

# **Chemical Time Bombs: Definition, Concepts, and Examples**

**W.M. Stigliani, Editor**

**EXECUTIVE REPORT 16  
(CTB Basic Document 1)  
January 1991**

**Participants:**

**P. Doelman, DHV Consultancy, The Netherlands**

**W. Salomons, Institute for Soil Fertility, The Netherlands**

**R. Schulin, Swiss Federal Institute of Technology, Switzerland**

**G.R.B. Smidt, VROM, The Netherlands**

**W.M. Stigliani, IIASA, Austria**

**S. Van der Zee, Agricultural University Wageningen, The Netherlands**

**INTERNATIONAL INSTITUTE FOR APPLIED SYSTEMS ANALYSIS  
A-2361 LAXENBURG, AUSTRIA**

**International Standard Book Number 3-7045-0103-4**

---

*Executive Reports*, which summarize research conducted at IIASA, are independently reviewed before publication. However, the views and opinions they express are not necessarily those of the National Member Organizations or other institutions that support IIASA's work.

---

Copyright © 1991  
International Institute for Applied Systems Analysis

All rights reserved. No part of this publication may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopy, recording, or any information storage or retrieval system, without permission in writing from the publisher.

---

Activities of the Chemical Time Bomb Project are coordinated in the Netherlands by the Foundation for Ecological Development Alternatives (Mondiaal Alternatief), Hoofddorp, The Netherlands.

Cover design by Martin Schobel

Printed by Novographic, Vienna, Austria

# Foreword

The environments of industrialized countries have long been the recipients of high doses of polluting chemicals from all kinds of societal activities. In the face of perceived threats posed by these chemicals, policies have been enacted for safeguarding public health and protecting the natural environment. While these policies have been certainly beneficial and necessary, they are often implemented as a reaction to a pollution problem that has already occurred. A preventive policy rather than a reactive one would certainly be a better approach. However, our ability to enact preventive policies is hindered by our limited knowledge of the complex linkages between chemical inputs and environmental effects.

In fact, the literature abounds with references to “chemical sinks” as the ultimate environmental depositories of pollutants. The image that the word “sink” conjures up is one of a bottomless hole into which chemicals may be washed away never to be encountered again. In reality, is the environment a “bottomless pit” or is it more like a sponge? This is far from a trivial question, for if the latter analogy is true it implies that, just as for a sopping-wet sponge, environmental systems can eventually become saturated from accumulated chemical inputs. At that point they may be transformed from a sink to a source of harmful chemicals. Moreover, during the time over which the system is capable of absorbing toxic chemicals, overt environmental effects may not be evident or expected. When the effects are finally manifested (after saturation occurs) they are usually displaced in time from the activities causing the problem in the first place. Because of the delayed environmental response and because such responses may be unanticipated, the term “chemical time bomb” has been coined to describe the phenomenon.

This publication introduces the concept of chemical time bombs, describes, by way of example, why we should be concerned about them, and provides some guidance in how to anticipate their occurrence. Subsequent publications will provide further elaborations of the general ideas expressed

in this document. Moreover, a series of workshops focussing on potential time bombs in specific European regions will be conducted over the next several years.

We hope that these efforts will raise awareness of potential problems associated with long term accumulations of chemicals in the European environment, and assist in formulating wise public policies for their mitigation.

C.J. van Kuijen  
Director for Chemicals  
and Risk Management  
VROM

Bo Döös  
Leader  
Environment Program  
IIASA

# Preface

This report, based on the deliberations among six scientists at a three day workshop in the Netherlands in August 1990, discusses the question of the potential long-term impacts of the accumulation and mobilization of toxic and environmentally harmful chemicals in the environment. It is meant to be an introduction to an environmental problem deserving of far more extensive research. This paper sets forth the potential problems caused by long term accumulations of chemicals in the environment, cites examples of economic costs of such occurrences, and defines the means by which, under certain conditions, such accumulations behave like "time bombs." Subsequent sections of the report provide actual examples of such behavior, and discuss, in a preliminary way, how chemical time bombs may be predicted. Finally, the conclusions are cited, based on the consensus of the participants at the workshop.

This publication is the first in a series of five. Subsequent reports, based on workshops planned in the future, include: Scenarios Pertaining to Chemical Time Bombs, Vulnerability Mapping, Landfills and Contaminated Lands, and Models and Adjustments of Data Sets.

We gratefully acknowledge the Netherlands Ministry for Housing, Physical Planning, and Environment (VROM), Directorate for Chemicals and Risk Management for providing financial support for the workshops.



# Contents

Foreword	iii
Preface	v
1. Problem Statement	1
2. Examples of Economic Costs of Long-Term Chemical Pollution	2
3. Definition and Demarcation of the Chemical Time Bomb Concept	4
3.1. Definition	4
3.2. Mathematical formulation	6
4. Examples	8
4.1. Acidification and leaching of aluminum	8
4.2. Microbial induced CTBs	11
4.3. Biological time bombs	14
5. Prediction of Future Chemical Time Bombs	14
5.1. Lessons from the most vulnerable areas	15
5.2. The “bottom up” approach	15
5.3. Listing of system parameters	18
6. Conclusions	21
References	22



# Chemical Time Bombs: Definition, Concepts, and Examples

## 1. Problem Statement

Man-made chemical contaminants have been accumulating in soils and sediments for the past 2000 years. An early example is the pollution caused by the mining of heavy metals. Since the beginning of the Industrial Revolution 200 years ago, the scale and pace of environmental contamination caused by industrial, commercial, agricultural, and domestic activities have steadily increased. The pattern of pollution may be characterized not only by local, highly concentrated sites such as toxic waste dumps or mine tailings, but also by lower concentrations of pollution widely dispersed over the landscape, including pastures, crop lands, forests, and the sediments of rivers, lakes and estuaries.

The short-term economic benefits from industrialization, through which potentially toxic and environmentally harmful chemicals are concentrated, processed, manufactured, consumed and inadvertently discharged to the environment, are obvious. What is less visible are the societal costs over the long-term, caused by the legacies of the chemical loads stored in the environment. Apart from the visible signs of contamination (e.g., heavily polluted rivers with observed fish extinctions), account should be taken also of the vast amounts of unnoticed contamination.

Due to the capacity of soils and sediments to store and immobilize toxic chemicals in so-called “chemical sinks,” direct effects of pollution may not be directly manifested. This positive function of soils and sediments does not guarantee, however, that the chemicals are safely stored forever. Factors

influencing the storage capacity of soils and sediments or the bioavailability of the stored chemical can change and indirectly cause sudden and often unexpected mobilization of chemicals in the environment (Stigliani, 1988).

