

# ENVIRONMENTAL SOIL SCIENCE

ANTHROPOGENIC CHEMICALS

AND

SOIL QUALITY CRITERIA

PROCEEDINGS OF A JOINT SYMPOSIUM

OF

THE CANADIAN LAND RECLAMATION ASSOCIATION

AND

THE CANADIAN SOCIETY OF SOIL SCIENCE



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# ENVIRONMENTAL SOIL SCIENCE

## ANTHROPOGENIC CHEMICALS AND SOIL QUALITY CRITERIA

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## **PREFACE**

The Environmental Soil Science conference was held August 8-13, 1992 at the University of Alberta, Edmonton, AB. It was sponsored jointly by the Canadian Land Reclamation Association (CLRA) and the Canadian Society of Soil Science (CSSS). The objective of the conference was to share theoretical and applied aspects of soil science. It also served to get participants from the sponsoring groups together to find areas of mutual interest. There were 330 participants from Austria, Bangladesh, Canada, England, France, Germany, India, Japan, New Zealand, Norway, Spain, the Netherlands, and USA.

Abstracts of the oral and poster papers were published in the Canadian Journal of Soil Science (Vol.72, No.3, August 1992. (p.299-353). Volunteer papers covered all aspects of land reclamation, soil science, and public participation in the environmental review process. Seventy six of the 164 volunteer papers were presented as posters.

The invited papers presented in the plenary sessions focused on soil quality and interaction of soils with anthropogenic chemicals, and are published in this proceedings. Publication of the proceedings has taken an unduly long time due to unavoidable circumstances and we apologize for the delay.

Grateful acknowledgement is expressed to our colleagues on the organizing committee (J.A. Robertson, Chair) for their contributions to the success of the conference.

Y.P. Kalra and W.W. Pettapiece, Compilers



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# SOIL : THE ENVIRONMENTAL INTEGRATOR

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## ABSTRACT

Soil is defined in terms of dynamic circulation patterns of water, air and minerals driven by solar energy. The soil is the reactor and exchanger of energy and matter and, as such, is the terrestrial environmental integrator and supporter of life on Earth. The environment as expressed in this context is a permeable membrane which shapes life forms, with an inherent capacity and resilience to function and respond to stimuli. Soil is an open and metastable thermodynamic system. It functions because of an external energy supply. The soil is remarkably resilient but its capacity and resilience are limited. Although soil is important for plant production for agriculture and forestry, its role in Nature is more vital in fundamental earth processes and moderating the effects of human manipulation. The soil is finite, scarce and fragile. Human activity may affect the soils' capability to function as an environmental integrator and moderator, if rates of human interference are greater than the rates that sustain soil processes.

## ACKNOWLEDGEMENTS

I express my gratitude to the students at the University of British Columbia, who make my tenure not a job but a life-style. Their free energy contributes to my pleasant and increasing entropy. To my colleague, Professor Hans Schreier, simply thank you; he knows what I mean. I am indebted to Ms. N.A. Dick, Ms. P. Schreier and Ms. S. Brown for their dedication and support, and for making this manuscript presentable. The efforts of Ms. C. Heaver in preparing the Figures is appreciated.

## 1.1 INTRODUCTION

Earth, fire, water and ether were espoused by early philosophers as the element (substance), component, feature or principle of a thing, a basic part and a constituent of all physical matter. Further, any of these substances were thought of as the natural (physical) environment of living things. If one modernizes the words of the early philosophers, the four elements may be called soil, energy (solar?), water and the atmosphere. It was the belief of the early philosophers that these four substances were the key to the planet Earth and to its unique characteristic as a living entity.

Lucretius (99-55 B.C.) illustrates the prevailing scientific concepts before the beginning of the Christian era in Book V, "On the Nature of Things". He states:

"First of all, since the body of the earth and water and the light breath of air and burning heats, out of which this sum of things is seen to be formed, do all consist of a body that had a birth . . . the world must be reckoned of like a body . . . parts of the world are destroyed and begotten anew . . . there has been a time of beginning and there will be a time of destruction."

Lucretius anticipated our concept of Nature's Laws that were formulated several thousand years later as the Laws of Thermodynamics. He goes on further to speak of soil:

"Part two of the soil is put under water by rains, and rivers graze against and eat into the banks. Again whatever increases something else, in its turn replenished; and since beyond a doubt earth the universal mother is found at the same time to be the general tomb of things, therefore you see she is lessened and increases and grows again."

Sir Francis Bacon (1561-1626), in describing a new methodology in the experimental interpretation of nature (*Novum Organum*), stated:

"Now the empire of man over things depends wholly on the arts and sciences. For we cannot command nature except by obeying her."

Although humans have progressed immeasurably in art and science since these concepts were promulgated, their fundamental truth and simplicity begs one to reflect on their significance. Have the fundamental Laws of Nature changed because humans have devised complex institutions, elaborate language (including mathematics), and a better understanding of Nature? This question cannot be answered unequivocally, precisely or simply. Basic

human behaviour has not altered much through time. Human ingenuity has replaced labor and toil with substitutes ever since the first human discovered fire or used a wooden stick to till the soil. Humans have had, and continue to possess, greater capabilities to destroy and kill than to save and nourish their own kind. Consider for example the expenditures in resources that are allocated to military endeavours because of the perception that our life-styles may be altered or changed and compare this to the amount of financial resources that are utilized for the existence (not change) of Homo sapiens and, in fact, life on Earth. Thus, although the sophistication and magnitude of human behaviour has changed, basic human behaviour has not, just as the fundamental Laws of Nature have remained.

If one reflects on the ancients' perception of earth, fire, water and ether, these four elements have a common feature. They are what economists and legislators term the "commons" (common property or common pool resources). There is little doubt that without the intricate interaction of soil, solar energy, water and air, that life as we know it could exist on Earth. Things that seem plentiful are little appreciated by humans, until one or more facets becomes limiting to the needs, wants and desires of humans, either individually or collectively. Personal health is taken as given, until one becomes ill; personal finances are paramount until bankruptcy; life is of incalculable value until death; and soil, energy, water and air are common goods (priceless and essential) but until their quality or quantity are exhausted, not worthy of concern. All things, the Universe, the Earth, and living entities have a beginning and an end. Laws of Nature and Time govern our environment and thus our very existence. Although heralded authors (Hardin 1968; Leopold 1949) have brought attention to these issues, little change has been implemented by society. We continue to use soil, air and water with little respect for their essentiality.

## 1.2 ENVIRONMENT

There are many usages of the concept of environment. We hear of the physical environment, the cultural environment, the social environment, the biophysical environment, the economic environment, the political environment and even the sociopolitical economic environment. In recent years environment has become an increasingly popular cliché employed by individuals, private groups, public servants, politicians and educators. The



concept has taken on even more interesting interpretations since the publication of the World Commission on Environment and Development report on "Our Common Future" (W.C.E.D. 1987) and with it the popular concept of sustainable development, i.e., "development that meets the needs of the present without compromising the ability of future generations to meet their own needs" (W.C.E.D. 1987:43). Many people have embraced the concept to reinforce their beliefs or actions. It is not uncommon to read such phrases as "sustainable economic development" or "sustainable socio-economic development" and, in an attempt to capture all audiences, "environmentally sustainable socio-economic development". This is but one example of how humans utilize language and pragmatism to justify their own needs and promote their singular beliefs and adherence to neoclassical dogma. It is an attempt to explain human activity as being rational and in concert with one's own view of Nature.

In an attempt to avoid catapulting into the above abyss, I choose a simple definition of environment: the membrane that shapes life into the form in which it exists. The attributes of the membrane are defined in operational terms by which we categorize the continuum of Nature. Central to this definition, is that the focus is on the phenomenon of life, as we know it on Earth. If we accept this simplistic, somewhat vaguely defined, concept of environment, as those intrinsic properties and values that shape the existence of life, it becomes evident that a living thing is affected and responds to its environment. If response and adaptation of the living entity to its environment is too slow, the living thing will perish. This brings into focus the element of time.

While human populations were small, humans could live with their natural (physical) environment and be shaped by this environment. The environment did little to directly alter the living thing and life-forms adapted to the changes in the environment or became extinct. Homo sapiens being largely unspecialized are highly adaptive life-forms to different environments; from forest to grassland to alpine to arctic. Homo sapiens also possess the ability to modify their environment, unlike most other animals, by the use of tools and energy (fire). As human populations grew, became more social in behaviour, and developed their ability to modify their environment for their own needs and desires, they increasingly changed the very environment that had shaped them. The Earth's permeable skin of soil, water and air is the environment of man and all living things. It is this environment

that provides water, oxygen, food and shelter; the necessities of life. Homo Sapiens, however, demand more!

The brain allows the species to gain power, to gather resources from the environment far in excess of those of their biological needs. Early humans extracted from the atmosphere only the oxygen that was required for respiration; today humans extract oxygen not only for life but to support combustion, factories, extraction and processing industries. The resulting production of gases, such as carbon dioxide, appear to be far in excess of those that can be assimilated by the Earth's natural photosynthetic machinery or by the oceans and similar sinks. Technology has shifted the balance between demand and supply, and increasingly is introducing new and foreign things (synthetics) into Nature's system. Take, for example, the application of fertilizer technology to replace or augment the basic nutrients for crops in agriculture or forestry. Inorganic forms of fertilizers, such as nitrogen, dramatically increase crop production but impoverish the soil in organic carbon, which in turn affects the physical properties of the soil. Resulting changes in soil physical properties, in turn, affect the balance of the interrelationships between air and water in the soil, making the plant less efficient in utilizing the added fertilizer (Young 1989). The unused fertilizer, if soluble such as nitrogen, leaches into groundwater, streams and lakes, which through contamination or overproduction of aquatic plants renders water unacceptable for human consumption (Greenland and Hayes 1981). In addition, microorganisms which function in the natural process of nitrogen fixation are disrupted by additions of inorganic fertilizer nitrogen (Brady 1990). Thus, nitrogen fixation slows or ceases and certain of these microbes may be unable to survive. The growth of plants therefore becomes increasingly dependent on nitrogen fertilization. Possibly more significant is that fertilizers (and other materials added to soil) may deplete the natural populations of nitrogen fixing and other organisms. As has been shown, the effectiveness of this symbiosis is microbe and plant species specific. Current management agricultural practices may be eliminating varieties of organisms that could overcome total dependence on inorganic nitrogen fertilization. Thus we are using up the biological "capital" of the environment and may be destroying the capability of the soil to recover (Hillel 1991).

Haberen (1991) argues that a "soil health index" is needed. He states that "soil quality is like the weather. People talk about it, few understand it, and still fewer do anything about it." Haberen argues that soil biology remains a "virtual unknown" and hypothesizes that losses of species at the far end of the food chain may be less important to the world's ecosystem than those species at the start of the living chain, the living soil.

The addition of foreign materials to soils such as synthetic plastics, chemicals or sludges may exceed the assimilative capacity of the soil. One may argue that side-effects of any management scheme are to be expected in order to gain from that management, usually in terms of economic return. The point, however, is that human's abilities to modify, manipulate and possibly destroy the capability of the environment may exceed the time frame to remedy or reverse any undesirable side-effects. In fact, the above discussion mandates that as humans modify their environment to meet their needs and desires, they must in fact have a much better understanding of the Laws of Nature, than when the natural environment merely shaped their lives; for by modifying the environment, humans in fact are shaping themselves and ultimately influencing their destiny.

Most of us today were educated in a fashion that is popularly termed as reductionist science. We are the product of the era of the specialists, drawing imaginary yet largely impermeable boundaries between perceived segments of Nature's continuum.

Descartes (1596-1650) in Part II, "Discourse on Method" gives four precepts of logic:

"The first was never to accept anything for true which I did not clearly know to be such . . . avoid precipitancy and prejudice . .

The second, to divide each of the difficulties under examination into as many parts as possible, and as might be necessary for its adequate solution.

The third, to conduct my thoughts in such order that, by commencing with objects the simplest and easier to know, I might ascent little by little . . . to the knowledge of the more complex; assigning in thought a certain order . . .

And the last, in every case to make enumerations so complete, and review so general, that I might be assured that nothing was omitted."

Humankind has oscillated between the extremes of holism (e.g., Gaia) and intense specialization. We hear criticism of today's educational system as being too specialized and that more generalists (often equated with better educated rather than trained) are needed. Neither extreme has been shown to be satisfactory. Society should seek a balance of both approaches in order to meet the magnitude of issues and concerns facing our increasingly complex institutionalized world. We need to strive for a balance of views and approaches to science rather than intellectual snobbery of singular alternative approaches espoused by one group or another.

Relatively recently the literature has abounded with questions of scientific ethics. Collins (1991) cites three components of ethical thinking: the recognition of (a) intrinsic values in nature; (b) the instrumental or utilitarian effects of decision making on human welfare; and (c) the long term consequences of behaviour that may be unsustainable. Ethics, therefore, is dependent on time and circumstance, which govern choice. Growing populations, education and scarcity of resources will alter ethical judgements. Here too, humans can take advantage of their intellectual capabilities and technologies to aid in achieving the goals of improving human perception and behaviour by the employment of the extension of the human brain, the computer. Computer technology and application can assist people to better understand the complexities of Nature both with human and without human interaction. This process must be conducted with perception, caution and care. The utilization of computers must be regarded as a tool of science and humanity, and not an end in itself. Like the human brain, today's computer is limited by the information available, the understood relationships among pieces of information, various perceptions and bias inherent in the information, and the situation (time) under which the facts of Nature's system were collected.

Concern about the environment and the survival of the human species is not new, nor will society refrain from expressing concern about the environment that shapes their lives. Over time Malthusian philosophy developed advocates and skeptics of equal conviction. Resource economists such as Krutilla (1972) and Pearse (1992) argued that technological progress broadened the resource base on which humans depend so that the scarcity foreseen by Malthus has not materialized. Rather than argue the nuances of



Malthusian philosophy, it is more constructive to view resources and the environment in terms of Nature's Laws. As Loehman and Conner (1974) pointed out almost three decades ago, environmental quality arises from the use of resources; the key problem is scarcity, i.e., both resources and the ability of the environment to restore itself are limited. Neo-classical economists focus only on resource availability, neglecting the inherent temporal limitations of the environment to restore itself.

A crucial issue that has been more vividly popularized in the past few decades is the ratio of human population to resources and the shifting of that ratio regionally on the globe. Rising demands for resources make increasing demands on the environment, parts of which deteriorate while others are enhanced for human use. Holgate and White (1977) identified four key processes essential for environmental maintenance:

1. conversion of solar energy into chemical energy;
2. the biogeochemical and hydrological cycles by which essential mineral nutrients are passed through the biosphere to sustain plant, animal and human life;
3. the processes of organisms achieving complete life cycles and adapting by evolution; and
4. the perception, communication, processing and transmission of information to allow all living things to interact with each other and their environment.

It is within these perceptions that I wish to discuss soil: the environmental integrator. By necessity and choice, the following will be largely restricted to the natural (physical) environment, rather than the "socioeconomic-political and cultural environment".

### 1.3 SOIL: THE ENVIRONMENTAL INTEGRATOR

If one accepts the definition of environment, as in common usage by ecologists (including human ecologists), as "the unique skin of soil, water, gaseous atmosphere and organisms that covers the planet", and incorporates the beliefs of the ancients of the four fundamental substances (elements) that are essential for physical matter (including human life), this may be schematically presented as a mechanical model shown in Figure 1.1.

The three interacting phases of the environment; solid, liquid and gaseous, driven by energy from the sun, give rise to soil and terrestrial life as we know it. It is at the points of interaction of the various circles that life begins and ends. It is this envelope that depicts the region in which life can function. As the static and mechanical model (Figure 1.1) attempts to illustrate, life is not a single point but a spatial area with various amounts of air, water and minerals. These interact to give rise to various combinations of living habitats or niches in the terms of ecology, ranging from almost all air, almost all water, to almost all mineral. Each component of the environment by itself is devoid of life. It is at the intersection of the environmental components that life exists, e.g., air and water (viruses); water and mineral (anaerobic organisms); mineral and air (chemoautotrophs). Of paramount importance, to have a functioning environment, is energy.

Attention is once more brought to the spatial envelope identified by soil sustaining life. The spatial area has boundaries among the three essential components. The region within the envelope may be termed the carrying capacity of the system, and the resilience of the system or its buffering or tolerance. Once these characteristics are exceeded: e.g., no air, no water, no mineral (no equating to both quantity and quality); the soil system collapses and life ceases.

The components of Figure 1.1 are dynamic and cyclical. During this process there is the opportunity to renew or rejuvenate the component and hence the system to a degree. Some cycles are relatively short (atmospheric circulation), others intermediate (hydrologic cycles), while others are of long-time durations (tectonic cycles). One can see from the diagram that there are interactions of phases, of the components in an open system driven by an external source of energy (that is, it is a thermodynamic system). Each component has intrinsic attributes that are defined, finite and have tolerable ranges (resilience) within which each operates. Extrinsic attributes arise from the interaction of components on each other (the environment). The shaded portion is the soil, the physical environmental integrator. It is also the realm wherein the vast majority of life both in terms of numbers and diversity are found. Cairns-Smith and Hartman (1986), as an example, argue that "life" originated on land, not in aqueous environments as is commonly held; with the clay minerals providing the template for molecular organization. Both "biological life" and "soil life" are

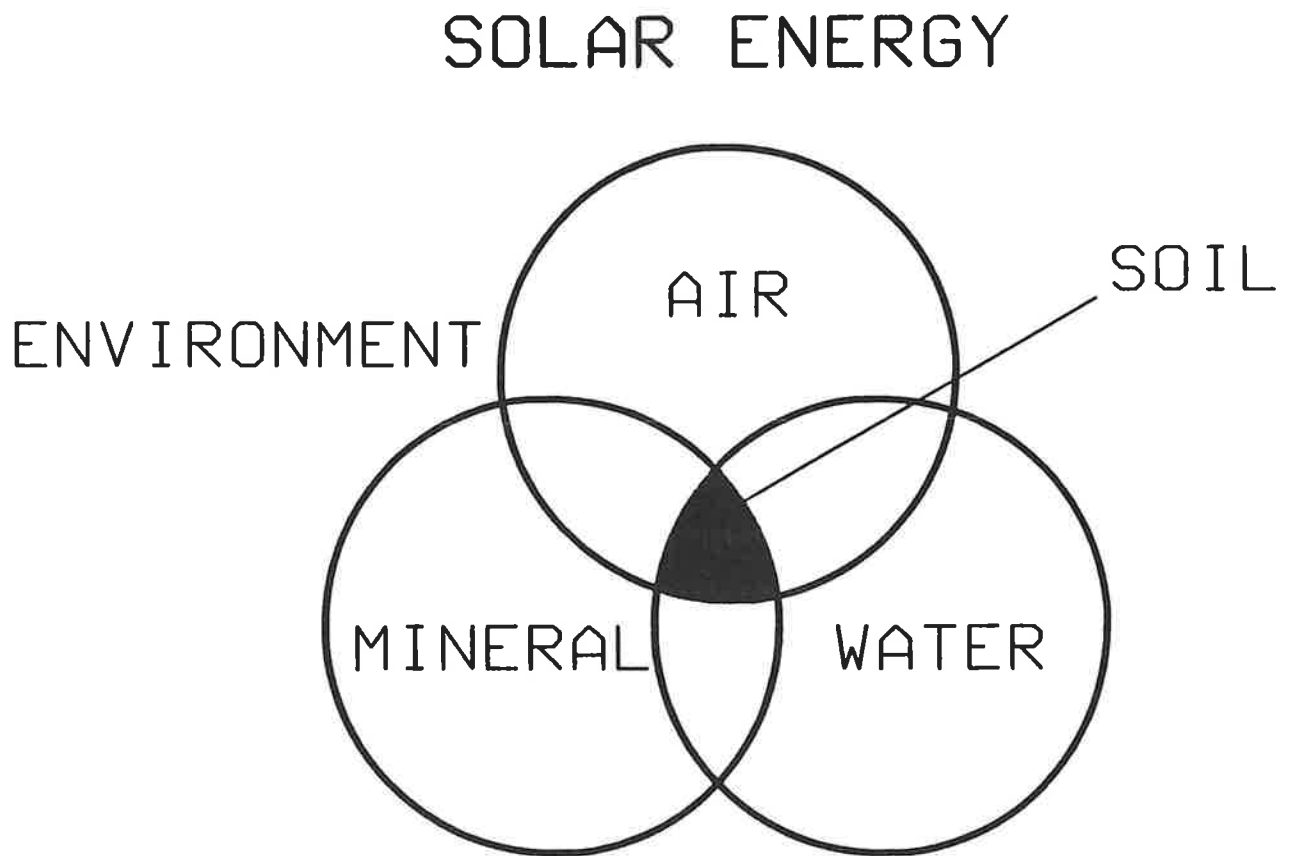


Figure 1.1 Conceptual diagram of the physical environment.

open systems and in terms of thermodynamics, unstable. The reason they exist and function is because of the external energy received from solar energy, which is converted to chemical energy and in turn allows work to be done.

### 1.3.1 Development Concepts and Models

Science has long recognized soil as a natural body. Joffe (1949) quotes Vernadskii as defining a natural body as "any object in nature which attains the status of individuality, endowed with an independent existence, capable of being distinguished and isolated from its environment, with an internal constitution, and controlled by specific laws in nature". Whether Fallou, Thaer, Dokuchaev or some other nineteenth century scientist is the founder of soil science as a discipline is of historical interest and debate. However, it was the school led by Dokuchaev that developed the concept that the principles applied in elucidating the natural sciences such as botany and zoology are applicable to the study of soil. This school looked upon soil as a distinct organism, with defined morphological features and inherent compositional character, with physical, chemical and biological make up. "The pedological method of the study of soil is analogous to that used in other sciences: chemistry, physics, and biology " (Joffe 1949). Joffe goes on to quote from Dokuchaev:

"The parent materials which have undergone changes by the mutual activities of air, water and plant, I call soil. Soils are the surface mineral and organic formations, always more or less colored by the humus, which constantly manifest themselves as a result of the combined activity of the following agencies; living and dead organisms (plants and animals), parent material, climate, and relief."

Thus soil is different from geology or geological formations in that soil is distributed over the Earth by natural laws that govern living things. Each climatic type has a definite flora, fauna, and soil. Geologic formations are distributed with no definite relation to the climatic conditions of the region.

Natural scientists have recognized the soil as a product and part of nature. The early writings of Dokuchaev challenged many earlier utilitarian and pragmatic approaches to the study of soil. The classical book by the late Professor Hans Jenny in 1941, Factors of Soil Formation, has had a tremendous impact upon the manner in which we study soil today.



The so-called factors of soil formation (parent material, climate, biota, topography and time) in fact form the integrating model of the environment at the Earth's surface that results in soil and terrestrial life. The model of Jenny was conceptually sophisticated and modified by others to help explain their approach to the natural world (Billings 1952; Crocker 1952 and others). This conceptualization has brought debate and scientific enquiry about independent and dependent factors; of attempts to evaluate the effects of single factors on soil evolution (e.g., toposequences, chronosequences); and the application of semi-quantitative and quantitative methods to understand and predict soil history and evolution (chronofunctions, biofunctions). The success of unifactoral approaches has been disappointing because the factors themselves are not independent and covary. However, Jenny's formulation of the Factors of Soil Formation spawned and nurtured reflective enquiry (science) in soil-environment studies for over one-half a century. In this sense, Jenny's contribution to natural science has extended far beyond his writings about soil or pedology. The stimulation of others, provoked by Jenny's work, to adopt, refute, adapt, modify, quantify, redefine etc. has been one of the greatest contributions to natural earth science.

As an aid to help visualize soil as a fundamental and natural entity, one may consider the analogy of the soil as a living organism — a body. In this analogy, generalized and simplistic similarities are stressed, recognizing that there are fundamental intrinsic differences between the soil and a living body, in the sense in which humans understand life.

A body is the result of inherent characteristics (genetic make-up) and modified characteristics resulting from the body's surroundings (environment). A body occupies space, is a physical entity and has shape (morphology). In other words, a three-dimensional thing in nature that has intrinsic and extrinsic characteristics (properties). The body is contained within a flexible membrane and as such can vary in size and shape within limits governed by its intrinsic properties. This membrane is selectively permeable to the transport of energy and matter from outside and inside the body. The body is an open system. At any time there is an equilibrium or steady state developed between the inside and the outside of the body with respect to energy and matter. The body is composed of a number of inter-connected objects, called organs. Each of these organs has a unique shape and function. If the body is to perform effectively, each organ must function in an appropriate fashion. The appropriateness

of the functional process varies within limits. If these limits are exceeded, the functional process slows and may cease. As this process within an organ changes so do processes in other organs change in response. If one organ ceases to function, this may lead to the cessation of the entire body. It is the process of exchange of matter and energy that allows a body to perform. In order to continue this performance, matter and energy must be continually added as the processes consume energy in their functioning (work).

The body has a capacity to carry out its functions (accumulative functions of its constituent organs) and a resilience or ability to return to its normal functions, if perturbed by "abnormal" or unnatural flows of energy or matter. If the unnatural flow is greater than the resilience, the organ (or body) decreases in its performance and may cease to function and the body dies. Some organs can be replaced if non-functional as a result of human ingenuity and technology. As a result, the body may function once again, usually at a somewhat lower level of effectiveness and a permanent scar is left that affects either the body's capacity to function or its inherent resilience. Often too, for the body to continue to function, outside additions of matter or energy (medicines) must be supplied. Rarely does the body regain its full potential to perform following such a perturbation. Thus, in order to have the body function at all, additional economic cost must be incurred.

So too the soil. The soil occupies space, has a morphology, has inherent or intrinsic characteristics (derived from the parent material), is affected by its surroundings (the other classical factors of soil formation), and bonded by a selective "membrane" that governs the flow of matter and energy through the so-called "open-system". The soil is meta-stable in terms of thermodynamics and thus is constantly changing and using up energy as work is done to affect these changes; yet at any instantaneous moment it appears to be in equilibrium (steady-state). The soil too, has "organs" and a concomitant array of processes which mediate interaction. The solid particles of various shapes, sizes and elemental composition; the pore spaces with their variable composition of gases and solutions; electrical charges; exchange phenomena of elements, aqueous constituents and atmospheric gases; and various combinations of solids, liquids and gases that interconnect all the parts. Thus each soil has an intrinsic hydraulic conductivity, cation exchange capacity, heat capacity, water holding

capacity, permeability, etc. Each of these characteristics has a capacity and a limit or resilience imposed by the intrinsic and extrinsic characteristics of the soil.

Parts of the soil or the whole soil may cease to perform effectively if the capacity (quantity) or resilience (quality) of these "organs" are exceeded. The soil, like the body, has extraordinary capacity and resilience to the transfer of energy and matter. But each body has a finite limit. If exceeded, technology may rejuvenate or regenerate the soil to somewhere near its natural condition, but at a cost and usually with a permanent scar that decreases the original performance of the soil.

Although an understanding of the functions and processes of the parts is necessary, it is how they interrelate that allows the thing to function. This is as true of a life form as of soil. Reductionist science is important in order for humans to comprehend nature's organization. The re-introduction of the reductionist parts into the whole allows an understanding of how and why some part of the system functions and, just as importantly, allows us to predict functioning of the whole if a part is affected (or managed).

Human beings have been taking advantage of the soil's capacity and resilience since the dawn of the agricultural revolution; but, more importantly, they have increased demand on the soil throughout the Industrial Revolution. Today's environmental revolution is forcing human beings to rethink their expectations and demands on the body upon which their lives depend. The agricultural revolution took thousands of years to achieve, the Industrial Revolution a few hundred. Will or can the environmental revolution succeed in a matter of decades?

Homo sapiens may be on a collision course with the Laws of Nature. Some would argue that this type of scare tactic has been professed 1,000's or 100's or 10's of years ago and yet the human species continues to survive. They cite the fact that there are more healthy people today, with a longer life expectancy and with a higher standard of living than ever before in the history of human life (Pearse 1991) as evidence of the fallacy of Malthusian philosophy and the predictions of Limits to Growth (Club of Rome 1972). There are, however, more unhealthy people today living under poverty than ever before (Worldwatch 1992). The point is there are more people! We live on a finite planet if in no other terms than in terms of energy (required to do work to allow bodies to perform). Human

populations are growing at exponential rates. Physical goods cannot grow forever, yet human populations appear to do so. It is not my intention to delve into the issues facing the future of Homo sapiens. The point is that the physical planet is finite, the energy (or matter) of the planet is finite, the environment is finite, as is the integrator of the environment finite.

The planet (and all things on the planet) was born, evolved and will die (cease to function). What we do not know with any precision or accuracy is when. This is controlled by the Laws of Nature. Our ultimate fate is known! As yet we cannot alter this fact by human intervention. The rate at which we approach that ultimate fate, in some measure, can be modified, that is we can affect the rate of the process or kinetics. If human intellect chooses rates at which process functions accelerate or speed up, the eventual end is reached sooner than if one chooses to work more closely at the rate governed by natural processes, or if by the application of intellect and technology, humans slow the rate without consequence. In terms of simple physical phenomena science describes this process on the basis of thermodynamics and kinetics. However, our understanding of thermodynamics and kinetics, especially as applied to natural things, such as soil, is most imperfect. The cliché that the "whole is greater than the parts" applies. We can analyze by rather sophisticated techniques the composition, structure and behaviour of a living organism, yet we do not understand the "magic", which somehow arranged matter and energy into a myriad of unique forms and functions, called life. So it is with soil! We can analyze, mix the components and manipulate the mixture, but the soil is a natural body with intrinsic and extrinsic characteristics. It has unique functions and that it can exist and perform without human intervention is also "magic".

### 1.3.2 Thermodynamics and Kinetics

The planet is a bundle of energy. Our natural (physical) resources are energy provided by Nature, useful to human beings and governed by natural laws. The Laws of Thermodynamics are a set of rules conceived by science to describe the physical world. The First Law simply states that energy is neither created nor destroyed, although it can change form. Energy in this sense is the total of kinetic (motion) and potential (state) of the component molecules, atoms, and subatomic particles. This energy is an extensive property;



that is it depends upon the quantity of matter being considered and is independent of the path by which that matter was brought to that state. Any change in energy of a system as a result of a process results in work or heat. A system is simply a specified part of the universe which we have isolated for our specific purpose. If  $E$  represents the energy of a substance or system, then a change in energy  $\Delta E$  is:

$$\text{State 1}(E_1) \rightarrow \text{State 2}(E_2)$$

$$\Delta E = E_2 - E_1$$

It can be seen that if work is performed and/or heat is generated;

$$E_2 = E_1 + q - w, \text{ and}$$

$$\Delta E = E_2 - E_1 = q - w$$

where  $q$  = heat and  $w$  = work

The above equations represent a reversible process, i.e., the conversion of State 1 to State 2 can be reversed by some external factor (in the case of soil by the addition of solar energy). A reversible process is one that may be visualized as consisting of a series of successive equilibria. Thus, to carry out a finite process reversibly requires an infinite time. Reversible processes yield the maximum amount of work (performance) that may be obtained for a net change in energy. When a process is not reversible, less work is obtained. An irreversible process can only occur when an external source of energy is applied. Soil and soil components are found in open and not closed systems and most processes are irreversible. Thus for the soil to function (to do work or perform) energy must be supplied. A process is only truly reversible if no heat or no entropy is produced. True reversible processes do not exist in Nature. There are processes where heat or entropy production is small, however, so we utilize the simplified concept of reversible processes in our deliberations.

Bohn and Bohn (1986) describe the application of thermodynamic concepts to natural soil minerals, which are impure and exist as solid solutions or contain isomorphous substituted components. These solid solutions dissolve nonstoichiometrically. They demonstrate how approximate solid activities in soil can be calculated and present modified

solid activity coefficients for soil solutions. The proposed procedure is applicable to studies concerned with ion retention (adsorption), as well as coprecipitation and precipitation of solid solutions. This approach is most useful when one wishes to develop mathematical models to describe soil processes. Cosby et al (1986) have developed a mechanistic, process-oriented model on the effects of acidic deposition on the chemistry of drainage water to associated streams. The model incorporates thermodynamic considerations of anion retention, aluminum solubility, dissociation of carbon dioxide, cation exchange, and weathering. The authors stress the fact that such models must be viewed with caution, because calibrating and verifying the model requires long-term data and, possibly, a truly predictive model may not be necessary or feasible.

Richter (1987) describes the soil in terms of a reactor. He discusses the soil as a dynamic system, which entails the study of the interactive flows between a complex, arbitrary part of reality and its surroundings (environment). It is this investigation that reveals and expresses how a system behaves. Each system is by nature part of a larger system. An open system, therefore, is a natural, arbitrarily spatially limited entity which consists of elements or subsystems. As an open system, soil can only reach a stationary state, i.e., a system characterized by constant mineral composition, by minimum production of entropy and by maximum energy efficiency and minimum energy dissipation (Ulrich 1986).

The world as a whole may be considered a closed system and thus entropy can only increase. In open systems entropy can decrease by exchange of matter with its surroundings. Thus an open system develops or organizes (Morowitz 1968), structure, horizons, mineral-organic interactions, etc. For a more detailed discussion of these principles, the publication of Richter (1987) is recommended. He describes thermodynamic forces in terms of free energy, free enthalpy, and relates these to chemical potentials of gas, liquid and solid phases, and explains how moisture potential and nutrient potential can be formulated, for example in respect to plant nutrient availability.

All processes in soil may be viewed in a long term or short term perspective. Changes in composition (genesis) are long term, while function, e.g., crop production (utility) are of shorter term. Thus humus formation, podzolization, and the like are relatively complex

and of long duration; while leaching of soluble salts, ion exchange, mineralization, compaction, etc. are less complex processes and are of a short time range duration.

Thermodynamics can only allow prediction of the final state of a system from a non-equilibrium beginning. It tells us little about how fast the reaction will proceed towards equilibrium or the reaction pathways that may occur during the transition. The rate of processes is termed kinetics. Kinetic studies are difficult to assess for even homogeneous systems; the complexities involved in heterogeneous systems, such as soil, are phenomenal. As Sparks (1989) observed:

"Kinetics of soil chemical processes is one of the most important, controversial, challenging, enigmatic and exciting areas in soil and environmental chemistry".

Thermodynamics deals with equilibria: soil is rarely, if ever, at equilibrium. In an attempt to utilize kinetic concepts in the context of soil the environmental integrator, a brief overview of the Rate Law is introduced. By definition a rate equation is written as:



Rates are expressed as a decrease in A and/or B concentrations (number of molecules or ions) or an increase in C and/or D concentrations over time. Thus if one monitors the change in A over time (t), the rate is:

$$\frac{-d[A]}{dt} + a$$

or for C the rate is:

$$\frac{dC}{dt} + c$$

or

$$\frac{dC}{dt} + c = \frac{-dA}{dt} + a = k[A]^{\alpha} [B]^{\beta} \dots$$

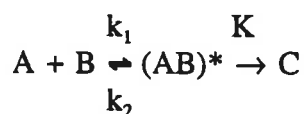
where k is the rate constant and  $\alpha$  is the "order" of the reaction with respect to A,  $\beta$  is the order for reactant B and so on. The sum of the  $\alpha$ ,  $\beta$ , etc. give what is termed the reaction order, i.e.

$$n = \alpha + \beta + \dots$$

Usually the reaction order, n, is determined experimentally.

Kinetic phenomena in soil can be described by apparent rate laws, mechanistic rate laws, or apparent, or mechanistic rate laws including transport processes. As an example, Stumm (1986) discusses the importance of surfaces and interfaces as they affect the composition of the environment. His examples of the oxygen donor atoms present on oxide surfaces as they undergo protolysis, form complexes with metal ions, or exchange for other ligands, show how these processes govern the rate of precipitation and dissolution of minerals, weathering of rocks and minerals, and heterogeneous nucleation. Chemical weathering is a key process in the neutralization of both internal production and anthropogenic input of acid into soil. The rate of chemical weathering in soil is a function of mineralogy, temperature, flow-rate, surface area ligand, CO<sub>2</sub> activity, and hydrogen ion activity (pH). Thus an increase in weathering rate upon an increase in hydrogen activity is not linear, thus increased soil acidification cannot be fully compensated by an increase in the neutralization rate in the soil. It is beyond the scope of this article to expand on these approaches. The interested reader is referred to Skopp (1966), Sparks (1986) and the more comprehensive volume by Sparks (1989).

One aspect that has significance to the discussion presented is the application of transition-state theory. The application of this theory often aids in understanding, or at least explaining, why a soil appears to be at equilibrium (steady-state) when in fact it is only metastable in the thermodynamic sense. Consider, for example:



where  $k_1$  and  $k_2$  are the rate of formation and the rate of destruction of the "activated complex" (AB)\*. According to this theory, the energy status of the activated complex (AB)\* governs whether A and B will in fact form C. More useful perhaps is the equation:

$$\Delta G^\circ = -RT \ln K^*_{eq} = \Delta H^\circ - T\Delta S^\circ$$

where  $\Delta G^\circ$  is the change in free energy of the reaction,  $R$  is the gas constant,  $T$  is temperature,  $\Delta H^\circ$  is the change in enthalpy,  $\Delta S^\circ$  is the change in entropy, and  $K_{eq}^*$  is the so-called pseudoequilibrium constant of the activated complex. [Thus  $K_{eq}^*$  is related to the more generally used thermodynamic state functions, i.e., the equilibrium constant  $K_{eq}$  is related to the thermodynamic state functions of enthalpy and entropy.]

The relationship discussed above is shown in the form of a diagram (Figure 1.2, adapted from Lavkulich 1969; Sparks 1986) where  $\Delta G$  is the change in free energy,  $\Delta G_1$  is the free energy change as  $A + B$  react to form the activation complex ( $AB^*$ ) at rate,  $r_1$  and  $\Delta G_2$  is the change in free energy as the activation complex ( $AB^*$ ) reacts to form  $C$  at rate,  $r_2$ . Thus, thermodynamic and kinetic considerations are related.

The amount of energy change to go from 1 (reactants) to the activated complex is commonly termed the activation energy. Once the activated complex is formed, the reaction can proceed. Whether a reaction will proceed depends on factors affecting this  $\Delta G_1$ . If  $\Delta G_2$  is less than  $\Delta G_1$  the reaction proceeds at rate  $r_2$ . Catalysts may be present or added to a soil system to aid in the reaction rate. Common examples are the role of surfaces that adsorb reactants (e.g., colloidal clay or organic matter) allowing the adsorbate to remain in proximity to a surface and increasing the probability that an effective collision will occur and a new entity can form (Mortland 1986). In other words, the catalyst (surface) ensures effective collisions will take place. Enzymes and transition elements (Fe, Mn) are examples. On the

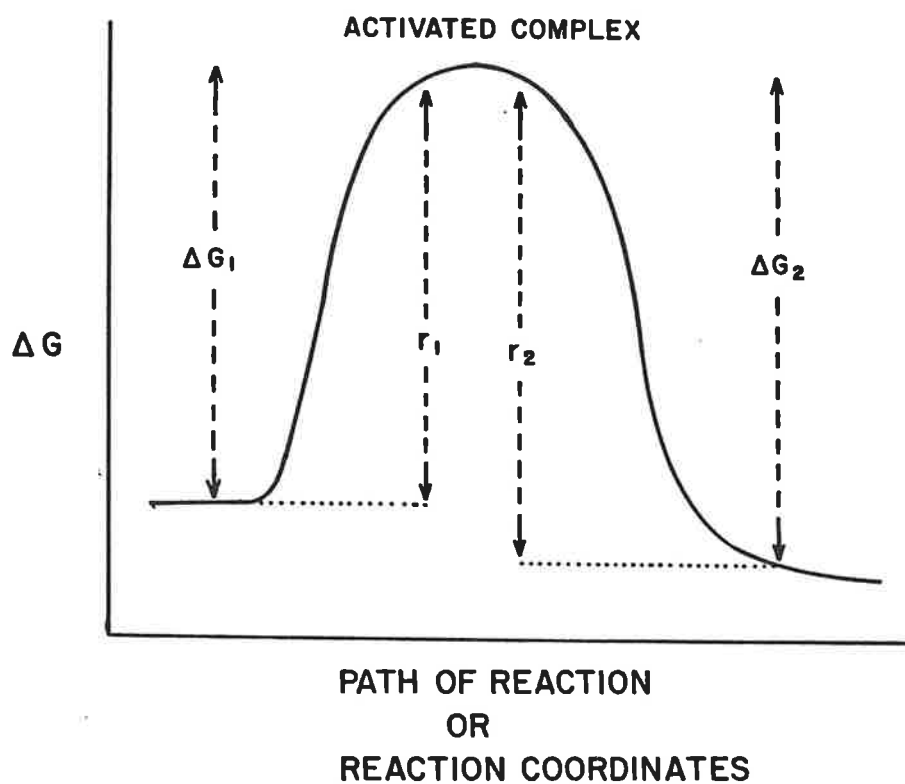
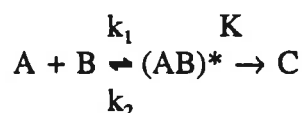


Figure 1.2 Generalized illustration of free energy changes.

other hand, soil systems have or may have added to them reaction inhibitors which slow reaction rates. Nitrogen mineralization rates may be slowed temporarily by certain chemicals or by the build-up of nitrite (Brady 1990). Heavy metals may inhibit enzymes by replacing the natural metal coenzyme (Tiller 1989). Most elements in soil cycle rapidly between soil solids, soil solution, organisms and the atmosphere, often faster than the rates at which they reach their most stable thermodynamic state. Thus the soil is thermodynamically metastable and the understanding of kinetics is becoming an increasingly important area of investigation in order to understand process and behaviour.

