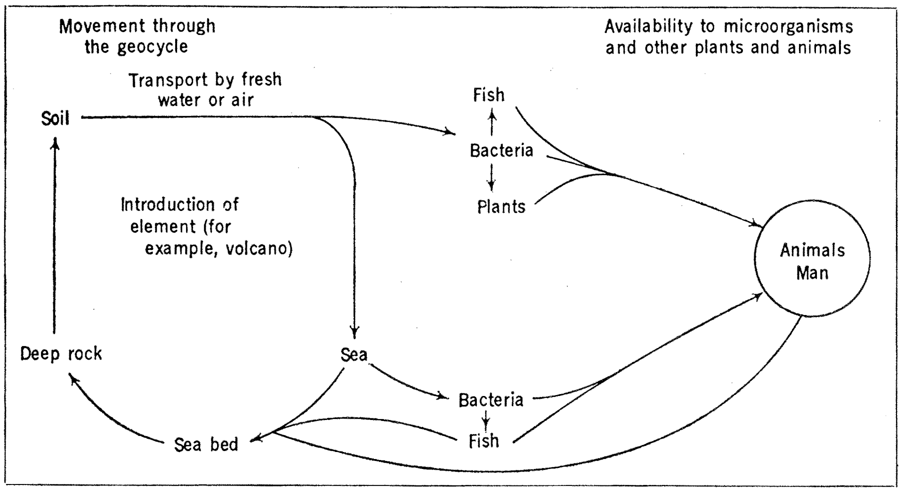


Fig. 1. The movement of toxic elements through the geocycle and their availability to microorganisms and other plants and animals.

Similar conclusions may be drawn about other transition metals in biocatalysis. This concept is of great importance because when a metal is introduced into a microbial ecosystem, each formal valence state of that metal is available for chemical or biochemical reactions.

With mercury we must consider the following disproportionation reaction at all times

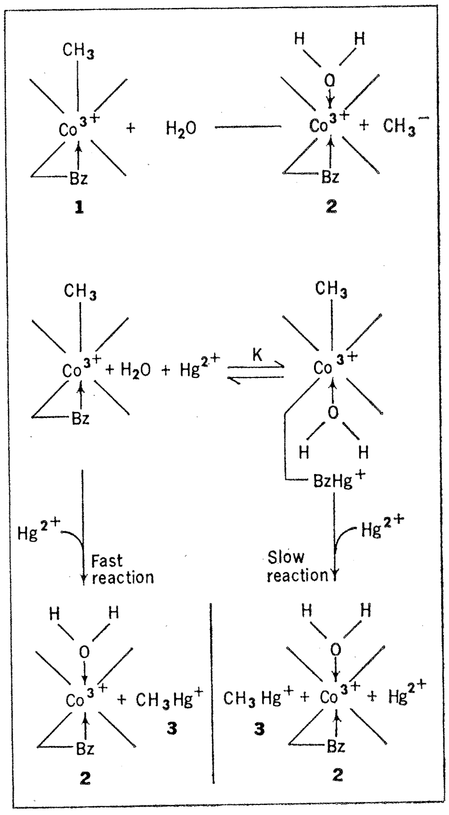
$$Hg_2^{2+} \rightleftharpoons Hg^{2+} + Hg^0$$

Vaporization of elemental mercury (Hg^0) shifts the equilibrium to the right, but return of Hg^0 from the atmosphere to the earth's crust shifts the equilibrium to the left. Interconversions of these three inorganic forms of mercury can be catalyzed by microorganisms. Aerobes can solubilize Hg^{2+} from HgS (solubility product $10^{-53}M$) by oxidizing the sulfide through sulfite to sulfate (*2*). Once Hg^{2+} has been solubilized it can be reduced to Hg^0 by an enzyme which is present in a number of bacteria; this enzyme has been shown to require reduced nicotinamide adenine dinucleotide (NADH) as a coenzyme for catalysis (*3*):

$$Hg^{2+} + NADH + H^+ \rightleftharpoons Hg^0 + 2H^+ + NAD^+$$

The conversion of Hg^{2+} to Hg^0 can be regarded as a detoxification mechanism because the Hg^0 has sufficient vapor pressure to be lost from the aqueous environment into the vapor phase.