Because loading of the chemical to the environment can occur long before effects are observed, the term “chemical time bomb” has been coined to describe such phenomena. Moreover, when the overt environmental effects are finally manifested they may be much more serious than would have been initially foreseen. Forest dieback in the early 1980s, due at least in part to soil acidification and air pollution, is a recent example of a sudden, unanticipated environmental problem resulting from delayed responses to inputs of chemical pollutants.

## 2. Examples of Economic Costs of Long-Term Chemical Pollution

As noted by Brooks (1986), while the economic benefits of the applications of chemicals are visible on relatively short time scales, the disbenefits (defined here as the effects of chemical time bombs) become obvious only on relatively long time scales. Economic planning, as currently practiced, overlooks the problems caused by the legacy of chemicals accumulated in the environment over time.

For example, consider the price of purifying drinking water in the Netherlands, where about 70% of the supply is withdrawn from ground water. Costs (given in US dollars-cents) of purifying one cubic meter of ground water from various commonly occurring hazardous chemicals are shown in *Table 1*.

The annual use of drinking water in the Netherlands is two to three billion cubic meters. A combined purification removing heavy metal salts and chlorinated propane requires two or three treatments each, costing 20 – 40 US cents per cubic meter. An annual cost of one to two billion US dollars can be expected for such treatment.

For phosphate contamination, it is estimated that currently ground water underlying at least 60,000 ha (2% of the total Dutch surface area) requires purification at an annual cost of 30 million US dollars. Even if one stops pollution, these costs would be incurred each year for the next 200 years or more, the time scale over which phosphates from the saturated overlying soils would continue to leach into the ground waters. Costs for sanitizing the soil of phosphate contamination to a depth of 5 meters vary between about 50

**Table 1.** Average additional costs per m<sup>3</sup> water of various treatments for purifying drinking water from chemicals.

Chemical	Treatment	Cost in Cents <sup>a</sup>
Simple chlorinated organic compounds	Air stripping	1-1.5
	Ozone	8-12
	Peroxide	2-12
Other organic compounds	Charcoal filter	10-12
Phosphate	Charcoal filter	2-12
Nitrate	Charcoal filter	25-50
Heavy metals	Charcoal filter	20-25

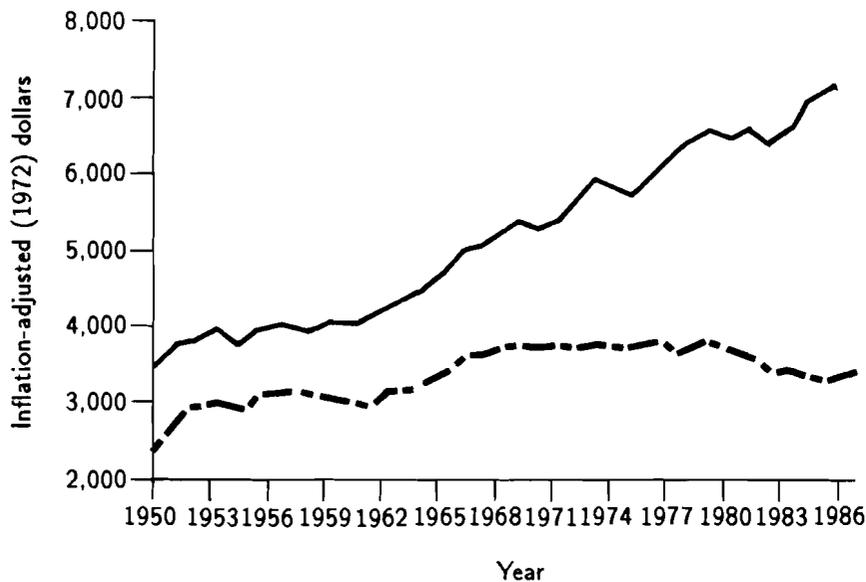
<sup>a</sup>Assumes 1 Dutch guilder = 50 US cents.

million and one-half billion US dollars, depending on the treatment process (extraction, incineration or microbial degradation).

Recently, Daly and Cobb (1989) have calculated the gross national product (GNP) of the United States for the period 1950-1986, adjusted for a variety of pollution factors. As shown in *Figure 1*, the "adjusted" GNP per capita exhibits hardly any growth during this period. It is estimated to be \$3300 (in 1972 dollars), rather than the value of \$7200, determined by classical economic calculations.

As noted by Norgaard (1990), "all decisions over time have been treated by economists as investment sources, as if all resources were always this generation's resources." Within this context, it has been implicitly assumed that soils and sediments could for eternity serve as free receptacles for storing or eliminating pollutants. Since subsequent effects may be large in scale, costly, and in some cases irreversible, main stream economic planning should take into account the potential impacts of chemical time bombs. As part of such an accounting, monitoring systems should be developed for early warning and prediction of chemical time bombs. Without such long term planning it may be increasingly difficult to ensure ecological and economic sustainability.

Before such planning can be undertaken, it will be necessary to develop the theoretical foundations for studying chemical time bombs. This paper is a first attempt at delineating the mechanisms, processes, and conditions evoking chemical time bombs.



**Figure 1.** Trend in per capita GNP in the USA determined by classical economic indicators (solid line), and adjusted for the costs of environmental damage (dashed line). (Source: Daly and Cobb, 1989.)

### 3. Definition and Demarcation of the Chemical Time Bomb Concept

#### 3.1 Definition

*A chemical time bomb (CTB) is a concept that refers to a chain of events resulting in the delayed and sudden occurrence of harmful effects due to the mobilization of chemicals stored in soils and sediments in response to slow alterations of the environment.*

This concept applies to a set of environmental problems having certain characteristics in common. Firstly, CTBs refer to environmental problems for which the release or activation of chemicals leads to effects considered harmful. Usually, the ecosystem has a capacity to buffer against adverse effects of perturbations, such as chemical pollution. Such buffering mechanisms may be, for example, the immobilization (retention) of pollutants, or a limitation of their bioavailability. Only when the buffering capacity of an ecosystem is too small to retain or otherwise counteract inputs of chemical

pollution will harmful effects become manifested, and will the ecosystem be rendered vulnerable to adverse effects of pollution.

Another characteristic of the CTB concept is that in contrast to conventional types of pollution, systems in which CTBs are active exhibit a time delay between chemical accumulation and adverse effects due to this accumulation. Hence, harmful effects from the pollutants may not be apparent and their eventual appearance may be quite unexpected.

A third characteristic of CTBs is that the adverse effects manifest themselves suddenly – on a time scale that is short relative to the time between initial accumulation and manifestation of the effect. Such behavior may be ascribed to mechanisms occurring on two time scales, one in which slow alterations gradually predispose the system to adverse effects (the “fuse” of the time bomb), and a second mechanism acting on a rapid time scale in which the effect is manifested (the “explosion”).