To obtain a better appreciation, the equation:



may be rewritten in the form:

$$\frac{-\Delta[A]}{\Delta t} = \frac{K[B][A]}{K_m + [A]}$$

where  $k_m$  is the function of  $k_1$  and  $k_2$ . This is illustrated in Figure 1.3. The equation for the curve in Figure 1.3b is represented by:

$$\frac{\Delta[\text{Rate Factor}]}{\Delta t} = \frac{\Delta[A]}{\Delta t}$$

This equation may be modified to express a variety of soil processes, such as the evolution of  $\text{CO}_2$  from the addition of organic carbon, the appearance of nitrate from introduced nitrogen fertilizer, or the adsorption of water by soil colloids.

The above application of thermodynamics and kinetics is merely an introduction to the subject in order to show how one may predict the behaviour of soil as the

environmental integrator. Thermodynamics and kinetic theory are only useful tools to aid in the understanding of soil processes.

These principles may be illustrated by the well known growth curve of microbial populations (Figure 1.4). Point 1 is considered the lag phase or in reference to Figure 1.2 prior to the formation of the activated complex ( $AB^*$ ); at portion 2 of the curve, the population grows exponentially (or the reaction rate is at  $r_1$ ), until a steady state is reached (the activated complex ( $AB^*$ ) persists (position 3); gradually at first and then again exponentially death of organisms occurs because of environmental conditions (activated complex moves to lower free energy at rate  $r_2$ ), and a new steady state is reached at 5.

The above generalized illustration gives an overall framework to the functioning of systems whether the system be simply two molecules reacting, the more complex growth of organisms, or the behaviour of a soil that has been subjected to externally induced factors. The Figure shows that there is a beginning and an end,  $r_1$  and  $r_2$  govern the time from birth to death, and region 3 illustrates the capacity of the system to function as a thermodynamically metastable system.

Another schematic diagram may aid in appreciating the approach (Figure 1.5). The areas under curves A and B are the same (capacity) but the rate at which X is achieved is different. Nature's Laws hold! Homo sapiens can control the rate (time) at which X is arrived at. Because the soil is an open-system, the areas under curves A and B need not be the same. Mineral weathering, N- fixation, fertilizers, airborne particles, etc. may increase the area. The area under the curve, however, is finite (capacity).

Harmsen (1992) illustrates the behaviour of Cd in soil following zero, first and second order reaction rates over a period of 200 years and the actual concentration of Cd found in soil at 56 years. He shows that depending on soil conditions, rates of addition or environmental parameters, the long term predictions regarding Cd sorption by soil varies. This demonstrates the strength of kinetic modelling that is both predictive and dynamic. It also shows that the same soil may behave differently (i.e., with different rates) depending on the driving force (environment). The shapes of the resultant curves fall between those presented schematically in Figure 1.5a and 1.5b.



### REACTION RATE DEPENDENCE ON EXTERNAL FACTORS

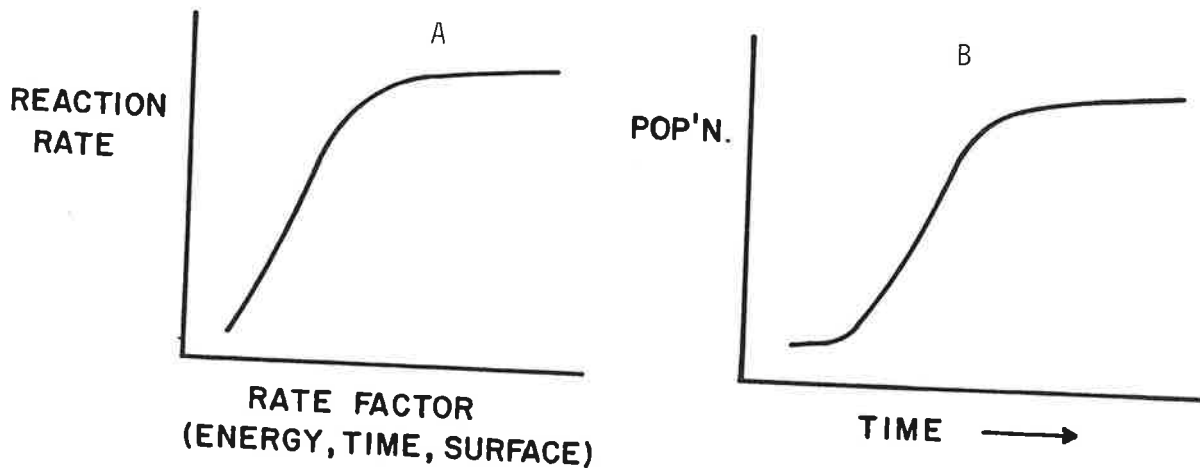


Figure 1.3 Reaction rate dependence on external factors (A) and analogy to population growth dependence on time (B).

### GENERALIZED GROWTH CURVE OF ORGANISMS

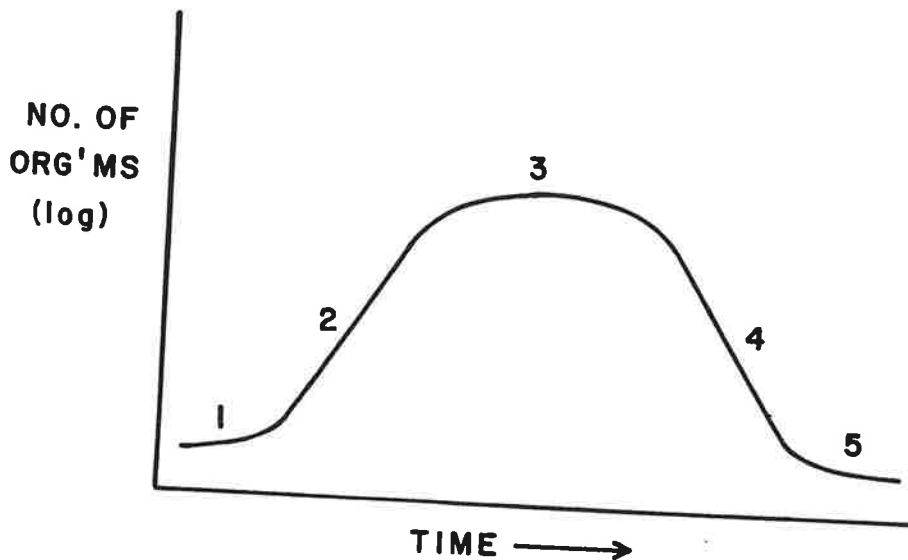


Figure 1.4 Generalized growth curve of organisms.

In my view, Malthusian theory holds. What society has been able to do by the adoption of technology is to increase the time interval until finite  $X$  is reached and thereby postponed the eventuality put forth by Malthus. The planet has a finite capacity. In terms of human life-span or history "they are not making any more". Soil, water, and air are remarkably resilient (buffering) but do have limits beyond which they cannot be utilized without irreversible change.

By appreciation of the soil as a "reactor", one is able to understand what is the capacity and the resilience of a particular soil body. Laws of thermodynamics and kinetic theory allow a better understanding of how the soil functions as the integrator of the environment, that is, the fundamental integrator of the atmospheric, mineralogic, hydrologic and biologic components of the Earth's terrestrial skin. It is by the understanding of these fundamental relationships that human activities (management) can be judged as to their impact on the functioning of the soil, the impacts of human intervention, and the remedial processes that are necessary to maintain the soil as a living entity.

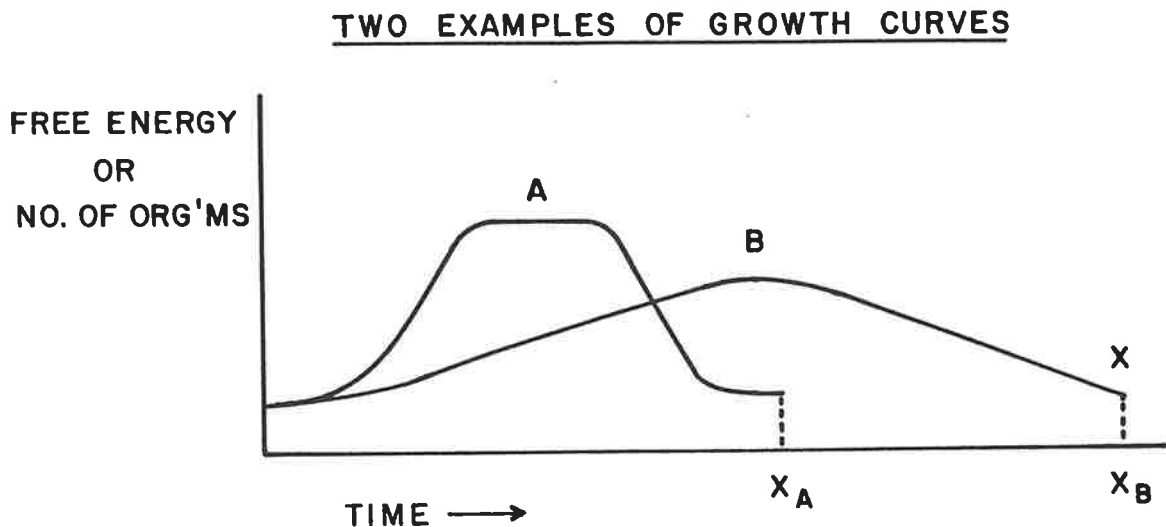


Figure 1.5 Two examples of growth curves proceeding at different rates (area under curves A and B are equal).

### 1.3.3 As a Geographical Entity

From the previous discussion it is apparent that the soil is a three dimensional entity on the terrestrial portion of the Earth. Too often, authors write and speak about the soil as an individual spot or a two-dimensional object, e.g., the soil profile. In fact, soil is a relatively continuous membrane on the Earth's surface. Within this membrane are things that are considered non-soil such as water, permanent snow or ice, rock and human constructs. As a result of science, and especially reductionist science, humans, not having the capacity to comprehend complex and continuous phenomena, have artificially segmented nature into what they perceive as "homogeneous" categories. This only holds if one can quantitatively and unequivocally define soil from non-soil, or life from death. Nature is a continuum; but in our attempt to understand nature we subdivide this continuum on perceived similarities in morphology, process or function, emphasizing and thereby focusing on similarities and minimizing or ignoring differences. Usually this process is conducted through various levels of generalization, abstraction or comprehensiveness (Cline 1949, 1962). Pedologists have focused much of their attention on the soil profile (two-dimensional) and more recently on the soil pedon (three-dimensional) with a consequent emphasis on soil processes that give rise to vertical differentiation (horizons) of the land surface. Relatively less attention has been given to processes that are related horizontally and spatially across landscapes, be it a depression, hillslope, watershed, or physiographic region. The reality that soil is a geographical (spatial) three-dimensional entity has been largely neglected in research. Many scientists view soil science as a "spot" science. If one accepts that soil is the integrator of the mineral, atmosphere, water and biota, it is obvious that the soil is in fact a spatial volume. The pioneering work of Jenny (1941) and the formulation of the factors of soil formation has been misinterpreted in that Jenny's soil was not a single isolated spot on the Earth's surface. Traditional soil surveys recognize soil as a landscape unit (polypedons) and have developed cartographic concepts to demonstrate this conceptualization (association, catena) yet characterize the soilscape by the modal soil, the profile, and the site (a single isolated spot). There has been a lack of communication among soil scientists, other earth scientists, agricultural scientists, and ecologists in understanding the membrane of soil as having horizontal as well as vertical relationships in components, processes, functions and

morphology. This lack of communication and understanding has resulted in numerous debates and pages of scientific literature on soil versus site versus land versus ecotype. The conceptualization is common, the landscape is common, the applied objective may be less common (Rohdenburg 1989). The soil is in fact a landscape; a landscape that may be described and studied at various levels of generalization from a few metres cubed, to hectares, to hundreds of hectares to kilometres squared. It is important in all of these observations and studies that it be recognized that properties, processes and functions form a continuum, sometimes abruptly different but more often changing gradually both vertically and horizontally. The problem still exists as to how we characterize a natural continuum, such as soil.

There is no insurmountable problem if soil is perceived as a single "spot" science, if sufficient spots are examined. With the utilization of geographical positioning systems, geographical information systems and statistical tools such as kriging, spatial relations about the continuum of soil can still be empirically ascertained. This process simply involves rather sophisticated satellite and computer technology.

This approach changes the way in which soil inventories are generated and how soil variability, interpretation and risk assessments are proposed. Rather than the conventional approach of determining soil landscapes as mapping units and determining soil variability (Wilding 1985), a more reliable and statistically more rigorous procedure may be to prepare soil inventories from "spot" sources and then generate "iso-similar" soil landscape polygons. This approach has been utilized in determining forage parameters of quantity and quality by Smith et al. (1991).

A legacy of this historical perception of soil and the fact that most scientific observations about soil have been made by agricultural scientists is that soil is considered by most only as the medium for the growth of agricultural crops and that soil erosion and degradation are important only to agriculture and to agricultural policy. This is unfortunate. Soil erosion and soil degradation as a result of agricultural and forestry practices are important indeed; but the functioning of the soil and its role in integrating the physical environment of air, water, energy and minerals is more vital. It is this integrative nature that allows soil to regulate and buffer the factors that support terrestrial life. Perhaps, keeping in

vogue with present times, the term soil should be replaced by a more appealing word such as "ecoterra". The importance of soil as a product of nature would not change but the perception and understanding of its vital role in the environment and the dependence of life on this pervious skin might become more appealing to society. To many, soil is equated to dirt - a negative connotation.

1.3.3.1 Some Examples. If one accepts the soil as a thermodynamic system which follows the predictions of Nature's Laws, then one must accept that soil changes, sometimes slowly, sometimes more rapidly, governed by intrinsic and extrinsic factors. The soil is the integrator of the environment. It is through the soil that the component cycles reach steady states and maintain quasi-stability in terms of capacity and resilience.

As one example, consider the role of soil in the hydrologic cycle. The following table is adapted from Black (1991):

| Global Water<br>Time | Volume<br><br>m <sup>3</sup> | Percent of Total | Residence<br><br>years |
|----------------------|------------------------------|------------------|------------------------|
| Total Fresh          | 4 x 10 <sup>16</sup>         | -                | -                      |
| Shallow Ground Water | 4.3 x 10 <sup>15</sup>       | 11               | 760                    |
| Biosphere            | 9.7 x 10 <sup>13</sup>       | 0.24             | 17                     |
| Soil Moisture        | 4.1 x 10 <sup>13</sup>       | 0.06             | 4.2                    |
| Atmosphere           | 1.4 x 10 <sup>13</sup>       | 0.04             | 2.4                    |
| Rivers               | 1.2 x 10 <sup>13</sup>       | 0.03             | 2.1                    |

Of the total freshwater (which accounts for 89%), the above table does not include lakes, deep groundwater, and ice and glaciers. One notes that about 0.06% of the Earth's fresh water is held as soil moisture with a residence time only longer than the atmosphere or flowing rivers.

If the infiltration rate and consequent water storage capacity of soil is decreased by 10% as a result of agriculture and forestry practices and human structures such as roads and cities, this is equivalent to 4 x 10<sup>12</sup> metres cubed of water that is no longer in the soil and is re-distributed within the hydrologic cycle in such forms as run-off or increased evaporation. This exceeds the amount of water discharging through all rivers in Canada per year (Pearse et

al. 1985). Thus, as a result of interruption of Nature's cycles, the capacity of the soil has been altered, the hydrologic cycle perturbed and a new steady state must be established. The effects of this decreased water storage and cycling and new steady state are rate (or time) dependent.

Bohn (1976) estimated that the amount of organic carbon in world soils to a depth of one metre is  $3.1 \times 10^{15}$  tonnes. Again assuming a 10% decrease in organic carbon as a result of anthropogenic activities, this amounts to  $3 \times 10^{14}$  tonnes of carbon that is no longer in the soil "sink" and has found its way into other portions of the carbon cycle. This represents an amount greater than the carbon calculated to come from the burning of fossil fuels in 1980 on a global scale (Hengeveld 1991). This does not consider other effects such as decreased infiltration (loss of structure), water storage capacity, cation exchange capacity, pH, nitrogen, porosity etc., resulting from the loss of organic matter.

The calculated figures presented above are themselves unimportant. What is significant is the process that is being affected and the impact of the process on the ability of soil to re-adjust to new capacity and resilience conditions, and the readjustment of air and water cycles. In addition, the rate at which anthropogenic effects can occur in comparison to the rates by which the soil can re-adjust to these effects may be quite different, and the results and effects on other circulation patterns unknown.

To quote Lucretius once again:

"... whatever increases something else, in its turn replenished ... earth the universal mother is found at the same time to be the general tomb of things, therefore you see she is lessened and increases and grows again."

Forest floor soils tend to be the most dynamic in terms of rates of change over short periods of time, and the processes during the transformation of organic matter to soil organic matter have been widely examined. The roles of organic matter decomposition and synthesis products have been implicated in numerous pedogenic and ecological investigations. Sanborn and Pawluk (1983) presented some interesting observations in their study of litter decomposition. In comparing the decomposition rate of litter from two species of Populus and one species of Cornus the %C evolved as CO<sub>2</sub> over a 70 day period was higher for

Cornus than Populus and the trends over time were similar. When these authors compared the nutrient content (Ca, Mg and K) of the decomposing litter over a 12 month period the trends were similar for the two genera with respect to Mg and K, however the trends were different for Ca between the two species of Populus. Casual observation showed that in some respects one species of Populus was more similar to Cornus, although the data for the two Populus species appeared to converge towards the end of their experiment. This exemplifies the importance of recognizing that rates and processes which take place during pedogenesis are different and illustrates that process studies rather than only static approaches are needed for better prediction and understanding of the role of organic materials in soil.

In the popular press it is common to stress the effects on the atmosphere of CO<sub>2</sub> resulting from industrialization and the consequent "greenhouse effect". The atmosphere, like soil, behaves as a thermodynamic system. Hengeveld (1991) presents data on atmospheric change. A commonly used diagram showing CO<sub>2</sub> in the atmosphere is presented in Figure 1.6.

If one superimposes a similar trend with respect to land conversion to cropland (Figure 1.7), it is clear that the period following 1900 has had the greatest impact on the amount of carbon in the atmosphere attributed to industrialization. However, it also coincides with the rapid increase in cropland and the concomitant increase in cultivation of soils and increased CO<sub>2</sub> release from soil organic matter. During this same period the area of pasture and grassland remained essentially constant and the area in forests and woodland decreased by over 18%. The question that arises is can the Earth's absorptive capacities of biota, oceans and soil assimilate this combined effect of increased CO<sub>2</sub> from soil organic matter decomposition and industrial activity? The figures also show an exponential tendency of increased CO<sub>2</sub> production and cropland conversion. The questions raised are where is the threshold (the plateau of the growth curve), and can humankind alter the rate at which the plateau will be reached by the adoption of appropriate technology?

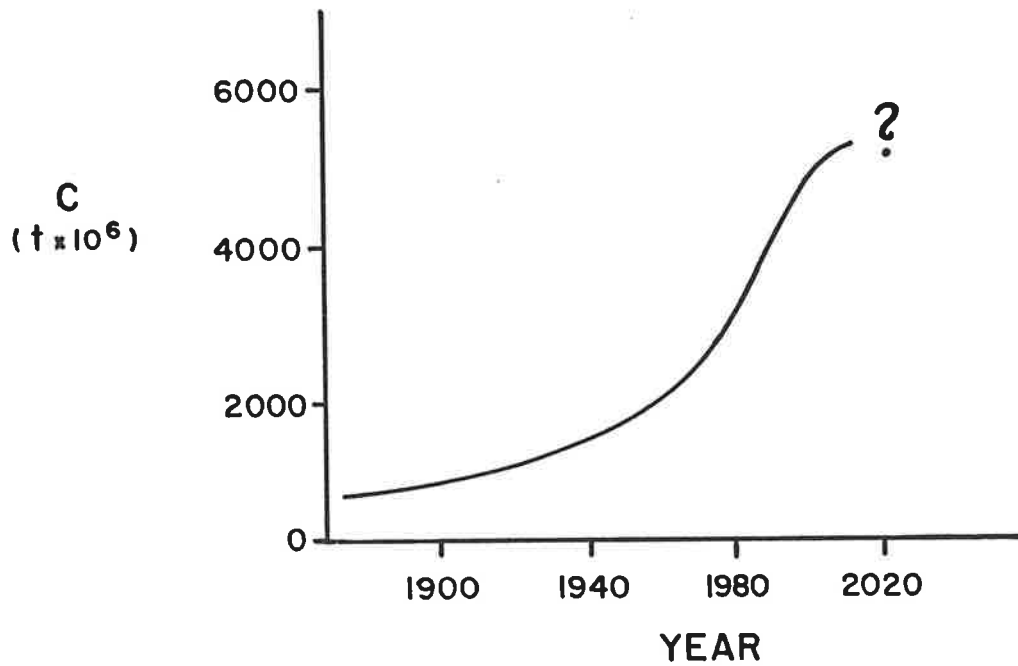


Figure 1.6 Carbon content of global CO<sub>2</sub> emissions from fossil fuel combustion and cement production (adapted from Hengeveld 1991).

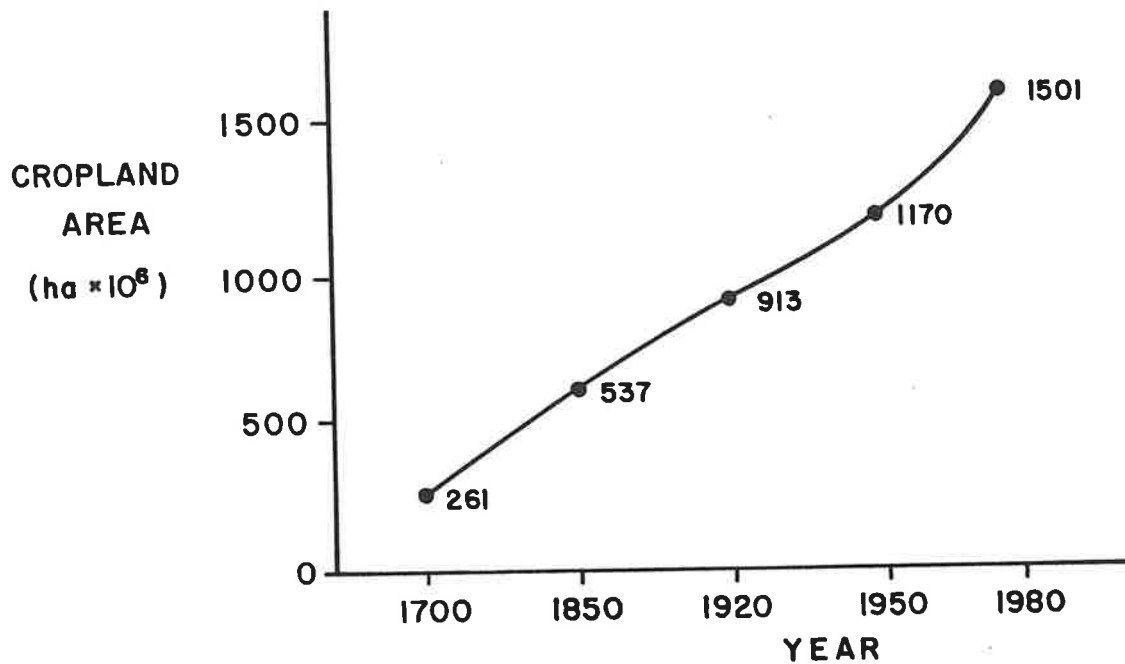


Figure 1.7 Land area of the Earth under cultivation (adapted from Richards 1990).



Other environmental factors also play dominant but poorly understood roles in soil reactions and reaction rates. It is commonly held that reaction rates increase with temperature. Barrows (1992), in examining the effects of temperature on sorption of inorganic ions in soil, argues that in sorption studies evidence about the interaction between time and temperature should be evaluated and stated. He discusses the differences in the direction of temperature effects on the activity of anions and cations, as well as reactions at surfaces. In general, anions shift towards less adsorption with increase in temperature; with cations exhibiting the opposite behaviour. There are however competing reactions that need to be considered.

The usefulness of chronosequences, albeit with the well recognized assumptions, allows the simulation of soil processes over time. Singleton and Lavkulich (1987a, b) presented the following data in their study of the Cox Bay chronosequence on Vancouver Island, British Columbia. Figure 1.8 shows that there is a general relationship of increasing organic matter and extractable Al in a 500 plus year period in the chronosequence. The rate of increase is low for about the first 400 years, then increases exponentially. This illustrates the typical "growth-curve" pattern and the postulation that a certain threshold (activated-complex) must be obtained before reaction rates increase. This is governed by the intrinsic properties of the system, and the rate will be modified by extrinsic factors (the environment). In the above example, a steady state (curve plateau) does not seem to have been reached in 600 years. This emphasizes the significance of an understanding of processes for periods of time longer than most soil investigations address. The soil is dynamic and responds to the Laws of Thermodynamics but only reaction rates (kinetics) will allow prediction of the length of time that is necessary to reach a steady-state and the beginning of the death-phase or decline in the accumulation of organic matter and extractable aluminum. Pedogenesis causes the soil to lose constituents, e.g., soluble ions, and therefore inherent soil fertility and reach a new and different steady state. This loss of plant nutrients is shown in Figure 1.9.

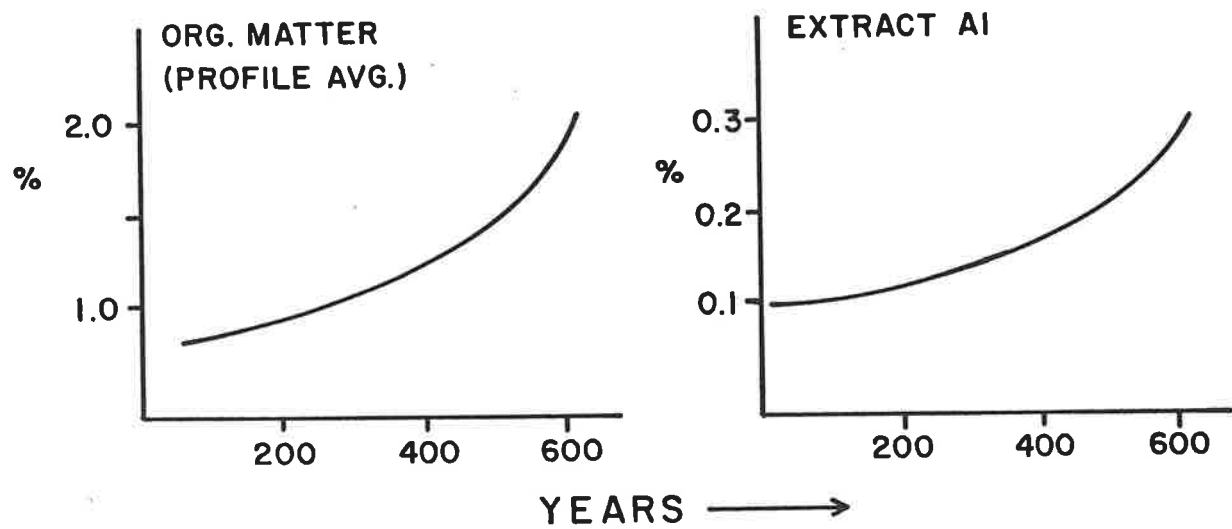


Figure 1.8 The relationship between organic matter accumulation and extractable aluminum (oxalate) over a period of > 600 years.

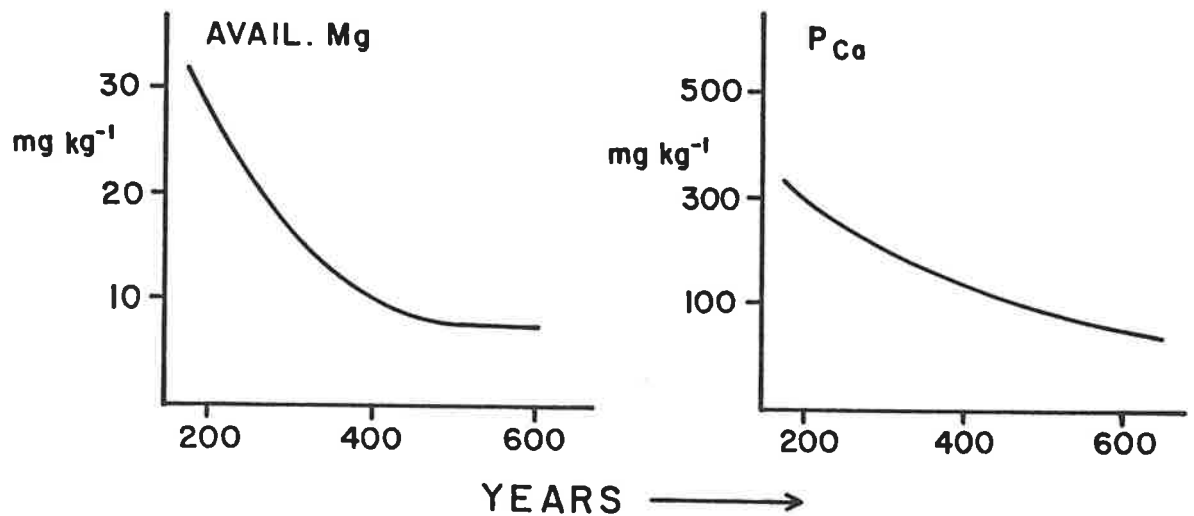


Figure 1.9 Loss of weighted profile average of available Mg and calcium phosphate in a 500 year Cox Bay chronosequence.

Bulk density and soil texture, among other soil factors, play important roles in affecting the relationship of the soil atmosphere as an exchanger of  $\text{CO}_2$  and  $\text{O}_2$  with the atmosphere above, for a "biologically healthy" soil environment. Richter (1987) provides an interesting treatment of the gas regime in soil. As an example, he shows that the role of a vegetative cover can have a pronounced effect on the  $\text{CO}_2$  flux in a soil (Figure 1.10). The example above leads one to speculate how the overall atmospheric cycle is being affected by human activity in managing the vegetative cover of the soil.

The effects of soil management on estimates of soil properties has been studied by several authors (Gregorich and Anderson 1985; Haas et al. 1957; Lavkulich and Rowles 1971; Tiessen et al. 1982). Goldin (1986) showed that with land clearing, pH values increased from about 5 to around 6 following 50 years of cultivation (i.e., one-order of magnitude) as a result of management (liming?). Cultivation resulted in a decrease of 20% organic matter in 35 years with the most rapid decrease occurring in the first 15 years, and steady state did not appear to have been reached. Cultivation over the same period increased bulk density by 26% to 58% on the soils examined and appeared to have reached a steady state in about 25 years. This shows that although soil properties may often be statistically correlated between each other, e.g., organic matter content and bulk density or organic matter and pH, each property is governed by its inherent intrinsic features and its response to the environment.

A commonly held belief is that soil can bioremediate all of society's wastes. Juste and Mench (1992) have shown that the continual application of sewage sludge to soil is not without limit. An example from their work is shown in Figure 1.11.

The data show there is a relationship between sludge application rate and amount of Zn in a crop and in the surface of the sludge amended soil. The data also demonstrate that the soil does not have an infinite bioremedial capacity to offset the continued application of sewage sludge. The soil has an inherent limit.

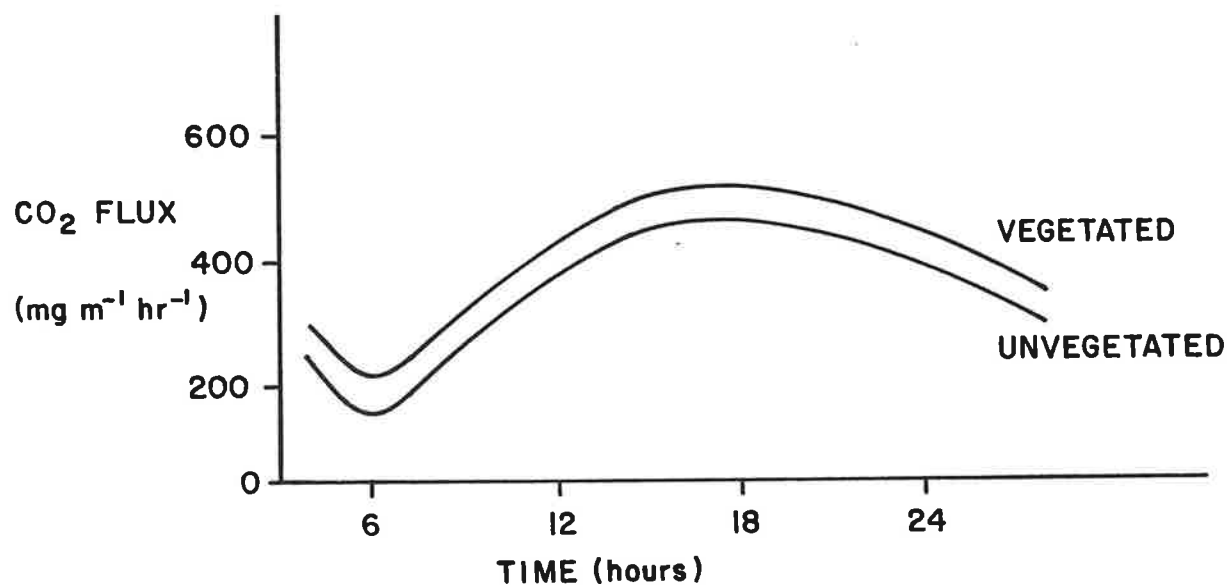


Figure 1.10 Schematic representation of CO<sub>2</sub> flux over a 24 hour period of a sandy soil (adapted from Richter 1987).

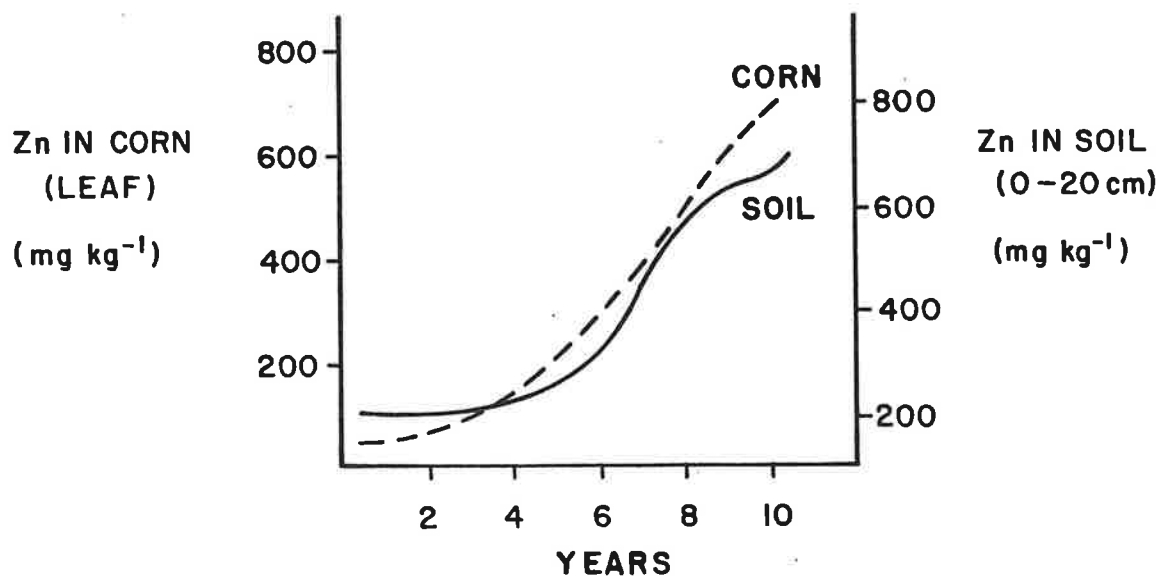


Figure 1.11 Increase in concentration of Zn in 6th leaf of corn and 0 to 20 cm soil from additions of sewage sludge (Bordeaux) at a rate of 100 (dry matter) hectare<sup>-1</sup> 2 year<sup>-1</sup> (adapted from Juste and Mench 1992).

The examples given are not meant to be inclusive but merely a representation of the role of soil in the hydrologic, energy and mineral circulation systems of the planet and the implications for biological systems. The examples attempt to illustrate the significance of reductionist approaches, process studies and studies at various scales within the hierarchy of systems in Nature. The attempt is also to draw attention to more holistic approaches to the study of soil as the environmental integrator. The soil is complex, dynamic and not static, a reactor, moderator and an exchanger; it is remarkable, mysterious and fascinating and, most important, essential for life on planet Earth.

Homo sapiens are relative newcomers to the planet. They too are remarkable and mysterious. Humankind has been shaped by its environment and has modified the same environment so that it must now adapt. The Laws of Nature appear to be inviolate even for Homo sapiens. The Earth has an enormous capacity and resilience to the activities of humans; it is however finite.

#### 1.4 The Challenge:

The Earth is a closed system, with the exception of solar energy, the soil is not. The soil exists because of its unique position among the components of the physical environment viz minerals, energy and water. The term "soil" in common usage usually relates to agriculture, other users refer to sediment, land or biosphere when considering non-agricultural aspects of soil. Unfortunately, the concept prevails that soil is merely an admixture of inorganic and organic matter to which management practices such as fertilizers, pesticides, and water can be added for crop production with no effect on the inherent capacity of the soil to function in its significant roles in hydrologic, mineral and atmospheric circulation systems. It is in the holistic sense that life on Earth is dependent on soil. The popular notion that all and any wastes of human activity may be applied to the soil for bioremediation neglects the very truth that the soil is a living system with a finite inherent resilience. The soil is not an equilibrium product, nor a homogeneous body. It is

thermodynamically metastable, varies horizontally and vertically and each soil landscape has varying capacities and resilience components that form a continuum on the terrestrial portion of the planet. Soil degradation (erosion, compaction, salinization) only affects immediate biomass production that technology may overcome. More importantly degradation is a strong signal that the balances and cycles of energy, water and atmosphere are being altered and therefore life, itself is ultimately affected. The soil, like air and water, is common property, thus no one is individually responsible, yet everyone is collectively affected.

Soil scientists may be proud of their contributions in agricultural production over the last several decades. More people are better nourished on a decreased land base than ever in the history of humankind. Soil surveys and other natural resource inventories have been most successful in accepting the challenges of the day and have evolved in their utility to resource issues from their original goals to serve agriculture. The demands and utility of soil survey information are varied as is the appropriateness of the present information. Zinck (1990) discusses the vital need for, and yet the recession if not the demise of, soil survey. He discusses soil as a resource limited in time and space and advocates that the three main resource attributes (scarcity, vulnerability and low resilience) beg for more care and that economics deal with soil as a non-renewable resource. He raises a number of questions that are fundamental to soil science. Do we need soil survey? Should soil survey be technology-driven or problem oriented? Can he have a more critical review of basic reasoning and fundamental concepts of structure, hierarchy etc. that support our understanding of soil formation, distribution and potential uses? What about the utility of our basic soil vocabulary such as soil, land, landscape, map unit, entity, etc? To this one may add, are soil scientists addressing the soil as a vital resource, a vital link, an integrator of the environment, in an

attempt to understand Nature and the appropriate use and management of this component of Nature for sustained life on Earth?

Wild (1989) raises the question of whether soil scientists are agricultural scientists or earth scientists? As agricultural scientists, Wild argues that our concern has been mainly with plant nutrition, denitrification, nitrate leaching fluctuations in organic matter, acidification and erosion. Are we, as earth scientists, concerned about preserving a healthy environment that can assist archeologists, ecologists, geologists, planners, economists, and sociologists, etc.? Wild suggests that if we are to make a contribution to earth science, we must treat soil as part of the natural environment, and we must, as a consequence, be concerned with global transfers of gases, water and solids between the atmosphere and the soil.

I would argue that it is the responsibility of soil scientists to indeed consider the broader issues. We are trained and educated to understand physical and biological processes and hopefully the interactions between the two. No other area of specialization (discipline?) is better prepared to do so. To do otherwise is shirking a trust and responsibility placed upon us by our colleagues and society. We must also question the basic tenets and practices of our science as we attempt to explain the insights for our science to our colleagues, governments, and the general public. We must learn to communicate better, so that the environmental integrator is given its rightful role in vital decisions made by engineers, economists, sociologists, planners and politicians. Soil scientists must awaken to a new holism. No longer will an informed public allow single answers to complex environmental problems.