Some bacteria employ a second detoxification mechanism that converts Hg^{2+} to methylmercury and dimethylmercury. A survey of the methylating agents that are available for methyl transfer reactions in biological systems reveals that there are three coenzymes that are known to participate in this reaction: (i) *S*-adenosylmethionine, (ii) N^5-methyltetrahydrofolate derivatives, and (iii) methylcorrinoid derivatives. The *S*-adenosylmethionine and N^5-methyltetrahydrofolate derivatives are not capable of transferring methyl groups to Hg^{2+} because for both these coenzymes the methyl group is transferred as CH_3^+. Therefore, the only known methylating agents capable of methyl transfer to Hg^{2+} are methylcorrinoids because they are capable of transferring methyl groups as CH_3^- (*4*). In the following reaction Bz represents the 5,6-dimethylbenzimidazole in a methyl-B_{12} (vitamin B_{12}) derivative, **1**, that is converted to aquo-B_{12}, **2**. The Bz in **1** can be displaced by other bases, however; in fact, the stronger the base, the greater the electron density on CH_3 which facilitates its displacement as CH_3^-.



Recent studies have elucidated the details of the mechanisms for the synthesis of both methylmercury and dimethylmercury from methyl-B_{12} compounds (*5, 6*).

The rate of synthesis of methylmercury (**3**) depends on the equilibrium constant, *K*. The slow reaction is about 1000 times slower than the fast reaction. Dimethylmercury (**4**) is synthesized by an identical mechanism, except that CH_3Hg^+ is the reacting species instead of Hg^{2+}. However, the synthesis of dimethylmercury is about 6000 times slower than the synthesis of methylmercury. The *p*H optimum for the synthesis of methylmercury either under laboratory conditions or in natural sediments is 4.5 (*7*). Dimethylmercury is volatile, and once in the atmosphere it is photolyzed by ultraviolet light to give Hg^0 plus methane and ethane:

$$\underset{\mathbf{4}}{(CH_3)_2Hg} \xrightarrow{\text{light}} Hg^0 + 2CH_3^\bullet$$

methyl radicals ($CH_3^\bullet$) can abstract hydrogen or couple to give methane plus ethane.

Other microorganisms can detoxify their environment of methylmercury by reducing it to Hg^0 plus methane. This detoxification reaction converts the deadly poisonous neurotoxin, methylmercury, to the more volatile Hg^0 (*8*), which is, however, also toxic to man and other mammals.

From the preceding examples it is clear that there are biological cycles for the synthesis and degradation of toxic compounds. The biological cycle for mercury is summarized in Fig. 2. The interconversions of mercury compounds set up a dynamic system of reversible reactions which leads to a steady state concentration of methylmercury in sediments. Because these steady state concentrations of methylmercury need not reflect the rate of synthesis of methylmercury, the determination of the concentration of methylmercury in a sediment would be a meaningless exercise (*6*). To assess a particular case of mercury pollution only measurements of the concentration of total mercury in sediments and the rate of methylmercury uptake in fish would give meaningful results. The kinetics of the process are important, as is the case

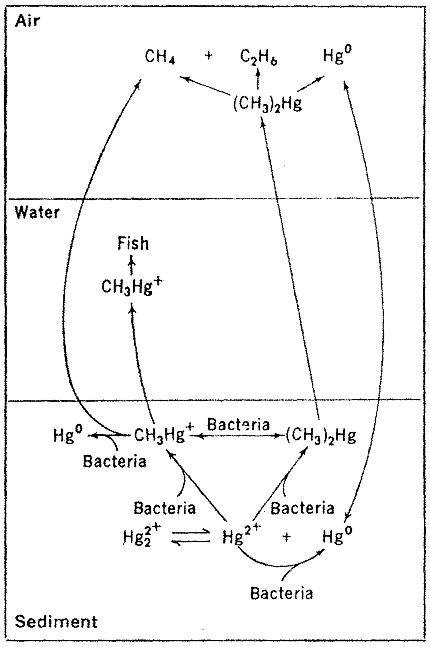
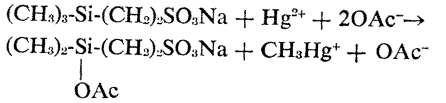


Fig. 2. The biological cycle for mercury.

for all problems of environmental significance.

It is possible to predict which other heavy metals can be transformed in the same way as mercury. For example, by using the same approach as that used with methylmercury, one can predict that tin, palladium, platinum, gold, and thallium will be methylated in the environment, but that lead, cadmium, and zinc will not be methylated. This is because the alkylmetals of lead, cadmium, and zinc are not stable in aqueous systems, and methyl-B_{12} does not transfer methyl groups to these elements. All these predictions have proved to be correct (*9*). For example, although cadmium does form coordination complexes with a variety of ligands in biological systems, no metabolic interconversions have ever been demonstrated for this element. The heavy metals that are methylated should be watched closely by environmental agencies. Platinum and palladium catalysis and other heavy metal alkyls as gasoline additives in place of lead alkyls, should be of particular concern.