A final characteristic, in fact a corollary of the third, is that the effects of CTBs are discontinuous and non-linear. Due to a chain of events whose interrelations may not be obvious, the vulnerability of the system is gradually increased. Once the vulnerability has passed a certain threshold, the system starts to behave differently from before. Whereas previously it served as a sink for the chemical, it suddenly loses this function and serves to mobilize or reactivate the chemical, leading to environmentally hazardous situations. Sometimes such events may be caused by an unlikely coincidence of normally non-interfering events.

Essential to such discontinuous and sudden behavior are changes in certain environmental conditions, for which the chemical’s behavior with respect to mobility or biotic activity is critically dependent. Thus, environmental “surprises” caused by CTB-phenomena will occur when changes in known critical conditions are unnoticed, or when the relationships governing non-linear interactions between chemical activity and the changing conditions has not been scientifically established.

This background provides some clues as to where to look for CTBs. One precondition is the accumulation/immobilization of the CTB. For man-made pollutants it may be possible to identify “hot spots” from information on the geographical pattern of deposition of chemical inputs. However, CTBs may include naturally occurring chemicals that are inherent to the system, for example aluminum (Al) in the acid rain context described below. In such cases, “hot spots” may be more difficult to locate.

A second clue may be provided by seeking to determine the potential range of environmental conditions upon which suppression of mobility/biological activity depends, and the means by which the range of these conditions could change in the future, thus prompting non-linear and sudden changes in mobility and bioavailability. Such behavior depends upon two time scales. One is slow, corresponding to the time over which the system retains the capacity to buffer against chemical inputs. During this time the buffering capacity is slowly depleting. The fast time scale corresponds to the nonlinear response of the chemical sink, during which chemicals are mobilized due to a saturation of the buffering capacity. When attempting to anticipate nonlinear chemical behavior as characterized by CTBs, it may be useful to consider depleting capacities, chemical reactions (with often exponential relationships between concentrations of different dissolved compounds), amplifiers (bioaccumulation through food chains, for example) or erratic fluctuations in physical factors (drought, floods, earthquakes). Systemic CTB-problems may occur over broad geographical areas when large scale changes occur. For instance, the climatic changes anticipated by many climatologists may bring about changes in factors, hitherto considered to be constant, that are critical elements in the retention of chemicals in soils and sediments.

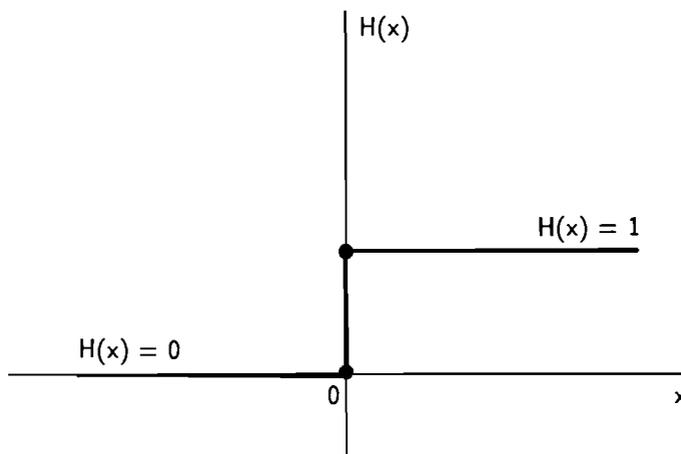
### 3.2 Mathematical formulation

Inherent in the CTB concept is the notion that environmental effects in soil or sediment systems depend in a nonlinear way on stress factors. In the simplest case, as shown in *Figure 2*, the effect is an “all-or-nothing” one, in which case it can be expressed mathematically as a “Heaviside” step function of the form:

$$C = H(Y - 1/V)$$

where  $C$  is the *effect* (e.g., release of aluminum into the soil solution);  $Y$  is a function of *stress* factors  $S_i$ ,  $i=1, \dots, n$  (e.g., the addition of acidic inputs to the soil);  $V$  is the *vulnerability* of the system, depending on the system properties  $X_j$ ,  $j=1, \dots, m$  (e.g., the soil’s buffering capacity which may decrease as acidic inputs increase).

Thus a time bomb effect may result from a continuous increase in external stresses, in a continuous increase in the system’s vulnerability, or both.



**Figure 2.** Schematic of the “Heaviside Function”  $H(x)$ . It is characterized by the following conditions:  $H(x) = 0$  when  $x < 0$ ;  $H(x) = 1$  when  $x \geq 0$ . In the case described here,  $x = Y - 1/V$ . Hence,  $H(x) = 0$  when  $1/V > Y$ ;  $H(x) = 1$  when  $Y \geq 1/V$ .

The system properties determining vulnerability may be the same as the stress factors, as in the case by which acidic inputs decrease the soil’s buffering capacity, but vulnerability is not necessarily coupled to a given stress factor. For example, a system’s vulnerability to leaching of toxic heavy metals depends on the magnitude and duration of the inputs of heavy metals to the soil (stress factor) and the soil’s capacity to bind the metals (a system property determining vulnerability). The binding capacity depends on several factors, one of the most important of which is the organic content of the soil. This content can change over time (e.g., due to climatic change or intensive agricultural practices) independent of whether heavy metal inputs occur or not.

If we have a large number of systems, we may consider  $V$  and  $Y$  to be random variables; i.e., variables which assume different values at random for the various soil sites. A probability  $\Pr[Y \geq 1/V]$  may be defined as the risk that a harmful environmental effect may occur at a given site. The spatial coverage of this probability may be determined to obtain risk maps.

## 4. Examples

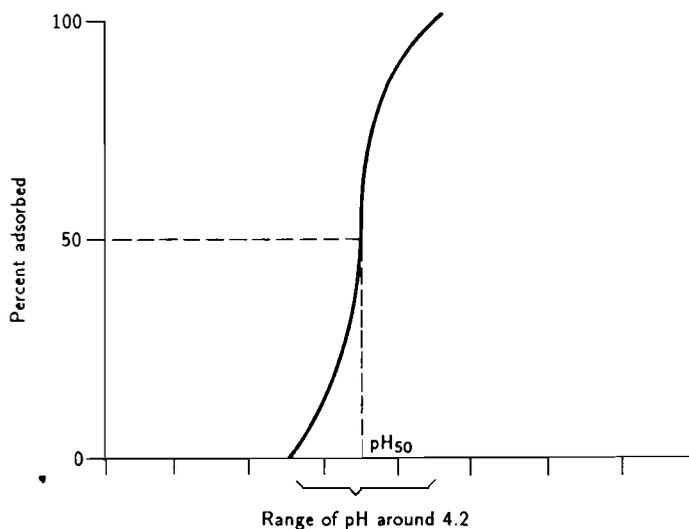
### 4.1 Acidification and leaching of aluminum

