

U.S. ENVIRONMENTAL PROTECTION AGENCY
SCIENCE ADVISORY BOARD
ENVIRONMENTAL POLLUTANT MOVEMENT AND TRANSFORMATION COMMITTEE

Advisory Papers on the Development and Calculation of Global
Material Balances for Selected Chemical Substances. #1

General Background Concepts

This is the first in a series of advisory papers on the problems of developing global material balances for selected chemical substances in all parts of the environment and the methodologies needed to exploit these material balances to make predictions on the movement and behavior of the chemicals being studied. This paper is based largely on the material developed in a draft of a consultant paper prepared by Dr. Robert A. Duce, University of Rhode Island, a member of the Environmental Pollutant Movement and Transformation Committee.

Dr. Elliott W. Montroll
Chairman of the Committee

Dr. Joel L. Fisher
Executive Secretary

August 24, 1978

EPA NOTICE

This report was prepared by members of the Science Advisory Board for the Environmental Pollutant Movement and Transformation Committee. The Science Advisory Board is chartered to provide independent advice to the EPA. This report has not been reviewed or approved by the EPA, and therefore it should not be considered to reflect official Agency policy, nor should mention of trade names or commercial products be considered as an endorsement. The report has been approved by the Environmental Pollutant Movement and Transformation Committee as an advisory document. The report has been endorsed by the Chairman of the Executive Committee for transmittal to the Agency.

TABLE OF CONTENTS

EPA Notice	2
Table of Contents	3
Introduction	4
Global Material Balances	6

INTRODUCTION

A fundamental method of assessing the movement and distribution of a chemical substance in the environment is to establish a material balance for that substance. Such a material balance is an inventory, or method of bookkeeping, which totals the amount of the material which enters the system, the amount which circulates within the system, the amount which changes chemical form, and the amount which leaves the system. The "system" is that part of the environment of interest at the moment with respect to the chemical substance which is being inventoried. Thus, the "system" is an expression of "scale" or "size." One may speak of planetary material balances -- the inventory of substances that enters and leaves the planet at large. Here the inputs could be meteorites, the outputs could be space satellites or rocket boosters, and circulation is movement within the planet. The chemical substance of interest is assessed in terms of its concentration within the various input and output materials. One may also speak of global material balances -- the dynamics of movement through the atmosphere, aquatic systems (rivers, lakes, estuaries, and oceans), terrestrial media (soils, then groundwaters), and biota (organisms and tissues) -- and ignore the "planetary" inputs and outputs as not being relevant. Or one may speak of a continental balance -- the dynamics of input, output and circulation within a large land mass which has been "intellectually isolated" from all other land masses for study purposes. Material balance scales continue downward through regional, urban or rural, local, individual, cellular, subcellular, etc.

The Environmental Pollutant Movement and Transformation Committee of the Science Advisory Board is concerned with how pollutants move through the environment and change. The Committee is concerned with environmental distributions of natural and manmade chemicals, and with processes affecting environmental distributions of these chemicals; with methods of predicting what impacts particular changes in pollutant distributions have on exposed animal, plant, and human populations; with the impacts of distributions on methods of control or utilization of possible pollutants; and with decision making and policy making which depend on maintaining or changing particular distributions. This Committee is specifically concerned with advising the EPA on methods of calculating and utilizing material balances for selected chemicals in the environment and in predicting effects that modification of environmental distributions of selected chemicals will have on regulatory policies. The Committee requested its member, Dr. Robert A. Duce, to begin to explore how to advise EPA with respect to material balances.

The importance of this project has been underscored by some recent problems within the Environmental Protection Agency. Of note has been the desire of various regulatory groups within the Agency, especially the Office of Toxic Substances, to establish guidelines to use the "fate of a pollutant" as a means of predicting environmental impact and the types of regulatory strategies needed for control of toxic chemicals.

Unfortunately, of all of the things usually known about a given chemical pollutant, e.g., its toxicity and physical and molecular properties, the "fate" in the environment is usually the least known. In fact, the "fate" of environmental chemicals is only "known" in a very few cases. One such case is the "nitrogen cycle," which has been studied by agronomists, limnologists, and microbiologists, for many years. Although some of the data may be questionable, there seems to be large scale agreement among scientists as to the mechanisms involved.