Under certain circumstances the industrial synthesis of methylmercury can upset the balance of the biological mercury cycle. DeSimone has shown that water-soluble methylsilicon compounds react with Hg^{2+} to give methylmercury (*10*).



$$(CH_3)_3\text{-}Si\text{-}(CH_2)_2SO_3Na + Hg^{2+} + 2OAc^- \rightarrow (CH_3)_2\text{-}\underset{\displaystyle OAc}{\underset{|}{Si}}\text{-}(CH_2)_2SO_3Na + CH_3Hg^+ + OAc^-$$

Jernelöv has shown that contaminating methyl groups in ethyl-lead compounds yield the chemical synthesis of methylmercury from Hg^{2+} (*11*). The chemical synthesis of methylmercury as a fungicide can also upset the balance of the biological cycle of mercury. When neurotoxins such as methylmercury are synthesized as by-products of industrial processes it is necessary to recognize that such compounds are also produced by natural processes which are influenced by a variety of factors. For example, the rate of synthesis of methylmercury depends on the concentration of available Hg^{2+}, the composition of the microbial population, the *p*H, the temperature, the redox potential, and the synergistic or antagonistic effects of other metabolic or chemical processes (*12*).

The Metalloids

By examining the periodic table and utilizing current knowledge of the properties of the toxic elements, one can predict how most of these elements will behave in the environment. Arsenic compounds are reduced and methylated by anaerobes to give dimethylarsine and trimethylarsine as volatile products of extreme toxicity (*13*). Fortunately, these arsines are readily oxidized to give products less toxic, such as cacodylic acid. However, cacodylic acid has been shown to be an intermediate in the synthesis of dimethylarsine from arsenic salts. Therefore, there is a biological cycle for arsenic just as there is for mercury (Fig. 3). Alkyl-arsenic compounds have been found to accumulate in shellfish analyzed in Norway (*14*). On the basis of our understanding of arsenic chemistry, we can predict similar metabolic reactions for selenium, tellurium, and sulfur. Such reactions have already been found to occur (*13*).

It is evident that with evolution of

Table 1. Classification of elements according to their toxicity. Elements omitted from this table should not be neglected in the environmental sense. For example, iodine and manganese are important elements, but they fit more than one category for the above classification.

Noncritical			Very toxic and relatively accessible			Toxic but very insoluble or very rare	
Na	C	F*	Be	As	Au	Ti	Ga
K	P	Li	Co	Se	Hg	Hf	La†
Mg	Fe	Rb	Ni	Te	Te	Zr	Os
Ca	S	Sr	Cu	Pd	Pb	W	Rh
H	Cl	Al	Zn	Ag	Sb	Nb	Ir
O	Br	Si	Sn	Cd	Bi	Ta	Ru
N				Pt		Re	Ba

* Some may argue with this designation, but we do add fluoride to drinking water. † All the lanthanides are very insoluble and some are very rare.