Food production merely to feed the under-nourished is no longer acceptable if, by doing so, the atmosphere or the water become no longer life sustaining. Whether existing institutions will rise to the challenge is a moot point. As society begins to understand the essential role of soil as an integral part of life, the challenge will be accepted by natural earth scientists. They may not be called soil scientists, but their challenge will be that of a holistic soil scientist.

The soil is the environmental integrator as it is the Planet's terrestrial reactor and exchanger of minerals, air, water and energy.



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## **2. INADVERTENT ADDITIONS TO SOILS: METALS**

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This paper was unavailable for publication at time of press and therefore is unfortunately not included herein.



### **3. ENVIRONMENTAL FATE AND TRANSPORT OF ORGANIC CONTAMINANTS IN SOILS AT WASTE DISPOSAL SITES**

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#### **ABSTRACT**

Current approaches for describing the environmental dynamics of organic constituents in complex waste mixtures are reviewed. Factors controlling equilibrium and nonequilibrium sorption of organic contaminants from aqueous solutions are summarized, and extension of these concepts to predict the effects of mixed solvents are discussed. Presence of organic cosolvents increases solubility in a log-linear manner, leading to proportional decreases in sorption and retardation of nonpolar organic contaminants. Available data support the use of a log-linear cosolvency model and the UNIFAC model to predict the cosolvency effects. For predicting dissolution of aromatic hydrocarbons from multi-component organic liquid wastes, available data for gasolines, diesel fuels, and coal tars support the adequacy of approaches based on the assumption of ideal mixtures (Raoult's law). Examples are presented where the cosolvency model and the Raoult's law approach were applied for designing remediation of contaminated soils at industrial waste disposal/spill sites and for predicting the concentrations of aromatic hydrocarbons in the leachate from a source area.

#### **3.1. INTRODUCTION**

Environmental contamination problems at most industrial waste disposal sites or spill sites commonly involve wastes consisting of complex mixtures of organic and inorganic chemicals. Several researchers have made considerable efforts during



the past decade to investigate the primary processes (e.g., solubility, sorption, transport) governing the environmental dynamics of organic chemicals in complex mixtures. Earlier efforts were usually limited to investigations of the behavior of single solutes in aqueous solutions, or to systems that were simple in composition relative to many waste mixtures found at or near disposal/spill sites. Complex mixtures are defined here as those systems comprising multiple organic solutes and multiple solvents. The solute mixtures of interest might consist of various combinations of nonpolar or hydrophobic organic chemicals (HOCs); hydrophobic, ionogenic organic chemicals (HIOCs); and ionic organic chemicals (IOCs). The solvent may be a mixture of water and one or more organic cosolvents (either completely- or partially-miscible in water). Solvent mixtures of interest may consist of water and cosolvents in a single, homogeneous liquid phase, or multi-phases that form at least two distinct liquid phases.

The release and migration of organic constituents from a waste disposal or spill source will produce a contaminant plume, either in the vadose zone or in the saturated zone or both. The contaminant plume composition will vary with time and distance as the plume size increases. For discussing solubility and sorption processes within the plume, three separate regions may be considered: a near-field region, a transition zone, and a far-field region. The basis for such a distinction is not the distance from the contaminant source. Rather, the criterion employed to designate these regions is the chemistry of the contaminant mixture within the plume as contrasted to the waste composition.

In the near-field region, corresponding to the source itself and its immediate vicinity, the composition and concentrations of most waste constituents are similar to that in the waste. There are usually two, possibly three, liquid phases in this region. This would be the case, for example, at waste disposal sites where we may find both "dense" and "light" organic immiscible liquids (OILs) and an aqueous phase as well as a vapor phase. In the transition zone, the solution phase is likely to be predominantly a single-phase, homogeneous liquid made up of water and varying amounts of cosolvents (if they were present in the near-field region). The

concentration of one or more waste constituents may be sufficiently high such that approximations based on behavior in dilute aqueous solutions are found to be inadequate. Finally, the far-field region corresponds to that region of the contaminant plume in which the waste constituents are present in an aqueous solution. Most of these chemicals will be at concentrations well below their aqueous solubility limits. During migration of the contaminant plume through the vadose zone and the saturated zone, chromatographic separation of the waste constituents occurs due to their different mobilities. Furthermore, dilution resulting from hydrodynamic dispersion and attenuation resulting from abiotic and/or biotic transformations could decrease contaminant concentrations. Thus, high concentrations of multiple contaminants are less likely to be found as the distance from the source increases. Nevertheless, it is possible that these contaminant concentrations may be higher than the standards set by regulatory agencies.

This paper presents an overview of recent experimental and theoretical developments in describing: (1) solubility of HOCs in aqueous and mixed solvents; (2) sorption of HOCs and HIOCs by soils and other geologic media from water and mixed solvents; and (3) partitioning of HOCs from multi-component OILs into water. Applications of this information to definition, prediction, and remediation of soil and groundwater contamination problems will also be discussed.

### 3.2.           SORPTION FROM AQUEOUS SOLUTIONS

Most of the available data and theories for predicting sorption and transport of organic chemicals may be successfully applied to predict contaminant behavior in the far-field region (i.e., dilute aqueous solutions). The following section will highlight the information available on equilibrium and nonequilibrium sorption of organic chemicals.

#### 3.2.1.       Equilibrium Sorption

Equilibrium sorption of HOCs by soils and sediments has been successfully predicted in many cases by the "solvophobic theory" and the use of linear

free energy relationships (LFER). Excellent log-log, linear relationships have been reported between  $K_{oc}$ , the sorption coefficient normalized to the mass-fraction organic carbon content (OC) of the sorbent, and the octanol-water partition coefficient ( $K_{ow}$ ) for several HOCs (c.f., Dzombak and Luthy 1984; Karickhoff 1981, 1984; Kenega and Goring 1980). Linear relationships have also been found between  $\log K_{oc}$  and solute hydrophobic surface area (HSA) (Dzombak and Luthy 1984; Rao et al. 1985) and solute molecular connectivity (Sabljic 1984, 1987). The different slopes and intercepts found in these regression equations are predominantly determined by the characteristics of a group of compounds (i.e., class, degree of hydrophobicity, and structure) (see Gerstl 1990), while the sorbent properties other than OC appear to have only minor impact in most cases (Karickhoff 1981, 1984; Schwarzenbach and Westall 1985). The equations derived from LFER and experimental data obtained for only a few sorbents provide reasonable predictions of HOC distribution in diverse soil-water and sediment-water systems. However, the limitations of the  $K_{oc}$ -concept have been pointed out by a number of authors (e.g., Green and Karickhoff 1990; Mingelgrin and Gerstl 1983). The two main concerns involve the contribution of adsorption on mineral constituents and the possibility of site-specific interactions between functional moieties of the solute and the sorbent.

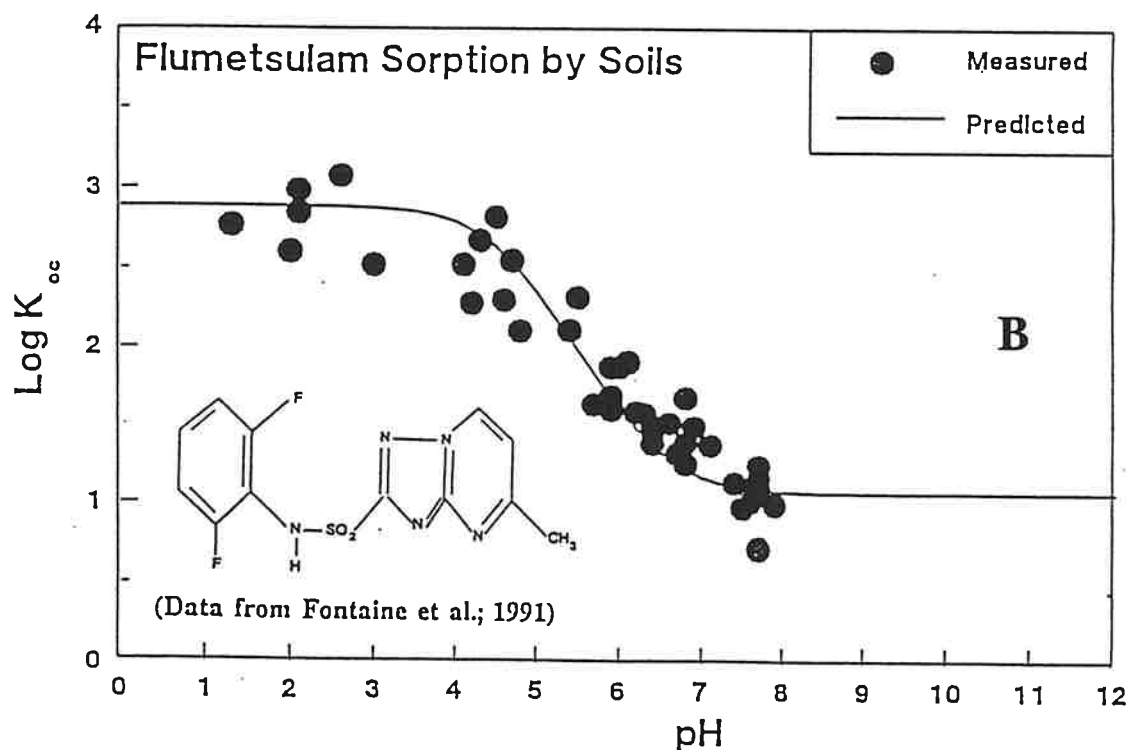
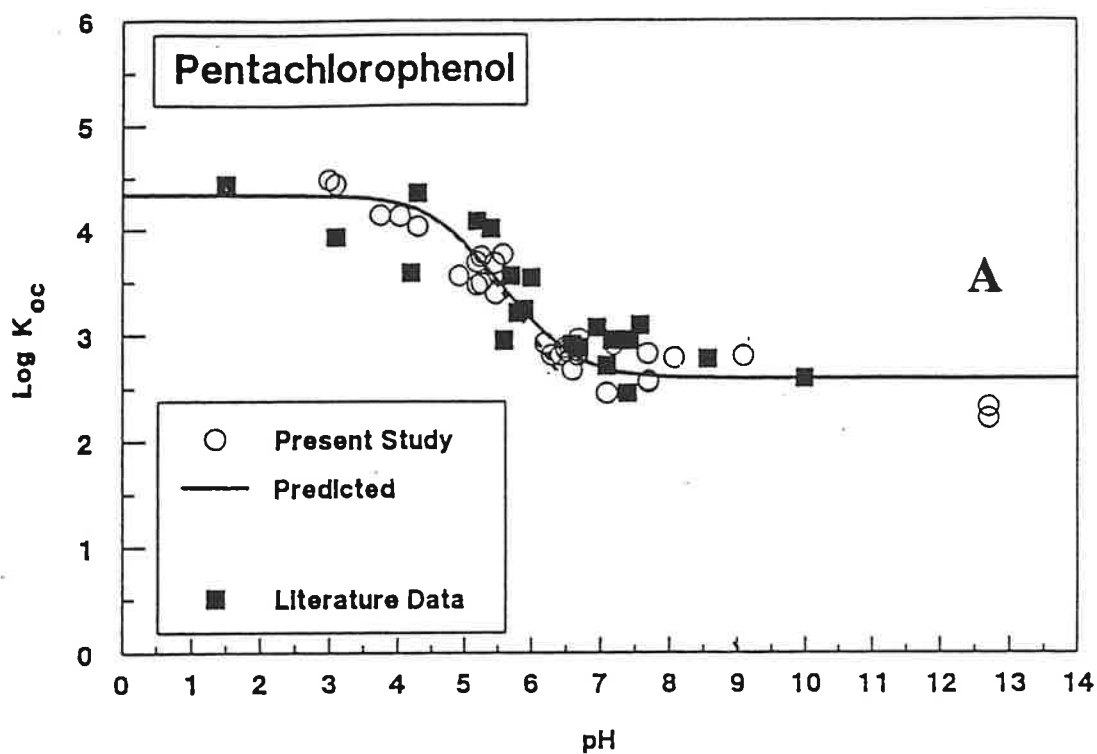
For HIOCs, predicting sorption from a single parameter becomes difficult due to additional processes that must be considered (i.e., speciation, ion-exchange, ion-associations, etc.). For example, on the basis of an analysis of a large data set for pentachlorophenol (PCP) sorption from aqueous solutions by several sorbents over a broad pH range (Figure 3-1A), Lee et al. (1990) showed that equilibrium sorption could be described by the following model:

$$K_{oc} = K_{oc,n} \phi_n + K_{oc,i} (1-\phi_n) \quad (1a)$$

where

$$\phi_n = (1 + 10^{pH-pK_a})^{-1} \quad (1b)$$

$K$  is the measured distribution ratio for the sorbed- and solution-phase concentrations for sorption by a specific sorbent;  $K_{oc} = (K/OC)$  is the OC-normalized distribution ratio;  $OC$  is the soil organic carbon content (mass fraction);  $\phi_n$  is the fraction of the neutral



1. Examples of pH-dependence of sorption of organic acids by soils from aqueous solutions. (A) Pentachlorophenol sorption by several sorbents, as reported by Lee et. al. (1992); (B) Flumetsulam herbicide sorption by several soils, based on data reported by Fontaine et. al. (1991) and interpreted by Lee (1993). The solid line in both cases is prediction based on eq (1a).

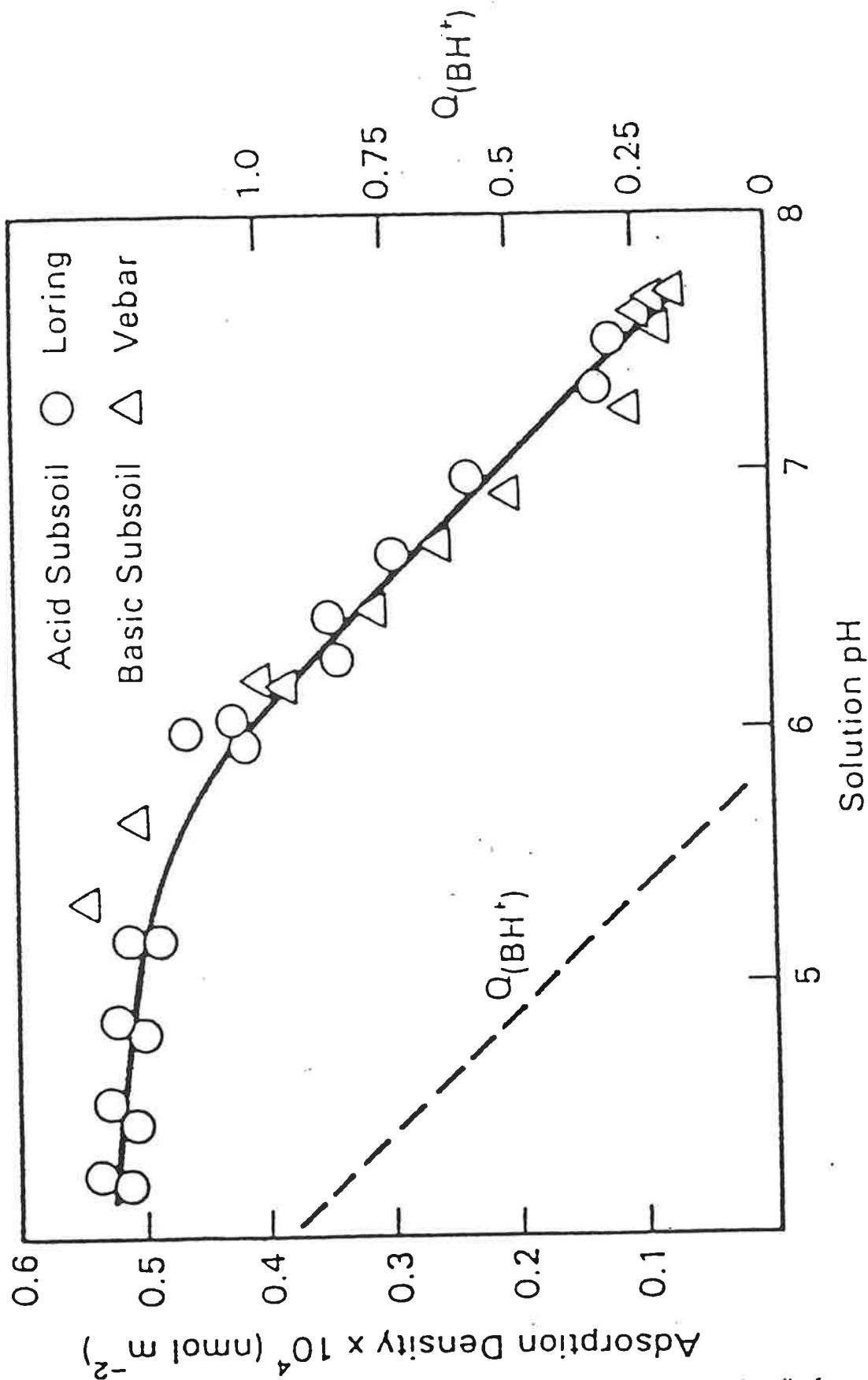
HIOC; the subscripts n and i refer to neutral and ionized species, respectively; and  $pK_a$  is the organic acid dissociation constant. Substantial deviations from eq (1a) suggest the predominance of specific sorption mechanisms (e.g., hydrogen bonding, ligand exchange). Lee (1993) applied eq (1a) to sorption data compiled from the literature for several other organic acids, and found that in most cases eq (1a) adequately described the sorption observed as a function of pH; Figure 3-1B shows an example of the agreement between the eq (1a) predictions and the reported pH-dependency of flumetsulam herbicide sorption by soils.

For sorption of organic bases, ion-exchange has been shown to be the controlling sorption mechanism even at pH values as much as two units greater than the solute  $pK_a$  (Ainsworth et al. 1987; Zachara et al. 1986, 1987, 1990). Figure 3.2 presents an example of the data reported by Zachara et al. (1986) for quinoline sorption by two subsoils. Note in Figure 3-2 that the observed change in quinoline sorption with bulk soil pH is not in direct response to the protonation of the organic base; enhanced protonation of quinoline at the soil-water interfaces accounts for the increased sorption (Zachara et al. 1986).

Competitive sorption in multi-component mixtures has been observed for N-heterocyclic compounds when pH is low enough that protonated form is the dominant species (Felice et al. 1985; Zachara et al. 1987). In contrast, for HOCs and neutral HIOCs competition has been reported to be minimal (Chiou et al 1983; Karickhoff et al. 1979; MacIntyre and deFur 1985; Rao et al. 1986; Schwarzenbach and Westall 1981; Zachara et al. 1987). The predominance of ion-exchange in the sorption of organic bases suggests the use of a sorption coefficient normalized to the cation exchange capacity of the sorbent as a first approximation, analogous to the use of  $K_{oc}$  for describing sorption of HOCs.

### 3.2.2. Sorption Nonequilibrium

The importance of accurately describing the effective travel time and recovery of a contaminant plume has stimulated the characterization of sorption nonequilibrium processes for organic chemicals. Brusseau and Rao (1989a) have



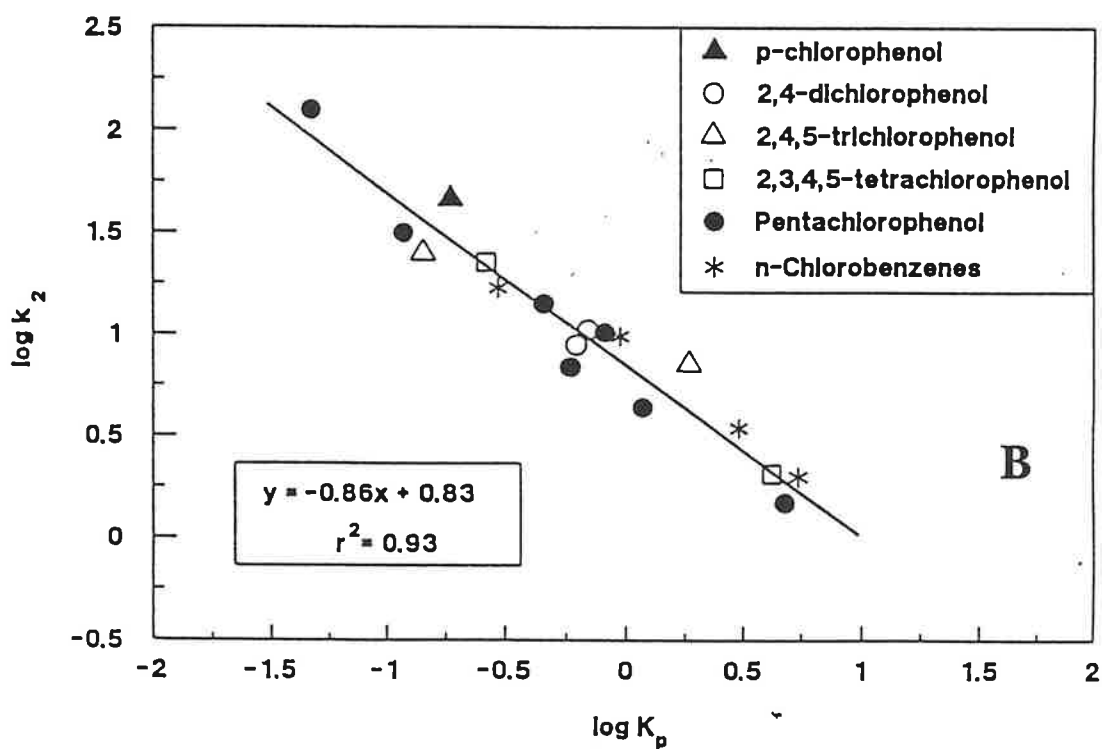
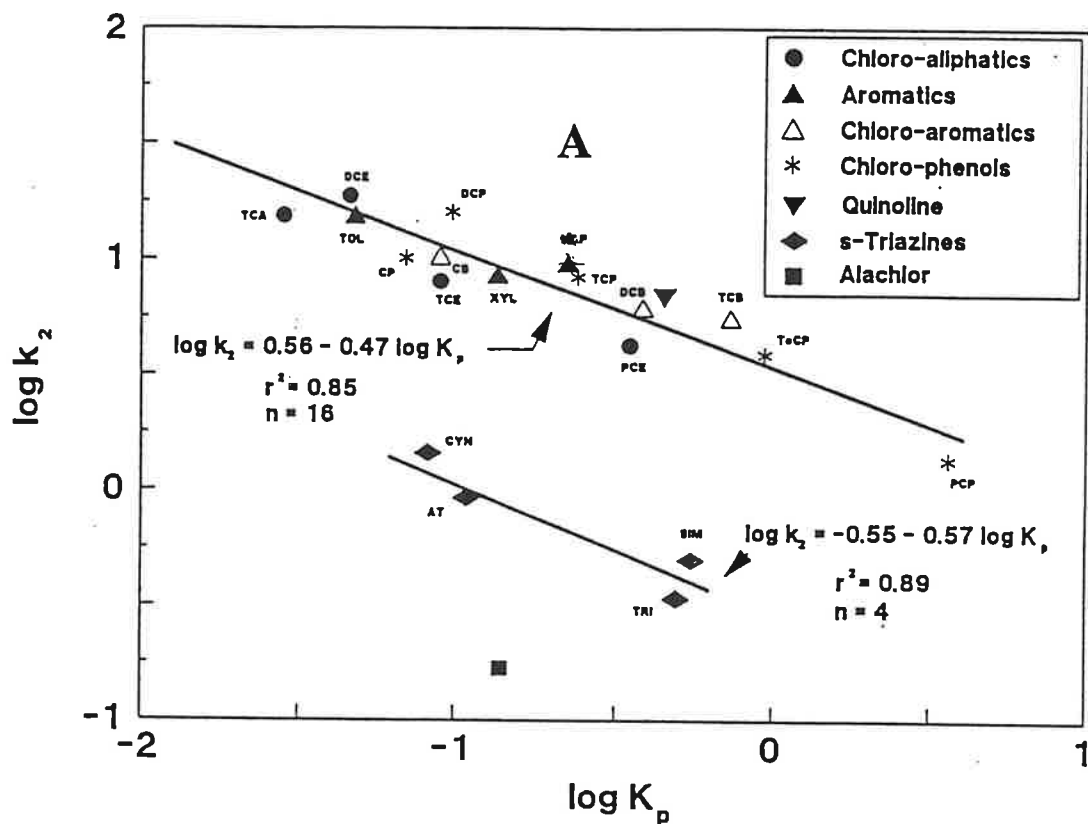
- Examples of pH-dependence of quinoline sorption by two subsoils from aqueous solutions. The dashed line shows the fraction of total quinoline present as the quinolinium cation. Taken from Zachara et al. (1986).

compiled and analyzed an extensive data base for sorption nonequilibrium; they noted an inverse log-log linear relationship between sorption rate coefficients ( $k_2$ ,  $h^{-1}$ ) and corresponding equilibrium sorption constants ( $K_p$ , mL/g). This inverse relationship has been confirmed by data collected from more recent studies (Brusseau et al. 1990, 1991a,c); see Figure 3-3A for an example of the sorption data compiled for several classes of organic solutes. Brusseau and Rao (1989a) postulated that the sorption nonequilibrium observed with HOCs in soils was due to intra-organic matter diffusion (i.e., diffusion into the organic matter matrix). Other researchers have proposed intra-granular (i.e., retarded diffusion within the pores of mineral particles) as the predominant mechanism for sorption nonequilibrium, especially for aquifer materials (Ball and Roberts 1991a,b). A detailed discussion on the processes affecting nonequilibrium sorption and transport is given by Brusseau and Rao (1989b).

Lee et al. (1991) also noted a single log-log inverse relationship between the  $k_2$  and  $K_p$  for several chlorophenols (regardless of ionization status) and for a series of chlorobenzenes (Figure 3-3B). This  $k_2$ - $K_p$  relationship was also similar to that observed by Brusseau and Rao (1989a) for HOCs suggesting that the processes controlling nonequilibrium sorption for chlorophenols are similar to those experienced by HOCs. For other classes of organic acids (e.g., carboxylic and phenoxy-acetic acids) and for organic bases (e.g., N-heterocyclic compounds), sorption nonequilibrium may be significantly influenced by pH and chemical nonequilibrium processes (i.e., rate-limited interactions between the solute and specific sites on the sorbent; chemisorption) (Brusseau and Rao 1989a; Brusseau et al. 1991c); however, limited data prevents any further assessment of their behavior.

### 3.3. COSOLVENCY

The effects on solubility and sorption (hence, on transport) of organic chemicals upon addition of one or more organic cosolvents to an aqueous solution are defined here as cosolvency. This section will focus on the most significant interactions affecting solubility and sorption of both HOCs and HIOCs. Such interactions include solute-cosolvent, cosolvent-cosolvent, and cosolvent-water



3. Examples of log-log inverse relationship between the sorption mass-transfer rate coefficient ( $k_2$ , hr<sup>-1</sup>) and equilibrium sorption coefficient ( $K_p$ , mL/g). (A) Taken from Brusseau and Rao (1991); (B) Taken from Lee et al. (1993).



interactions for solubility; for sorption, solvent-sorbent interactions must also be considered.

### 3.3.1. Solubility in Mixed Solvents

The log-linear cosolvency model and the UNIFAC model are among the theoretical approaches that have been used to examine cosolvent effects on solubility (Fu and Luthy 1986a; Pinal et al. 1990). The log-linear cosolvency model (Yalkowsky and Roseman 1981) is based on the central assumption that the logarithm of the solute solubility in a mixed solvent is given by the weighted-average of the logarithms of solubilities in the component solvents in the mixture; the weighing coefficient is taken to be the volume fraction of each solvent component. Thus,

$$\log S_m = \sum f_i \log S_i \quad (2)$$

where  $S$  is solubility (mg/L),  $f$  is volume fraction of the solvent, and the subscript  $m$  denotes mixed solvent and  $i$  the  $i$ -th cosolvent. Note that averaging the logarithms of solubilities is equivalent to averaging the free energies of solution in different solvents in the mixture. The UNIFAC model (Fredenslund et al. 1975) is a group-contribution scheme for calculation of the activity coefficients. This model is based on the UNIQUAC model (Abrams and Prausnitz 1975) and the solution-of-group concept (Wilson and Deal 1962). In this model, a mixture of different chemicals is treated as a mixture of the functional groups constituting the components in solution.

In many cases the UNIFAC model may be preferred over the log-linear model because: (1) it has a more sound theoretical basis, (2) activity coefficients in mixtures can be calculated given only pure component data, and (3) all possible interactions among the components in the mixture are explicitly considered. A limitation of the UNIFAC model, however, is that although the group interaction parameters required to estimate the solute activity coefficients are continuously reviewed and updated, their values are not available for a number of systems of interest here. Furthermore, the UNIFAC model provides poor estimates of HOC solubility in predominantly aqueous solutions (Fu and Luthy 1986a).

A convenient measure of the impact of a cosolvent on the solubility of an organic chemical is the cosolvency power ( $\sigma$ ), which is defined as:

$$\sigma = \log [S_c / S_w] \quad (3)$$

where the subscripts c and w refer to neat cosolvent and pure water, respectively. HOC solubility in organic solvents is larger than that in water, thus  $\sigma > 0$ . Larger values of  $\sigma$  indicate a greater solubilizing power of the solvent for a specific solute.

Rubino and Yalkowsky (1987a) and Pinal et al. (1990) have shown that  $\sigma$  values can be viewed as being equivalent to hypothetical partition coefficients for the HOC between a cosolvent and water. Morris et al. (1988) have shown that  $\sigma$  values can be correlated to HOC octanol-water partition coefficient ( $K_{ow}$ ) as follows:

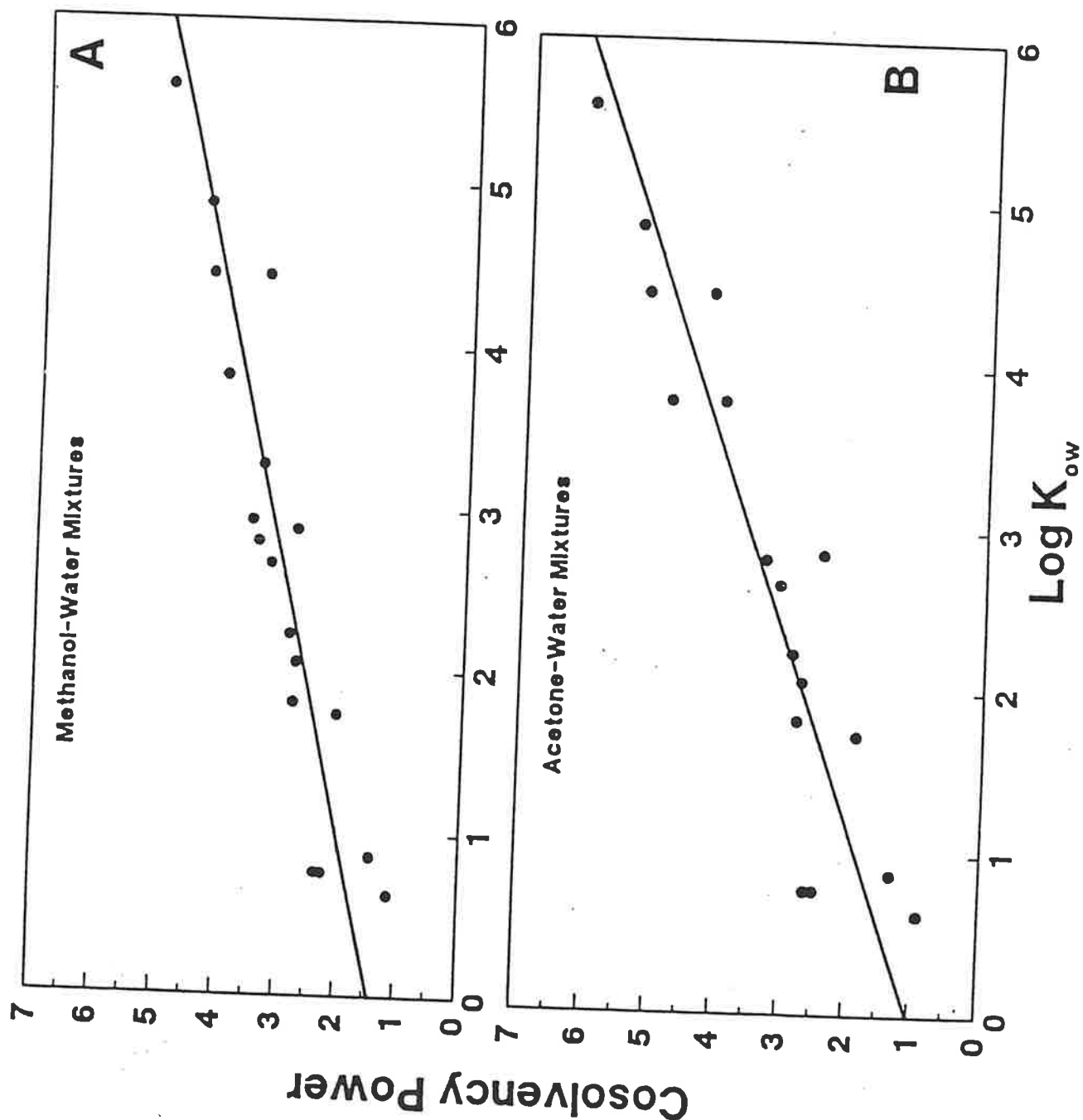
$$\sigma = a \log K_{ow} + b \quad (4)$$

where a and b are empirical constants unique for a given cosolvent. Figure 3-4 presents a plot of eq (4), where the  $\sigma$  values were estimated from HOC solubility profiles measured in methanol-water and acetone-water mixtures. It should be noted that other cosolvent and solute properties may also be used to estimate  $\sigma$  values (Morris et al. 1988; Rubino and Yalkowsky 1987a,b).

Although both eqs (3) and (4) provide useful first-order approximations of the cosolvency power of a solvent for a solute, measured HOC solubility profiles in solvent mixtures often exhibit deviations from the expected log-linear behavior primarily due to solvent-cosolvent interactions. The observed cosolvency in a binary mixed solvent can be more generally defined as,

$$\log S_m = \log S_w + \beta \sigma_c f_c \quad (5)$$

where  $\beta$  is an empirical constant that accounts for water-cosolvent interactions. Note that  $\beta = 1$  implies the absence of water-cosolvent interactions. Equation 5 provides only a reasonable approximation of the expected cosolvency effects, because solvent-solvent interactions are not constant over the entire  $f_c$  range. Pinal et al. (1991) proposed a modified log-linear model for estimating the solubility of HOCs in nonideal solvent mixtures which used the UNIFAC model to estimate expected deviations due to solvent nonideality as a function of  $f_c$ .



4. Relationship between cosolvency power ( $\sigma$ ) and log octanol-water coefficient ( $K_{ow}$ ) for several hydrophobic organic chemicals. Data compiled for solubility in methanol-water mixtures (A), and acetone-water mixtures (B) are shown. Taken from Rao et al. (1991).

### 3.3.2. Equilibrium Sorption from Mixed Solvents

#### 3.3.2.1. Hydrophobic Organic Chemicals (HOCs)

A log-linear cosolvency model describing the decrease in sorption of HOCs with increasing  $f_c$  in a binary solvent is given by (Fu and Luthy 1986b; Rao et al. 1985):

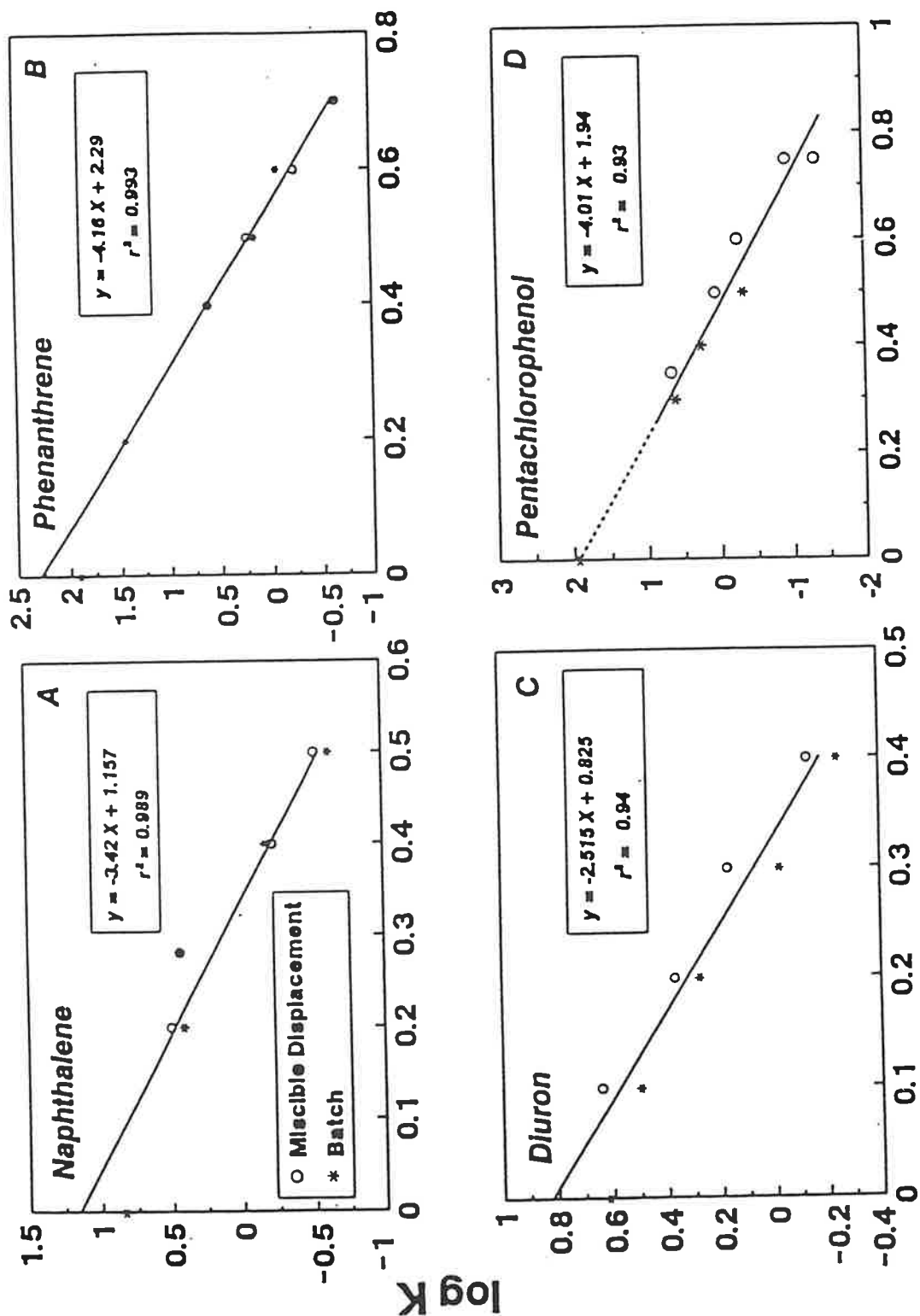
$$\log K_b = \log K_w - \alpha \beta \sigma_c f_c \quad (6)$$

where  $K$  is the equilibrium sorption coefficient (mL/g),  $\alpha$  and  $\beta$  are empirical constants for describing solvent-solvent and solvent-sorbent interactions, and the subscript  $b$  stands for binary mixed solvent. For a mixture of water and multiple cosolvents, eq (6) may be extended as follows (Rao et al. 1985; Rao and Lee 1987; Woodburn et al. 1986):

$$\log K_m = \log K_w - \sum \alpha_i \beta_i \sigma_i f_i \quad (7)$$

where the subscript  $m$  denotes mixed solvent and the other terms are as defined earlier.

An extensive amount of data has shown that in binary mixed solvents, HOC solubility increases and sorption decreases in a log-linear manner as the volume fraction of the organic cosolvent increases (Fu and Luthy 1986a,b; Nkedi-Kizza et al. 1985, 1987, 1989; Rao et al. 1985, 1986, 1989, 1990; Rubino and Yalkowsky 1985, 1987a,b,c; Walters and Guissepi-Ellie 1988; Woodburn et al. 1986; Yalkowsky 1985, 1987). Examples of the log-linear decrease in sorption of several organic solutes are presented in Figure 3-5. These experimental findings are consistent with the predictions of both the UNIFAC model and the log-linear cosolvency model. The successful application of the log-linear model to describe solubility and sorption in ternary and quinary mixed solvents has also been demonstrated (Rao and Lee 1987; Rubino et al. 1984; Rubino and Yalkowsky 1985; Yalkowsky and Rubino 1984). Lane and Loehr (1992) measured the dissolution/desorption of several polycyclic aromatic hydrocarbons from tar-contaminated soils. They successfully applied the log-linear cosolvency model to predict the aqueous phase concentrations by extrapolating from data collected in a few binary solvents mixtures.