In order to better illustrate what is meant by chemical time bombs according to the definition provided above, let us consider the example of aluminum ( $\text{Al}^{+3}$ ) and the vulnerability of soils to its mobilization. This example contains all the elements described in the definition. A chain of events, at first glance unrelated, causes the sudden mobilization of aluminum from soils due to slow alterations in the capacity of soils to buffer acidification. The chain of events may be described as follows:

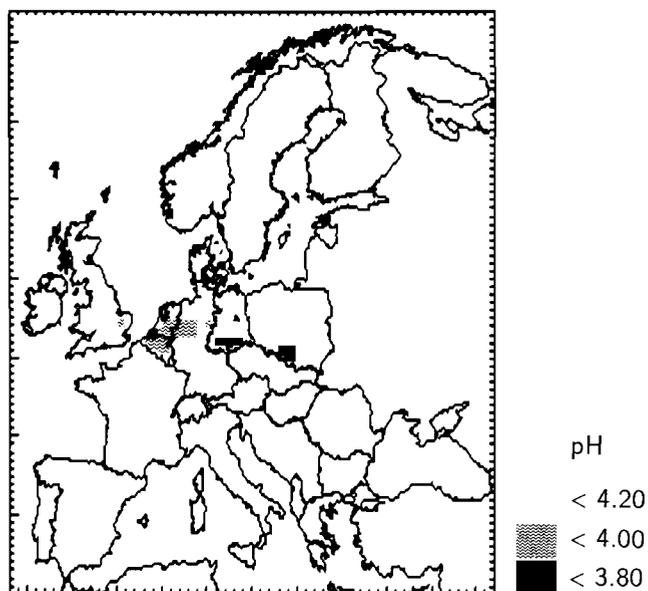
- (a) Aluminum present as a natural component of soils is immobile at soil pHs greater than around 4.2. As the pH shifts into the range  $<4.2$ , mobilization is greatly enhanced (see *Figure 3*).
- (b) Acid deposition begins to acidify the forest soils containing the Al. For some time, the pH is unaffected by the acid inputs because the soil contains a store of "base cations" that buffers against acidic inputs.
- (c) After the buffering capacity of the soil is depleted, the soil pH drops rapidly.
- (d) Around the threshold value of 4.2, the soil begins to leach Al.
- (e) Adverse effects in the ecosystem (e.g., damage to trees, fish mortalities) begin to be manifested.

It should be noted that soils replenish their buffering capacities through the weathering of rocks containing base ions that can neutralize acidity. However, in areas receiving high inputs of acid deposition, the natural rates of replenishment are usually not able to keep pace with the rate of acidification.

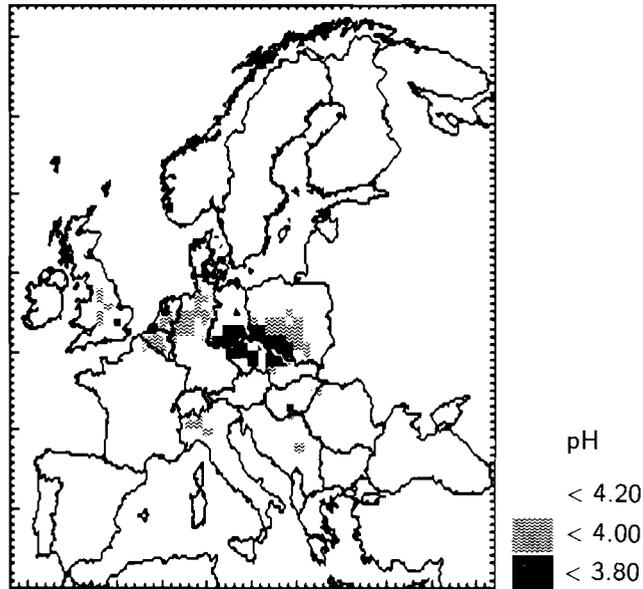
*Figure 4* shows the state of acidification of European forest soils in 1980. It can be seen that the pH was 4.2 or lower in some regions of Central Europe, particularly at the borders of Poland, Czechoslovakia, and East Germany. Leaching of Al has been noted as a possible cause of forest dieback in Central Europe in the early 1980s (Ulrich and Pankrath, 1983; Hauhs and Wright, 1986; Mathy, 1988; Schulze, 1989). It is important to note that the soils in these regions have been receiving acidic inputs since the dawning of the Industrial Revolution 200 years ago. It has taken two centuries to acidify these soils, which initially were highly resistant to acidification. Now that this valuable property of buffering against acidification has been depleted, the soils in the region are much more vulnerable to further acidification.



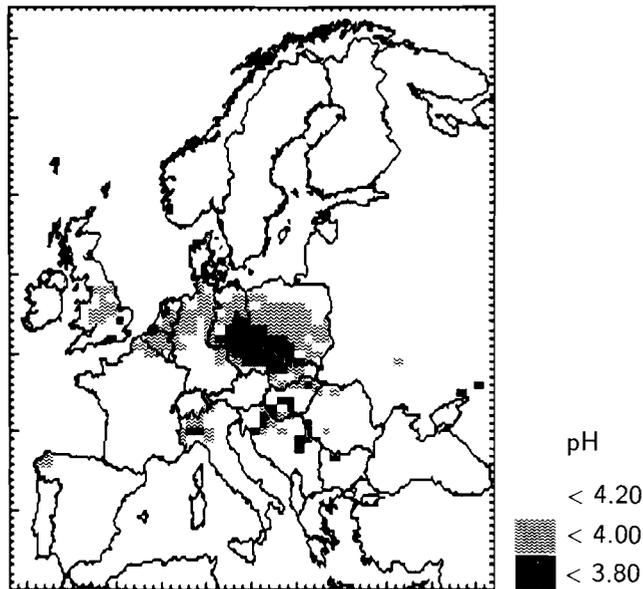
**Figure 3.** Relation between adsorption of aluminum in soils and pH.  $\text{pH}_{50}$  is defined as the pH at which 50% of the aluminum is adsorbed and 50% is mobilized. The rate of pH change is dependent on soil type.



**Figure 4.** State of soil acidification in the forest soils of Europe, 1980. (Source: Alcamo *et al.*, 1990.)



**Figure 5.** State of soil acidification in the forest soils of Europe, 2000.  
(Source: Alcamo *et al.*, 1990.)



**Figure 6.** State of soil acidification in the forest soils of Europe, 2040.  
(Source: Alcamo *et al.*, 1990.)

Moreover, once these soils have lost their buffering capacities, it will take many decades, perhaps several centuries for natural replenishment to occur. *Figures 5 and 6* illustrate how forest soil acidification could spread in the future, even in the case when current plans for reducing acidification are employed.