Also of note is the feeling among those Agency regulators who are concerned with proposing effluent guidelines for selected chemicals in industrial dischargers that knowledge of the "fate of the chemicals" from the discharge may be of considerable value in choosing ambient standards in the aquatic environment without having to rely solely on the safety factors applied to limited toxicological data with selected aquatic species. It would be nice, for example, to be able to state that a dilution factor of 100 or 500 was applicable to certain discharge situations and that mixing zones are either usable or unusable without having to cite toxicological data for aquatic species not indigenous to the waterbodies of interest.

This first paper is adapted from Dr. Duce's consultant paper. It deals with global material balance concepts and is primarily introductory. Future papers in the series will deal with specific methodologies and cases, and in order to be of maximum advisory benefit to the Agency, will consider topical inputs from the Agency.

GLOBAL MATERIAL BALANCES

Over the past 10-20 years there has been a growing realization that man can affect and sometimes significantly change the global environmental cycles of many substances. Public concern relative to global-scale problems has arisen because of (1) possible climate modification due to carbon dioxide and atmospheric particle increases, (2) human health effects due to possible changes in the ozone levels in the stratosphere as a result of increased aircraft operations at high altitude and chlorofluorocarbon and nitrogen fertilizer use, and (3) the impact of pollutants on marine and terrestrial ecosystems. These three problems have probably been the primary driving forces behind increased research directed toward understanding global material balances, but they have also led us to an awareness of how poorly we understand biogeochemical cycles and global material balances in general. None of these problems can be adequately addressed unless the mass flow and accumulation of the substances of interest in various compartments of the environment are known and unless the natural and anthropogenic source strengths of the substances are quantified.

Geochemists have been concerned with global chemical balances for decades. Only recently, however, have they had adequate analytical tools and sampling techniques to evaluate the importance of the marine and atmospheric environments in the global material balances of many substances. On the basis of recent data, it appears that anthropogenic sources may be dominating, or at least measurably altering, major components of the natural geochemical cycles of a number of substances, specifically elemental lead, sulfur dioxide, carbon monoxide, carbon dioxide, nitrous oxide, ozone, and atmospheric particulates.

An understanding of the complete environmental cycling of certain classes of toxic substances is necessary to develop adequate models for the environmental behavior of similar substances and to plan for their control and containment. Evaluation of global balances identifies environmental compartments in which individual substances are being concentrated. Research emphasis can then be directed toward evaluation of the effects of these substances on the ecosystems residing in these compartments. In addition, information can be obtained about the general features and mechanisms of transport processes using the distribution of flux of certain chemical tracers. For example, the extent of tropospheric air mass exchange across the Equator has recently been evaluated from atmospheric carbon monoxide measurements in both hemispheres.

For global scale considerations, decades to centuries are involved for marine transport. The atmosphere is the primary transport path for global transport processes on time scales of less than a few years. In evaluating the global balance of any substance, we must consider its distribution, sources and sinks, fluxes and transport, and reactions and transformations. In general, the discussion below will relate to the atmospheric part of global biogeochemical cycles and material balances. It is only used as an example of the kinds of questions we must ask about all components of the environment, be they marine, fresh water, terrestrial, or atmospheric.

Obviously, a measurement of concentrations or burdens in various compartments of the environment is the first step in evaluating a biogeochemical cycle for any substance over any significant geographic scale. For many substances, however, we are not really "off the ground," literally and figuratively, with this first step. For example, atmospheric information on the vertical distributions of chemicals, information which is critical to assessing atmospheric burdens, is virtually nonexistent. For most substances, measurements are restricted to near surface urban regions, with little surface data and almost no vertical data from remote marine and continental regions. Although advances in analytical methodology have been remarkable in the past few years, determining of global material balances for many substances is still analytically limited. For example, satisfactory methods are still in the development stage for measuring atmospheric nitric oxide in remote regions. Reliable measurements for DDT in open ocean waters are still not available.