Volume Fraction Methanol

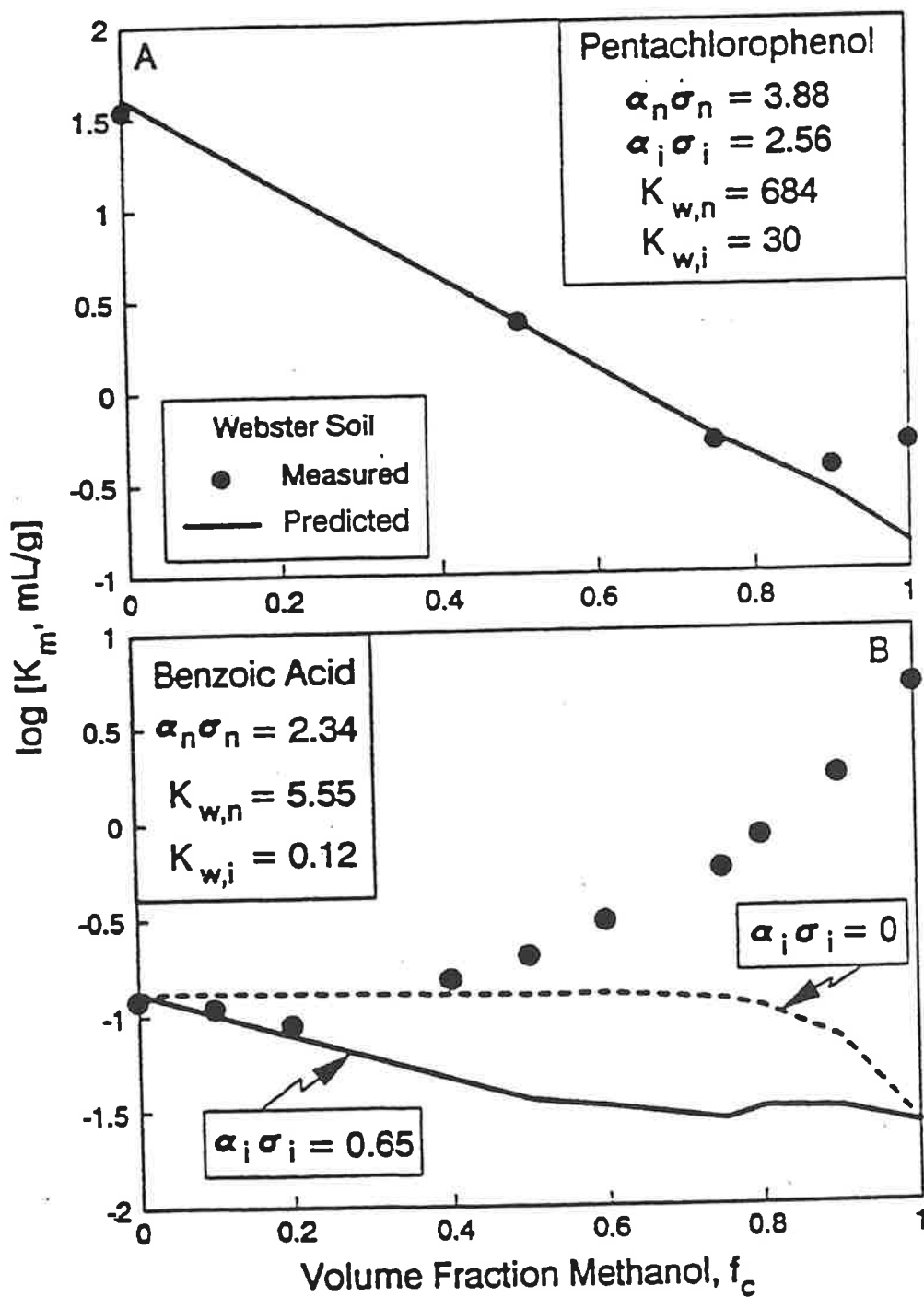
5. Log-linear decrease in equilibrium sorption coefficient (K, mL/g) and volume fraction methanol for sorption of several organic solutes. Taken from Rao et al. (1991).

### 3.3.2.2. Hydrophobic Ionogenic Organic Chemicals (HIOCs)

For hydrophobic ionogenic compounds (HIOCs) of environmental interest, data on solubility, sorption, and transport in mixed solvents are limited. However, pharmaceutical literature contains solubility data for several drugs spanning a wide polarity range. Yalkowsky and Roseman (1981) observed that as solute polarity increases relative to the solvent, the solubilization curves become increasingly more parabolic in shape until an inverse relationship occurs (i.e., decreased solubility with cosolvent additions). Such behavior is explained on the basis of the solute-solute and solute-cosolvent interactions.

The sorption of HIOCs from mixed solvents has received little research attention to date. For several HIOCs of environmental relevance ( $\log K_{ow} > 1.0$ ), solubility does increase with increasing  $f_c$ , thus a decrease in sorption is expected. However, prediction of HIOC sorption from mixed solvents is confounded by a number of indirect effects resulting from cosolvent-induced phenomena occurring either in the solution phase or on the sorbent. For an organic acid in solvents of low dielectric constants (e.g., methanol, acetone, dimethylsulfoxide) an alkaline shift in the solute  $pK_a$  results in an increase in the fraction of neutral species.

Zachara et al. (1988) evaluated the sorption of quinoline by a clay isolate and montmorillonite in methanol/water solutions over a range of 0 to 60 volume per cent methanol, but the log-linear relationship was confirmed only up to 40% methanol by volume. In soil thin-layer chromatography studies (Hassett et al. 1981), dicamba (3,6-dichloro-2-methoxybenzoic acid) moved with the solvent front in both aqueous and 50/50 (v/v) ethanol/water solutions, but was strongly retained by soil with neat ethanol as the mobile phase. The greater retention of dicamba in neat ethanol over that in aqueous solutions was attributed to solute-solvent interactions. Lee et al. (1993) investigated the sorption by soils of several substituted phenols and carboxylic acids in methanol/water solutions. As shown in Figure 3-6A, they successfully described the cosolvency behavior of the substituted phenols by a model incorporating both speciation and cosolvent effects (i.e., summation of eqs 1 and 6). However, large positive deviations from the proposed model were observed for the



6. Comparison of measured (data points) and predicted (dashed and solid lines) impacts of methanol on equilibrium sorption coefficient ( $K_m$ ) for sorption of pentachlorophenol (A) and benzoic acid (B) from methanol-water mixtures. Taken from Lee et. al. (1993).

sorption of benzoic acid (Figure 3-6B), especially at high cosolvent contents, suggesting the role of some type of cosolvent-enhanced surface complexation mechanism(s). Further investigation is needed to better understand the impacts of cosolvents on HIOC interactions with soils.

### 3.3.3. Sorption Nonequilibrium in Mixed Solvents

Cosolvents have been shown to influence the rate at which sorption equilibrium is attained. The inverse log-log relationship between the sorption rate constant ( $k_2$ ) and the equilibrium sorption coefficient ( $K_w$ ) for aqueous systems, and the inverse, log-linear relationship between sorption coefficient and volume-fraction cosolvent ( $f_c$ ) suggests that  $k_2$  would increase in a log-linear fashion with increasing  $f_c$ :

$$\log k_{2,m} = \log k_{2,w} + A \alpha \beta \sigma_c f_c \quad (8)$$

where  $A$  is an empirical coefficient, and other parameters are as defined previously. Figure 3-7 presents a compilation of experimental data from column studies confirming eq (8). Brusseau et al. (1991b) suggested that as the cosolvent content increases, the polymeric organic matter swells; this leads to enhanced rates of solute permeation and is reflected in faster intra-organic matter diffusion rates (i.e., increased  $k_2$  values).

### 3.3.4. Cosolvency and Contaminant Transport

Sorption effects on contaminant transport can be conveniently expressed using the retardation factor ( $R$ ) defined as follows:

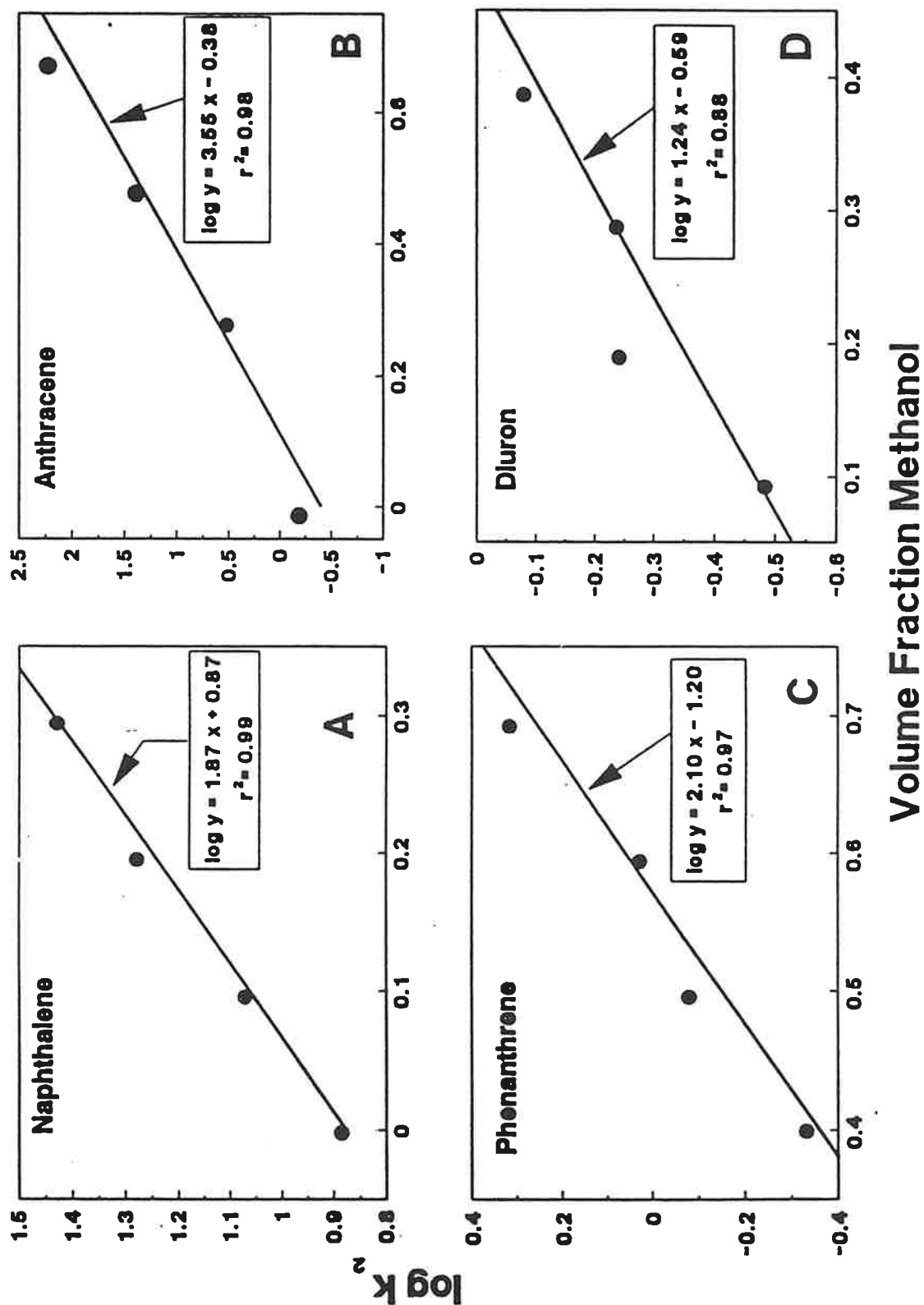
$$R_w = [1 + (\rho K_w / \theta)] \quad (9)$$

where  $\rho$  is the soil bulk density,  $K_w$  is equilibrium sorption coefficient (for sorption from aqueous solutions), and  $\theta$  is the volumetric soil-water content. Note that for a nonsorbed solute,  $R=1$  since  $K_w=0$ . Equation (9) can be modified to account for cosolvent effects by substituting eq. (6) for  $K_w$  in eq (9), and rearranging, to give:

$$\log (R_m - 1) = \log (R_w - 1) - \alpha \beta \sigma_c f_c \quad (10)$$

Therefore, an increase in solubility upon cosolvent addition is reflected in a decrease in sorption and retardation. Nkedi-Kizza et al. (1987) and Wood et al. (1990) have demonstrated the validity of eq (10) with experimental data collected from soil column





7. Log-linear dependence of sorption mass-transfer rate coefficient ( $k_2$ ,  $\text{hr}^{-1}$ ) and volume fraction methanol. Taken from Rao et al. (1991).

studies with several organic contaminants under conditions of isocratic elution (i.e.,  $f_c$  was time invariant).

### 3.4. PARTITIONING FROM MULTI-PHASIC LIQUIDS

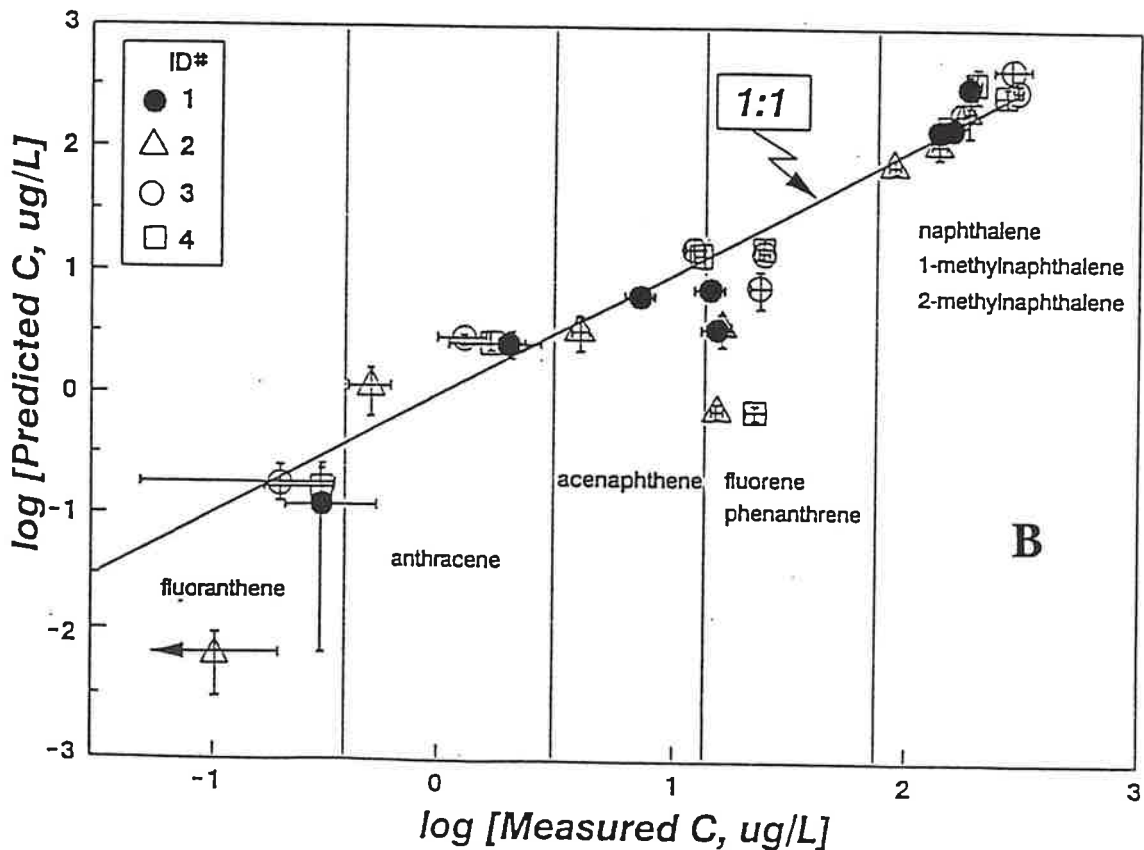
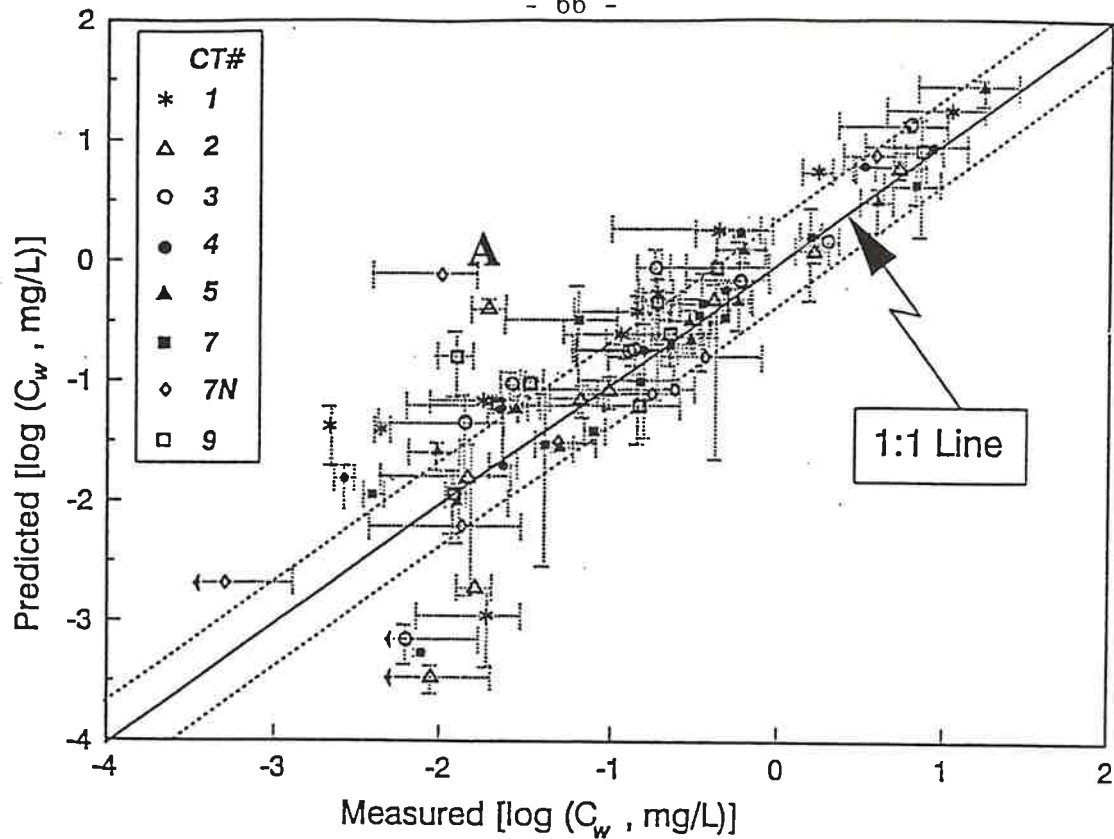
An understanding of solubility (or partitioning) of HOCs from complex liquids is essential for predicting contaminant release from mixtures such as fuels (e.g., gasoline, diesel, kerosene) and industrial wastes (coal tar, creosote). The solubility of a given component in a mixture may be altered by other components that may act as cosolutes or cosolvents. According to the model based on Raoult's law, the concentration of an organic constituent in the aqueous phase ( $C_w$ ) in equilibrium with an "ideal" organic mixture is equal to the product of the mole fraction ( $X_o$ ) of that constituent in the organic phase and the pure compound solubility ( $S_l$ , moles/L) in its liquid phase (i.e.,  $C_w = X_o S_l$ ). Note that for solids,  $S_l$  is the solubility of a hypothetical super-cooled liquid. Examining the ideality of the entire system in a single, graphical representation is made feasible by considering the liquid-liquid partition coefficient ( $K_D$ ). Application of Raoult's law and the assumption of ideal behavior yields the following relationship (Cline et al. 1991; Lee et al. 1992b):

$$\log K_D = -\log S_l - \log \bar{V}_o \quad (11)$$

where  $\bar{V}_o$  is the molar volume of the organic phase which can be estimated by the ratio of the average molecular weight ( $MW_o$ , g/mole) and the density of the organic phase ( $\rho_o$ ). It is evident from eq (11) that a linear inverse relationship exists between  $\log K_D$  and  $\log S_l$  where the slope is negative one and the intercept is dependent on the molar volume ( $\bar{V}_o$ ) of the particular organic mixture. Using this relationship, the assumption of ideal behavior can be conveniently assessed for a complex mixture with minimal number of easily obtained parameters.

Cline et al. (1991) and Lee et al. (1992a,b) presented data for liquid-liquid partitioning of hydrocarbons from several gasolines, diesel fuels, and coal tars. As indicated by the data shown in Figure 3-8, their analysis suggests that deviations from ideal behavior (Raoult's law) are within a factor-of-two or less in most cases.

Agreement between the model predictions based on Raoult's law and measured liquid-



8. Comparison of measured and predicted aqueous-phase concentrations of several polycyclic aromatic hydrocarbons partitioning from coal tars (A) and diesel fuels (B) into water. The predictions were based on eq (12) with the assumption that ideal behavior is valid. Taken from Lee (1993).

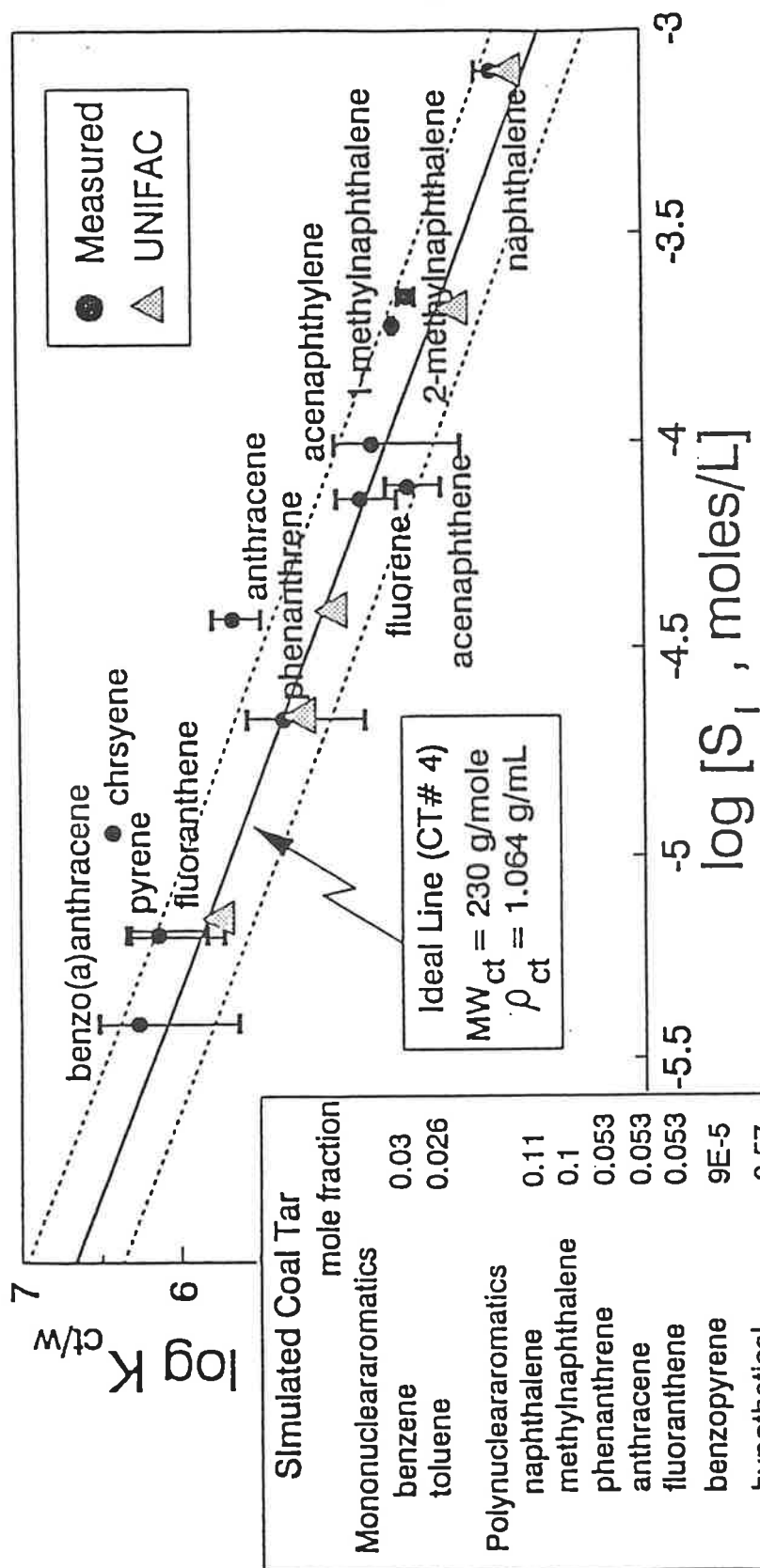
liquid partitioning data is not to be taken as evidence that complex organic wastes are indeed ideal mixtures. Rather, the assumption of ideal behavior might suffice for practical considerations in providing first-order estimates for maximum contaminant concentrations likely to be found in groundwater leaving such a waste source.

The magnitude of the deviations from solute-solute interactions that might lead to nonideal partitioning behavior for complex liquid mixtures may be evaluated using the UNIFAC model. Two problems are encountered in such attempts. First, it is extremely difficult to characterize (either qualitative or quantitative) the composition of these wastes. For example, no more than about 60% of the coal tar constituents can be identified and quantified using sophisticated chromatographic techniques. Second, even if the compositional information were available, the necessary UNIFAC model parameter values may not always be available in existing compilations. Thus, it is often necessary to replace the complex mixture with a simpler, hypothetical mixture comprising of fewer compounds, as was done by Lee et al. (1992a,b) in analyzing the data for gasolines and diesel fuels. A comparison of the UNIFAC model predictions with measured tar-water partition coefficients is shown in Figure 3-9.

Peters (1992) investigated the dissolution of coal tar in binary mixed solvents. She evaluated the feasibility of representing coal tar as a single "psuedo" component in order to evaluate an approach based on ternary phase diagrams. Parameter estimation techniques for describing the tar/solvent/water system was successful. However, Peters (1992) concluded that the predictive power of the model is currently limited by a lack of accurate binary data and the need to use several tie lines.

### 3.5. ENVIRONMENTAL APPLICATIONS

The likely presence of organic cosolvents at waste disposal/spill sites will result in higher concentrations of organic contaminants in pore water, since an increase in the concentration of organic cosolvents is reflected in decreased sorption. Decreased sorption, in turn, will lead to organic contaminants being transported farther than predicted from aqueous-based transport data. While this manifestation of cosolvency can exacerbate environmental problems, judicious application of the



9. Comparison of measured (solid circles) tar-water partition coefficients and predictions based on the UNIFAC model (triangles) and the Raoult's law approach (solid and dashed lines). The assumed composition of the coal tar, used in UNIFAC model calculations, is shown in the inset. Taken from Lee (1993).

principles of cosolvency can assist in alleviating existing problems. For example, removal of contaminated soils from a disposal/spill site and extraction with solvent mixtures (so-called "solvent washing") is one remediation technique that is receiving considerable attention.

#### 3.5.1. Magnitude of Cosolvent Effects

A variety of organic cosolvents may be expected at and near waste disposal sites, especially if codisposal of a number of wastes had been practiced. However, protocols for site investigations usually do not call for monitoring of organic cosolvents in groundwater. Site-specific information on concentrations and types of cosolvents that may be present can be surmised only if waste composition is known. Thus, estimating the magnitude of cosolvent impacts in enhancing solubility and decreasing sorption/retardation is often difficult. Although direct field-scale evidence for cosolvency is lacking, anecdotal evidence from site investigations suggests that organic cosolvents are present and may have contributed to facilitated transport of organic contaminants at waste disposal facilities. Our data and model calculations suggest that solubility enhancement for most organic contaminants is likely to be small (< 20% increase) as long as cosolvent concentrations in pore water are < 2% by volume (or about 20,000 mg/L). Thus, dramatic alterations of chemodynamic properties are to be expected only in close proximity to a disposal site (i.e., the "near-field" region) where high concentrations of cosolvents are likely. With increasing distance from the site, cosolvent effects should diminish in proportion to decreasing cosolvent concentrations.

#### 3.5.2. Dissolution of Multi-Component OIL Constituents

Available data (Cline et al. 1991; Lee et al. 1992a,b) indicate that Raoult's law can be used to provide reliable estimates of organic contaminant concentrations in groundwater in contact with multi-component OILs, such as gasolines, diesel fuels, and coal tars. Even though these wastes are complex liquid mixtures, the nonideality resulting from interactions with other constituents is apparently sufficiently small to be

neglected for most practical applications. Equilibrium or maximum concentration of a multi-component OIL constituent in groundwater,  $C_w$  (mg/L), can be estimated as follows:

$$C_w = M_o \frac{MW_o}{S_l} \quad (12)$$

where  $M_o$  is the concentration (mg/g) of a specific constituent in the organic phase,  $MW_o$  is average molecular weight of the organic mixture (g/mole), and  $S_l$  is the super-cooled liquid solubility (moles/L).

Table 3.1 summarizes the range of likely maximum concentrations of selected hydrocarbons in groundwater which is in contact with some multi-component OILs. Equation (12) was used along with information on the composition of the waste mixtures (Cline et al. 1991; Lee et al. 1992a,b; Millner et al. 1992). Equilibrium for liquid-liquid phase partitioning was assumed in calculating the values in Table I. The range in calculated  $C_w$  values is a direct reflection of the wide diversity in waste composition (both within and between waste types). Note that the aqueous-phase concentrations will reflect the changes in composition of the waste, as it "ages". Nonequilibrium conditions, arising from various mass-transfer constraints, as well as dilution and degradation processes will result in the actual concentration being smaller than those shown in Table 3-1. The possibilities of sampling artifacts (e.g., formation of emulsions during pumping) (Thomas and Delfino 1991) need to be examined when the measured aqueous-phase concentrations are found to be much larger than those estimated assuming ideal behavior (i.e., Raoult's law).

### 3.5.3. Remediation of Contaminated Soils

Contaminated aquifers have traditionally been remediated by pump-and-treat methods. With increasing awareness of the limitations to "pump-and-treat" methods to effectively clean up groundwater contaminated with organic pollutants, interest exists in new remediation techniques based on chemical additives that increase the efficiency of rate at which contaminants are removed (Palmer and Fish 1992). In situ soil flushing is one such remediation technique that involves the injection of a mixed solvent (water plus organic cosolvents) or a surfactant at a site

Table 3-1. Maximum  $C_w$  values (25°C) for Several PAHs Based on the Data Compiled for Thirty Gasolines, Four Diesel Fuels, and Eight Coal Tars. Liquid-liquid Partitioning Data Reported by Cline et al. (1991) and Lee et al. (1992a,b) Were Used to Calculate the  $C_w$  Values.

| Compound            | Aqueous Solubility<br>$S_w$ (mg/L) | Range of Maximum $C_w$ (mg/L) |              |            |
|---------------------|------------------------------------|-------------------------------|--------------|------------|
|                     |                                    | Gasolines                     | Diesel Fuels | Coal Tars  |
| Benzene             | 1780                               | 1 - 130                       | 0.05 - .4    | < 30       |
| Toluene             | 515                                | 20 - 200                      | 0.3 - 6      | < 10       |
| Ethylbenzene        | 150                                | 1 - 6                         | 0.03 - .15   | < 5        |
| Xylenes             | 200                                | 2 - 25                        | 0.2 - 2      | < 10       |
| Naphthalene         | 32                                 | --                            | 0.1 - .3     | 1 - 26     |
| 1-Methylnaphthalene | 27                                 | --                            | 0.1 - .2     | 0.2 - 2    |
| 2-Methylnaphthalene | 26                                 | --                            | 0.2 - .35    | 1 - 1.4    |
| Acenaphthylene      | 3.93                               | --                            | --           | 0.01 - 0.5 |
| Acenaphthene        | 3.42                               | --                            | 0.004 - 0.02 | 0.02 - 0.3 |
| Fluorene            | 1.9                                | --                            | 0.01 - 0.03  | 0.1 - 0.3  |
| Phenanthrene        | 1.0                                | --                            | 0.01 - 0.03  | 0.1 - 0.4  |
| Anthracene          | 0.07                               | --                            | < 0.002      | < $S_w$    |
| Fluoranthene        | 0.27                               | --                            | < 0.005      | < 0.01     |
| Pyrene              | 0.16                               | --                            | --           | 0.02 - 0.1 |
| Benzo(a)anthracene  | 0.0057                             | --                            | --           | < $S_w$    |
| Chrysene            | 0.006                              | --                            | --           | < $S_w$    |
| Benzo(a)pyrene      | 0.0038                             | --                            | --           | < 0.001    |



contaminated with organic chemicals (U.S. EPA 1991). Site remediation efforts may involve any of the described regions. Soil flushing would be most logically applied for clean up of the source area, since removal of the source prevents further contamination of groundwater. Excavation of the soil from the source area is an alternative option, but the contaminated soil still requires treatment (e.g., incineration, solvent washing) before it can be safely disposed. Excavation can also be very expensive, especially when a large volume of soil is contaminated, and may not even be possible when, for example, the source is located under permanent structures. In such cases, soil flushing may be considered as a more plausible alternative.

In-situ soil flushing involves the following steps (U.S. EPA 1991): (1) the solvent mixture or surfactant is injected upstream of the contaminated zone, (2) the additives with the dissolved contaminants are extracted downstream and treated above ground to recover the solvent, and (3) the recovered additives may be reinjected. Physical barriers (e.g., sheet piling, slurry walls) or hydraulic control measures might be needed to prevent off-site transport of contaminants with the chemical additives. The cosolvency concepts discussed earlier may be used in developing criteria for the selection of solvents or solvent mixtures to achieve optimal extraction of the contaminants of interest. For example, other factors being equal, it may be preferable to choose a solvent with greater cosolvency power (larger  $\sigma$ ) so that the contaminants can be extracted using less solvent. If economic or other constraints prevent the use of pure organic solvents and a mixture of water and cosolvents are to be used, the log-linear cosolvency model might provide reasonable estimates of the level of extraction achievable with various combinations of cosolvents.

The use of surfactants for remediation of contaminated soils has been studied extensively (see review by Palmer and Fish 1992). The presence of surfactants increases the apparent solubility and decreases the sorption of HOCs. Surfactants are more efficient than mixed solvents; i.e., an equivalent increase in solubility is achieved at a much lower concentrations of a surfactant compared to a cosolvent. In addition, surfactants may facilitate emulsification of OILs (which enhances contaminant removal) to a greater extent than cosolvents. However,

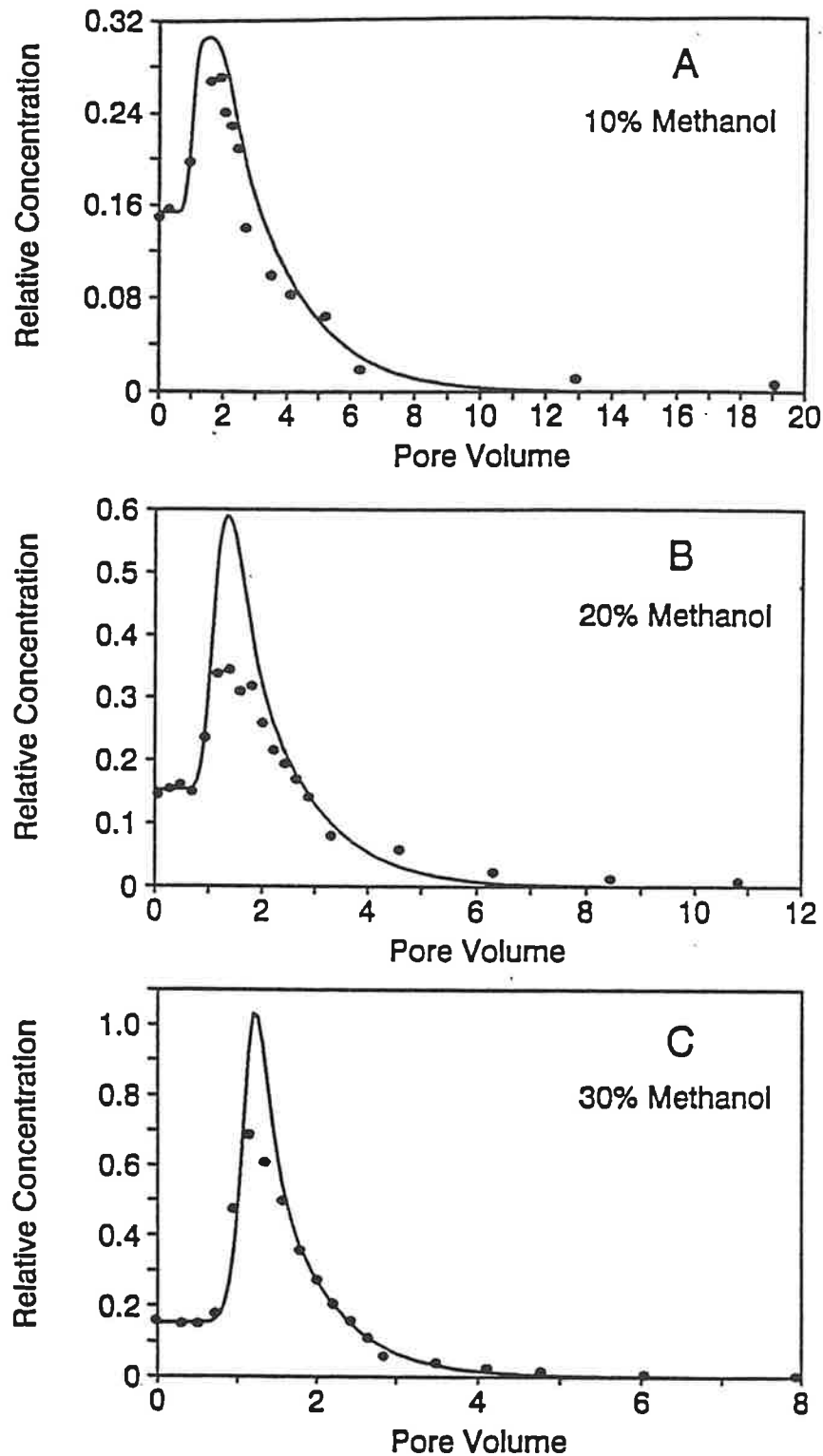
surfactants do not reduce nonequilibrium constraints as do cosolvents. Furthermore, when contrasted to cosolvents the delivery of surfactant solutions to the contaminated areas within a heterogeneous medium might be more difficult.

The use of cosolvents for extraction of organic contaminants from various environmental matrices has been successfully demonstrated either at the pilot-scale or in full-scale commercial applications (U.S. EPA 1990). Currently, laboratory research is being conducted to evaluate the use of solvent-flushing (Augustijn et al. 1993; Luthy et al. 1993). Augustijn et al. (1993) presented a simulation model to predict contaminant elution curves during solvent flushing for the case of one-dimensional, steady flow through a contaminated soil. They also conducted column experiments with a Eustis fine sand that was initially equilibrated with an aqueous naphthalene solution, and then eluted with methanol-water solutions (cosolvent content 10, 20, and 30%) to remove naphthalene. The model simulations, based on parameter values estimated using literature data, agreed well with the measured elution profiles for naphthalene displacement with methanol-water solutions (see Figure 3-10). In general, the higher the cosolvent fraction and the smaller the retardation factor in water, the faster the contaminant was recovered. Model parameter sensitivity analysis suggested that the presence of nonequilibrium conditions, soil heterogeneity and type of cosolvent will influence the required time to recover the contaminant.

### 3.6. SUMMARY

Industrial waste disposal/spill sites are characterized by the presence of complex organic mixtures of multiple contaminants, present at high concentrations. In addition, the waste may be composed of several distinct immiscible phases of solvent mixtures. Several empirical and semi-empirical relationships have been developed to describe contaminant behavior in these complex systems were reviewed.

Three separate regions within a contaminant plume have been discussed: a near-field region, a transition zone, and a far-field region. Most data are available for the environmental fate and transport of organic contaminants in the far-field region, where the waste constituents are present in an aqueous solution.



10. Elution profiles for naphthalene displacement from a soil column with mobile phases containing different methanol contents. Measured (data points) are compared with model predictions (solid lines) for cosolvent flushing of contaminated soils. Taken from Augustijn et al. (1993).

Sorption of HOCs can be predicted from various solute properties and the OC content of the soil or aquifer material. Due to their polar nature, adsorption of HIOCs is subject to specific interactions with the solid surface. Adsorption of HIOCs has been shown to be a function of pH, OC and  $pK_a$ . In all regions nonequilibrium conditions may be present. Again, this has been best quantified for the far-field region where the sorption rate coefficient has been found to be inversely related to the equilibrium sorption coefficient.

In the transition zone, contaminants may be dissolved in a solution phase that is made up of water and varying amounts of cosolvents. Solubility increases linearly in the presence of cosolvents, while sorption decreases proportionately and nonequilibrium constraints are reduced. The effects of cosolvents in solubility and sorption for HOCs have been successfully described by a log-linear model. The UNIFAC model or a modified log-linear model are available to account for nonideal behavior due to solute-solvent-cosolvent interactions. Limited available data indicate that the log-linear cosolvency model may not always predict the cosolvent effects on solubility and sorption of HIOCs, especially at higher cosolvent contents. Further research is needed to explain the deviations observed from the predicted sorption of HIOCs from mixed solvents.