As soil acidification spreads, so will the region over which aluminum will be leached. Thus, leaching of aluminum is a delayed response to acidification of the soils in which the aluminum had been safely immobilized. The time scale of the delay depends on two factors. One is the intensity of the acidic inputs, and the second is the initial buffering capacity of the soils. Soils with low initial buffering capacities and receiving high acidic inputs will be the first to acidify and leach Al. Soils with high initial buffering capacities and receiving low acidic inputs will be the last soils to acidify.

Historically, the Scandinavian soils were the first to acidify in Europe, effects such as fish depletions having been observed in the early part of this century. The soils of Central Europe have received higher acidic inputs for a longer time period, but their soils have begun to acidify about five decades after the soils of Scandinavia. This difference in response is due to the much larger initial buffering capacities of the soils of Central Europe. After acidification had appeared in Scandinavia, the eventual acidification of Central European soils would have been foreseeable had more environmental awareness existed 50 years ago. Were that the case, prudent policies for protecting the soils of Central Europe might have been enacted much earlier. Now it is inevitable that, despite plans for reducing acidic inputs to the soil, much of Central Europe will be acidified, with subsequent leaching of Al. (For a more complete discussion, see Stigliani and Shaw, 1990.)

## 4.2 Microbial induced CTBs

Soil chemistry is to a large extent determined by microbial populations that propagate a vast array of biochemical reactions in the life-sustaining processes of respiration and metabolism. These reactions exert a great influence on the soil's capacity to immobilize toxic chemicals. On the other hand, chemical pollutants in the soil affect the quality of the microbes present. Thus, there are complex interactions and feedbacks between pollutants and microbes, some of which have a direct bearing on CTB phenomena.

Gradual and diffuse pollution of soils causes a shift within the microbial community. In general fungi are more resistant to heavy metals than are actinomycetes, the latter are more resistant than are Gram negative bacteria,

and Gram negative bacteria are more resistant than Gram positives as first noted by Doelman (1985). Hence, the ratio eukaryotes/prokaryotes increases in soils stressed by heavy metal pollution. This shift will in turn cause a change in the potential of the soils to degrade harmful chemicals to harmless inorganic end products (mineralization potential).

Another shift within the bacterial community is an increase in the ratio of strains relatively resistant to heavy metals to strains sensitive to them (Duxbury and Bicknell, 1983; Doelman and Haanstra, 1979). Resistance has been defined as growth in the presence of high concentrations of a heavy metal (e.g., 10 mg Hg/kg in the growth medium). Sensitivity has been defined as death in the presence of low concentrations of heavy metals (e.g., 0.1 mg Hg/kg in the growth medium).

The sensitive bacteria have a greater ability to grow on aromatic compounds than do the resistant ones (Reber, personal communication, 1990; van Til, 1988). Hence, the alteration of the environment favors the predominance of a heavy-metal-resistant microbial community with subsequent loss of the ability of soil micro-organisms to degrade certain persistent organic compounds. When this chain of events is followed by pollution of the ecosystem by chemicals such as polycyclic aromatic hydrocarbons or chlorinated organic compounds (e.g., anthracene, PCBs and dibenzofurans), their persistence will increase significantly relative to what would be anticipated in a system not contaminated by heavy metals. Subsequently, the concentrations of these toxic chemicals and their bioaccumulation in the food chain could be greatly enhanced.

Not only heavy metals, but also the presence of other organic chemicals can unexpectedly inhibit bacterial degradation of certain pesticides. For example, dichloropropene-dichloropropane (DD) has been used for many years as a nematicide against *Heterodera rostochiensis*. One of the perceived advantages of DD was its apparent rapid degradation in the environment. However, now it has been discovered that the simultaneous use of other pesticides can inhibit DD degradation (van Fassen, 1985). Because of its long life time in the environment, it has contaminated ground waters and drinking water supplies in the Netherlands. Currently in Drente Province, about 30,000 ha are contaminated with DD. It has been estimated that the ground waters which provide drinking water in this region have to be treated (by air-stripping) until the year 2050. For better or worse this may convert a drinking-water problem to an air-pollution problem.

Mercury pollution of Minamata Bay in Japan first aroused consciousness about the "Minamata disease". Due to the unforeseen capability of bacteria

to convert Hg to highly toxic methyl mercury, a chain of events emerged triggering the chemical time bomb. While the production of methyl mercury by bacteria and its release to the aquatic environment is a defence mechanism protecting the microbes from mercury poisoning, methyl mercury is at least 100 times as toxic to fish as is metallic Hg. Moreover, fish was a major part of the diet of Japanese villagers living in the vicinity of the Bay, and many became seriously ill before the cause of the disease could be discerned. Within the chain of events, bacterial methylation caused the mobilization of the mercury stored in sediments of the Bay and turned a "normal" pollution episode to a catastrophic chemical time bomb.

The same chemical time bomb phenomenon is occurring now in the gold mining area of the Amazon Basin in Brazil. Mercury is used for concentrating the fine gold particles through amalgamation. The gold is separated from the amalgam by application of heat to drive off the mercury which is volatilized to the atmosphere. Mercury, through atmospheric transport and deposition, is contaminating a vast area of the Amazon River (Malm *et al.*, 1990). Currently about 200 tons of mercury per year is being deposited. All of the conditions for a new "Minamata" exist, but on a much grander scale. The process may proceed as follows:

- (1) Concentration of mercury from the basin to the river by runoff or flooding;
- (2) Sedimentation of the mercury;
- (3) Production of methyl mercury by bacterial activity in anaerobic sediments;
- (4) Biomagnification in fish; and, finally
- (5) Human consumption of fish.

The problem may not only be specific to mercury alone, since it can be argued that arsenic (As) and antimony (Sn) are also subject to methylation by microorganisms under specific physico/chemical conditions (Summers and Silver, 1978).

In principle, microbial transformation of heavy-metal salts, induced by a change of environmental conditions such as redox potential, may cause chemical time bombs. One example is the dumping of dredged anaerobic harbor sludge containing heavy metal sulfides (very low solubility) at land fill sites. In this occurrence, the sludge environment, now exposed to the atmosphere, switches from anaerobic to aerobic conditions. *Thiobacilli*, which are usually present and active in the presence of oxygen, oxidize the insoluble metal sulfides to more soluble metal sulfates (Silver and Torma, 1974). The

metals are then more prone to mobilization and leaching from the dump to soils, ground and surface waters. Problems associated with the land-filling of harbor sludge have occurred in Rotterdam, the Netherlands, and at various harbors on the Mississippi River.