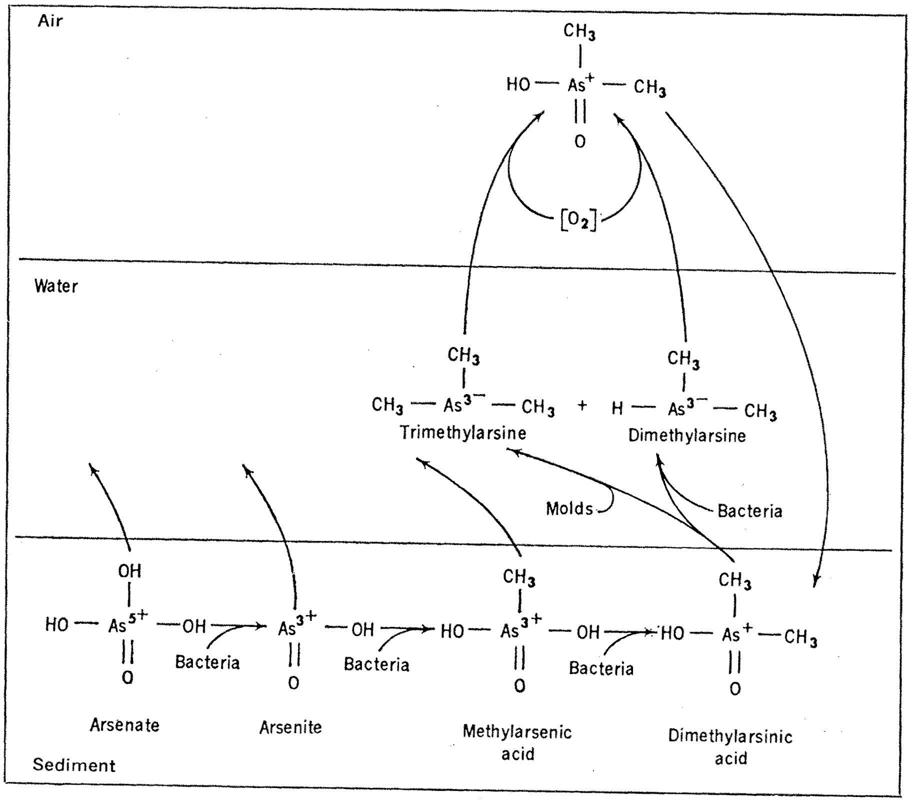


Fig. 3. The biological cycle for arsenic.

such a dynamic system of biological cycles for the toxic elements, small disturbances in these cycles will affect the natural equilibriums which will in turn affect the concentrations of toxic intermediates. Great care must therefore be taken in deciding which species of a toxic element should be monitored in the environment, because neglect of these biological transformations can make the development of models for the flow of chemicals through the environment a futile exercise.

References and Notes

1. When a new synthetic compound is produced by the chemical industry and laboratory tests indicate that it is not biodegradable, it is then important to know the solubility of this compound in water and in lipids. The maximum concentration of this new compound in water or in lipids will represent its "bioaccumulation potential." In the environment this potential may never be reached, but "bioaccumulation potential" does give us a good guideline for the concentration of this new compound which should be of concern when testing it toxicologically. Jernelöv has used the term "bioaccumulation potential" to describe this concept [A. Jernelöv, in *Proceedings of the Environmental Protocols Meeting*, San Antonio, Texas, 11 to 16 February 1973 (National Academy of Sciences, Washington, D.C., in press)].
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The Economics of Resource Recovery from Municipal Solid Waste

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Environmental concern has drawn attention to means for recovering material and energy resources from urban solid waste, particularly from the household portion (*1*). Recently, federal support has been given for this purpose (*2*). The public viewpoint is that the metal, glass, and other materials found in ordinary refuse are resources to be saved, preserved, and recovered rather than discarded. Recovery, outside of separation by the householder, depends on the availability of suitable separation technology operated at a reasonable cost to the community.

Unfortunately, progress in affecting the installation of recovery facilities to meet the needs of communities has been slow. Much of the work done has been beset with technical, and, more often, economic difficulties. However, the rising cost of traditional and environmentally acceptable means of disposal may allow new systems to become economically competitive. New systems hold promise. The Environmental Protection Agency in late 1972 announced four grants, under Section 208 of the Resource Recovery Act of 1970 (*3, 4*), for the construction of resource recovery plants of at least 200 tons per day capacity to demonstrate new technology. Many unit operations familiar in chemical, mechanical, and minerals processing engineering practice can be, and already have been, applied to refuse processing and resource recovery (*5*). Their final adoption will depend on their costs to the community being competitive with traditional methods of disposal, such as sanitary landfilling or incineration.

Raw Materials

Before considering the costs of resource recovery, one must examine what there is to recover—that is, what is likely to be in the solid waste stream. This article is focused on the household portion of the urban solid waste.

The results of several analyses (*6*) of the composition of household refuse by weight resulted in the values given in Table 1. Unfortunately, there is no such thing as an average refuse composition: The composition varies from city to city—probably geographically and no doubt seasonally and temporally, from year to year and on shorter time scales, all making definitive analysis difficult. There are, however, some general trends in composition that can serve as design input for technical and economic analysis. First, some nominal composition figures can be computed, using one's judgment, from the available data (*7*). Second, it is apparent that municipalities with a "high" refuse assay have an economic advantage in implementing recovery facilities. A high assay means that the content of the valuable, nonferrous metals must be about 1 percent.

Recovery potential falls into two basic groups of materials (see Table 1). The first group of items is labeled "mechanical recovery" and refers to that portion of the refuse stream which is available for essentially mechanical extraction and for reuse as a relatively pure raw material. The second group includes what are primarily organic materials, which, because of their physical characteristics, can only be recovered through conversion. Organic materials are generally suitable for some sort of derived product, such as com-

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