Differentiation between natural and anthropogenic sources and sinks is often extremely difficult but is necessary to evaluate global material balances. For some substances, such as many synthetic organics, this is not a problem, as nature does not (or we often think it does not) produce many of these materials. For substances which have both natural and anthropogenic sources, several approaches can be taken:

Isotopic studies are often useful. Due to differences in source materials or exchange processes, certain natural sources may produce substances with altered isotope ratios relative to anthropogenic sources. This has proven useful for elemental lead, elemental carbon, and elemental sulfur, some compounds of nitrogen, and recently for hydrogen and oxygen isotopes in the molecules of water itself.

Within a given elemental cycle, certain sources may emit different chemical forms, or species, of the element. For example, smelters usually emit arsenic as the trivalent arsenic trioxide, while the biosphere, through microbial activity, converts elemental arsenic and its oxides to methylated species such as methyl arsine.

For atmospheric particulate matter, SEM/EMP can be helpful, as particles from specific anthropogenic sources often have morphology, composition, and mineralogy different from particles from natural sources.

For a broad scale effort to determine whether the overall cycle of a particular substance is dominated, or at least significantly affected, by man on a global or hemispheric scale, an historical record may be of great use. This includes both glaciers and major icecaps in the north and south polar regions as well as fresh water or even near shore marine sediments.

Detailed meteorological analysis, particularly air parcel trajectory analysis coupled with simultaneous atmospheric measurements, can allow one to relate substances to certain source areas.

Sophisticated statistical techniques such as factor analysis, pattern recognition, and hierarchical clustering allow one to relate the distributions of substances of unknown origin in a sample to substances of known origin, thus suggesting common sources which should be evaluated further.

Finally, one can simply compare the global or regional fluxes of material from (or to) natural and pollution sources (or sinks). In most cases, our knowledge of the numerical values for these fluxes is so uncertain that this approach gives us only a crude and often misleading approximation of the importance of pollution sources. Quantitative information on direct emissions from anthropogenic sources is only now becoming available for the U.S. and is largely missing for the rest of the world. This problem is complicated by second and third order processes not directly related to the primary emission process. These include changes in land use patterns, chemical transformations in the atmosphere, etc. Nevertheless, it is safe to say that estimates of the input of most chemical substances to the atmosphere from pollution sources are considerably more accurate than estimates from natural sources. Our understanding of the importance of the terrestrial and marine biosphere, volcanoes, forest fires, surface weathering, etc. as sources for most trace substances in the global atmosphere is abysmal.

Fluxes are usually more difficult to measure than are ambient concentrations. As formulated in material balance equations these fluxes are often linearized by equating them to a ratio of inventories over residence times. This approach assumes that the rate of removal (or input) of a substance is independent of the quantity of that substance already in the reservoir. This is rarely the case for removal processes and is not that common for source functions. However, until more is known about the factors controlling the fluxes of substances in and out of reservoirs, this assumption is the easiest to make. If possible, fluxes should be measured as a function of ambient concentration so that the relationship between these two quantities may be evaluated. With respect to removal mechanisms from the atmosphere, the correct relationship will probably involve exponentials in most cases.

The real action in most cases occurs at interfaces in the environment. An understanding of the chemistry, physics, and biology of surfaces is fundamental in all biogeochemical cycles. Sources, sinks, and associated fluxes are all concerned with transport across some interface, be it air/sea, air/leaf, river/sea, gas/particle, soil/water, etc. For simple physical and chemical exchange processes we must know the specific form of the exchanged substances at the interface (which may be different from its form away from the interface), the effects of temperature, pressure, light, moisture, and other chemical substances on the exchange process and the fundamental surface forces and properties which control exchange across each interface. The presence of organisms on a surface (and in many cases we are concerned with a biological surface to begin with) will often affect chemical fluxes across the surface. In this case, not only must the parameters affecting simple physical and chemical exchange be considered, but also such factors as the state of organisms development, growth, and season.