### 4.3 Biological time bombs

Time bombs, although inherently chemical in nature, can also be manifested in biological systems in which sudden and surprising changes may occur under certain conditions. An example of a "biological" time bomb is the sudden, broad-scale die-off of rye grass (*Lolium perenne*) on the English coast after a severe winter. The population of grasses over the years had gradually shifted to a more acid-tolerant population due to pollution by high levels of acid deposition. These more acid-tolerant grasses however, were not as resistant to cold weather as the population that had preceded them (Davidson and Bailey, 1982). This inherent vulnerability, while not apparent during mild winters, led to their unexpected extinction, as a result of a period of extremely cold weather.

Another example is the toxification of predators in areas highly contaminated by heavy metals. Bengtsson and Rundgren (1984) reported that the soil fauna in areas around metal smelters are generally resistant to heavy metals. The isopod *Oniscus asellus* protects itself by accumulating heavy metals in its hepatopancreas (Coughrey *et al.*, 1977). Predators feeding on this isopod may ingest concentrated levels of heavy metals and die. This sudden occurrence is again initiated by an unanticipated chain of events beginning with alterations in the soil fauna community as a response to chemical pollution.

## 5. Prediction of Future Chemical Time Bombs

We have discussed how chemical and biological time bombs are triggered by a chain of events that is often difficult to anticipate. In this section we address the question of how to predict time bombs. There may not be a unique methodology for doing so since inherent in the problem is the daunting task of "predicting the unpredictable." Nevertheless, some useful approaches to developing anticipatory strategies that foresee time bombs before they explode are formulated in this section.

## 5.1 Lessons from the most vulnerable areas

In designing a program that will provide early warning of sudden ecological changes, one logical place to start looking for such changes is in the most vulnerable areas. As we have seen, two factors determine vulnerability: 1) the level of inputs of polluting chemicals; and 2) the size of the reservoir accumulating them.

The history of the acidification of European soils and waters demonstrates both the potential utility of this approach, and the lost opportunity in foreseeing the spread of acid deposition from initially a very small region in southern Scandinavia to most of the central part of Europe. One lesson to be learned from this experience is that, as a general principle, we should pay closer attention to what appear to be local-scale environmental effects, but which may in fact be harbingers of future problems on a grander scale. If these events are good natural experiments or test cases for what is to come, then perhaps we should find out why the effects appeared at the particular location, and try to discern whether the episode is indeed only of local significance, or whether the same event could happen elsewhere under changing conditions.

## 5.2 The “bottom up” approach

Processes for immobilizing and storing toxic chemicals (or alternatively, for remobilizing and releasing them) are related to key properties of soils and sediments, many of which are well known through numerous scientific investigations. Moreover, the environmental conditions that govern these processes have also been investigated. What is less well known are how the processes and key properties may change over a time scale of decades to centuries in ways that affect the mobility of the stored toxic materials. Changes may occur either because the capacity for storage of toxic materials in the soils and sediments becomes saturated, or because changes in environmental conditions cause the capacity to shrink or expand (rendering the release of stored chemicals more or less likely, respectively).

The “bottom-up” approach for identifying chemical time bombs uses what we know about processes and environmental conditions and then works backward to predict or anticipate potential time bombs. The method consists of four basic steps:

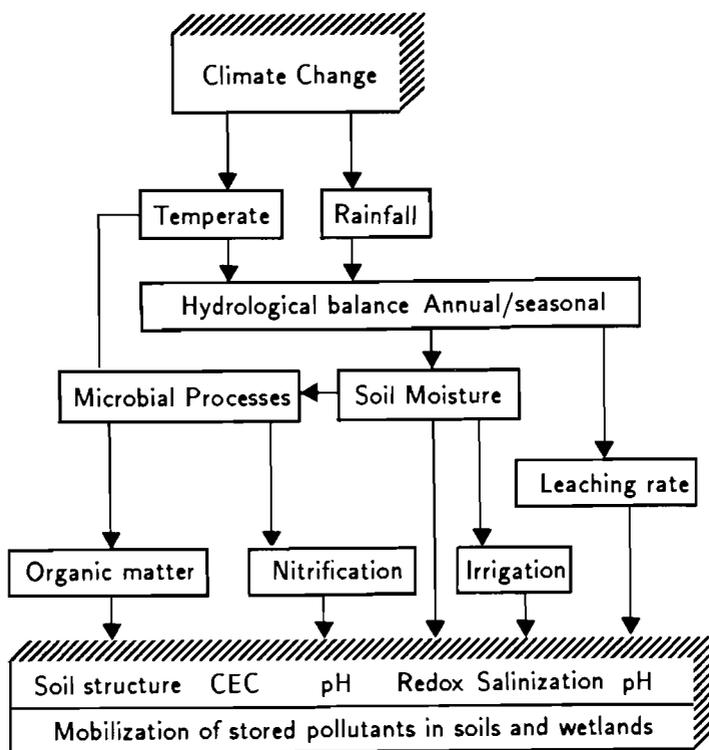
- (1) Identification of the key factors influencing the mobility of a particular class of chemicals, and how these factors are linked to soil and sediment properties;
- (2) Determination of the environmental conditions and their relevant ranges that cause the soils or sediments to possess the given properties;
- (3) Construction of scenarios by which the environmental conditions could change; and
- (4) Assessing the effect of changing environmental conditions on storage capacities.

In parallel to this analysis, a map identifying “hot spots” (regions of high inputs of toxic materials) should be prepared. Areas susceptible to chemical time bombs might be those in which the hot spots overlap with large changes in soil properties caused by changing environmental conditions.

By way of example, we discuss here the potential for mobilization of heavy metals during an era of strong climatic change. The capacity of soils and sediments to adsorb and immobilize heavy metals is strongly influenced by certain prevailing properties. The most important of these are pH, redox potential, salinity, and organic matter contents, the latter of which directly affects the cation exchange capacity (CEC) and soil structure. The linkages between these properties and climatic change are shown in *Figure 7*.

Two of the linkages, between organic matter and soil structure and CEC and between soil moisture and redox potential and salinization, are of particular importance. (For a more detailed discussion of *Figure 7* see Stigliani and Salomons, 1991.) Following the arrows on the left side of the figure, it is shown that soil temperature and moisture affect the kinetics of microbial processes, and that these processes determine the content of organic carbon in soils. The effect of increasing soil temperature is to increase microbial decomposition, with a subsequent decrease in the soil’s organic content. In contrast, increasing soil moisture has the effect of increasing the organic matter content (and vice versa).

Changes in organic matter content of soils will affect the mobility of heavy metals in two ways. Firstly, decreases in organic matter will cause increases in the erosion of soils. Since pollutants tend to accumulate in the upper part of the soils, this will cause an increase in flux of metals from soils to the aquatic environment. Extreme climatic events, which could be more frequent in the future (Dickinson, 1986), could cause an even more increased rate of erosion. Secondly, the CEC is directly proportional to organic matter



**Figure 7.** The linkages between the mobility of heavy metals stored in soils and wetlands and climatic change. (Source: Stigliani and Salomons, 1991.)

content. A decrease in organic matter content leading to a decrease in the CEC will result in a decreased capacity of the soil for adsorbing heavy metals.