Phase partitioning is the primary process that determines the release of contaminants from the near-field region, which includes the source. Raoult's law has been shown to adequately describe equilibrium phase partitioning for several multi-components OIL wastes, including gasolines, diesel fuels, and tars. However, limited information is available on the rate-limiting processes controlling contaminant release in the near-field region of sites containing OIL wastes.

The cosolvency concepts are useful in defining the magnitude of enhanced contaminant transport at waste disposal/spill sites. It is apparent that high cosolvent contents required to produce dramatic alterations in contaminant solubility and sorption are likely only in close proximity to the source (i.e., in the near-field region). Cosolvents may be used for remediation of contaminated soils. Commercial-scale applications of solvent extraction have been demonstrated. The use of

cosolvents and surfactants for in-situ flushing of contaminated sites appears promising, as evident from laboratory-scale tests. Field-scale studies are underway to evaluate the use of surfactants for remediation of contaminated soils. Similar studies for the use of cosolvents are in the design stages.

### 3.7. ACKNOWLEDGEMENTS

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### 3.8. DISCLAIMER

Although the research presented in this article has been partially funded by the U.S. Environmental Protection Agency and the U.S. Department of Energy through cooperative agreements, it has not been subjected to technical and policy review by either Agency, and therefore this manuscript does not necessarily reflect the views of the Agencies, and no official endorsement should be inferred.

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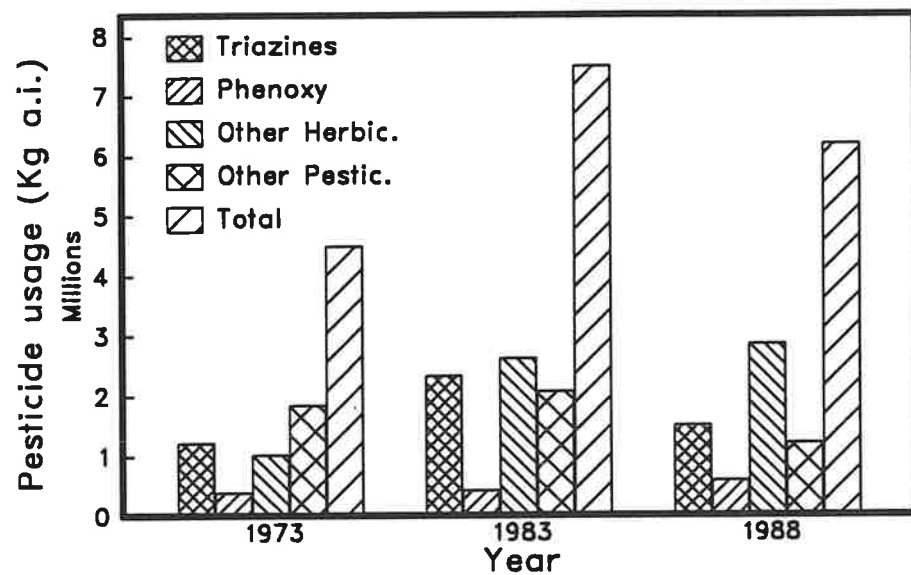
#### 4. INTENTIONAL ANTHROPOGENIC ADDITIONS TO SOILS: PESTICIDES

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##### 4.1 INTRODUCTION

Although agricultural pesticide usage in Canada began to increase following World War II, its rate did not increase rapidly until the early 1970's. From 1971 through 1976, pesticide sales in Canada more than tripled from approximately \$200 M to almost \$700 M (Hall 1981). By 1981, over 400 pesticides, based on active ingredient, were registered for use in Canada, appearing in over 3000 registered formulations. In Ontario, the total pesticide usage was 4.5 M kg in 1973 (Roller 1975), increasing to 7.5 M kg in 1983 (McGee 1984), and decreasing to 6.2 M kg (Moxley 1989) in 1988 (Figure 1). The non-herbicide component (insecticides, fungicides, growth regulators) has steadily decreased from 41.2% (1973) to 27.8% (1983) to 19.6% (1988). Canada's Research/Development in the pesticide industry has been rather minuscule, forcing us to use products developed in other countries, primarily in the U.S.A. We have developed our own set of registration protocols which, although often a subset of American protocols, usually steered a middle course between U.S. Environmental Protection Agency and European Organization of Economic Cooperation and Development (O.E.C.D.) protocols, with additional testing specific for Canadian conditions, such as for regional climatic and soil differences.

In the late 1950's and early 1960's, the widespread availability of commercially formulated pesticides ushered in a new era in which farmers were able to increase greatly both the yield and quality of their agricultural products, as well as improving their profitability. Application recommendations were often based on amounts necessary to prevent, or greatly suppress, a pest problem throughout the production season, rather than simply controlling it when the particular pest was a problem (the definition of "pest" in this context is broadly based, including any unwanted species, including plants and fungi as well as insects). The perception existed that farmers were now able to "control" or "manage" their production environment in a way never before possible in the history of agriculture. This led to the



Note: Other Pesticides includes insecticides, fungicides, growth regulators  
Source: Economics Information, O.M.A.F., Prov. of Ontario

**Figure 1.** Pesticide usage trends in Ontario, 1973, 1983, and 1988.

concept that large-scale monoculture practices for crops, such as corn and soybeans, were not only possible, but the economical and logical way to proceed.

Little attention was paid to the effects of pesticides upon non-target organisms (pests or plants), nor the long-term consequences of such practices upon soil and water quality. By the late-60's the "miracle" herbicides, such as the triazines, combined with a new generation of larger agricultural equipment made it possible for farmers to convert quickly considerable acreages of idle pastureland into productive cornland. Those practices often resulted in moderate-to-severe soil erosion where excessive and careless herbicide application severely damaged grassed waterways and fence bottoms. By 1973 in Ontario, almost 1.8 million kg of herbicides were used on corn, while approximately 355000 kg were applied to soybeans (Roller 1975).

In the early 1970's, an awareness began to develop of negative side-effects of organochlorine insecticides upon non-target species, especially in those avian species which preyed upon those lower in the food chain. Biomagnification of these fat-soluble, hydrophobic pesticides in these species manifested itself in the form of gross abnormalities, and in lowered survivability of the egg hatch and of the remaining young (Peakall 1970). Most of the organochlorine insecticides were banned from the marketplace by the latter part of that decade, to be largely replaced with another class of pesticide, the carbamates. Although this group of pesticides did not tend to exhibit the adverse biomagnification effects of their predecessors, they were actually much more toxic to a wide variety of species, including earthworms, honeybees and, in general, mammals (Broadbent and Tomlin 1982; Harris and Miles 1975). However, the negative side effects of pesticide usage were now better recognized, and integrated pest management techniques became more widely accepted and used. Instead of applying blanket pesticide applications throughout the production season, attention was focussed on the most susceptible period for the target species (Harris 1972), and on how much pesticide was required to suppress, but not necessarily totally wipe them out.



During the 1980's, environmental issues grew rapidly in importance, and more sophisticated modelling scenarios were developed as an aid in predicting the transport and persistence behaviour of pesticides in various ecosystems. In most of the pesticide transport models, two particular parameters are of prime importance: a parameter to describe the partitioning between soil and water, the soil-water partitioning coefficient ( $K_d$ ); and a parameter to describe the time required for one-half of the applied pesticide to disappear ( $T_{1/2}$ ) based on first-order kinetics, where  $T_{1/2} = 0.693/k$ , and  $k$  is the first-order disappearance rate constant. Much of the discussion that follows deals with issues and techniques surrounding the use of these key parameters, and problems associated with accurately measuring and correctly using them.

## 4.2. PHYSICAL, BIOLOGICAL AND CHEMICAL REACTIONS WITH SOIL

### 4.2.1 Soil Sorption of Pesticides

The bonding mechanisms responsible for pesticide retention by soil components include most of the classical physical (and some chemical) bonding forces, which have been reviewed elsewhere (Chesters et al. 1989). "Sorption" is a general term used to describe solute or vapour uptake by soil without being specific about the mechanism. "Adsorption" onto a solid refers to condensation of solute or vapour on the surface of the adsorbent, and depending on the definition, usually includes interior pores of a porous adsorbent such as soil aggregates, or the interlamellar surfaces of clay minerals. Mingelgrin and Gerstl (1983) defined "adsorption" as the "excess of solute concentration at the solid-liquid interface over the concentration in the bulk solution, regardless of the nature of the interface region or of the interaction between the solute and the solid surface causing the excess".

The sorption of nonionic pesticides by soils is influenced by a wide range of both chemical and soil factors, including solute and solvent properties, soil organic and mineral properties, and soil moisture content. Chiou (1990) stated that a wide range of organic sorption behaviour can be accounted for by considering the soil as a dual sorbent, in which the

mineral fraction functions as a conventional solid adsorbent and the organic matter functions as a partition medium. In aqueous systems, adsorption on mineral matter is suppressed by water, and soil uptake consists primarily of solute partitioning into the organic matter. Chiou suggested that the presumed partition with organic matter was supported by several facts, including: (1) observed linearity of soil-water isotherms, (2) absence of competitive effects between solutes, (3) low equilibrium heats, and (4) difference in limiting sorption capacity for liquid and solid compounds.

In an earlier paper, Mingelgrin and Gerstl (1983) argued that linear isotherms, per se, were not evidence of a partitioning process rather than an adsorption process if the surface concentrations were low. They further stated that correlations between solubilities, liquid-liquid partitions and soil uptake were insufficient proof for a partition process, as had been previously proposed (Chiou et al. 1979). Many pesticides exhibit predominantly non-linear adsorption isotherms (Freundlich slope,  $N < 0.95$  or  $N > 1.05$ ) on soils and clays (Bowman 1973; 1981). Reference smectitic clays saturated with divalent or trivalent cations often result in pesticide adsorption isotherms with slopes greater than 1.05, whereas mineral soils with varying amounts of organic matter usually produced slopes less than 0.90 (Bowman 1981; 1989). Chiou's concept of organic matter acting as a partitioning medium would be at odds with that of Gamble and Khan (1992) and Wang et al. (1991) who have related atrazine sorption by soil to carboxyl-group sites on the organic matter.

Pesticide adsorption by soils has most frequently been described using the empirical Freundlich adsorption isotherm (Chesters et al. 1989), although there are some instances, such as organo-cations (paraquat, diquat) where the theoretically-based Langmuir adsorption equation is more appropriate (Singh et al. 1989). The Freundlich isotherm equation can be expressed as:

$$X/M = K_d C_e^N \quad (1)$$

where the defined parameters (with examples of units) are:

$$X/M = \text{unit mass of adsorbate adsorbed/unit mass of adsorbent} \\ \mu\text{g/g (mass); } \mu\text{mole/g (molar)}$$

- $C_e$  = equilibrium concentration of solute,  $\mu\text{g/mL}$  (mass);  $\mu\text{mole/mL}$  (molar)  
 $K_d$  = Freundlich constant,  $\mu\text{g}^{(1-N)} \text{g}^{-1} \text{mL}^N$  (mass);  $\mu\text{mole}^{(1-N)} \text{g}^{-1} \text{mL}^N$  (molar)  
 $N$  = unitless Freundlich constant, a measure of curvature of the isotherm,  
 $N > 1$ , convex downwards;  $N < 1$ , convex upwards;  $N = 1$ , linear

The Freundlich constants are obtained by performing linear regression on the log-transformed adsorption data and the Freundlich equation in Log format is given by:

$$\text{Log } X/M = \text{Log } K_d + N \text{ Log } C_e \quad (2)$$

The Freundlich  $K_d$  value, commonly referred to as the soil-water partitioning coefficient, is the most frequently-used means of reporting pesticide adsorption by soils and is extensively used by modelling algorithms to predict pesticide mobility in soils. Sensitivity analysis conducted for a number of transport models has shown that relatively small variations in  $K_d$  values used to calculate pesticide movement can have a major influence upon their predicted movement (Boesten 1991; Boesten and Van Der Linden 1991; Jernlas 1990). The  $K_d$  value is therefore one of the most important environmental parameters used to assess pesticide behaviour, and top priority should be given to its accurate determination. Adsorption isotherms for a number of nonionic pesticides at low solution concentration ranges often approach linearity ( $N$  within 5% of unity). Consequently a considerable number of researchers (Karickhoff and Brown 1979; Tim and Mostaghimi 1989) have calculated partitioning coefficients based on a linear modification of the Freundlich isotherm (assuming  $N = 1$ ) given as:

$$X/M = K_p C_e \quad (3a)$$

The linear partitioning coefficient is shown as  $K_p$ , since its units will be different than  $K_d$ , and re-arranging Equation (3a) we obtain:

$$K_p = \frac{X/M}{C_e} \quad \text{Units :} \quad \frac{\mu\text{g/g}}{\mu\text{g/mL}} \equiv \text{mL/g} \quad (3b)$$

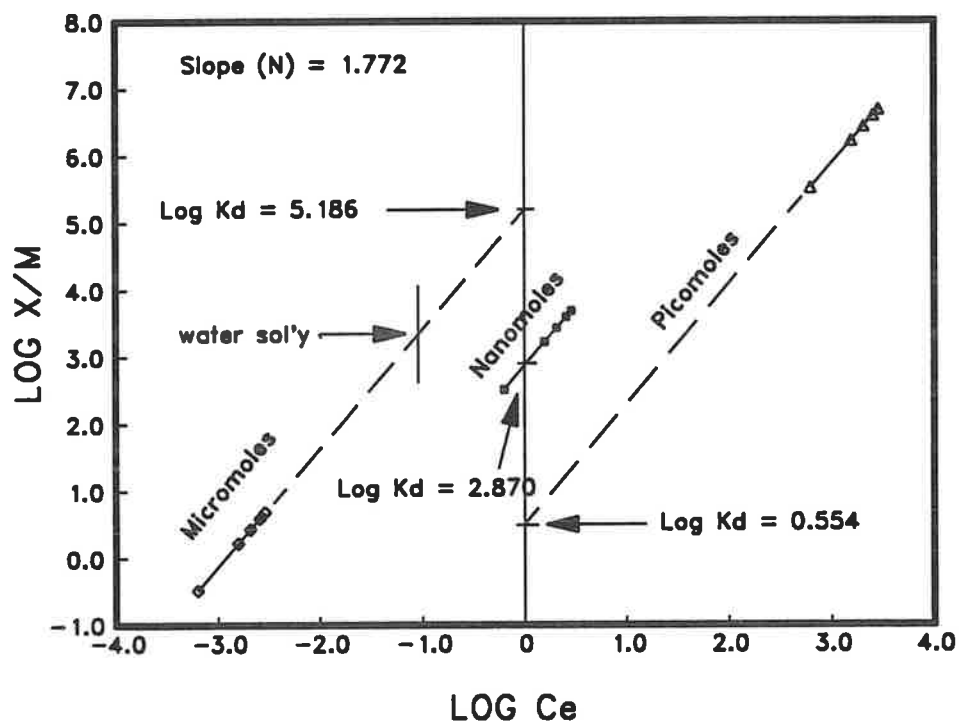
When calculating the  $K_p$ , linear regression is forced through the origin since all isotherms must converge at that point. The downside of using linear isotherms is the introduction of a less precise version of the partitioning coefficient, with its own set of units. The magnitude of  $K_p$  is somewhat different from  $K_d$  values calculated for the same data set, therefore creating a

consistency problem in their use in models. There is no convention recommending when isotherm data would be better plotted in Freundlich form to properly account for nonlinearity.

The presence of  $N$  (Freundlich slope), in the units of  $K_d$  complicates its use. When  $N$  is not unity, the magnitude of  $K_d$  does not change by factors of 1000 when changing sets of units (e.g.,  $\mu\text{g}$  to  $\text{mg}$ , or  $\mu\text{mole}$  to  $\text{nmole}$ , etc.) (Bowman 1981). Thus, great care must be exercised in converting literature  $K_d$  values into another unit set for comparison or modelling purposes. By definition, the  $K_d$  value is always evaluated at  $\text{Log } C_e = 0$ ,  $C_e = 1.0$ , in whatever set of units is being used. Therefore  $K_d$  is not a numerical constant unless  $N = 1$ , and consequently, modellers should be very aware that the units of  $K_d$  are consistent with the requirements of their model. The proper way to set up an adsorption isotherm experiment is to ensure that  $C_e = 1.0$  always falls within the equilibrium concentration range of that data set.

In a previous study (Bowman and Sans 1977) we found that the adsorption of the insecticide fenitrothion by  $\text{Fe}^{3+}$ -saturated montmorillonite was quite nonlinear, giving a Freundlich slope ( $N$ ) of 1.772. If the adsorption data were plotted in nanomolar units (nanomole/mL, nanomole/g) as shown in Figure 2, then  $\text{Log } K_d = 2.87$  ( $K_d = 741 \text{ nmole}^{(1-N)} \text{ g}^{-1} \text{ mL}^N$ ). However, if the same data set was plotted in either micromolar or picomolar units,  $K_d$  would have been  $153460 \mu\text{mole}^{(1-N)} \text{ g}^{-1} \text{ mL}^N$ , or  $3.58 \text{ pmole}^{(1-N)} \text{ g}^{-1} \text{ mL}^N$ , respectively. Of the three plots, only the nanomolar plot included  $C_e = 1.0$  within the data range. The concentration at which  $K_d$  was calculated in micromolar units ( $\text{Log } C_e = 0$ ;  $C_e = 1.0$ ) occurred far above the water solubility limit of  $0.092 \text{ nmole/mL}$  ( $\text{Log solubility} = -1.04$ ) for fenitrothion - a physical impossibility. Unfortunately there is no means for making  $K_d$  values totally consistent because of the wide water solubility ranges involved in the various classes of pesticides, and the impossibility of conducting all adsorption isotherm experiments within the same solution concentration range. The next best step is always to ensure that  $K_d$  falls within the experimental data range.

Over a decade ago, there was a keen interest to find a means for rating "pesticide adsorption potential" that would be independent of soil parameters, equivalent to a



**Figure 2.** Log-log Freundlich isotherm of fenitrothion-Fe-montmorillonite plotted in three sets of units; X-axis - "x"mole/mL; Y-axis, "x"mole/g, where "x" = micro, nano, or pico.

universal adsorption constant for each pesticide. The closest that anyone has come to that constant was the derivation of a  $K_{OC}$  value which was a  $K_d$  value normalized for soil organic carbon (Karickhoff et al. 1979; Karickhoff 1981). However, there was not universal agreement on the implementation of  $K_{OC}$  and some researchers instead based their normalized  $K_d$  on organic matter content ( $K_{OM}$ ) (Briggs 1981). The definitions are as follows:

$$K_{OC} = K_d / f_{OC} \quad (4a)$$

$$\text{or} \quad K_{OM} = K_d / f_{OM} \quad (4b)$$

where  $f_{OC}$  = organic carbon fraction of the soil,  
 $f_{OM}$  = organic matter fraction of the soil.

Since soil organic matter contains approximately 58% organic carbon (Nelson and Summers 1982), then

$$f_{OC} = 0.58 f_{OM} \quad (5a)$$

$$\text{and} \quad K_{OC} = K_{OM} / 0.58 \quad (5b)$$

The presence of both of these terms in the literature, as well as in modelling scenarios led to unnecessary confusion, especially for less technical personnel who could easily interchange the terms. The usefulness of the normalized  $K_d$  value (we'll use  $K_{OC}$ ) lies in the fact that adsorption by soil of nonionic pesticides can be largely attributed to the organic matter fraction in soil. However, this simple relationship starts to fall apart in soils with organic matter contents less than 1 to 2 %, at which time the clay mineral contribution to adsorption accounts for an increasing proportion of the adsorption capacity.  $K_{OC}$  values increasingly underestimate the sorptive capacity of the soil for a given pesticide as the organic matter content falls below the 1 to 2% range (Sanchez-Martin and Sanchez-Camazano 1991). Von Oepen et al. (1991) found that there was a large variation in adsorption behaviour for polar compounds between soils, and that  $K_{OC}$  values were of no use in predicting their adsorption.

Gustafson (1989) developed a useful relationship called the Groundwater Ubiquity Score (G.U.S.), for predicting pesticide leachability using the relationship between the logarithm of  $K_{OC}$  and the logarithm of the pesticide half-life in soil ( $T_{1/2\text{soil}}$ ). Two semi-empirical hyperbolic curves generated by the following equation for two numerical G.U.S.

values, 2.8 and 1.8, divided the Log  $K_{OC}$  vs Log  $T_{1/2}$  graph into three leachability zones (high, transition, low):

$$G.U.S. = \text{Log}_{10} (T_{1/2}\text{soil}) \times (4 - \text{Log}_{10}(K_{OC})) \quad (6)$$

This relationship, although not foolproof, was certainly a very good initial screening step in trying to predict whether a given pesticide would be a leacher, recognizing that compounds with low  $K_{OC}$  values are not necessarily leachers if they have short  $T_{1/2}$  values, and conversely, compounds having moderate  $K_{OC}$  values can be leachers if they are very persistent. Compounds falling into the "transition" and "high" leachability zones would require more detailed investigations before registration.

#### 4.2.2. Soil-bound Residues and Sorption Nonequilibrium

The subject of soil-bound pesticide residues has become a focal point for much attention in recent years because of the wide-spread implications it has for environmental as well as efficacy issues. Khan (1991) defined bound herbicide residues as "chemical species, originating from herbicide usage, that cannot be extracted by methods commonly used in residues analysis". This definition can be broadened to include almost all pesticide residues in soil. Extraction in this context refers to the exhaustive removal of the chemical species from a soil or plant matrix by a selected mixture of solvents. Khan's definition of bound residues excluded fragments of the chemical species possessing no pesticidal activity, and which are recycled into natural polymeric products through metabolic pathways of a biological system. The rates and extent of bound residue formation vary widely, depending on factors including properties of the specific chemical, soil type, amount and quality of organic matter, microbial activity and climatic factors (temperature, moisture). There is an indication that there is some association between chemical structure and the tendency to be bound by soil (Klein and Scheunert 1982; Roberts 1984). Chlorinated compounds appear to exhibit less binding tendencies than other structural groups, such as triazine, carbamates, phenols, anilines, or organophosphorus compounds. Khan (1991) reported that from 7% to 90% of a diverse group of soil-applied herbicides became soil-bound over periods ranging from several months to more than a year.

Sorption nonequilibrium of pesticides by soils is a different approach to describing soil-binding, emphasizing the kinetics (dynamics) of sorption processes, usually in aqueous media, as compared with soil-binding processes which were defined in terms of maximum extractability by various solvent systems. Pignatello and Huang (1991) defined nonequilibrium processes as "sorptive processes that are slow compared with concurrent transport or degradation reactions". Rao (1990) grouped these processes into two general classes, transport-related and sorption-related. Transport-related processes occur when sorption at the sorbent-solvent interface is instantaneous, but access to sorptive sites is rate-limited by solute diffusion rates within pore sequences in immobile domains. This process is of significance in aggregated or macroporous soils as well as in fissured/fractured aquifers, and in heterogeneous aquifers with layers and inclusions. Sorption-related nonequilibrium occurs in rate-limited solute interactions with specific sorption sites, including solute diffusion within the organic matter matrix.

The sorption dynamics of pesticides in soil-water systems influence their accessibility to microorganisms, which are greatly restricted in assimilating or transforming sorbed species relative to those molecules in solution (Steen et al. 1980). Sorption can also influence chemical reactions, such as base-catalyzed hydrolysis which is much slower for sediment-associated molecules than for dissolved molecules (Macalady and Wolfe 1985). There are other reactions, such as those involving humic materials or surface-catalyzed reactions on clays, which may occur only in the sorbed state.

Sorptive uptake processes appear to be biphasic, consisting of both rapid and slow phases. Pignatello (1989), in a review of sorption dynamics, stated that desorption processes are also biphasic in nature. The overall sorptive process, while initially quite rapid for freshly-applied pesticides, decreases in a multiphase exponential fashion over periods of hours, days, months, and even years, depending upon the compound and the soil. Scribner et al. (1992) found that field-aged simazine residues produced apparent sorption coefficients that were approximately 15-fold greater than freshly added simazine residues. Similarly, Pignatello and Huang (1991) reported that apparent soil-water partitioning coefficients for field-aged (2 to



14 mo.) atrazine and metolachlor residues were 2.3 to 42 times greater than for 24-hour equilibrium  $K_d$  values. Under these experimental conditions, 5.6% to 60% of the herbicides were considered to be labile.

Solute partitioning onto soil (sediment) adsorbents has been classified into "reversible" (labile) and "resistant" fractions (DiToro et al. 1982). Pignatello carried the classification one step further by subdividing the "resistant" fraction into a second "irreversible" fraction. In his definition, "resistant" refers to that portion of the adsorbed solute which has not desorbed within the time frame of the experiment, but given sufficient time eventually will desorb in its original form. The "irreversible" fraction was defined as that fraction that cannot be recovered in its original form, indicating that the compound has undergone a chemical or biological transformation. Pignatello pointed out that while some sorption processes may technically be "resistant", they will effectively be "irreversible" in environmentally relevant situations. This raises an interesting scenario for soil-bound pesticides, such as atrazine, which have been transported on eroded soil particles in runoff into streams. Given the very extensive, long-term usage of atrazine combined with the fact that the parent molecule may still comprise a considerable portion of soil-bound residues (Khan 1991), there may be a very large reservoir of eroded, soil-bound parent atrazine which has the potential to be slowly released into water courses. Perhaps this is a contributing factor as to why trace levels of atrazine are so widely detected in various bodies of water.

In the earlier discussion on sorption processes, it was noted that pesticide transport models tend to be quite sensitive to relatively small variations in  $K_d$  (or  $K_{oc}$  or  $K_{om}$ ) values. As an example, Boesten and Van der Linden (1991) reported that changing the  $K_{om}$  or transformation rate by a factor of two typically changed the dose leached by a factor of 10. Under some circumstances, existing transport models may considerably overestimate the amounts of soil-aged chemicals predicted to leach, especially for extended time frames. There have been a number of recent efforts to incorporate sorption nonequilibrium processes into pesticide transport models (Brusseau 1991; Brusseau et al. 1991; Pignatello and Huang 1991). Brusseau (1991) reported that the multiprocess nonequilibrium (MPNE) model provided a good

description of breakthrough curves at different flow velocities, and seemed to yield a valid representation of sorption dynamics and solute transport for layered systems influenced by sorption capacity heterogeneity and multiple sources of nonequilibrium.

#### 4.2.3 Enhanced Microbial Degradation

Microbial degradation has long been recognized as a major route by which pesticides are dissipated in soil and water ecosystems. The balance between pesticide dissipation and leaching rates in the soil profile determines their potential to reach groundwater. Ideally, the suitability of a pesticide for a given application would be based upon its ability to persist sufficiently long to perform its task, and then to degrade before it leached to groundwater. Most microbial activity in soil resides in the organic matter-rich surface layer, where there is an abundance of carbon and nutrients necessary for their activities. Hence most pesticide degradation processes occur in this surface layer, and residual pesticides which migrate to lower horizons have an increased probability of reaching groundwater before completely disappearing.

Enhanced microbial degradation in soil refers to the increase in decomposition rate of a pesticide in a soil that has been previously treated with the same or a chemically-related compound, compared to that pesticide's decomposition rate in an identical medium not previously treated (Roeth 1986). Although enhanced herbicide degradation was first reported by Audus (1949) for 2,4-D (2,4-dichlorophenoxy acid), the phenomenon did not attract much attention nor was perceived to be of economic importance at that time. In the case of foliar herbicides, such as 2,4-D, enhanced degradation in the soil was not a serious problem since they were not targeted for soil application. Later studies showed that the monochloro analog of 2,4-D, MCPA (2-methyl-4-chlorophenoxyacetic acid) was also susceptible to enhanced degradation in the field (Kirkland and Fryer 1966). In the early 1970's, enhanced biodegradation began to be associated with insect control failures (Sethunathan 1971).

Of all the classes of pesticidal compounds reported to be susceptible to enhanced degradation, the methyl carbamate insecticides and the thiocarbamate herbicides have been the most thoroughly investigated (Felsot 1989). One of the first reported carbamate control failures was for carbofuran (2,3-dihydro-2,2-diethylbenzofuran-7-yl methylcarbamate) on grape phylloxera (Williams et al. 1976). During the 1970's in the mid-western cornbelt of the U.S.A., reported failures of carbofuran to control corn rootworm damage quickly grew from only 6% during 1969 to 1974, to 28% during 1976 to 1980 (percent of test plots exceeding economic injury levels; Kuhlman and Steffey 1981). Initially it was believed that the corn rootworms had developed an increasing resistance to carbofuran, although western corn rootworm beetles collected in Illinois exhibited continuing low resistance levels (Felsot 1981). Felsot et al. (1981) suggested enhanced degradation as an alternative to the resistance theory for carbofuran control failures, based on: (1) the fact that poorest control occurred on fields where carbofuran had been repeatedly applied and, (2) the ample time for significant degradation to occur between carbofuran application and corn rootworm egg hatches.

There are a number of factors influencing the development and longevity of enhanced microbial degradation in soils, in addition to the nature of the chemical classes of pesticide involved. Chapman and Harris (1990) found that the degree of developed enhanced activity was greater when pure chemicals rather than formulated products were used, and that granular formulations presented a heterogeneous system with respect to the micro-location and accessibility of the insecticide to the microbial population. They also found that there was no enhancement of carbofuran degradation in soils maintained at 3°C following initial treatment, but that enhancement increased by 16 and 41 fold (first-order half-life ratios) at 15 and 28°C, respectively. Moisture contents for enhanced carbofuran degradation in their soils had a broad optimum range from about 9 to 36%, with enhancement factors reaching 54 fold at 27% moisture. At low soil moisture contents, enhanced carbofuran degradation failed to develop. Once enhanced microbial populations for carbofuran degradation had developed, they appeared relatively insensitive to temperature and moisture changes, even in the more extreme portions of the above-discussed ranges. Carbofuran soil concentrations of 1.0 µg/g were sufficient to trigger enhanced activity in mineral soils, but 10 µg/g levels were required in organic soils.

Cross-enhancement is the enhanced degradation of a chemical in a soil in which enhanced microbial activity was initially generated by a different chemical (Chapman and Harris 1990). Both Felsot (1989) and Roeth (1986) have cited numerous instances of cross-enhancement in their reviews. Cross-enhancement studies can provide valuable information on the nature of the adaptation process since the occurrence of cross-enhancement is a test of specificity for microbial adaptation. The incidence of cross-enhancement is much greater within chemical classes (e.g.; carbamates, organophosphorus compounds), although the degree of enhanced activity is often less than with a repeat application of the same chemical (Roeth 1986).

Despite the fact that soils are very heterogeneous in nature, most theoretical descriptions of pesticide dissipation kinetics have been based on models assuming various degrees of soil homogeneity. Gustafson (1990) developed a nonlinear pesticide dissipation model using the concept of a spatially-variable first-order rate constant to deal with the issue of heterogeneous domains in the soil. This model recognizes the fact that although most pesticide degradation processes probably follow first-order rates, there are many factors that can spatially vary on a micro-scale in the soil including microbial population density, temperature, amount and intensity of precipitation, solar intensity, soil properties (moisture, organic matter, texture, sorptive capacity), tillage and cropping practices. Gustafson found that the relative variability in rate constants was similar for both laboratory and field experiments, suggesting that the repeating scale for spatial variability may well be on the order of pore-size dimensions.

The trend towards monoculture cropping practices in many regions of North America over the past two decades may have hastened the more widespread development of enhanced degradation, since repeated soil applications of the same pesticide appear to be the most common means for its development. There has been a very intensive scientific effort during the past decade to characterize the processes involved in the development of enhanced microbial degradation and to identify the most susceptible classes of compounds. These efforts have been thoroughly covered in several excellent reviews published elsewhere (Felsot 1989; Racke and Coats 1990; Roeth 1986).

#### 4.2.4      Adsorbent Concentration Effects on Sorption Partitioning

During the past two decades there has been an ongoing controversy regarding the influence that adsorbent concentration appears to have upon the partitioning of nonionic organic compounds between aqueous and solid phases (soil, sediments). The phenomenon has commonly been referred to by many terms, including soil (solid)-solution (water, liquid) ratio effects (Boesten 1990), solids (particle, (ad)sorbent) concentration effects (Bowman and Sans 1985; DiToro et al. 1982; Van Hoof and Andren 1991; Voice and Weber 1985), or third-phase effects (Gschwend and Wu 1985; Mackay and Powers 1987; Schrap and Opperhuizen 1989). The range of reported  $K_d$  shifts with changing adsorbent concentration can span several orders of magnitude, which would have very significant implications for use in modelling. In this discussion, factors contributing to observed adsorbent concentration effects in solute partitioning experiments are grouped into two categories, Experimental Design, and Experimental Technique.

##### 4.2.4.1      Experimental Design

4.2.4.1.1.      Solute Removal and Measuring Errors      When setting up a solute partitioning experiment, one must carefully examine the quantities being measured, including their associated errors. Partitioning coefficients are obtained from adsorption isotherm experiments in which the adsorbed concentration is derived from the difference between initial and equilibrium solute concentrations, and therefore the measuring errors of the difference are additive. To demonstrate this effect (Table 1), a scenario was set up for three different percentage solute removals (5%, 10%, 50%) by a hypothetical adsorbent, with an initial solute concentration of 10  $\mu\text{g/mL}$ , a 100 mL solution volume, and assuming a 3% error in determining solution concentrations (typical analytical error for gas/liquid chromatographic analyses). The "Range" columns beside the initial and equilibrium concentration columns show predicted analytical ranges, based on the 3% error. For a 5% solute removal, it would be possible to observe a negative adsorption because of measuring errors. Maximum measuring errors in the adsorbed amounts occur when the difference between initial and

Table 1. Effect of analytical measuring errors in the determination of adsorbed amounts in adsorption isotherm experiments as a function of percent solute removal.

| Percent Solute Removal | Initial                     |                    | At Equilibrium |            | Adsorbed Amount <sup>c</sup> |            | Range/<br>Mean |
|------------------------|-----------------------------|--------------------|----------------|------------|------------------------------|------------|----------------|
|                        | C <sub>e</sub> <sup>a</sup> | Range <sup>b</sup> | C <sub>e</sub> | Range      | Mean                         | Range      |                |
| 5                      | 10.0                        | 9.7 to 10.3        | 9.5            | 9.2 to 9.8 | 50                           | -10 to 110 | 2.40           |
| 10                     | 10.0                        | 9.7 to 10.3        | 9.0            | 8.7 to 9.3 | 100                          | 40 to 160  | 1.20           |
| 50                     | 10.0                        | 9.7 to 10.3        | 5.0            | 4.7 to 5.3 | 500                          | 440 to 560 | 0.24           |

Assume constant 3% measuring error based on initial concentration of 10 µg/mL = 0.3 µg/mL

<sup>a</sup> solution concentration, µg/mL.

<sup>b</sup> measured range, based on 3% error

<sup>c</sup> adsorbed solute, µg

equilibrium concentrations are small, most likely to occur for weakly adsorbed species in an adsorption system using low adsorbent concentrations. This type of error increases rapidly as solute removal from solution drops below 10% of the total. Boesten (1990) performed a detailed mathematical analysis of random and systematic experimental errors associated with sorption coefficients. He recommended that to minimize experimental errors, the adsorbent concentration should be kept as large as possible, unless this results in an equilibrium concentration too low to measure accurately. In practice it was found that designing adsorption experiments to remove from 10% to 90% of initial adsorbate from solution would generally minimize this type of error.

Measuring errors also become significant for sorption systems having very low solution concentrations, or which approach detection limits for that particular solute (more likely for very hydrophobic, low water solubility compounds). Under such circumstances, the uncertainty in measured values increase, compounded by interferences (chemical or electronic), and become increasingly significant as the detection limit is approached for that compound.

4.2.4.1.2. Sorption Nonequilibrium Failure to achieve equilibrium in sorption partitioning experiments may lead to nonsingularity in adsorption-desorption branches of the isotherm, and may be a major source of apparent adsorbent concentration effects. Before sorption experiments are conducted, equilibrium-time studies should be conducted to determine appropriate equilibration times. Van Hoof and Andren (1991) reported that partitioning coefficients for a chlorinated biphenyl congener-polystyrene system became independent of adsorbent concentration after 96 days, and suggested that the effects of particle concentration on solute partitioning requires a kinetic rather than a thermodynamic explanation.

4.2.4.2 Experimental technique. There are numerous pitfalls in sorption techniques which can result in anomalous partitioning coefficients, especially for those experimental setups discussed above which are already quite sensitive to additive measuring errors.

4.2.4.2.1 Incomplete Phase Separation Failure to completely separate the solid and liquid phases in sorption studies can produce anomalous partitioning coefficients, especially for strongly adsorbed solutes (hydrophobic, low water solubility) in sorption systems with low equilibrium concentrations and very fine particle-size sediments. Under such conditions, amounts of solute associated with unseparated adsorbent may represent a significant fraction of the amount in the solution phase (Voice et al. 1983). In our experience, centrifugation times and speeds of at least 0.5 to 1.0 hr and 40000 x g are necessary to ensure complete phase separation. Careful attention must also be paid to the deceleration phase of centrifugation as well as to post-centrifugation handling of the samples. Improperly balanced high-speed centrifuge rotors frequently experience strong vibration nodes during deceleration, resulting in resuspension of very fine materials. Samples of the supernatant solution should be withdrawn from the centrifuge tube without removing it from the rotor to minimize the possibility of resuspension. Occasionally, light mineral or organic debris in the form of a thin film will remain floating on the surface of centrifuged samples, which can be avoided when sampling by keeping a finger over the pipette as it is lowered into the tube.

Some researchers have invoked a "third-phase" effect to explain  $K_d$ -adsorbent concentration effects (Gschwend and Wu 1985; Voice et al. 1983; Voice and Weber 1985). This theory contends that dissolved concentrations are essentially in error because a portion of the measured solute in solution is actually sorbed to colloidal or non-filterable matter. Mackay and Powers (1987) stated that the magnitude of the  $K_d$  shifts, in their opinion, were too large to be completely accounted for by the "third-phase" explanation. When filtering techniques are employed for primary phase separation, it should be followed by a secondary high-speed centrifugation of the filtrate to ensure complete separation. Rigorous centrifugation techniques may well minimize or eliminate the occurrence of "third-phase" effects.

4.2.4.2.2 Strong Solute Adsorption by Adsorption Vessels. When conducting adsorption partitioning studies, caution must be taken in selection of the materials used in handling, equilibrating and storing the solutes. In general, avoid the use of plastics for storing, equilibrating or transferring aqueous solutions of the test solute. Recent studies have clearly



shown that soft plastics, such as Tygon® or Nalgene®, can quickly adsorb a large fraction of moderately hydrophilic compounds, such as the herbicides atrazine or metolachlor, from aqueous solution, whereas some harder plastics such as low or high density polyethylene remove considerably lesser amounts (Topp and Smith 1992). It would be prudent to check possible sorption by teflon stir bars in experiments using very hydrophobic compounds.

Hydrophobic compounds such as dieldrin, an organochlorine insecticide, can be strongly adsorbed from aqueous solution by certain types of glass surfaces, and removed only by organic solvents such as acetone (Bowman and Sans 1985). Dieldrin adsorption by glass was concentration-dependent, precluding the use of standard adsorption blanks to correct for a constant amount of depletion by adsorption vessels. Glass adsorption of dieldrin was also bottle-specific for certain types of glass, such as flint. A sequential blank-sample equilibration procedure should be used for very hydrophobic compounds (such as polychlorinated biphenyls (PCB) or polyaromatic hydrocarbons (PAH)) in which the different concentrations of aqueous solute solutions are initially equilibrated in their respective adsorption vessels. A sub-sample of that equilibrated volume is analyzed to determine the "actual initial concentration". An appropriate amount of adsorbent is then weighed into the remaining glass-equilibrated solution for the isotherm experiment. As a further precaution, replace plastic liners, which come in screw-capped glass bottles used in sorption studies, with tin foil-lined caps. In general, the two best materials for minimizing unexplained solute losses in sorption studies are Pyrex® glass and stainless steel.

4.2.4.2.3 Radiochemical impurities. Radioisotopes are a very convenient means for detecting very small amounts of solute in sorption systems and for maintaining mass balance calculations. However, radioisotope detection is specific only for the tagged entity and does not distinguish between the primary tagged compound and any tagged metabolites or impurities present in the system. McCarthy et al. (1986) found that minute amounts of radiolabelled impurities in sorption systems using low adsorbent concentrations (100 mg/L) resulted in anomalous partition coefficients, leading to erroneous conclusions regarding the reversibility of

the sorption process for that solute. They presented a list of five criteria which should be followed in validating solute partitioning when using radioisotopes.