In general, the spatial scales over which one might begin to attempt a mass balance are related to substance residence times in the system. The shorter the residence time, the smaller the spatial scale one may wish to cover. In such cases as elemental sulfur and nitrogen, hemispheric (i.e., northern and southern) mass balances may be most appropriate. For substances whose atmospheric residence time is one to two years or less and whose biogeochemical cycle is

suspected to be significantly altered by man, a comparison of northern and southern hemisphere mass balances, inventories, etc., etc., can often be extremely valuable. This has been particularly useful for carbon monoxide, some halogenated organic species, and certain heavy metals.

Chemical transformations and reaction rates in the atmosphere and aqueous systems must be evaluated in any material balance. Many harmful substances are rapidly transformed to less harmful species; others are not. With an understanding of reaction rates and transport processes, the appropriate time and distance scales can be evaluated for any substance. Information on the physical and chemical transformations of a substance is sometimes available before the distribution of the substance is well known. Modelling, based on laboratory reaction kinetics, can predict, sometimes fairly accurately, the concentrations of certain species in the atmosphere, but these models must be verified by actual ambient air measurements. In many cases, the real world measurements have lagged behind the models.

The presence of unmeasured or poorly measured species can sometimes be deduced from conservation of mass considerations. This is difficult at present in most biogeochemical cycles because the overall uncertainties in the various components of the cycles are usually so great that it is hard to identify any "holes." Certainly, there appears to be such a "hole" in the global atmospheric sulfur cycle, and many forms of sulfur from several sources have been suggested to fill this hole. It still has not been filled. As measurement techniques and area coverage improve, the information on sources, sinks, and reservoirs will improve, thus decreasing the cycle uncertainties. This will undoubtedly reveal "holes" in other cycles.

It should be pointed out that important intermediate species will often be completely missed in a simple mass balance approach, and thus important mechanisms involved in material fluxes or transformations can be overlooked. For example, a substance with a very short residence time in the atmosphere may be transformed into a longer residence time component, and the longer lived component may be the only one measured. It is likely that the primary flux of arsenic into the global troposphere is via a vapor phase. However, the vapor phase comprises only about 2% of the total arsenic burden due to its very rapid conversion to or uptake by particles. A simple mass balance in which only particulate arsenic is considered would be quite accurate relative to the total tropospheric burden of arsenic, but would miss the very important fact that this burden is apparently controlled by a short-lived arsenic vapor phase.

The time scales over which quasi-steady states may be expected in the atmosphere vary tremendously depending upon the particular substance evaluated. For substances dominated by certain rapid photochemical reactions, the presence or absence of clouds could affect the steady state, and thus a time scale of minutes would be important. Diurnal time scales are appropriate for other photochemically controlled cycles, e.g. NO_x , and seasonal cycles may be dominate for biologically controlled atmospheric cycles. For cycles of other substances, e.g. the freons, the time scale is likely to be decades. Determining these critical time scales is one of the fundamental questions to be answered in any global mass balance or biogeochemical cycle.

The cycles of many substances interact and couple. Obvious examples are cycles for nitrogen, chlorine and ozone. We are constantly being surprised in this area, however. The relationship between the methane cycle and the carbon monoxide cycle through the hydroxyl free radical is a good example. The "discovery" of the hydroxyl radical has perhaps more than any other single event, catalyzed our thinking toward watching for and seeking out this coupling of cycles.

Finally, we must know the ultimate sinks of the substances of interest, particularly pollutants. Ultimate must be used in a relative sense here -- on a time scale of hundreds to thousands of years, perhaps. Many substances undergo chemical reactions, are destroyed, and thus do not accumulate indefinitely in the environment. Others may be destroyed but only after accumulating to potentially harmful levels in certain compartments, e.g., the freons in the atmosphere. Others may be deposited in the ocean sediments over various time scales and become largely decoupled from the dynamic part of biogeochemical cycles.

For any substance with a significant pollution source, the determination of an accurate global material balance and a realistic evaluation of its biogeochemical cycle will not be easy. It will require close communication between the field and laboratory scientists studying the fundamental processes involved in pollutant transport and distribution in the environment and the national and international agencies responsible for pollution control and source strength evaluation.