*Figure 7* also shows that soil moisture directly affects the redox potential. Wet and waterlogged soils rich in organic matter, as are found in extensive peat regions and wetlands, typically have low levels of dissolved oxygen and thus low redox levels. Dry soils, particularly if they are porous and well aerated, tend to have higher redox potentials. Thus, a drying out of wetland areas could cause extensive changes in redox potential. Such changes could affect the mobility of heavy metals that were stored in wetland areas as insoluble sulfides. Under dry conditions these metals may be mobilized as soluble sulfates.

Soil moisture is indirectly linked to salinization. If soils dry out in summer in agricultural regions, farmers may resort to increased reliance on

irrigation to maintain crop productivity. In extensive regions of Europe, particularly in parts of Hungary, the USSR, Bulgaria, Romania, the Iberian peninsula, and coastal areas of the western Mediterranean region, the ground waters are highly saline. If the rate of evapotranspiration is greater than the rate of precipitation, soils irrigated with these waters will become increasingly saline. Soils experiencing increased salinity will have a decreased capacity to store heavy metals.

From these observations, it is apparent that the capacities of European soils for storing heavy metals could be significantly reduced, under warmer, dryer conditions. Several climatic models (Goddard Institute for Space Studies, British Meteorological Office) and soil moisture models (Manabe and Wetherald, 1987) predict such changes from the Greenhouse Effect. The most vulnerable areas are those with simultaneously high accumulated chemical loads and high storage capacities (in which the total and rate of loading of chemical inputs does not exceed the assimilative and storage capacity of the system under current environmental conditions). Their vulnerability is due to the potential for the capacities to be drastically reduced in the future owing to climatic change. Such areas would include soils with high organic content, for example the chernozem and chestnut soils characteristic of the Ukraine, wetland areas of northern Europe, and areas with salty ground waters such as those previously indicated. Also, coastal areas prone to sea level rise and salt water intrusion to ground waters should be considered.

### **5.3 Listing of system parameters**

By definition, a chemical time bomb occurs rapidly without an overt warning. How then is it possible to predict the occurrence of such an event? Advantage must be taken of the fact that the changes in the system that render it increasingly susceptible to CBTs are not instantaneous. Rather, they generally occur on a time scale that is slow relative to the actual manifestation of the effect. Therefore, a key to the identification of future time bombs might be a systematic analysis of how long term changes in soils and sediments occurring simultaneously with accumulations of chemical pollutants predispose ecosystems to CTBs. Given below are lists of categories and parameters that might serve as a rough and preliminary guide to such an analysis.

The CTB syndrome consists of two components: the "explosion" and the "trigger," the latter being displaced in time from the former. Important aspects of the first component (the explosion) are:

- (1) Type of chemical;
- (2) Loading and unloading mechanisms and processes;
- (3) Retention mechanism and characteristics;
- (4) System properties (state variables) affecting retention;
- (5) Release processes and pathways; and
- (6) Targets and effects of release.

Chemical releases are triggered by environmental changes causing transgressions of vulnerability thresholds. Such events lead to irreversible changes in retention parameters, and thus to discontinuous changes in the rates of release. Important points to consider are:

- (1) Environmental conditions having a dominant effect on system properties (temperature, water regime, etc.);
- (2) Processes affecting these environmental conditions (e.g., changes in patterns of atmospheric deposition);
- (3) Feedback mechanisms, such as effects of systemic changes on environmental conditions (e.g., changes in soil surface properties such as albedo).

The following is a description of key words (without being complete) associated with these components.

- (a) *Chemicals*: Persistence, metabolism, reaction products, toxicity, quantity in system in relation to potential hazard when released.
- (b) *Loading*: Pathways, mechanisms, carriers (atmospheric deposition, fertilization, pest control, waste disposal, capillary rise, infiltration, flooding, sedimentation, erosion, leaching, transformation, phase transition).
- (c) *Retention*: Compartment of the biosphere (solid, liquid, gaseous or biota phase, interfaces); binding mechanism (physical occlusion or barriers, adsorption, ion exchange, surface complexation, precipitation, coprecipitation, solid solution, incorporation into organic matter); effects on system properties (soil structure, hydraulic conductivity, nutrient availability etc.).
- (d) *System properties*: Variables directly related to retention characteristics and storage capacity (i.e., extensive properties), including CEC, organic matter composition and content; indirectly-related variables (governing intensive properties) such as pH, redox potential, T, water content; amplifier mechanisms (high sensitivity of storage capacity and binding strength on changing system parameters, feedback mechanisms).
- (e) *Release*: Overloading of storage or buffering capacities, transgression of buffering rates (assimilation capacity), decrease in binding strength

(change of retention characteristics), diminishing storage compartment (e.g., degradation of organic matter, dissolution of clays), reduction of unloading processes (such as microbial detoxification or dilution).

- (f) *Targets and effects*: Targets including human health, biota, gene pools, fertility, soil functions, competitive status; pathways, i.e., exposure (air, food, water, soil), uptake, partitioning, accumulation and dilution, excretion; effects, i.e., dose-response, residence time, threshold levels.
- (g) *Dominating environmental factors (conditions)*: Fluxes of energy and matter: radiation, heat, precipitation, deposition, infiltration, surface runoff, deep seepage, ground water rise, deflation, sedimentation, erosion, application of chemicals, irrigation, drainage; state variables including chemical composition, humidity, temperature, water potential, aerosol content of air, vegetation cover, ground water table, frequency and amplitude of variations of state variables; conditions such as geological status, topography, surface water, type of land use.
- (h) *Environmental changes*: Mean and fluctuations of temperature, humidity, atmospheric circulation, radiation, aerosol content and chemical composition of atmosphere, chemical composition and sediment load of surface water, chemical composition of groundwater, vegetation cover, microbial populations, gene pools of biota, type, amount and frequency distribution of precipitation, composition of aerosols and sediment load of surface waters.
- (i) *Feedback effects*: Environmental energy balances (partitioning energy fluxes between compartments), distribution of moisture (evapotranspiration, surface runoff, infiltration deep seepage), gas exchange between environmental compartments (e.g., nitrogen cycle), particle suspension in air and water (e.g., due to changes in erosion potential), volatilization of organic compounds (enhancing e.g., Greenhouse Effect), change in biota.

Chemical time bomb candidates are compounds which are persistent, toxic, and available in the environment in sufficiently high concentrations. A chemical that is not a time bomb *per se* may become one if it is metabolized into a toxic product under certain conditions and released. An example is the methylation of heavy metals such as mercury under anaerobic conditions, or the oxidation of metal sulfides under aerobic conditions.