4.2.4.2.4 Adsorbent/Adsorbate Losses and Measuring Errors. Errors in measuring adsorbent weights used in generating partitioning coefficient data are usually not significant when using adsorbent concentrations exceeding 100 mg/L. This type of measuring error or loss does become increasingly important with decreasing adsorbent concentrations. Baker et al. (1986) reported uncertainties in the order of 2% (0.1 mg/L at 5 mg/L) for filtering suspended solids through tared glass fibre or membrane filters. Such errors, while nominally small, compound analytical measuring errors of the same order of magnitude. Glass microfibre filters also have a small adsorptive capacity for insecticides such as parathion, which could further augment the above-mentioned measuring errors for more hydrophobic compounds.

In situations where adsorbent concentration effects have been reported, the partitioning coefficient ( $K_d$  or  $K_p$ , the linear partitioning coefficient) frequently decreases linearly at a slope of -1.0 (Log partition coefficient vs Log adsorbent concentration plot) with increasing adsorbent concentration at low adsorbent concentrations (< 100 mg/L) (Lodge and Cook 1989). In some cases the partition coefficient approached constancy at higher adsorbent concentrations (DiToro et al. 1982; O'Connor and Connolly 1980). In the linear region at lower adsorbent concentrations, a given increase in adsorbent concentration would be completely offset by the decrease in partitioning coefficient, meaning that a 1-L volume of 1 mg/L suspension would remove the same amount of solute as a 10 mg/L or 100 mg/L suspension - in other words, the total solute adsorbed is independent of adsorbent concentration in this region. These results are consistent with a secondary source of solute removal, such as glass or plastic surfaces which, while removing a constant amount, would gradually become the dominant source of removal at very low adsorbent concentrations. For studies using adsorbent (soil) concentrations exceeding 1.0 g/L, there were no consistent conclusions as to whether adsorbent concentration influenced partitioning (Farmer and Aochi 1974; Karickhoff et al. 1979; Koskinen and Cheng 1983; Lotse et al. 1968).

4.2.4.3. The Law of Mass Action: Experimental Consequences. Consider the case of a nonionic pesticide that is distributed between aqueous solution and suspended soil phases. The soil adsorbent will generally have a sorption capacity for the pesticide in the same sense that it has an ion exchange capacity for metal ions and thus the sorption capacity can be defined and measured as a saturation limit, expressed fundamentally as  $\theta_c$ , the (moles/g) of sorption sites in the solid soil, or operationally as  $C_c$ , the (moles/L of slurry). When the system is at equilibrium, the pesticide distribution is governed by the law of mass action, expressed by Equation (7) (Gamble and Khan 1988; 1992; D.S. Gamble, personal communication 1992).



$$\bar{K}_1 = \theta_A / \theta_o M_A = C_A / C_o M_A \quad (7b)$$

where P = pesticide molecules  $\bar{K}_1$  = weighted average equilibrium constant

$S_A$  = occupied sorption sites  $S_o$  = empty sorption sites

$M_A$  = aqueous pesticide concentration (mole/L) (equivalent to Freundlich  $C_e$ )

$\theta_A$  = adsorbed pesticide concentration (moles/g; equivalent to Freundlich X/M)

$\theta_o$  = concentration of unoccupied sites on soil (moles/g soil)

$C_A$  = adsorbed pesticide concentration (moles/L suspension)

$C_o$  = concentration of unoccupied sites on soil (moles/L suspension)

The empty sorption sites ( $\theta_o$  or  $C_o$ ) cannot be ignored in the most general case, because if the number of empty sites changes then this will change the equilibrium distribution ( $\theta_A/M_A$ ) between the two phases. This can be seen by examining the behaviour of the distribution coefficient,  $K_p$  (assuming a linear isotherm) which is defined by Equation (8), and which is equivalent to Equation (3b)

$$K_p = (\theta_A / M_A) \quad (8)$$

Note that  $K_p$  defined in this scenario has the units, (L/g). Combining Equations (7b) and (8) gives the relationship between  $K_p$  and  $\bar{K}_1$ , in Equation (9).

$$\bar{K}_1 = K_p / \theta_o \quad \text{or} \quad K_p = \bar{K}_1 \theta_o \quad (9)$$

The total concentration of sorption sites,  $\theta_c$ , is

$$\theta_c = \theta_o + \theta_A \quad (10)$$

Combining (9) and (10)

$$K_p = \bar{K}_1(\theta_c - \theta_A) \quad (11)$$

Equation (12) gives a useful units conversion

$$\theta_A/C_A = V/W \quad \text{or} \quad \theta_A = (V/W) C_A \quad (12)$$

where  $W$  = Adsorbent weight (g), and  $V$  = Solution volume (L)

and  $W/V$  = Soil/water ratio (adsorbent concentration, g/L)

Substituting for  $\theta_A$  in Equation (11)

$$K_p = \bar{K}_1(\theta_c - C_A/(W/V)) \quad (13)$$

For a given soil-pesticide system, the sorption capacity,  $\theta_c$ , is a constant.  $K_p$  is not inherently a rigorous constant in Equation (13), and approaches constancy only for certain special limiting conditions. Pesticide sorption by soils usually exhibits limited surface coverage because of low application rates and water solubility limitations on solution concentration, and therefore  $C_A \ll \theta_c$ . The ratio  $C_A/(W/V)$  usually increases only slightly for a several order of magnitude change in  $(W/V)$  (from 10 g/L to 10 mg/L, for example), and thus changes in  $K_p$ , as a function of  $(W/V)$ , would be small compared to experimental errors. In heterogeneous soil systems,  $\bar{K}_1$  might decrease modestly with increasing coverage of sorption sites since the most energetic sites are occupied first. Thus  $K_p$  would also change as sorption increased under this scenario, but not in the order of magnitudes that has been ascribed to adsorbent concentration effects.

Precautions should be taken to ensure that a possible experimental anomaly is not misinterpreted as a real equilibrium phenomenon. If the system has started with all of the pesticide in solution and has not attained equilibrium, then increasing the adsorbent concentration (g/L of solution),  $(W/V)$ , will put the system farther away from equilibrium. In such a case  $K_p$  would not only not represent true equilibrium values, but would decrease as the  $(W/V)$  ratio increased. The reason is that the  $(\theta_A/M_A)$  ratio in Equation (8) would be below the equilibrium value.

In general,  $K_d$ - adsorbent concentration interactions are reported most frequently under one or a combination of the following circumstances:

1. when the solute is a highly adsorbed (hydrophobic) nonionic organic compound which would tend to have low water solubility, leading to low equilibrium concentrations,
2. in presence of low adsorbent concentrations ( $< 100$  mg/L) which result in minimal removal of the solute from solution, making it difficult to accurately measure the removal by difference between initial and equilibrium solution concentrations,
3. when systematic, technical errors or unaccounted-for losses of adsorbent or adsorbate dominate solute removal under either or both of the above two situations.

If technique- and design-related sorption errors were minimized, would one expect to observe real  $K_d$  dependence on adsorbent concentration? If so, there are some rather far-reaching consequences for partitioning studies. Consider the scenario of suspended stream sediments carrying a load of PCB's, PAH's or hydrophobic pesticides. If  $K_d$  decreases with increasing adsorbent concentration, then one should expect a portion of the sorbed organics to desorb as the sediments settle out on the stream floor (increase in adsorbent concentration in the local domain). Should turbulent water re-suspend some of this sediment, then the adsorbent concentration would once again decrease, supposedly resulting in a re-sorption of organics, reflecting the increased  $K_d$ . Or, consider the fact that if  $K_d$  values were a function of adsorbent concentration, we would not be able to use centrifugation, or any other phase separation technique, to separate phases in order to analyze solution concentrations. As in the stream scenario, the separation process would, in itself, result in changes in the very solution concentration which was to be measured. Sorption of organics by soil and sediments are in fact driven by "intensive" type of processes (kinetics) rather than by "capacity" type of processes (volume), and if there are observed dependencies between  $K_d$  and adsorbent concentration, there are likely to be some unaccounted-for physical processes influencing the sorption processes.

#### 4.3. ENVIRONMENTAL IMPLICATIONS

##### 4.3.1 Preferential Water and Solute Transport in Soils

Preferential flow of water with accompanying solutes through cracks, fissures, or channels formed by soil fauna or by decaying plant roots, is now a widely recognized phenomenon, which under appropriate conditions can result in rapid non-equilibrium solute transport to considerable depths in a soil profile (Beven and Germann 1982; Ehlers 1975). This phenomenon was first reported by Lawes et al. in 1882 during studies at Rothamstead when they noticed "channel" drainage preceding the regular drainage in their soil. The first arrival of applied solute at any given depth in the soil profile may occur considerably before one pore volume has been displaced (Thomas and Phillips 1979; White 1985). The phenomenon has also been referred to by a number of other terms, including "channeling", "bypassing", "partial displacement", "sub-surface storm flow" and "short-circuiting" (Andreini and Steenhuis 1990; Bouma et al. 1981; Brusseau and Rao 1990).

Beven and Germann (1982) provided an in depth discussion of what constitutes a macropore, the various types of macropores, and experimental means for determining macroporosity in soils. At the microscopic scale, storage and flow of water in any particular soil void is related to the size and geometry of that void, and flow rates will be controlled by the void of smallest size in any continuous flow path (a pore neck). The most common means of classifying pore space in soil has been the soil moisture retention curve, in terms of pore sized classes. Although macropores may constitute only a small percentage of the total pore space, they may account for the bulk of water movement through the soil. Watson and Luxmore (1986) found that under ponded conditions on a forest floor, 90% of the water flux was through 0.32% of the soil volume. In agricultural soils, macropore space is in the order of 0.5% to 5% (Germann and Beven 1981; Kneale 1985).

Since macropores may permit spatial concentrations of water flow through unsaturated soil that can not be described by Darcy's Law, current physically-based flow

models do not properly cope with the transient nature of preferential flow under field conditions. There are many researchers currently developing models for preferential water and solute flows using approaches which incorporate multi-domain concepts for the hydraulic properties of the soil (Brusseau and Rao 1990; Jarvis et al. 1991 a, b; Chen and Wagenet 1992 a, b).

Steenhuis et al. (1990) reviewed a number of modelling approaches for preferential flow that have been used either in the laboratory or in the field, including the transfer function model (Jury et al. 1986) and a deterministic mathematical approach which was solved using analytical or numerical techniques (Rao et al. 1980 a, 1980 b). Although many computer models, such as PRZM (Carsel et al. 1985), GLEAMS (Leonard et al. 1987), CMIS (Nofziger and Hornsby 1986), or LEACHEM (Wagenet and Hutson 1986) have been based on the convective-dispersive equation, it now appears from tracer and dye studies (Addiscott et al. 1978; Andreini and Steenhuis 1990; Parlange et al. 1988) that it may fail to properly describe bulk-flow processes with accompanying dispersion under field conditions. An improved approach to this problem was to distinguish between mobile and immobile water as suggested by Van Genuchten and Wierenga (1976) and by Addiscott (1977) by dividing liquid water into two distinct pore size groups. Although this approach is superior to the convective-dispersive equation, it is still rather unrealistic to divide soil water into two arbitrary groups. A preferential flow model developed by Steenhuis et al. (1990) improved upon this by considering soil water to move with a range of velocities. In their review, Brusseau and Rao (1990) noted that the phenomena attributed to transport nonequilibrium (TNE) (constrained solute access to portions of the porous medium by diffusive mass transfer) are exhibited by both nonadsorbing and adsorbing solutes. Thus the mechanism influencing this nonequilibrium is transport- and not sorption-related.

Nonideality of a soil-water system usually increases as the soil-water content is reduced from saturation, and is dependent upon the pore-size distribution of the soil. Dispersive effects steadily increase with the degree of unsaturation because an increasing portion of the pores no longer easily transmit water, thereby creating immobile water domains.

Andreini and Steenhuis (1990) used a grid lysimeter to study the spatial variability of water flow through undisturbed soil blocks from conservation and conventional tillage practices (35 cm square, 34 to 46 cm in depth). They observed large spatial variations in both unsaturated water and solute (bromide, dye) flows through these soil blocks over extended periods (10 to 30 days) using a modest input rate of only 20 mm/day. Of the 52 collector cells below the blocks, water flowed from only 16 cells under the no-till block and 21 cells under the conventional tilled block. Selected horizontal slices through the blocks following the experiment showed that there were large areas apparently untouched by the dye. In current grid lysimeter studies using large undisturbed soil blocks (48 cm cube), we have found similar, very large spatial variations in water flow under unsaturated conditions (15 mm/hr input), which should not even involve the larger macropores (worm channels) in the system. Less than 20% of the collector cells transmitted the bulk of the water flow, and often full collector tubes (50 mL) were surrounded by empty or near-empty neighbouring tubes.

Rapid movement of pesticides may occur in soil profiles having a highly conducting, coarser horizon underlying a finer horizon (such as the A/B horizon interface), during periods when surface ponding exists. Under such conditions, unstable water flow (fingering or streaming) is enhanced whenever the lower layer's water entry is very low (controlled by the surface horizon hydraulic conductivity) while having a very high hydraulic conductivity at that suction (Baker and Hillel 1990; Hillel and Baker 1988). Essentially tension-free water accumulates at the interface and periodically streams down any available pore channels, carrying with it any dissolved solutes. In field lysimeter studies using medium-textured soil cores packed with an A and B horizon, rapid movement (up to 20 cm) has been repeatedly observed for various pesticides (terbuthylazine, a triazine herbicide; Bowman 1989; isazofos, a soil insecticide; Bowman 1990) following surface ponding of water. These chemicals moved only half as far (10 cm) in adjacent lysimeters uniformly packed with a much less adsorptive, coarser-textured Plainfield sand under the same water application conditions.

In recent laboratory studies, Baker and Hillel (1991) reported that in infiltration tests when the sublayer particle size was made smaller (closer to the texture of the surface



layer), or the sublayer particle size distribution was made wider (by addition of fines), or increasing amounts of water were uniformly mixed with the sublayer prior to infiltration, then the fractional wetted volume increased until fingering was no longer observed. Recently Steenhuis and Parlange (1991) reported that layered soils are not necessarily required to produce water flow instabilities (fingering), and that it can occur in a relatively homogeneous sandy soil at rainfall rates substantially below the saturated hydraulic conductivity. In a homogeneous sand profile, the fingers are quite vertical, but deviate more from their vertical paths as the sand becomes more heterogeneous. Similar preferential flow behaviour has been described by Jury (1991) in unstructured sandy soils in California. It therefore seems apparent that water flow and solute transport in unsaturated soils is a much more complex process than earlier-held concepts of relatively-uniform matrix flow, and that observed hydraulic conductivities in unsaturated soils may be very dependent upon input rates and antecedent moisture levels as well as upon the heterogeneous nature of the soil itself.

#### 4.3.2 Effect of Tillage Practices on Pesticide Transport in Soils

The portion of farmland in the U.S.A. employing some sort of conservation tillage has increased about 24 fold from 1963 ( $1.5 \times 10^6$  ha; Mannering et al. 1987) to 1987 ( $35.6 \times 10^6$  ha; Thornton 1987). In this discussion, "conservation tillage" practices include both "no-till" and "reduced tillage", which includes any practice leaving at least 30% crop residue on the soil surface (Allmaras and Dowdy 1985; Wauchope 1987). Conservation tillage has gained in popularity not only because it reduces soil erosion, but also because field operations can be significantly reduced, lessening input costs. There are ongoing arguments as to whether adoption of conservation tillage practices leads to increased pesticide use to compensate for lack of tillage. Wauchope (1987) stated that herbicide use would probably increase under conservation tillage, but not necessarily other pesticide usage. In many cases the development of conservation tillage practices has led to the development of different kinds and combinations of herbicide use patterns, but not necessarily greater total amounts applied.

Depending on the type of conservation tillage practiced, water infiltration may be significantly higher than on conventional tillage (Radcliffe et al. 1988), raising the potential for increased pesticide transport to groundwater. In some rainfall simulation studies on 1 m<sup>2</sup> plots (silt loam) using the Guelph Rainfall Simulator (Tossell et al. 1987), it was consistently observed that there was greater water infiltration on no-till plots compared to adjacent conventional tillage practices, and conversely, lesser runoff volumes. Edwards et al. (1988) and Dick et al. (1989) likewise reported much lower runoff volumes from no-till relative to conventional tillage, leaving more water for percolation. Much lower soil erosion losses can be expected from conservation tillage, which in turn translates into lower surface losses of strongly soil-adsorbed pesticides (nonionic pesticides of low water solubility (<1 µg/mL) and organic cations such as paraquat) (Wauchope 1987). Difference in pesticide runoff losses between the two tillage types are less distinct for more water soluble nonionic pesticides which tend to be transported in the aqueous phase. In field-plot rainfall simulation studies, it was found that about 85% to 95% of herbicides, such as atrazine and metolachlor ( $K_{oc}$  values about 50 to 100 µg<sup>1-N</sup> g<sup>-1</sup> mL<sup>N</sup>; N = Freundlich slope), were partitioned into the water phase in surface runoff. Leonard (1988) stated that the distribution of pesticide between solution and adsorbed phases can be assumed to follow relationships such as the Freundlich equation, and this has been found to be the case in these rainfall simulation studies.

The considerable amounts of crop residues remaining on the soil surface under conservation tillage increase the likelihood of significant washoff losses of freshly-applied herbicide (Felsot et al. 1990). Freshly-applied foliar pesticides are also quite susceptible to washoff losses but the hazard decreases substantially with time (Willis et al. 1992). In recent rainfall simulation studies at our research centre, substantial washoff losses of freshly-applied atrazine and metolachlor occurred on plots with high corn stover residue cover. It appeared that the herbicides did not strongly adhere to the crop residues, and a heavy rain following application quickly washed chemicals off the crop residue onto the wet soil surface, then transported them away in surface runoff water.

Isensee et al. (1990) found in their field studies that four to five times (unconfined aquifer) and 20 to 50 times (confined aquifer) as much atrazine leached into shallow groundwater under no-till than under conventional tillage. The amounts found far exceeded the level expected from piston-type displacement, which was strong presumptive evidence for preferential flow. Rainfall amounts, storm profiles and their timing following pesticide application greatly influence whether, and to what extent preferential transport of those chemicals is likely to occur. Shipitalo et al. (1990) found that a 1-hr, 5-mm rain followed by a 0.5 hr, 30 mm-rain one day later on no-till soil blocks (30 cm cubes) reduced atrazine transport through the blocks by 2-fold relative to replicate soil blocks receiving only the 30-mm rain. Light rain on herbicide-treated soil following application moved the chemicals slightly into the soil matrix, greatly reducing their susceptibility to preferential transport during subsequent storms. Even larger reductions in preferential flow of bromide ion (7 times) and strontium ion (10 times) were recorded for the same two rain scenarios. In subsequent water flow studies with the 30-cm cube no-till soil blocks they (Edwards et al. 1992) found very heterogeneous flow patterns as a result of the macroporous structure of the soil, and that average atrazine concentrations in the percolate did not seem to be influenced by rainfall intensity. Transport of the chemicals appeared to be dominated by percolate volumes rather than by rainfall intensity.

#### 4.4. CONTINUING RESEARCH PROBLEMS

In some respects there are less serious environmentally-related problems with agricultural pesticide usage than was the case a decade ago. There tends to be a much greater public awareness and sensitivity towards environmental issues today and as a result pesticides are now used more judiciously. Extensive well-water surveys taken here in Southwestern Ontario have found declining amounts of pesticides over the past several years (unpublished report, Agriculture Canada, 1992). There is also a growing interest in the agricultural community towards more holistic forms of farming which take a more balanced view of the ecosystem. Some of the ongoing research challenges facing agriculture through the next decade range from theoretical modelling of pesticide transport and dissipation to on-farm

related research problems, such as selecting the best management practices for an individual operation.

#### 4.4.1 Experimental Design and Data Quality

From a research viewpoint, efforts at modelling pesticide behaviour in agricultural systems have become increasingly sophisticated and complex. With this sophistication comes an increasing demand for better quality inputs, such as partitioning coefficients and dissipation rate constants. For more accurate long-term modelling scenarios, there is a need to include time-dependent  $K_d$  parameters in models that reflect the slow binding processes taking place in the soil. In the preceding discussion we have dealt in some detail with the numerous pitfalls that can and do occur in the generation of critical parameters such as partitioning coefficients. In setting up an experimental design it is of critical importance to the quality of the data generated that the researcher be aware of the errors associated with the measurements being made, and to minimize them as much as possible.

#### 4.4.2 Modelling Preferential Flow in Heterogeneous Media

As conservation tillage practices gain acceptance throughout this decade, the influence of preferential flow behaviour on pesticides, nutrients and manure bacteria will receive increasing scrutiny. Unsaturated water flow patterns in soil exhibit great spatial variability making it difficult to simulate in modeling scenarios. Extreme spatial variability in unsaturated water flow has been observed in soil block studies (includes A/B horizon interface) which suggests that both rainfall rate as well as the antecedent moisture status of the block determines which suite of pores conduct water for a given event. In successive rainfall simulations on the same block, different combinations of highly-conducting pores (not identified macropores or worm channels) may be involved in water conduction; the only change between simulations was the moisture status of the block. It would therefore appear that unsaturated hydraulic conductivity in a given soil block could vary greatly throughout domains within that block, depending on its "moisture history" as well as the current rainfall

rate. Unsaturated water flows in soil often seem to follow along "fracture planes" which may not appear evident until dye tracers are used to visualize the flow patterns. Such heterogeneous behaviour will prove to be a great challenge for modellers to deal with, and it is evident that preferential flow is a reality in unsaturated, as well as in saturated porous heterogeneous media.

#### 4.4.3 Farm Management Systems

Although conservation tillage practices in general are rapidly gaining acceptance, there remain lively ongoing discussions as to whether no-tillage or some form of reduced tillage is superior. While no-tillage practices have many supporters who correctly argue that no-tillage can greatly reduce soil erosion and improve soil quality, there remains the as yet-unresolved issue of the significance of rapid solute transport through the macroporous channels in the soil. In contrast, proponents of minimum tillage argue that light tillage at planting disrupts the surface access of preferential channels sufficiently long to permit pesticides to dissipate or move just below the soil surface where preferential flow is no longer a problem. The answer to these and other cropping and tillage practices may be found by developing more comprehensive approaches to farm management from an ecosystems viewpoint. In Ontario, and probably in many other jurisdictions, there is a rapidly growing movement among a broad-based coalition of farm organizations to develop environmentally-sustainable farm plans in cooperation with research and extension personnel. In Canada, this process is being stimulated by Environmental Greenplan funding, a joint Federal/Provincial program being currently put into place.

With new crop and tillage practices being tried by innovative farmers comes different requirements for pest management techniques. In some cases this may require new pesticides, improved formulations, new combinations of existing registered pesticides, or perhaps more holistic approaches to crop management which do not employ pesticides. Pesticide registration guidelines in Canada appear to be considerably more conservative and perhaps restrictive than their counterparts in the U.S.A., especially for the use of new tank mix combinations for already-registered pesticides. Often the market for such tank mixes will be

relatively small, especially for those required for new crop management techniques, and therefore there is no economic incentive for the agrichemical industry to do the necessary field efficacy studies required for registration. This fact, combined with the close proximity to, and the pressures of competition with the much freer U.S. market has driven some Canadian farmers to quietly use non-registered tank mixes. The access to new types of tank mixes is certainly an essential step for innovative farmers in successfully adapting to improved management practices.

The type of research issues involving pesticide use through the next decade will represent a cross-section of activities from the theoretical laboratory-based studies to the on-farm types of research activities alluded to above. Much more than ever before, there will be strong incentives for the research community to work closely with innovative farming groups, and to employ an ecosystems-based approach to solving and implementing new sustainable farming technologies for the next century. Pesticides, rather than being relied on as a means of controlling the production environment will instead become one of many tools available to the farmer in developing more comprehensive pest management strategies.

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## AGRICULTURAL SOIL QUALITY CRITERIA FOR CANADA

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### ABSTRACT

The concept of soil quality has evolved from an expression of productivity to an assessment of environmental sustainability. It now includes elements of health and time as well as biological production. This paper tracks the evolution from an agricultural context and defines specific, discrete components which can be managed separately within the environmental framework. A brief outline of agricultural soil suitability identifies some of the critical soil qualities such as the ability to supply nutrients and moisture and how we presently assess them. A discussion of emerging issues touches on the requirements to link various data sources and disciplines, the need for standardization and coordination, the need to establish and monitor sensitive environmental indicators and the challenge of putting a "value" on quality so that it can become an integral part of economic assessments and development planning.

### 5.1 INTRODUCTION

Soil quality per se is an abstract term which requires a description or context before it assumes specific meaning. For an assessment of soil quality one needs to know the purpose or use, the critical parameters by which it will be measured, and a rating standard to assess excellence (Pettapiece 1986). The term "soil quality" may be used for a variety of purposes including forestry, waste management or reclamation. Within an agricultural context, a number of terms and procedures such as rating index (cf Storie 1936), capability (CLI 1964) and land evaluation (cf Stewart 1968) have been used to describe soil quality. More recently, there has

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been a shift to emphasize a sustainability aspect (FAO 1976, Acton 1992) and a holistic ecological perspective (Dover and Talbot 1987, Lourance 1990).

The concept of sustainability, which has long been implicit in many assessments, is now a principal pillar of most definitions of soil quality and has been broadened to include the financial side of land use (Committee on Sustainable Agriculture, 1992). When one adds in the fact that the majority of soil quality considerations also include landscape, hydrology and particularly climatic components it is easy to see why there has been some confusion about this topic. In the past, with industries and disciplines relatively isolated and with a somewhat restricted number of people working on the issue, communication was not a major concern. That is no longer true today. Soil quality is now a major environmental issue that touches on an increasing variety of disciplines and jurisdictions and ranges in application from individual farms to international arenas. The need to integrate and cooperate has never been greater.

The number and usage of terms to describe soil quality is confusing at best and at worst can actually create problems and obstruct progress. The concept of soil quality and particularly the environmental perspective is critical to our future land use planning and management and needs to be clearly defined. The purpose of this presentation is to: (a) review the history and definition of (agricultural) soil quality, (b) place (agricultural) soil quality in a broad environmental perspective, (c) discuss the present criteria used to assess agricultural soil quality, and (d) consider emerging issues and concerns impinging on soil quality considerations.

## 5.2 BACKGROUND

Agricultural rating systems are actually assessments of soil quality for a specified purpose. They started in the early part of this century in a very qualitative Good-Fair-Poor style. However, by the mid 1930's there were a number of systems which provided some

specific structure. Most were based on yield predictions with very little attempt at defining processes or interrelationships. These deductive approaches were gradually replaced by systems which were based on some assessment of inferred response or inductive approaches. Both approaches were somewhat quantitative and were used by some as a relative (index) rating and by others, particularly those using the ratings to support land assessment for taxation purposes, in an absolute sense. Some used classes, others used multiplicative or additive procedures (Huddleston 1984).

While productivity was still a major consideration, the 50's and 60's saw the introduction of capability and suitability concepts (CLI 1965, Klingebiel 1958). These used a class format with a limiting factor approach and, even though based on more and better information, appeared less precise and therefore often gave the impression of being less reliable. However, the simple straight forward concepts were very useful for comparing land use options and they were quickly adopted by the planning community. Although the scope of interpretations was expanding, agricultural assessments still did not consider the environment or the idea of change.

In the decade of the 70's computer technology was introduced and process modelling began. Later, land evaluation (FAO 1976, Smit et al. 1984) added an economic component to soil quality assessments but the emphasis was still mainly on agricultural development. However, sustainability was becoming an underlying assumption and the concept of soil quality now included elements of time and "health". It was not simply the kind and amount of production but also would it stay healthy enough to maintain the production. Degradation and conservation became topical issues and the need for monitoring was introduced.

The next major change, coming mainly in the 80's, was inclusion of the holistic ecological concept. Soils were now considered part of a larger environmental system and added to soil quality was the idea of a filter in that system (Larson and Pierce 1992). For example, water was now seen not only in terms of plant

growth but also something that passed through or over the soil connecting it with other parts of the environment. Not only was the production system becoming more inclusive, but the concepts about what it should be were constantly evolving.

It is interesting to consider some of the scientific and institutional responses to the evolving concepts of soil quality and the emerging environmental awareness although cause and effect are often difficult to establish. For example, the 70's saw the development of land evaluation concepts but it is not clear whether it was a response to the multiple land use needs of planning or because the introduction of computers made it possible. Today, society is clearly responding to global environmental concerns and the idea of sustainability such as expressed in the "Brundtland report" (The World Commission on Environment and Development 1987). This in turn directs governments. We have recently had the National Soil Conservation Program and Federal-Provincial (agricultural) reports on environmental sustainability (1990) and now the Green Plan (Government of Canada 1990).

What then is an acceptable definition of soil quality?

### 5.3 DEFINITION OF (AGRICULTURAL) SOIL QUALITY

There are a number of definitions which capture our present concept of what we think soil quality should be. Leopold (1949) provided an early holistic concept which has been interpreted by Anderson and Gregorich (1984) as "the sustaining capability of a soil to accept, store and recycle water, nutrients and energy". More recently Larson and Pierce (1992) have suggested that "soil quality is the capacity of a soil to function within the ecosystem boundaries and interact positively with the environment external to that ecosystem". That is, the management of a soil within a particular set of environmental conditions, an ecosystem, cannot be judged without consideration of its impact on adjoining ecosystems. Others have specifically included profitability but that seems superfluous in addition to sustainability. In all cases there is an

implication of inherent soil capability and sustainability. Also, one understands that biological production is involved and that sustainability refers to both economic and environmental considerations. While the term 'soil' is used, the context indicates a broad concept which includes landscape and climatic attributes. There are situations where one may wish to specify soil or climatic quality for a particular use but in the general context it seems preferable to use 'land' as an explicit integration of the main contributing factors.

According to the FAO (1976) definition, "land quality is a complex attribute of land which acts in a distinct manner in its influence on the suitability of land for a specific use". Suitability is understood to include the aspects of biological production and sustainability and the definition emphasizes the need to specify a use or objective, an important point for clarity of communication. This is quite generic but can be adapted for any use or level of detail and would seem to be a good starting point. As quality also implies a "degree of excellence" it is clear that critical values for one purpose could be quite different from those for some other use. For example, a salinity level which is acceptable for barley might be limiting for onions or, topographic parameters which might be limiting for cultivation might be quite acceptable for grazing.

The previous discussions have noted a shift in the concept of soil quality from something that was almost synonymous with productivity to a much broader concept which includes sustainability and hence time and health aspects as well as an ecological perspective. Figure 1 is an attempt to illustrate the place of soil quality in the present context. The box in the middle defines the real geographic entity that we can analyse and monitor. This figure also "defines" the various components and identifies the linkages which must be developed to make the whole system function.

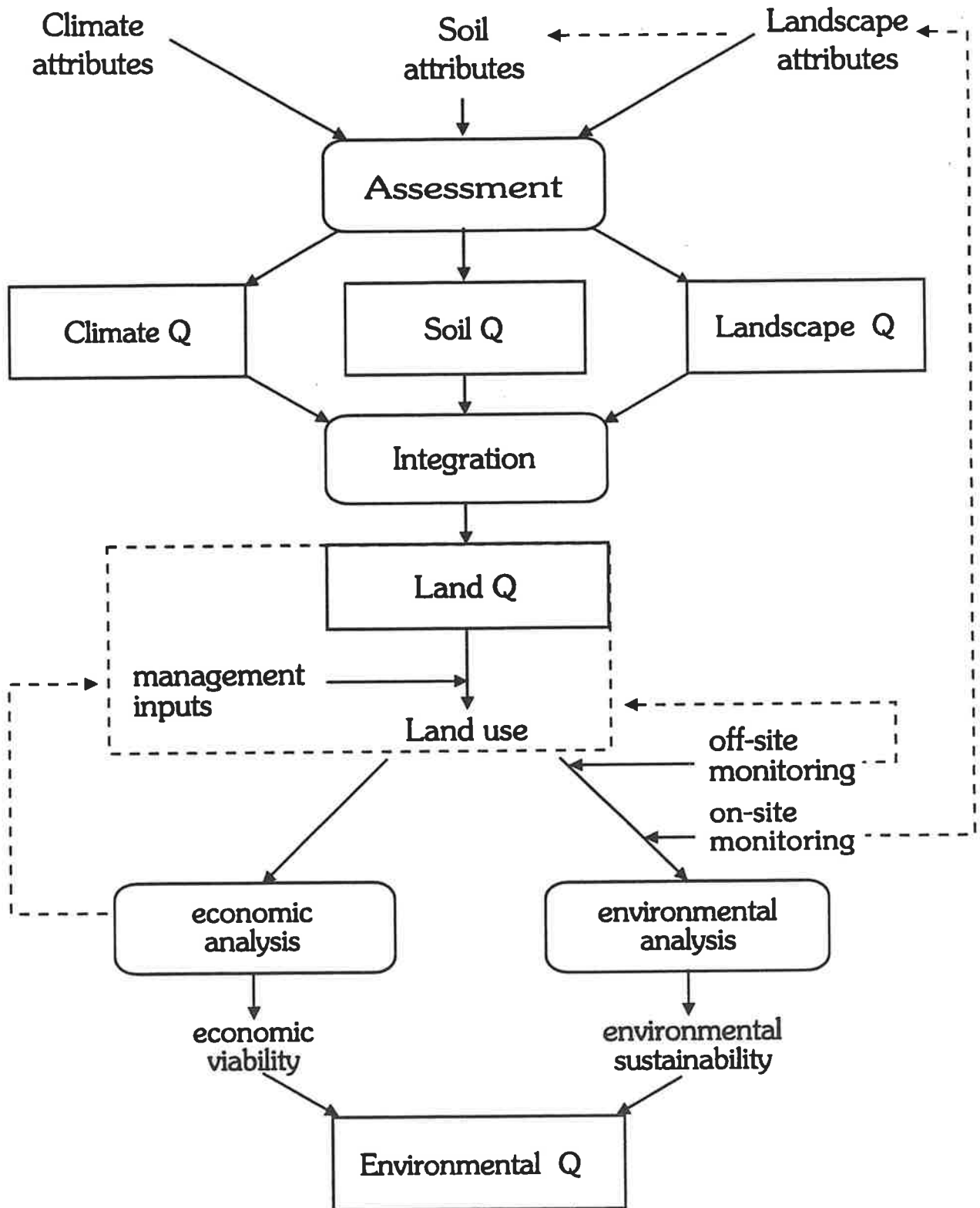


Figure 1. Components of environmental quality

It is difficult to deal with the whole package of "environmental quality" at one time or by one discipline. The next section will deal in more detail with the restricted scope of soil or land quality for agricultural purposes.

#### 5.4 AGRICULTURAL SOIL QUALITY

Agricultural soil quality as used here is identical with suitability for agricultural purposes. Indeed, even the term 'agricultural' is too broad for most discussions of soil quality which must at least specify arable vs nonarable. Therefore, this discussion does not cover the complete range of the soil quality definition but it is a definable sub-component which is basic to nearly all other socioeconomic and environmental assessments and evaluations. Our long term view is that we must deal with processes and that understanding and modelling them is the most effective approach for assessing and particularly monitoring soil quality. However at any point in time one needs to be able to assess quality based on current knowledge.

The following discussion is based on a recent initiative by an Expert Committee on Soil Survey / Agriculture Canada working group to quantify our assessments of soil interpretations. It will deal with the development of a standardized, quantified assessment of the suitability of a tract of land for a specified agricultural pursuit. Preliminary work defined a number of constraints and assumptions.

1. It must cover the range of Canadian conditions
2. It must be specific and explicit
3. It should follow the 7 class concept of the CLI
4. It must be flexible and adaptable
5. It should separate and rate individual components
  - climate, soils and landscape
6. It should be as inductive as possible
  - based on an expert system approach
7. It must be suitable for automation



8. It should use present or commonly available data
9. It should use a mathematical or continuous scale approach- not classes
10. It would be modified.

This provided a general framework but did not address the issue of the specific factors to be used for an assessment of soil quality. Huddleston (1984) concluded from a review of rating schemes in the U.S. that a mixture of inductive, process related, and deductive, direct measure, approaches would be effective and practical. With this in mind, the working group analysed systems presently in use and drew up a list of critical factors for determining land quality. The factors were selected according to 4 main criteria:

1. known to affect the ability of soil to produce crops,
2. known to affect the ability of soil to respond to management imposed stresses (resilience),
3. must be measurable or estimatable and
4. should be commonly available.

Because we wanted to deal with the whole land system it was necessary to consider the factors (qualities) and criteria<sup>2</sup> (measured parameters) for climate and landscapes as well as soils (Table 1).

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<sup>2</sup> The term 'criteria' is commonly used for assessments while the term 'indicators' is often used when discussing change.

Table 1. Selected criteria for assessing land quality for arable agriculture.

| Component | Factor (quality)         | Criterion                                 |
|-----------|--------------------------|---|
| Climate   | - heat or energy factor  | growing degree days<br>(growing season)   |
|           | - moisture factor        | precip.- potent.evap.<br>(growing season) |
| Soils     | - moisture supply        | texture (with climate)                    |
|           | water table              |   |
|           | - nutrient supply        | reaction (pH)<br>organic matter content   |
|           | - rooting condition      | surface structure<br>subsurface structure |
|           | - chemical problems      | salinity<br>sodicity                      |
|           | - drainage               | water table (climate)                     |
| Landscape | - erodibility/management | slope steepness                           |
|           |                          | slope length                              |
|           |                          | stoniness                                 |
|           |                          | flooding                                  |

Following the conclusions of Huddleston (1984) a mixture of inductive and deductive approaches was used. The next step was to develop ratings for each factor. This required a crop(s) designation and the small grains (wheat, barley, oats). a group of similar crops which could be grown across Canada, were selected. The approach was to establish critical values for each factor which related to our concept of excellence and then place these in a continuous value table or chart.

The following table for salinity was developed based on general relationships to crop yield.

Table 2. Critical levels of salinity for small grains.

| Salinity value<br>E.C. (dS/m) | Limitation                       | Point<br>deduction |
|-------------------------------|----------------------------------|--------------------|
| 2                             | no effect (class 1)              | 0                  |
| 4                             | slight effect (class 1-2)        | 20                 |
| 8                             | moderate limitation (class 3)    | 50                 |
| 12                            | very severe limitation (class 5) | 70                 |
| 16                            | growth stopped (class 7)         | 90                 |

This could also be represented as a graph (Figure 2).

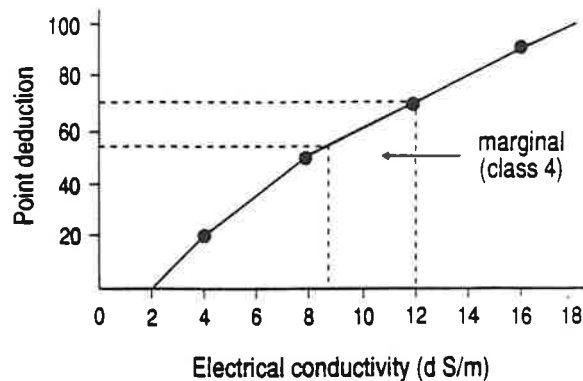


Figure 2. Relationship of point deductions to salinity for spring seeded small grains.

All the soil factors were combined into a final soil rating. The same procedure was used for the climate and landscape components. Each step is documented in the procedure so any discrepancies can be quickly identified and clarified. The overall rating is the most limiting of the three components, with accommodation made for the identification of significant limiting factors. This allows for informed land use comparisons including valuation of remedial measures.

This is a very pragmatic approach based on documented relationships which are linked together using an expert system procedure. The relationships, the use of a measurable soil attribute to assess another factor, have been termed 'pedotransfer functions' by Bouma (1989) and, along with 'proxies' for unmeasurable

attributes, are the key to the system. For example, we use % clay in the estimation of water supplying ability and % organic matter in the assessment of fertility and structural resilience. It would be nice to know every detail about every process but this is not the case and the need to utilize empirical relationships will be required for some time.

This suitability rating system documents our present knowledge and identifies problem areas for priority research. It integrates climate and landscape components into the analysis but maintains flexibility by dealing with each separately. It is explicit and quantitative and can be automated. It is best viewed as a relative index rather than an absolute value. While the approach can be used for other crops, the rating scales, as developed, are specific for small grains. Future work will address the factor ratings for other crops such as forages, corn, potatoes and specialty crops as required. This system does not model plant growth or predict change. Nor does it rate economic viability or best land use. These require additional considerations. It simply assesses the suitability (quality) of a particular set of biophysical conditions for a specified purpose. While links to more complex analyses were considered in the design of the system they also are the weakest part of the assessments and should be a focus for future work.

## 5.5 DISCUSSION

Soil (Land) quality includes a number of aspects which need to be related and integrated to support a variety of decisions ranging from individual field management to national policy development. The questions can vary from "can I grow onions", to "what is the most appropriate landuse", to "how might an international tariff affect sustainability". As a result, there is no single, simple answer or process for describing soil quality. It depends on the objective and may include a physical assessment, a comparison of alternative uses, socio-economic evaluations and environmental considerations. It may be a present determination, an analysis of change, or a prediction of sustainability.