Chemical time bombs may not necessarily originate from a human source. They may also derive from natural chemicals already present in the soil or sediment. They can become time bombs if they are mobilized as the result of

slow, continuous accumulations of another chemical load leading to sudden changes in soil conditions. A classical example is the mobilization of free aluminum ions due to a pH drop caused by soil acidification.

Another possible way to convert natural or man-made chemicals in the soil into time bombs is to interrupt and block degradation processes (as noted earlier in the example of the chemical DD). This effect can be the result of a collapse in critical microbial populations or a change to another substrate less conducive to degradation. The vulnerability of soils and sediments against such events might increase with a continuous “genetic erosion,” i.e., a decrease in genetic diversity and the flexibility of a population to adapt to environmental stress situations.

As is the case with all categories of environmental pollution, effects are only perceived as problems with respect to targets deemed worthy of protection. While effects on microbial activities in soils and sediments may not be a time bomb with respect to human health directly, they are certainly so with respect to microbial flora and fauna. Moreover, such effects may trigger other time bombs by a chain of unanticipated reactions resulting in effects that can directly affect human health.

## 6. Conclusions

- (1) Definition: A chemical time bomb (CTB) is a concept that refers to a chain of events resulting in the delayed and sudden occurrence of harmful effects due to the mobilization of chemicals stored in soils and sediments in response to slow alterations of the environment.
- (2) There is a strong likelihood that the behavior of contaminants under certain conditions is in accordance with the definition given for CTBs.
- (3) The concept implies that there exists a legacy of accumulated chemical pollutants in the environment stored in so-called “sinks” that can be mobilized in the future. Because the chain of events leading to mobilization may be indirect and not obvious, CTBs may not be anticipated.
- (4) The CTB concept implies the inherent variability in time of soil and sediment properties regulating retention and mobilization of chemical pollutants. Therefore, future standards/guidelines should as far as possible take this variability into account. Assessments calculating the risk of CTBs can be determined from estimation of changing vulnerability over time.

- (5) The basic tools for modeling the transport of pollutants in the environment are already available. Often, however, the models run on the assumption that environmental conditions (e.g., temperature, water availability, soil properties) will not change in the future. The further steps required for studying CTBs are developing scenarios for changing environmental conditions and incorporating these changing variables in the model calculations.

## References

- Alcamo, J., Shaw, R., and Hordijk, L. (eds.), 1990, *The RAINS Model of Acidification: Science and Strategies in Europe*, Kluwer, Dordrecht, The Netherlands.
- Bengtsson, G. and Rundgren, S., 1984, Groundliving invertebrates in metal polluted forest soils, *Ambio* 13:29-33.
- Brooks, H., 1986, The typologies of surprises in technology, institutions, and development, Chapter 11, pp. 325-348, in W.C. Clark and R.E. Munn (eds.), *Sustainable Development of the Biosphere*, Cambridge University Press, Cambridge, UK.
- Coughrey, P.J., Martin, M.H., and Young, E.W., 1977, The wood louse, *Uniscus acellus*, as a monitor of environmental cadmium levels, *Chemosphere* 12:827-832.
- Daly, H. and Cobb, J., 1989, *For the Common Good*, Beacon Press, Boston, MA, USA.
- Davidson, A.W. and Bailey, I.F., 1982, SO<sub>2</sub> pollution reduces the freezing of rye grass, *Nature* 297:400.
- Dickinson, R.E., 1986, Impact of human activities on climate - a framework, Chapter 9, pp. 252-289, in W.C. Clark and R.E. Munn (eds.), *Sustainable Development of the Biosphere*, Cambridge University Press, Cambridge, UK.
- Doelman, P., 1985, Resistance to heavy metals, in A. Kjuller (ed.), *Microbial Communities in Soil*, Elsevier, Amsterdam, The Netherlands.
- Doelman, P. and Haanstra, L., 1979, Effects of lead on the soil bacterial microflora, *Soil Biology and Biochemistry* 11:487-491.
- Duxbury, T. and Bicknell, B., 1983, Metal tolerant bacterial populations from natural and metal-polluted soils, *Soil Biology and Biochemistry* 15:243-250.
- Hauhs, M. and Wright, R.F., 1986, Regional pattern of acid deposition and forest decline along a cross section through Europe, *Water, Air, and Soil Pollution* 31:463-474.
- Malm, O., Pfeifer, W.C., Souza, C.M.M., and Reuther, R., 1990, Mercury pollution due to gold mining in the Madeira River Basin, Brazil, *Ambio* 19:11-15.
- Manabe, S. and Wetherald, R.T., 1987, Large-scale changes of soil wetness induced by an increase in atmospheric carbon dioxide, *Journal of the Atmospheric Sciences* 44:1211-1235.

- Mathy, P. (ed.), 1988, *Air Pollution and Ecosystems*, Reidel, Dordrecht, The Netherlands.
- Norgaard, R., 1990, Multidisciplinary look at a finite world, *Science* **249**:18-19. (Quote from report on first meeting of the International Society for Ecological Economics, May 1990, Washington, DC, USA.)
- Schulze, E.-D., 1989, Air pollution and forest decline in a spruce (*Picea abies*) forest, *Science* **244**:776-783.
- Silver, M. and Torma, A.E., 1974, Oxidation of metal sulfides by *Thiobacillus ferro-oxidans* grown on different substrates, *Canadian Journal of Microbiology* **20**:141-147.
- Stigliani, W.M., 1988, Changes in valued "capacities" of soils and sediments as indicators of nonlinear and time-delayed environmental effects, *Environmental Monitoring and Assessment* **10**:245-307.
- Stigliani, W.M. and Shaw, R., 1990, Energy use and acid deposition: The view from Europe, *Annual Review of Energy* **15**:201-216.
- Stigliani, W.M. and Salomons, W., 1991, Understanding "chemical time bombs." Pollution and some not impossible environmental problems caused by climate change, *New Scientist* (submitted for publication).
- Summers, A.O. and Silver, M., 1978, Microbial transformation of metals, *Annual Review of Microbiology* **32**:637-672.
- van Fassen, H.J., 1985, *De invloed van bestrijdingsmiddelen op de afbraak van grondontsmettingsmiddelen*, Rapport Instituut voor Bodemvruchtbaarheid.
- van Til, M., 1988, *De invloed van Zn verontreiniging in de grond op een verschuiving van de microbiële samenstelling; verminderde afbraak van aromaten*, Studenten verslag, Rijksinstituut voor Natuurbeheer.
- Ulrich, B. and Pankrath, J. (eds.), 1983, *Effects of Accumulation of Air Pollutants in Forest Ecosystems*, Reidel, Dordrecht, The Netherlands.