Our challenge is to clearly identify the component parts and requirements and to provide the linking procedures. This has long surpassed the purview of one discipline or even one industry. As the complexity of the issues and the solutions has increased so too has the need for cooperation and integration. This is not to say that we all have to develop and use a single procedure, but we must understand the needs and implications of the other players. Our information must be available in forms that are meaningful and useable by others. For example, people in agriculture must broaden their concept of soils to include other functions than those relating only to productivity; particularly those relating to water movement and "environmental filtering".

In a small region with relatively uniform conditions or limited number of options the complexity can be difficult but when considered for a country as large and varied as ours it often seems overwhelming. Indeed, it can be, without some overall logic or concept which provides for both the partitioning and linking of activities. For example, the development of a national ecological framework allows one to partition or separate parts of the country with similar environmental constraints and land use issues with defined boundary conditions. Within these limits, one could reasonably expect to have similar responses to external stresses whether environmental, economic or social in nature. For such a stratification to function it is critical that all concerned agencies agree to use a single standard. This agreement is much more important than being absolutely correct, a concern which often hampers the sharing of information and ideas. There does need to be reasoned background and documentation based on available research. There must also be continuing investigation, testing and validation, and a process for changing the standard when appropriate.

One of the requirements for cooperation and integration is consistency in terminology and standards. The people assessing soil suitability and those monitoring change should be measuring the same attributes or at least reporting on the same quality component. If we are going to exchange information and build on the experience of others it is essential that we have standards. Again agreement is

more important than absolute correctness. If a standard is found to be incorrect or inappropriate it can be changed and any system must be able to accept this inevitable occurrence. We are continually approximating and research to refine or change our assessments is essential.

The search for definition and establishment of environmental indicators is the source of much discussion (Hamblin 1992) and will be an important issue over the next few years. The consideration of sustainability demands a focus on quality change which in turn requires the identification of indicators sensitive to change. At present much of our knowledge about soil quality relationships is empirical. The future will see more emphasis on process based research and model development. Crop growth models are a good example. These will need to include feedback loops for changing conditions and will certainly be based on probability analyses. Such models will become the basic tools for predicting change or assessing sustainability. A current problem area is our inability to link or extrapolate experimental site data to an areal or geographic projection. This includes not only the single discipline concerns but the added links to other parts of the environment. For example, fertilizer-yield relationships when extrapolated to a field or watershed now need to consider movement of chemicals to a water table or off-site effects from surface runoff. As these kinds of initiatives progress more of our soil survey activity will be directed to validation and monitoring in contrast to basic data collection.

Another issue which will need to be addressed in the near future is the valuation of all aspects of environmental quality including soil quality. (MacNeil et al. 1991). That is, the assigning of dollar values and the internalizing of these factors in land evaluation. At the present time, environmental issues tend to be handled as external to assessment of economic viability and sustainability. Until they become an integral part of such evaluations, a balanced analysis which will stand up to public scrutiny will not be possible. The wildlife/recreation sectors have attempted for many years to put a value on the positive aspects of

our natural resource base with varying degrees of acceptance. Like human health, it is often the cost of correcting which is the only value available. For example, we don't have a value for a good, non-limiting subsoil but we can measure the loss in yield due to a restricting compacted layer or the cost of deep ripping to remove it. Following this line of reasoning, if it is easily (cheaply) fixed it is less valuable than if it is more difficult or expensive. That still does not put a positive value on a rural landscape or wildlife habitat or cover the cost of a sustainable management practice but it does provide some basis for decision making. We need to address this issue and we need help to do it. In many ways this is a societal as much as a technical issue and input from social scientists will be required. Society also influences our definitions of sustainability and acceptability. These can and will change as knowledge and awareness increases. The "value" of endangered species habitat and wetlands are examples. It is important that we understand this process and not get frustrated when the technical targets we identified yesterday are no longer valid today.

## 5.6 SUMMARY

The concept of soil quality has evolved over the past few years to include a holistic environmental context. It now includes time and change components as they relate to health and sustainability. The whole complex is dynamic and our definitions and assessments must be flexible enough to respond. We have tried to place agricultural soil quality in this broader context and to provide some working definitions which reflect process rather than static data. The need for clarity of definitions and standards is essential as is the need for cooperation and integration of many agencies and disciplines. The current assessment of soil quality for agricultural purposes is based on an expert system approach which is explicit, flexible and can be automated. It does not address the aspects of quality change or best land use which require additional inputs. This underlines the importance of defining

boundary conditions and the need to be able to partition as well as integrate.

Future activities will undoubtedly centre around process modelling, monitoring quality change, developing links with other data sources for holistic assessments of sustainability and the evaluation and internalizing of environmental and 'soil health' factors. An immediate challenge is to identify soil quality standards and indicators which are sensitive to environmental change. It should be remembered that there are rarely quantifiable absolutes in the natural resources and often many equally valid approaches may be used to address an issue. However, this should not be used as a reason to avoid setting or selecting standards. The establishment of standards highlights the difference between a research perspective which must keep probing and changing, and an application mode which requires some stability. Both are required and need to be accommodated in our overall approach to soil quality.

#### 5.7 ACKNOWLEDGEMENTS

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**SUSTAINING FOREST PRODUCTIVITY THROUGH SOIL QUALITY STANDARDS:**

**A COORDINATED U.S. EFFORT**

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**6.1 INTRODUCTION**

**Soil is more than farmer's dirt, or a pile of good topsoil,  
or engineering material; it is a body of nature that has  
its own internal organization and history of genesis.**

**Hans Jenny**

**The Soil Resource**

**"What will save the soil, then?" I ask.**

**"As soon as there is no food on their plates,  
people will start worrying about saving the soil."**

**Question posed to a forest soil scientist by Peter Steinhart**

**The Edge Gets Thinner**

Along with water and air, soil is the most fundamental of resources. This unconsolidated skin of the earth is the source from which many other resources and our most valued commodities flow. And along with clean water and air, healthy and productive soil is vital to a healthy and productive society. On a human time scale, soil is nonrenewable. Thus, in the fullest sense, soil is a heritage to be protected and, where necessary, to be repaired or improved as we pass it from one generation to the next.

Clear though this principle may be to some of us, it seems opaque to most of modern society to whom soil-derived resources simply are products of grocery stores, furniture shops, retail lumber yards and news stands. That soil is as common as air makes it just as invisible. Or, when thought is given to it, soil is seen in a negative sense. Soiled clothing must be cleaned. Soiled hands must be washed. Through the centuries, even landscape artists saw soil as little more than a platform for positioning deities and gentry (Jenny 1968). Even today, a cultural veil separates the earth from the eyes of most of humankind.

Despite today's general apathy, many cultures have emphasized soil stewardship through religion and philosophy. Abraham, in his covenant with God, was instructed to "Defile not therefore the land which ye shall inhabit, wherein I dwell" (Num. 35:34). Confucius saw in the earth's thin mantle the sustenance for all life and the source of minerals treasured by mankind. A century later, Aristotle viewed soil as the central mixing pot for the other elements of matter--air, fire and water--in the formation of all things. Donne, in Devotions Upon Emergent Occasions, used soil's relationship to earth metaphorically as man's relationship to mankind in that "No man is an Iland, intire of it selfe; every man is a peece of the Continent, a part of the Maine; if Clod be washed away by the Sea, Europe is the lesse, as well as if a Promontorie were, as well as if a Mannor of thy friends or thine owne were." Leopold (1949) expressed it too, in his Odyssey of an atom. From rock to soil, flower to acorn, deer to Indian, all in a single year.

In a sense, soil scientists carry a burden of raising a concern for saving the soil that approaches the fervor spent on whales, seals, owls, and redwood trees.

#### 6.1.1 Legislating Soil Stewardship

The Law. Irrespective of general apathy or ignorance, sustaining the long-term productivity of our forested lands should be an ethical and economic aim of enlightened forest management. For the USDA Forest Service, there is a legal reason, too. Among the World's nations, the United States and the Netherlands stand alone in their legal mandates for good land stewardship. In the Netherlands, the Dutch Soil Protection Act of 1987 requires that soil must not be treated in a way that degrades its capacity for such multiple functions as grazing, ground water recharge, or crop production (Moen 1988). In the United States, the Multiple Use and Sustained Yield Act of 1960, the National Environmental Policy Act of 1969, the Forest and Rangeland Renewable Resources Planning Act of 1974, and the National Forest Management Act of 1976 (NFMA) all bind the USDA Forest Service with managing renewable resources without permanently impairing the productivity of the land (USDA Forest Service 1983).

Section 6.(g)(3)(c) of NFMA specifically charges the Secretary with ensuring research and monitoring of the effects of each management system to protect the permanent productivity of the land (USDA Forest Service 1983). Responding to this, the Secretary appointed an independent Committee of Scientists to form a framework for implementing the law. These efforts led to a Code of Federal Regulations for Forest Planning which, among other things, requires the Forest Service to monitor the effects of prescriptions, including "significant changes in land productivity" (Code of Federal Regulations 1985). In response, the Chief of the Forest Service directed each of the nine Forest Service administrative Regions to develop monitoring procedures for detecting a

significant change in land productivity over a planning horizon (a timber rotation).

The Forest Service's first task was to define the scope of its monitoring responsibility. "Land Productivity" can be defined as the ability of a site to create goods or services of social value. Thus, land productivity might encompass a cornucopia of timber, wildlife, watershed, fisheries, and aesthetic values--each a legitimate measure of the land's "produce." Legitimate though they may be, they are not equally measurable. Some are intangible, others subjective or temporally unstable. Discussions with the Office of General Counsel eased the way to a more objective and usable definition (USDA Forest Service 1987)

6.1.1.2 Interpreting The Law. "Land Productivity" was defined as the soil's carrying capacity for vegetative growth within the constraints of local climate. "Vegetation" means the flora native to the region, but not necessarily that occupying the site before disturbance from management. "Carrying capacity" was defined as average periodic dry matter production when the site is stocked fully with the native flora of interest. Finally, "Significant Change" was defined as the minimal level of reduced carrying capacity that is detectable with operational monitoring technology. After much discussion, a working value of 15% was adopted (USDA Forest Service 1987). This does not mean that the Forest Service tolerates productivity declines of up to 15%, but merely that it recognizes problems with detection limits. Although smaller declines might be detected with a higher intensity of sampling, the consensus was that a decline would have to be at least 15% to be separated from extraneous variation under realistic levels of funding.

Obviously, vegetative growth is not the broadest measure of productivity. But what is better? Are any other measures more reflective of ecosystem health and potential? Clearly, reducing a soil's capacity to grow vegetation degrades the capacity of the site for sustaining the production of all other renewable resources.

### 6.1.2 A Site's Productive Potential

Although the definitions of productivity and significant change were clarified, assessing them under operational conditions isn't easy. Merely measuring current growth rates is not enough because rates vary both within and between plant species and are subject to changes as communities develop. Even in simple plant communities of a given age, competitive differences can cause confusion. For example, a community of forest trees spaced very widely will have less total tree growth per unit area than does a community where trees are spaced more tightly. However, if only merchantable growth is considered, the relationship is reversed because fixed site resources are apportioned among fewer trees. This is illustrated in Table 1 (Oliver 1990) where total stand volume is related inversely to tree spacing. Yet, when the focus is on larger trees of sawlog size, volume and spacing are directly related and the trend is reversed. The paradox is that depending on tree spacing and growth definitions, opposing conclusions could be reached about whether one land unit is more productive than another. In the Table 1 example, apparent productivities truly are different. But the land's productive potential--the inherent capacity of the site to sustain plant growth--has not changed at all.

Another problem facing productivity monitoring concerns the effects of other types of vegetation on tree growth. Tree volumes may be substantially less in stands with shrub understories than in adjacent stands without shrubs (Table 1). Poorer tree growth where shrubs are present creates the impression that productivity has been fundamentally reduced. But with or without shrub competition, the site's total resources have remained the same and the land's productive potential has not been altered. Failure to account for the effects of competing vegetation can lead to false conclusions and an immense problem for operational monitoring.

Measuring existing vegetation per se is a blind alley. Instead, we must turn to measures of site potential. Unfortunately, our knowledge of site potential is limited because it is conditioned by the way forests have been managed (Powers 1987, Stone 1975) (Figure 1). Where forests are merely exploited, as on many non-industrial private lands of



Table 1. Tree means and stand totals for 20-year-old Pinus ponderosa planted at five spacings with and without shrub understories (Oliver 1990).

| Square<br>Spacing<br>(m) | Average Height  |         | Average Dbh    |         | Total Volume                     |         | Merchant. Vol. |         |
|--------------------------|-----------------|---------|----------------|---------|----------------------------------|---------|----------------|---------|
|                          | With            | Without | With           | Without | With                             | Without | With           | Without |
|                          | ----- (m) ----- |         | ---- (cm) ---- |         | ----- (m <sup>3</sup> /ha) ----- |         |                |         |
| 1.8                      | 7.0             | 7.6     | 10.4           | 11.9    | 72                               | 92      | 0              | 0       |
| 2.7                      | 7.3             | 9.1     | 14.2           | 17.0    | 66                               | 103     | 0              | 0       |
| 3.7                      | 7.9             | 10.4    | 15.5           | 20.6    | 46                               | 88      | 0              | 5       |
| 4.6                      | 7.6             | 10.4    | 15.2           | 22.4    | 26                               | 65      | 0              | 14      |
| 5.5                      | 9.1             | 11.0    | 19.0           | 26.2    | 31                               | 67      | 2              | 37      |

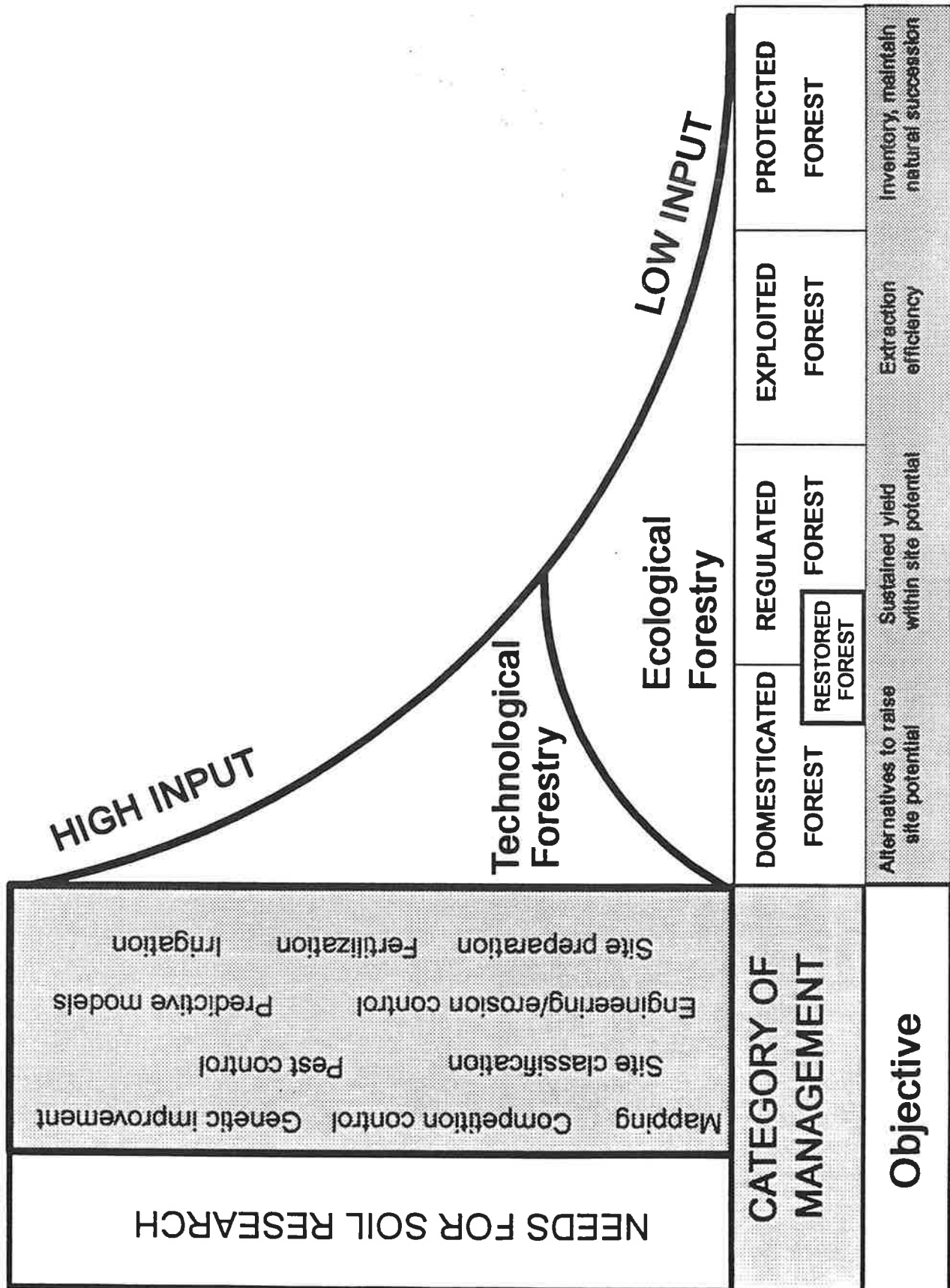


Figure 1. Site knowledge and soil information needs according to the level of technological input and category of management (Powers 1985, modified from Stone 1975).

the U.S. and the boreal region of Canada, knowledge about productivity is restricted at best to crude surveys of standing volumes. Technology is directed to efficiency of extraction, and very little is known about the site's potential for sustained growth. Where forests are regulated, as in most public and industrialized U.S. forests and portions of lower elevation British Columbia and the Atlantic Provinces, management has a working understanding of site potential in terms of site index and yield tables. There, the aim is to work within the inherent site potential and to find economic ways of capturing as much of the potential as possible. At the highest level of technological management intensity is the domesticated forest. There, inherent potential is viewed not as a limit, but rather as the foundation for raising productivity to a higher level by such intensive practices as soil modification.

While domesticated forestry is practiced extensively throughout much of the southern U.S., particularly on lands owned and managed by private forest industry, high cost, cumulative risks, and the inability to adjust crop cultures quickly to meet market demands means that most forests in the U.S. and Canada will be managed at lower levels of intensity. The aim there will be to work within the inherent site potential (Stone 1975). In a forestry context, at least for the present, this means working within concepts of site index and yield at culmination of mean annual increment. This is no panacea of course, because site index is simply an abstraction of potential productivity and must be related to yield functions to be useful in this sense (Powers 1987). Also, site index estimates are imprecise for stands much younger than 20 years, meaning that they cannot detect changes in early stand development following disturbance. Furthermore, stand yields reflect not only the productive potential of the site, but vagaries of stocking and competition (Table 1). And neither site index nor yield functions account for changes in non-tree vegetation. Although helpful, site index and yield have definite limitations.

## 6.2. THE FOREST SERVICE APPROACH

### 6.2.1 Soil Productivity as a Controlling Variable

The Forest Service knows that productivity standards cannot rely solely on tree growth. Instead, there must be a monitoring surrogate that is sensitive to changes in site potential, yet is buffered well against such factors as random fluxes in climate and stocking differences that affect vegetation from season to season and year to year. Soil is the best substitute. Within limits of climate, topography, and biology, soil sets the limits on productivity through its control of nutrients, moisture, and air supplies to plant roots. Furthermore, it is a controlling factor that is directly affected by management. "Soil productivity" has been coined to describe this, and the Forest Service's Watershed and Air Management staff has adopted a program for soil productivity monitoring that is based on the following rationale.

1. Management practices create soil disturbances.
2. Soil disturbances affect soil and site processes.
3. Soil and site processes control site productivity.

Monitoring soil and site processes directly is not feasible. Instead, monitoring strategy focuses on measurable soil variables that reflect important site processes. For example:

| Site Process          | Practicable Soil Monitoring Variables   |
|-----------------------|---|
| Soil erosion          | Soil loss thresholds, % soil cover, production, presence of rills, etc.                                     |
| Nutrient availability | Forest floor presence, soil organic matter content, surface soil loss through erosion or displacement, etc. |

|                                 |  |
|---------------------------------|--|
| Water availability              | Infiltration, saturated hydraulic conductivity, soil bulk density, soil organic matter, plant water potential, soil moisture, etc. |
| Gas exchange                    | Soil bulk density, air permeability, puddling, presence of mottles, waterlogging, etc.   |
| Root growth and nutrient uptake | Soil bulk density, soil strength, soil structure, water table depth, etc.  |

In putting this idea to practice, the Forest Service is establishing "soil quality standards" throughout its nine administrative Regions in the United States. Such standards are meant to be threshold values for operationally measurable soil properties that serve as early warning signals of impaired soil conditions. They are designed to help planning teams maintain or improve the health, suitability, or productive potential of soil. The standards become benchmarks for monitoring trends in soil condition, and for monitoring the implementation and effectiveness of soil and water conservation practices. For environmental assessments, standards are used in monitoring and evaluating the effects of management activities on the soil resource. Achieving these standards is taken to mean that the soil's potential for growing healthy and productive forest communities is sustained.

#### 6.2.2 Setting Soil Quality Standards

6.2.2.1 The Principle. In its most elementary form, the principle behind the Forest Service approach is illustrated in Figure 2A. For any given soil and site, a change in a key soil variable (for example, a loss in porosity) will lead ultimately to a change in potential productivity when the site is at carrying capacity. For the hypothetical relationship in Figure 2A, the change is negative. However, one should note that not all soil variable changes lead to productivity declines. In many cases, productivity may be enhanced to a certain degree. Such is the case when

moisture or nutrient constraints are modified by soil drainage, irrigation, or fertilization. Conversely, if the soil variable is not linked closely with productivity, changes in the condition of that variable will have little or no relevancy (potential productivity remains stable along the "line of no change" in Figure 2A). Obviously, the central feature of the concept is that the soil monitoring variable must be linked very closely with potential productivity when the forest has reached some specified stage of development.

The conceptual model in Figure 2A is simplistic. It implies that potential productivity is stable and known. In reality, there is a belt of uncertainty surrounding any productivity estimate that is due to climatic vagaries, the condition of the plant community, and to limits in our knowledge. Uncertainty about the true value of potential productivity leads to uncertainty about how much change a soil can withstand before productivity is affected. This uncertainty is shown as a shaded band about the line of no change in Figure 2B. Recognizing this, and based largely on collective judgement, the Forest Service has established a working hypothesis that a true decline in productivity would have to be at least 15% to be detectable. Therefore, the Watershed and Air Management branches of each Forest Service Region are charged with establishing soil quality threshold standards capable of detecting a 15% reduction in inherent soil productivity (USDA Forest Service 1987).

6.2.2.2 The Practice. Across the Nation, each administrative Region of the USDA Forest Service is establishing soil quality monitoring plans and soil quality thresholds (Table 2). Thresholds sometimes are rooted in scientific studies of direct applicability, but often they are based on the collective professional judgement of National Forest and Regional staff. In all cases, they are meant as interim guidelines that can be adjusted as knowledge improves. Some standards, such as those for compaction, are based on generalized models such as Froehlich and McNabb's (1984) linear model relating tree growth decline to increasing soil bulk density (Figure 3). There, a 15% decline in tree growth translates to about a 15% increase in bulk density. Erosion standards

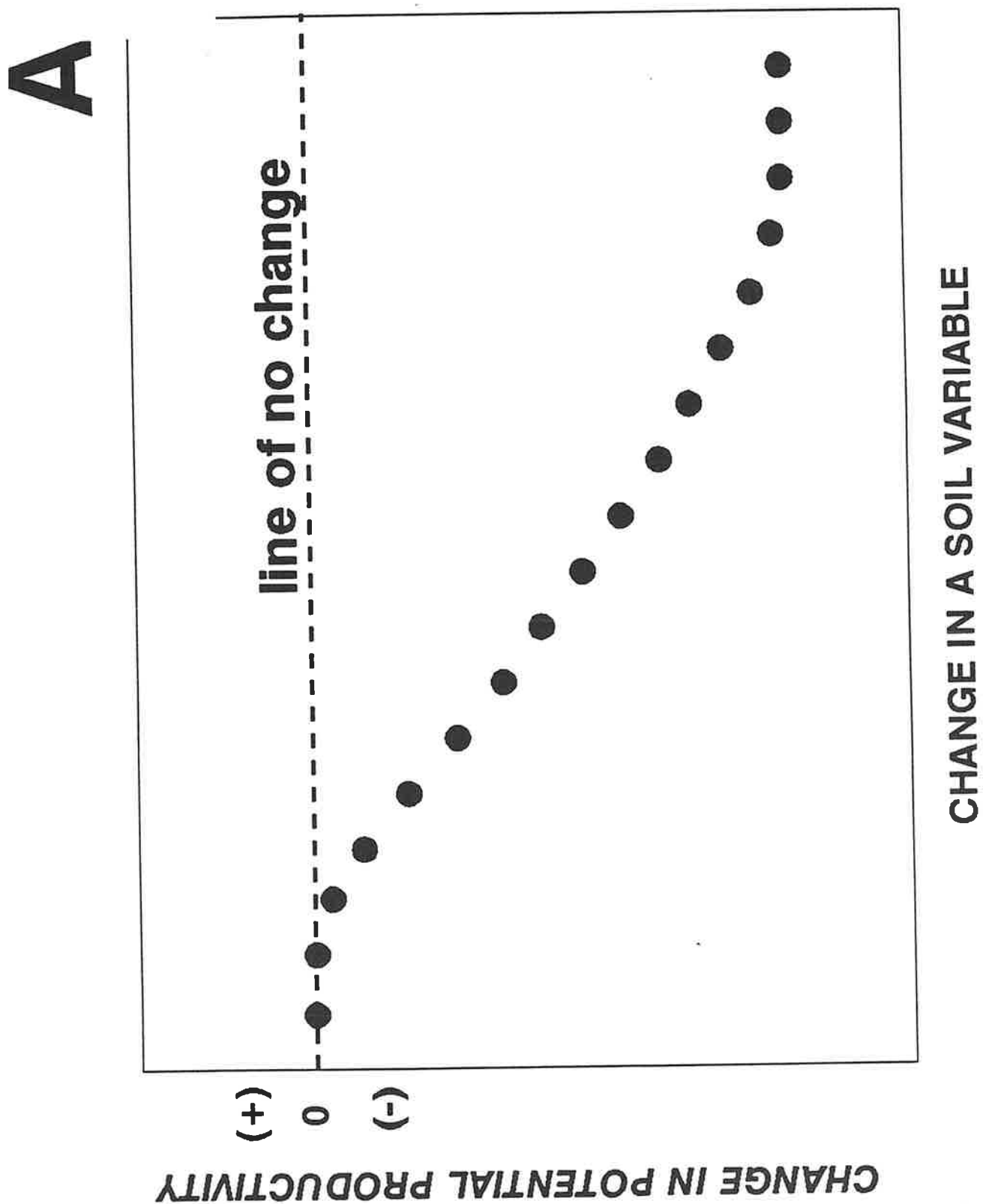


Figure 2-A. Conceptual relationship between potential productivity and a key soil variable. (A) In principle, as properties of a soil variable degrade, productivity declines from its potential (Powers 1990).

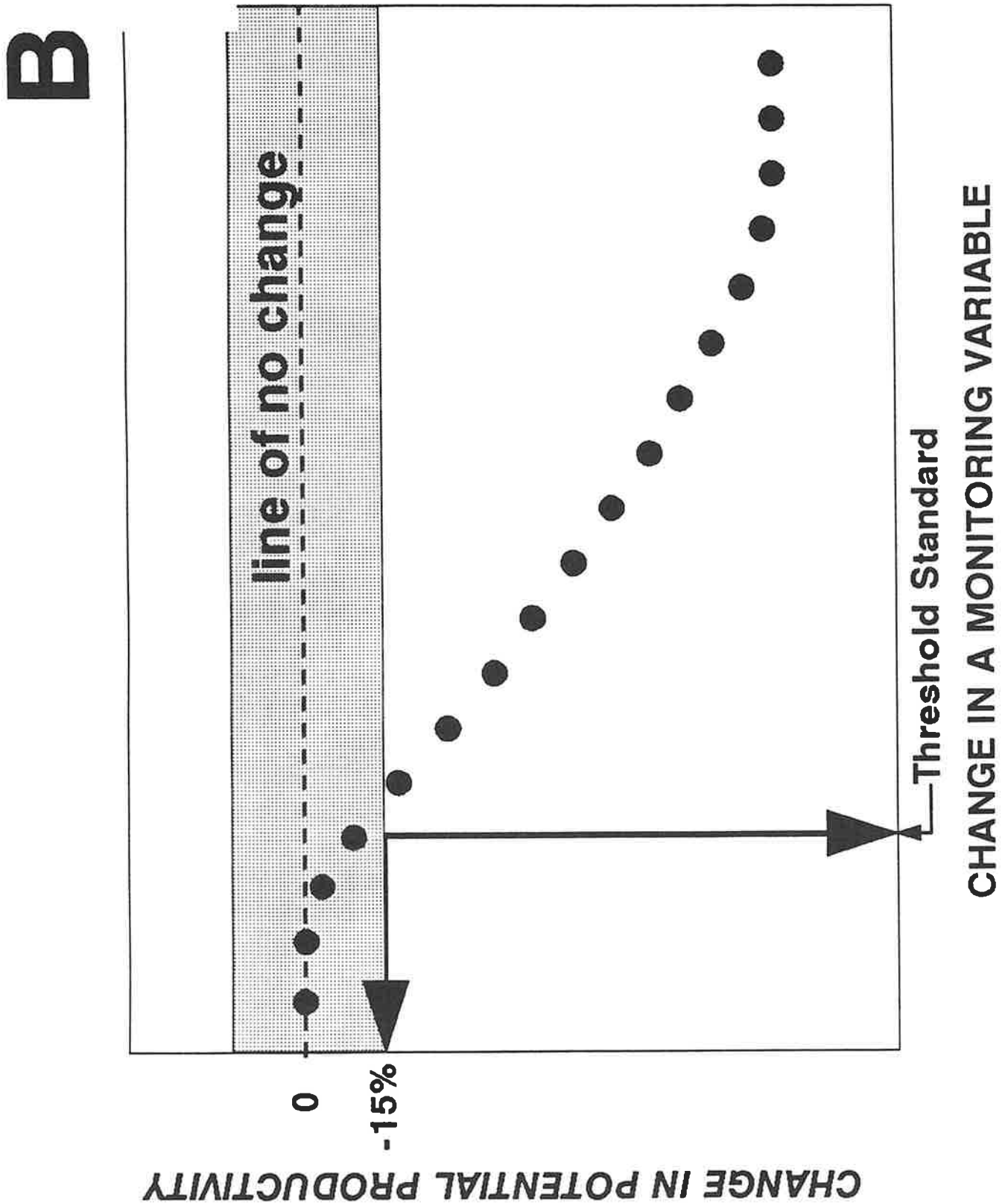


Figure 2-B. Conceptual relationship between potential productivity and a key soil variable. (B) In practice, variability exists about the estimate of productivity for an undisturbed site. Threshold soil quality monitoring standards indicate the degree of soil change needed to detect a 15% decline in potential productivity (Powers 1990).



Table 2. Soil quality standard threshold values for various disturbance variables for the nine administrative Forest Service Regions.

| Disturbance Variable | FS Region | Threshold Value   |
|----------------------|-----------|---|
| Erosion (surface)    | 1         | See "soil cover."   |
|                      | 2         | Appearance of pedestalled rocks and plants. Deposition of soil uphill of objects. Formation of an erosion pavement or of channels greater than 2.5 cm deep on more than 15% of the area.                            |
|                      | 3         | Any of the area exceeds soil loss tolerance values as determined by the universal soil loss equation (USLE).  |
|                      | 5         | See "soil cover."   |
|                      | 6         | See "soil cover."   |
|                      | 8         | Soil loss exceeds the allowable loss tolerance values set by the R-8 Guide on more than 15% of the area.  |
|                      | 9         | Sheet and rill erosion exceeds the average annual soil loss tolerance over a rotation, or exceeds twice the threshold level on more than 20% of the area.   |
|                      | 10        | Removal of 50% of topsoil or humus-enriched surface soil from 9.3 m <sup>2</sup> or more over more than 15% of the area.  |
|                      |           |   |
|                      |           |   |
| Soil cover           | 1         | Enough cover to prevent erosion from exceeding natural rates of soil formation on more than 15% of the area.  |
|                      | 2         | Depending on erosion hazard class, effective ground cover is less than 30% to 50% the first year, and 50% to 70% the second.  |
|                      | 4         | Too little to prevent erosion from exceeding natural rates of soil formation determined through the USLE.   |
|                      | 5         | Forest floor covers less than 50% of area.  |
|                      | 6         | Less than 20% cover on sites with low Erosion Hazard Ratings, 30% for moderate, 45% for high, and 60% for very high in first year after disturbance. Standards raise to <30%, 40%, 60%, and 75% in the second year. |
|                      | 8         | Cover guided by local standards.  |
|                      | 10        | Less than 85% cover on slopes under 35%. Less than 95% cover on slopes greater than 35%.  |
| Organic matter       | 1         | Enough to sustain site productivity.  |
|                      | 3         | Less than 22-34 Mg/ha organic matter throughout the area.   |
|                      | 4         | Large woody debris insufficient to sustain site productivity as determined through research.  |
|                      | 5         | <del>Litter and duff covers less than 50% of area.</del> Fewer than 12 decomposing logs/ha with diameters of at least 50 cm and lengths of 3 m.   |
|                      | 8         | Soil organic matter less than 85% of that in upper 30 cm of undisturbed soil on more than 15% of the area.  |
|                      |           |   |
| Infiltration         | 3         | Reduction of 20% from natural rates throughout area.  |
|                      | 5         | Reduced to ratings of 6 or 8 as defined by Regional Erosion Hazard Rating System. Extent depends on cumulative watershed effects analysis.  |

Table 2. Concluded.

|                      |    |  |
|----------------------|----|--|
| Compaction           | 1  | Bulk density at depths of 5 to 30 cm raised to between 1.35 and 1.85 g/cm <sup>3</sup> , depending on soil texture, on more than 15% of the area.  |
|                      | 2  | Bulk density increased more than 15% over natural conditions, or densities exceeding 1.25 to 1.60 g/cm <sup>3</sup> , depending on soil texture, on more than 15% of the area.                               |
|                      | 3  | 15% bulk density increase over natural conditions for soil other than Andisols and 20% increase for Andisols throughout the area.  |
|                      | 4  | Reduction of more than 10% in total soil porosity or a doubling of soil strength in any 5-cm increment of surface soil on more than 15% of the area.   |
|                      | 5  | Reduction of more than 10% in total soil porosity over an area sufficiently large that it reduces productivity potential.  |
|                      | 6  | 15% bulk density increase, 50% macropore reduction, and/or a 15% reduction in air permeability over natural conditions for soils other than Andisols and 20% increase for Andisols on more than 20% of area. |
|                      | 8  | 15% bulk density increase and more than 20% decrease in macroporosity over undisturbed conditions on more than 15% of the area.  |
|                      | 9  | 15% bulk density increase over undisturbed conditions on more than 20% of the area.  |
|                      | 10 | 15% bulk density increase over undisturbed conditions on more than 15% of the area.  |
| Rutting and puddling | 1  | Ruts to a depth of 15 cm or greater on more than 15% of the area.  |
|                      | 2  | See "compaction."  |
|                      | 6  | Ruts reach at least 15 cm depth on more than 20% of the area.  |
|                      | 8  | Ruts exceed 15 cm deep for a continuous distance of more than 15 m, ruts exceed 30 cm deep for more than 3 m, and ruts exceed 46 cm for any distance on more than 15% of the area.                           |
|                      | 9  | Ruts exceed 46 cm deep anywhere on site, or rut depths exceed 30 cm and extend for more than 3 m on more than 20% of the area.   |
|                      | 10 | Ruts or foot prints in mineral soil or 0a horizon of an organic soil on more than 15% of the area.   |

Table 2. Continued

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|                        |    |  |
|------------------------|----|--|
| Detrimental<br>burning | 1  | Standards set locally. Loss of O horizon and signs of mineral soil oxidation should not occur on more than 15% of the area.  |
|                        | 2  | Fine fuels entirely consumed, surface soil heated to redness, no organic structure recognizable, and/or no ash layer remains. Standards set locally but should not prohibit broadcast burning.   |
|                        | 3  | Most woody debris and entire forest floor consumed to bare mineral soil and fine roots charred in upper 1 cm of mineral soil on any of the area.   |
|                        | 4  | Standards set locally.   |
|                        | 6  | Top layer of mineral soil heated to redness and next 1 cm blackened from charring on more than 20% of area.  |
|                        | 9  | Consumption of the forest floor to mineral soil on an area of more than 4.6 m <sup>2</sup> . Bare soil exposure exceeds 5% on more than 80% of the area.   |
|                        | 10 | Most woody debris and entire forest floor consumed to bare mineral soil and fine roots charred in upper 1 cm of mineral soil on any of the area.   |
|                        |    |  |
|                        |    |  |
|                        |    |  |
| Displacement           | 1  | Loss of either 5 cm or more of the surface soil, or one half of the humus-enriched A horizon, which ever is less, on more than 15% of the area.  |
|                        | 2  | Soil loss from a continuous area of more than 9 m <sup>2</sup> on more than 15% of the area.   |
|                        | 3  | Removal of lesser of 50%, or 5 cm, of A horizon from a contiguous area of 9.3 m <sup>2</sup> or more.  |
|                        | 4  | Removal of lesser of 50% of humus-enriched surface soil or 5 cm of topsoil on more than 15% of the area.   |
|                        | 5  | Organic matter in the upper 30 cm of soil is less than 85% of the soil organic matter found under natural conditions. Affects an area sufficiently large that productivity potential is reduced. |
|                        | 6  | Removal of more than 50% of topsoil or humus-enriched A1 and/or AC horizons from an area of 9.3 m <sup>2</sup> or more and at least 1.5 m wide.  |
|                        | 8  | Removal of more than 50% of the humus-enriched A horizon over a continuous area more than 5.6 m <sup>2</sup> and more than 1 m wide for more than 15% of the area.                               |
|                        |    |  |
|                        | 9  | Removal to a depth of one-half the thickness of the A horizon over an area of more than 5.6 m <sup>2</sup> and more than 1-m wide on more than 20% of the area.                                  |
|                        | 10 | Removal of forest floor and 50% of topsoil from an area of 9.3 m <sup>2</sup> and at least 1.5 m wide on more than 15% of the area.  |

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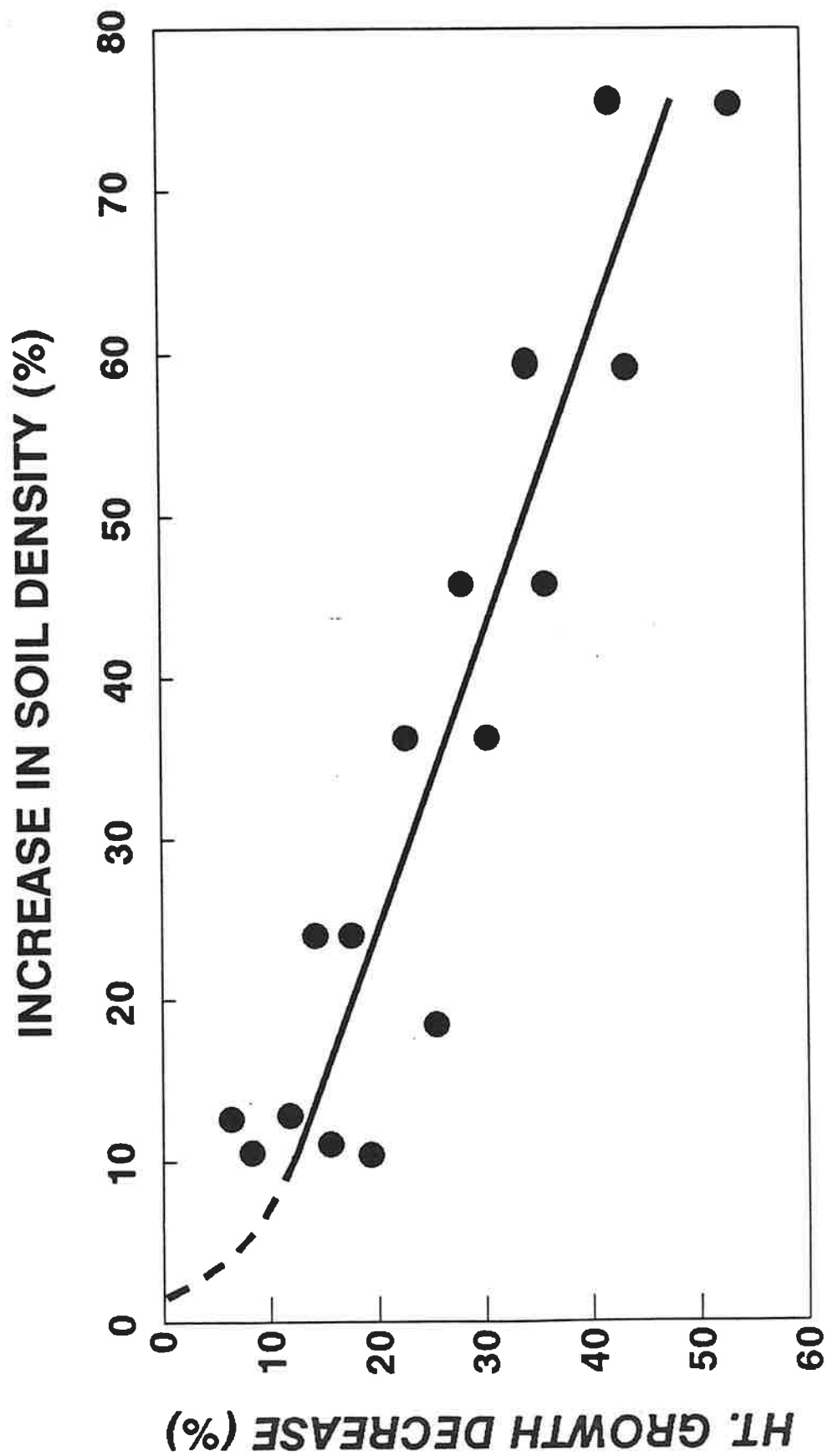


Figure 3. Relationship of soil bulk density increase to height growth decrease for a variety of sites (Froehlich and McNabb 1984).

largely are based on threshold tolerances from the Universal Soil Loss Equation (Wischmeier and Smith 1978) or potentially from such variants as the USDA Water Erosion Prediction Project (1987). In general, soil displacement and soil organic matter thresholds relate to our general understanding that soil fertility is most concentrated near the soil surface (Figure 4). Generic procedures for obtaining statistically reliable samples have been developed (Hazard and Geist 1984, Howes et al. 1983).

Soil quality monitoring is seen as a three-step procedure in the process of land management planning (Avers 1990). The steps are designed to address the following questions:

1. Implementation monitoring. Were prescribed soil management practices implemented as designed?
2. Effectiveness monitoring. Were the prescribed soil management practices effective in meeting management objectives?
3. Validation monitoring. Are the monitoring standards and guidelines appropriate for maintaining soil productivity?

Both implementation and effectiveness monitoring are the responsibility of soil scientists in the administrative arm of the Forest Service. The third stage, validation, is the responsibility of scientists in the research arm.

### 6.2.3 THE ROLE OF RESEARCH

6.2.3.1 Has Productivity Declined? Other than from mass wasting, is there sound evidence that soil productivity has declined from management activities? Findings from the United States tends to be confounded, or short-term and inconclusive (Powers et al. 1990). Many findings are based on retrospective analyses of data collected for other purposes. Characteristically, such studies are anecdotal and offer little insight into cause-and-effect mechanisms (Powers 1989).

The best report of an experiment designed specifically to test the deleterious impacts of management practices on soil productivity in

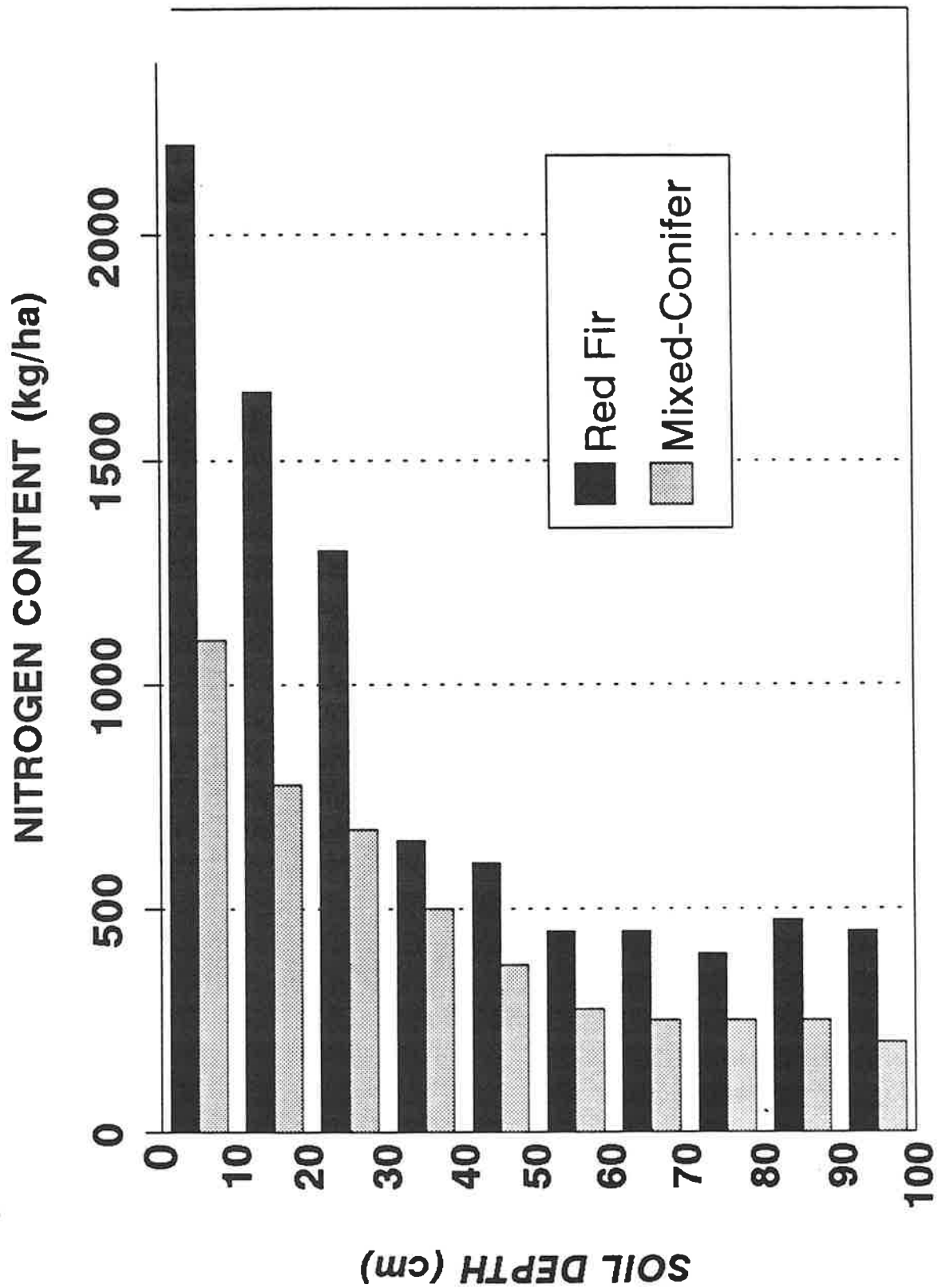


Figure 4. Content of total soil nitrogen and its distribution by depth averaged for two forest types in California.

North America is that by Compton and Cole (1991) for Douglas-fir (Pseudotsuga menziesii). Ten-year findings of a series of organic removal treatments following clearcutting on two sites are summarized in Table 3. The experiment was designed to test the hypothesis that increasing the amount of organic removal on sites low in soil nitrogen (N) leads to a decline in the productivity of the next forest. To avoid compaction, no equipment was allowed on the plots. Following treatment, plots were planted with Douglas-fir. The same treatments removed more N from the better site than the poorer because the better site had a much greater N capital. But expressed as a proportion of ecosystem N, the poorer site suffered the greatest relative loss. After 10 years, trees on the complete removal plots were about 30% shorter than those on the bole-only treatment. Fertilizing plots with N at year 5 led to rapid growth increases, supporting the hypothesis that growth decline was due to N removal, and not organic matter removal per se. (Cole 1992).

Work overseas has shown conclusively that losses of site organic matter, particularly on sandy soils and droughty sites, can trigger poor growth. Wiedemann's (1935) report of litter gathering in Pinus sylvestris forests of eastern Germany is a classic example. There, poor forest growth occurred on community-owned forests where, for decades, peasants had practised litter raking to provide bedding straw for farm animals. Growth in adjacent, estate-owned forests where litter gathering was not permitted averaged a full site class better.

In South Australia, Keeves (1966) showed that Pinus radiata planted on sandy soils grew much more poorly in the second rotation than in the first. Squire et al. (1985) demonstrated that the decline was due to the burning of logging slash following the first rotation. This led to both moisture and nutrient stress in the next forest, and the effect was evident by the time of crown closure. Productivity of successive plantations could be maintained either by retaining logging slash and avoiding burning (Squire et al. 1985), or by intensive silvicultural techniques such as cultivation, weed control, and fertilization (Cellier et al. 1985).

Table 3. Nutritional effects of organic matter removal on nitrogen budgets and plantation growth on two Douglas-fir sites in Washington (Compton and Cole 1991).

| Treatment <sup>a</sup> | Total<br>in<br>Ecosys. <sup>b</sup> | Removed<br>in<br>Harvest<br>----- (kg N/ha) ----- | Leached<br>in 3 Yrs.<br>----- | Total<br>Lost<br>(%) | 10-Year<br>Relative<br>Ht. Growth<br>(%) |
|------------------------|-------------------------------------|---|-------------------------------|----------------------|--|
| Site Quality III       |                                     |   |                               |                      |  |
| Uncut                  | 3,293                               | 0   | 0.3                           | 0                    | Not planted                              |
| Bole only              | 3,293                               | 478   | 4.4                           | 15                   | 100                                      |
| Whole tree             | 3,293                               | 728   | 0.5                           | 22                   | 92                                       |
| Complete               | 3,293                               | 950   | 0.6                           | 29                   | 71                                       |
| Site Quality IV        |                                     |   |                               |                      |  |
| Uncut                  | 1,032                               | 0   | 1.0                           | 0                    | Not planted                              |
| Bole only              | 1,032                               | 161   | 2.1                           | 16                   | 100                                      |
| Whole tree             | 1,032                               | 318   | 4.7                           | 31                   | 81                                       |
| Complete               | 1,032                               | 522   | 5.5                           | 51                   | 69                                       |

<sup>a</sup> Uncut (all vegetation left standing), Bole only (all logging slash retained), Whole tree (boles and crowns removed), Complete (whole tree plus understory and forest floor removed). Soil compaction was avoided by keeping machinery off the plots and removing organic materials using full suspension.

<sup>b</sup> Soils sampled to a depth of 50 cm.



In New Zealand, Dyck and Skinner (1990) have shown how windrowing first rotation *P. radiata* logging slash and an estimated 2.5-cm of pumice topsoil by tractor has led to growth losses in the second rotation. At 7 years, pines planted in windrows had volumes averaging 41 m<sup>3</sup>/ha, while those planted between windrows averaged only half of that. Combining data on an areal basis produced average plantation volumes of 28 m<sup>3</sup>/ha--only 84% of those in an adjacent plantation where logging slash had been retained. Differences were even greater by age 17, when volume in the windrowed plantation had fallen to 65% of that in the adjacent stand.

Such studies illustrate the significance of site organic matter in sustaining soil productivity. In the short run, surface organic residues provide a physical barrier to soil moisture evaporation--a particularly important factor in drier ecosystems before canopies have closed (Squire et al. 1985). During droughty summers in California, plant-available soil moisture lasts several weeks longer where surface residues are retained following timber harvesting than where they are absent (Powers unpublished). Surface materials also reduce soil particle dispersion from raindrop impact. Erosional losses where soil surfaces are exposed following prescribed burning can be 40% to 1200% greater than erosion from logging alone (Megahan 1987). In California, the mechanical exposure of mineral soil increased soil movement 3-fold in friable soils and 20-fold in compacted (Powers, unpublished).

Organic matter also supports soil productivity through the development of soil structure. Plant residues are the primary source of fixed carbon providing energy to surface and tunneling soil fauna that shred, digest, and transport organic materials beneath the surface. Earthworms feeding on surface litter create vertical, faeces-lined tunnels to the subsoil, promoting the entry of gravitational water, the movement of capillary water, and the exchange of surface and subsurface gases. Such altered, mixed materials provide energy substrate to microbes which drive ecosystem processes and promote soil stability. For example, microbially-produced polysaccharides promote soil aggregate formation through H-bonding and cation coordination (Stevenson 1982). Because

polysaccharides themselves are degraded easily by other microorganisms, fresh inputs of organic matter are needed to maintain aggregate stability, soil structure, and resistance to erosion.

Organic matter also is a reservoir for such nutrients as N and phosphorus (P) (Table 4) and probably is the main source of labile nutrients in closed-canopy forests. Nowhere is this more evident than in forest floors of temperate and cooler climates. There, forest floor mass is only a fraction of that in living vegetation, but its nutrient content is second only to that in the mineral soil (Table 4) (Powers and Van Cleve 1991). Therefore, major losses of site organic matter inevitably affect nutrient availability that may lead to nutrient stress. In young stands, nutrient deficiencies may not appear for several years because nutrient releases from roots and residual litter usually exceed the low uptake needs of very young vegetation (Smethurst and Nambiar 1990). However, deficiencies may appear as canopies close and readily available nutrient reserves are depleted. This will be most evident on sites with low nutrient storage but supplied well with water (Table 3).

Other nutritional effects of organic matter include chelation and ion exchange reactions. Organic acids produced during decomposition can form chelates with polyvalent metal ions such as aluminum (Al), rendering such metals innocuous at concentrations known to be toxic in the ionic form (Hue et al. 1986). Oxalate, common in most forest soils, adsorbs readily to Al-oxide surfaces, displacing P (Goldberg and Sposito 1985) and increasing its content in the soil solution (Fox and Comerford 1992).

Clearly, organic matter is a major factor affecting soil productivity, but it is not the only factor. On finer-textured soils, losses of soil aeration porosity through compaction may surpass the effects of organic matter losses. A unique experiment in New Zealand (Dyck and Skinner 1990) demonstrated that basal area growth of P. radiata was halved if bulk density was increased in the surface soil by 13% or in the finer-textured subsoil by only 4% (Figure 5). This indicates that Froehlich and McNabb's (1984) linear model of growth depression with increasing bulk density (Figure 3) is probably too simplistic.

Table 4. Ranges in total nitrogen (N) and phosphorus (P) contents found in young, mature Abies, Pinus, and Pseudotsuga ecosystems in North America. From Powers and Van Cleve (1991) as modified from Kimmins et al. (1985).

| Ecosystem<br>Component | Abies        |                    | Pinus       |           | Pseudotsuga                |             |
|------------------------|--------------|--------------------|-------------|-----------|----------------------------|-------------|
|                        | N            | P                  | N           | P         | N                          | P           |
| ----- (kg/ha) -----    |              |                    |             |           |                            |             |
| Trees                  |              |                    |             |           |                            |             |
| Above ground           | 80-686       | 12-83              | 180-556     | 12-31     | 84-728                     | 18-112      |
| Below ground           | 24-72        | 4-12               | 12-117      | 2-21      | 30-90                      | 5-18        |
| Understory             | 2-50         | t <sup>a</sup> -14 | 1-54        | t-5       | 5-66                       | 1-9         |
| Forest floor           | 666-2,300    | 9-103              | 80-1,240    | 9-103     | 110-1,249                  | 19-115      |
| Soil to 1-m            | 5,237-14,000 | 3,212-6,317        | 1,753-5,554 | 146-4,457 | <del>44,170</del><br>1,770 | 3,878-3,900 |

<sup>a</sup> t = trace.

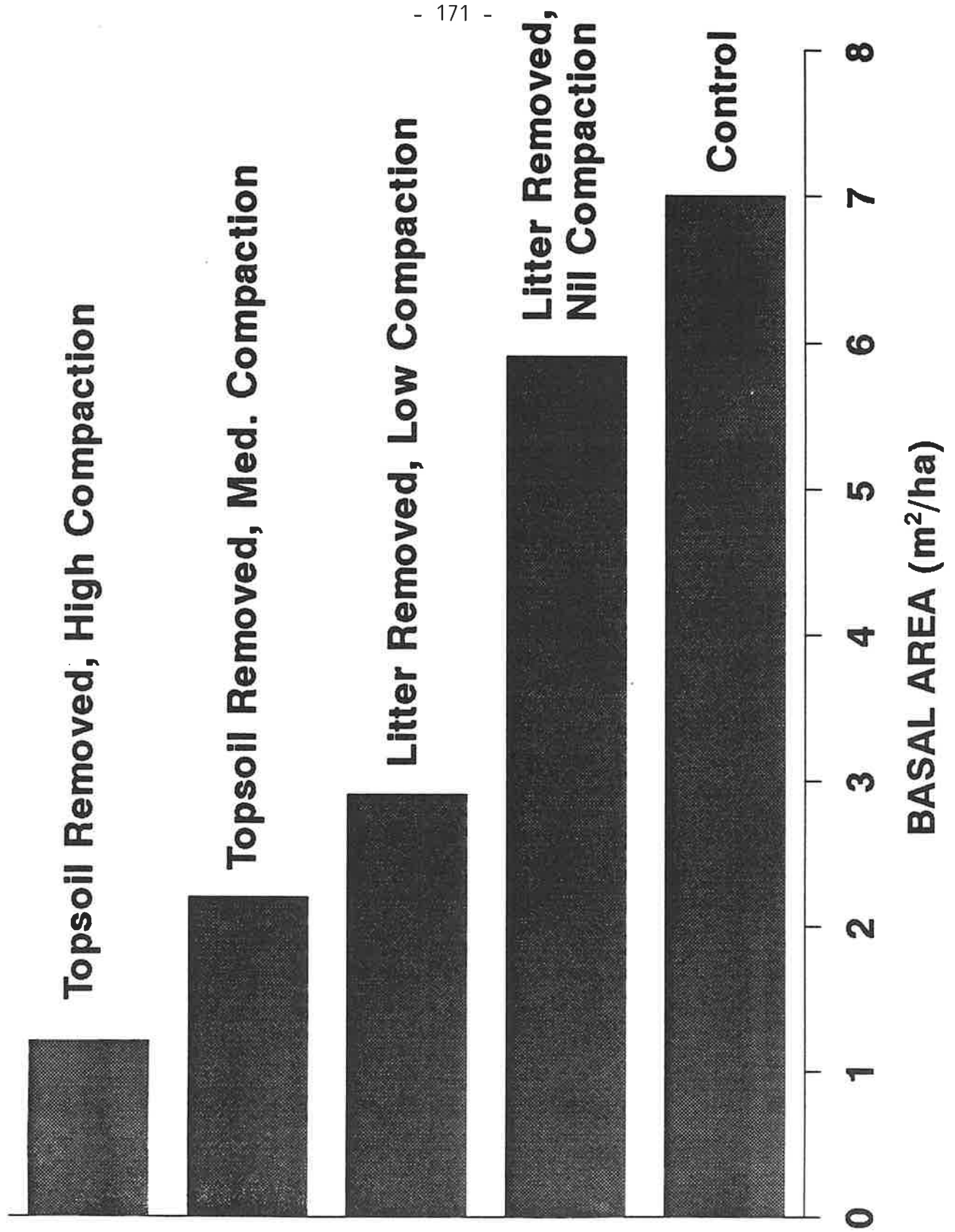


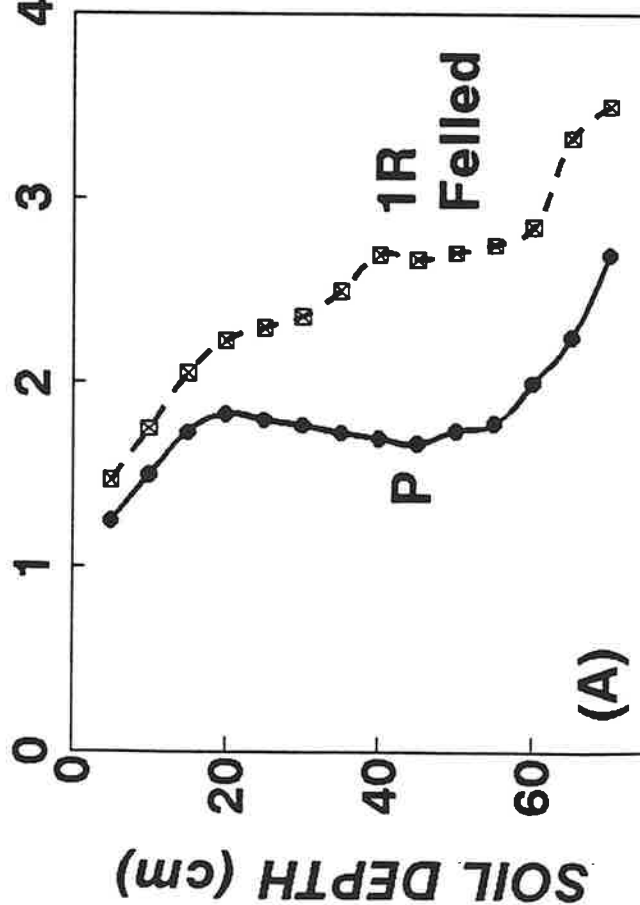
Figure 5. Average stand basal area at six years for a *Pinus radiata* plantation in New Zealand receiving a series of soil stress treatments (Dyck and Skinner 1990, supplemented with more recent data).

Soil densification affects productivity in several ways, including mechanical resistance to root penetration. Plant roots grow through the soil by following voids and by moving particles aside when pore diameters are narrower than those of elongating roots. If pores are large enough, root growth can continue. Using average pore size as a guide, Daddow and Warrington (1983) calculated theoretical growth limiting soil bulk densities where root growth should cease because of mechanical resistance. Growth limiting bulk densities varied by soil texture, ranging from  $1.4 \text{ g/cm}^3$  in clayey soils to  $1.8 \text{ g/cm}^3$  in sandy loams. Growing roots can exert forces of between 0.5 and 2.4 MPa to overcome particle resistances and enlarge soil voids (Wiersum (1957)). Greacen and Sands (1980) found root densities of pines were extremely low in soils with strengths at or above 3 MPa--values which are not at all unusual in compacted soils.

Mechanical resistance is not the only problem posed by compacted soils. Simmons and Pope (1988) have shown that compaction must be interpreted in terms of soil strength and aeration porosity. Under moist conditions, reducing air-filled pore volumes below  $0.1 \text{ m}^3/\text{m}^3$  creates anaerobic conditions that limit root growth in hardwood seedlings. Under drier conditions, aeration porosity is adequate, but soil strength may restrict root penetration into new soil volumes and increase the tortuosity of the flow path for water and nutrients to roots. Sands (1983) has demonstrated the cumulative impact of mechanized equipment on soil strength in sandy soils (Figure 6) where strengths in the subsoil approach 3 MPa, the threshold for root growth. Impacts extend deep enough into the profile that they probably are irreversible (Sands 1983). Even if compaction is not severe enough to inhibit plant growth altogether, it will shorten the growing season to a fraction of its potential. As soils dry in the summer, soil strength will reach a threshold that limits root processes much sooner on compacted sites (Figure 7).

The physical, chemical and biological means by which organic matter and soil porosity regulate productivity are suggested the conceptual model in Figure 8 (Powers et al. 1990). Clearly, process rates

# PENETROMETER RESISTANCE (MPa)



- (A) P = Pasture  
1R Felled = 1st rotation felled
- (B) 1R = 1st rotation  
2R = 2nd rotation

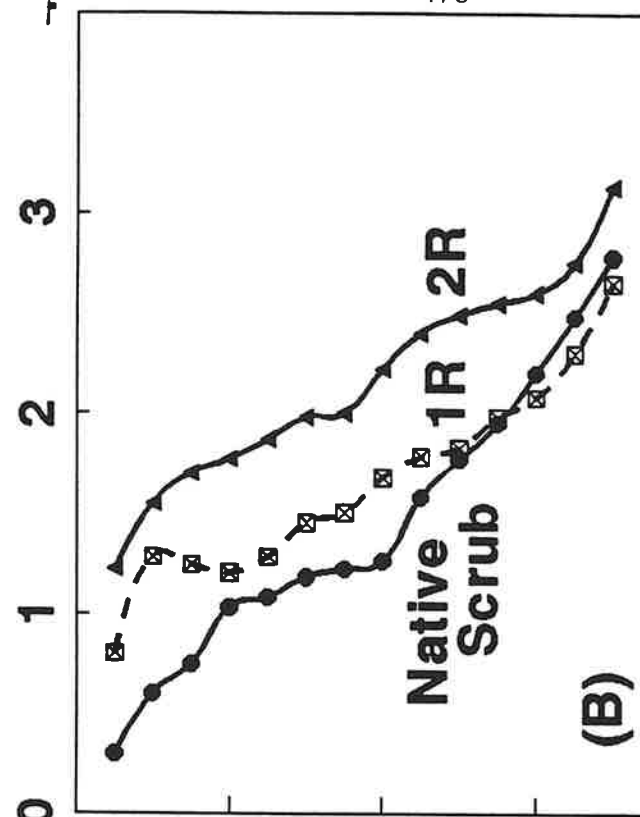


Figure 6. Penetrometer resistance (soil strength) as affected by land uses for adjacent sites on the same soil type in Australia (Sands 1983). Effects of each successive land use are cumulative.

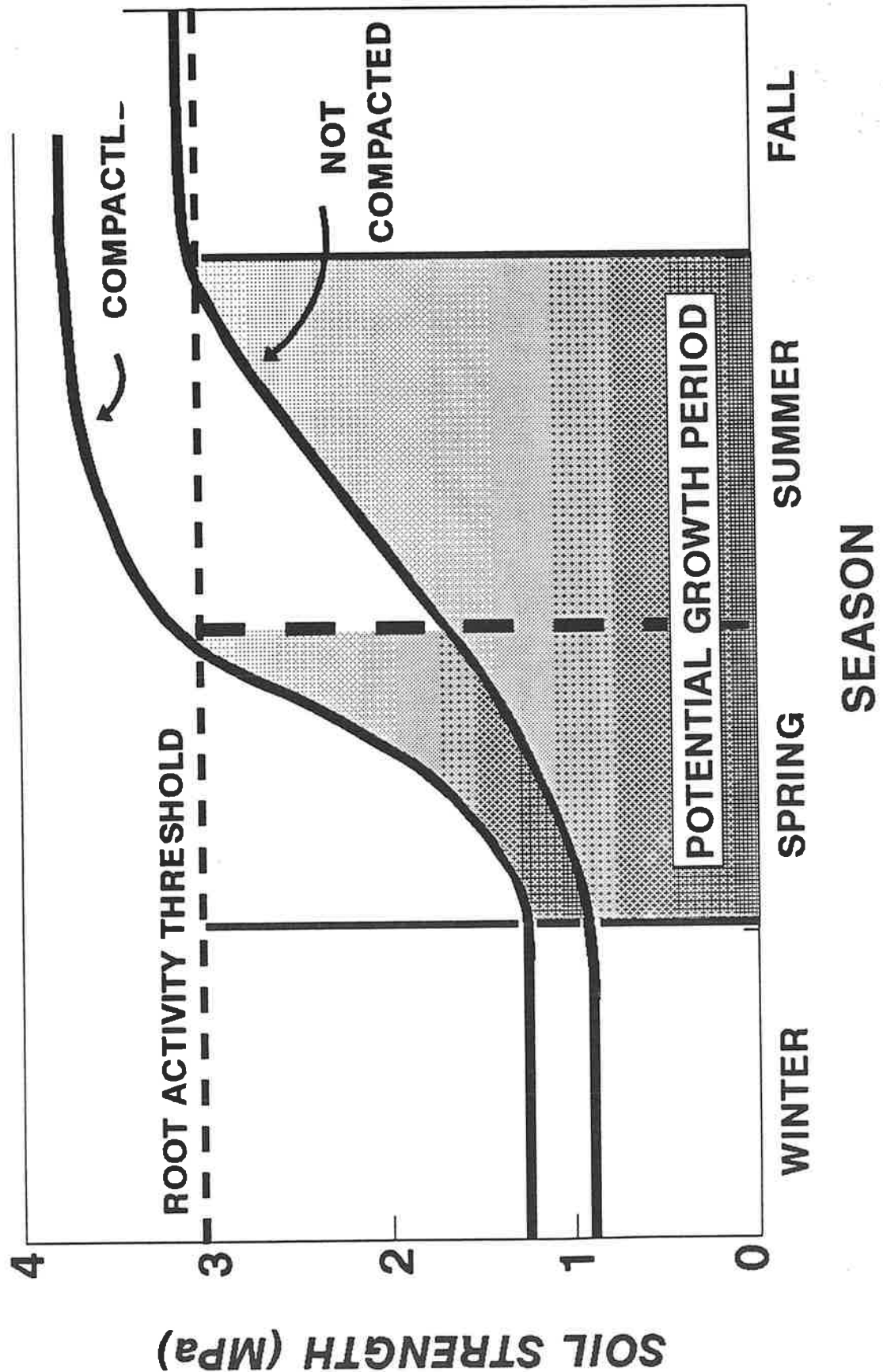


Figure 7. Conceptual model of how compaction affects soil strength and potential growing season (shaded area). Regardless of soil texture, root activity (growth, water and nutrient uptake) is presumed to slow and essentially cease as soil strength within the rooting zone approaches 3 MPa.





and productivity will be changed if site organic matter and soil porosity are altered substantially. But how much change is too much? Are some sites more resilient than others? Beyond conceptual models, we lack a specific understanding of what a given change in organic matter or porosity means for each site relative to long-term soil productivity. Uncertainty and skepticism will persist until we establish and maintain studies that help us document and understand the long-term effects. This gap in our knowledge means that soil quality standard thresholds described in Table 2 risk legal challenge because they are based largely on "best professional judgement."

#### 6.2.4 A COOPERATIVE NATIONAL STUDY

In 1989, a formal program of cooperation between research and administrative arms of the Forest Service was launched to address this problem through a national network of long-term soil productivity studies (LTSP) (Powers et al. 1989). A fundamental purpose of this is to help us understand how soil porosity and site organic matter jointly affect site processes controlling productivity through the conceptual model in Figure 8. An applied purpose is to validate soil quality standards and monitoring methods used by National Forest Systems. Specific objectives are to: (1) quantify the effects of soil disturbance on soil productivity; (2) establish site-specific calibrations such as are hypothesized in Figure 2; (3) validate standards and techniques for soil quality monitoring; and (4) improve our understanding of fundamental relationships between soil properties, long-term productivity, and forest management practices. Complementary "Research" and "Development" aspects include:

| RESEARCH                           | DEVELOPMENT   |
|------------------------------------|---|
| How does soil disturbance affect-- | Facilitate soil monitoring by--                       |
| <hr/>                              | <hr/>   |
| o Carbon allocation                | o Calibrating changes in soil properties against both |
| o Water and nutrient use           | stand productivity and total vegetative productivity  |

- o Soil biotic activity
- o Resistance to pests
- o Fundamental productivity
- o Evaluating/developing field monitoring methods
- o Developing means for extending results broadly

6.2.4.1 Coordination. National and regional coordination is achieved through three levels of control. First, national coordination and review for LTSP is provided by Washington Office staffs from Forest Management Research, Forest Environment Research, Timber Management, and Watershed and Air Management. Further coordination exists through a National LTSP Technical Committee of Principal Investigators from Forest Service Research and Regional Soil Scientists from National Forest Systems. Their main responsibilities are to establish and maintain research protocols, review study progress, and inform the Washington Office of significant findings, problems, and opportunities. Finally, a Regional LTSP Steering Committee consisting of the local Principal Investigator from Research and the Regional Soil Scientist and Silviculturist from National Forest Systems have responsibility for site selection, study establishment, and site maintenance. Their job also is to establish close working ties with National Forests, Ranger Districts, and other researchers. These ties are not merely to exchange information, but to foster a sense of partnership in the effort. Scientific aspects of LTSP are the responsibility of the local Principal Investigator. Supplemental research occurs through a group of collaborating scientists from nearly a dozen U.S. universities who are exploring ways for financing integrated studies on carbon cycling. International ties also have formed with British Columbia's Ministry of Forests and New Zealand's Forest Research Institute.

6.2.4.2 Research Protocol. A broad array of soil porosity and site organic matter manipulations are applied on benchmark soils within the major commercial forest types of the United States. Work began in 1989 in Louisiana and California, and now has expanded to Idaho, Michigan,

Minnesota, Mississippi, Missouri, North Carolina, Oregon, and Texas (Figure 9). Within each region and forest type, about a dozen timbered sites will be selected for treatment. Sites are characterized before treatment according to a standard protocol (Powers et al. 1989). Then a core series of organic matter and soil porosity treatments are applied to 0.4 ha treatment plots. This treatment core includes the following main effects and their interactions:

| Organic Matter Treatment                     | Soil Porosity Treatment   |
|--|---------------------------|
| <hr/>  | <hr/>                     |
| o Boles removed, only                        | o No compaction           |
| o Whole trees removed                        | o Intermediate compaction |
| o All vegetation and<br>forest floor removed | o Severe compaction       |

This produces nine factorial combinations that capture the range of site organic matter and soil porosity changes apt to occur under present or future forest management (Figure 10). Treatments were not chosen with any conventional management practice in mind. Nor are findings meant to apply exclusively to even-aged management systems. Instead, an experimental design is established in which site organic matter and soil porosity can be regarded as continuous variables in the development of general predictive models when data are combined. The product will be site-specific projections of the probable biological outcomes when site organic matter and soil porosity are altered. Where space permits at each LTSP installation, other treatments are added. These include conventional harvest and site preparation techniques and such ameliorative practices as tilling and fertilization. From this, one can compare the effects of operational practices, determine the value of timely mitigation, and examine possibilities for enhancing soil productivity.

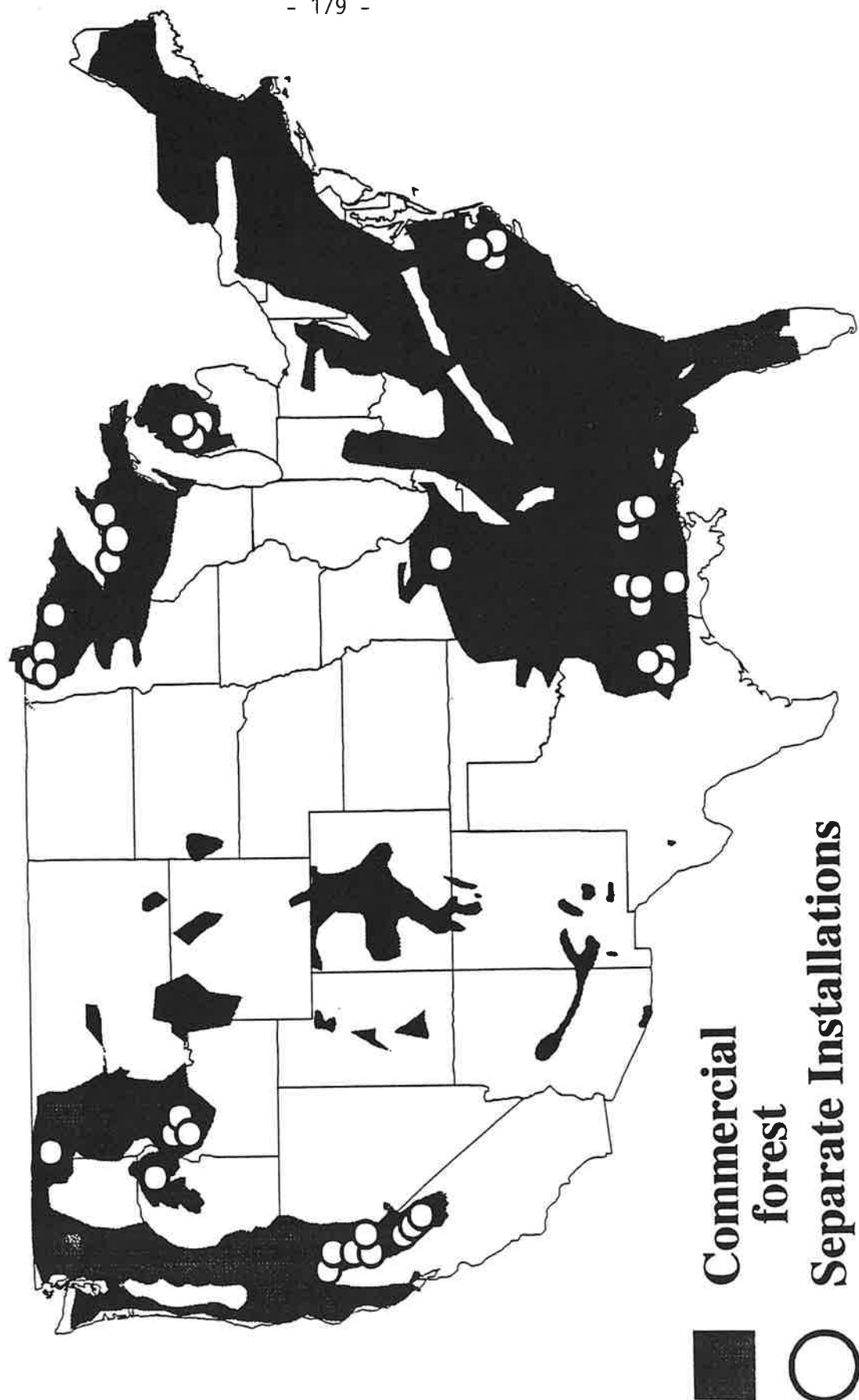


Figure 9. Location of Long-Term Soil Productivity installations through 1994 in relation to the commercial forest region of the United States (lands capable of producing  $14 \text{ m}^3/\text{ha}/\text{yr}$  at culmination of mean annual increment). Each LTSP installation is equipped with a recording climatological station.



Figure 10. Generalized layout of the 3 x 3 core arrangement of LTSP increasing stress treatments. Compaction levels reflect texture-dependent growth-limiting bulk density (Daddow and Warrington 1983). Each of the nine plots occupies 0.4 ha, and contains a split-plot subtreatment of vegetation control vs. no vegetation control. Ameliorative and operational treatments are included as space permits.

Each 0.4-ha treatment plot will be reforested with species of the appropriate forest type using a mixture of the best available genetic stock. The aim is to favor superior growth without narrowing genetic diversity. Each treatment plot will be split in half, creating two subplots with a measurement plot established centrally in each. One subplot will be kept weed-free. In the other, regional vegetation will develop with the trees. This provides the opportunity to study soil productivity and plant growth processes in simple and complex plant communities which are developing side-by-side. Installations will be maintained to at least the culmination of mean annual increment.

6.2.4.3 Site Measurements. Standard climatological stations and dataloggers will be installed at each LTSP installation to monitor air and soil temperature, wind speed and direction, relative humidity, total and photosynthetically active solar radiation, precipitation, and potential evapotranspiration. Stations will be compatible with others installed throughout the country, and will add to our monitoring base for detecting climatic change and its possible impacts on productivity. Variables measured on each plot include, but are not limited to, the following:

| Variable   | Measurement interval    |
|--|-------------------------|
| o Climatological data  | Continuously            |
| o Soil moisture and temperature                              | Monthly                 |
| o Soil strength  | Seasonally each 5 years |
| o Plant survival, damage from<br>pests, growth, NPP          | Years 1, 3, 5, 10, etc. |
| o Soil bulk density and porosity                             | 5 years                 |
| o Water infiltration and<br>saturated hydraulic conductivity | 5 years                 |
| o Soil organic matter content and<br>chemical composition    | 5 years                 |
| o Foliar chemistry and standing<br>nutrient capital          | 5 years                 |

- o Biomass modeling and prediction      As vegetation develops

6.2.4.4 Process Measurements. Data from these periodic measurements will provide basic information on how stress affects water and nutrient use, carbon allocation, and resistance to pests. Because all treatment plots are adjacent with trees all at identical spacing and age, comparative growth rates offer precise measures of site productivity and avoid the confounding caused by stand (not site) factors mentioned previously. Comparing each treatment against the "nil disturbance" control will be the standard for judging whether soil changes have affected the potential productivity of the land. Wood and total tree biomass production in "trees only" subplots provide an assessment of how soil disturbance affects traditional measures of timber site productivity. "Total vegetation" subplots provide a more comprehensive measure of total site productivity. The first indication of long-term effects is expected to occur about the time of crown closure, when vegetation is fully capturing all the factors of site (Squire et al. 1985).

Beyond this, several key soil and site processes invite more detailed investigations. Many of these processes will be studied by individual Forest Service researchers, but the National LTSP study would be served more effectively by a comprehensive, nation-wide collaborative attack on some or all of the following topics:

- o Soil erosion      o Plant biochemistry      o Residue dynamics
- o Soil respiration      o Nitrogen fixation      o Soil faunal dynamics
- o Process models      o Soil structure dynamics      o Microbial dynamics

To this end, a national group of university scientists has formed to develop the means for supporting collaborative LTSP research on fundamental aspects of carbon cycling. This group includes scientists from the following institutions:

- o The University of California      o Purdue University
- o Michigan State University      o Texas A&M University

- o Michigan Technological University
- o The University of Nevada
- o The University of New Hampshire
- o Oregon State University
- o Virginia Polytechnic University
- o The University of Washington
- o The University of Wisconsin

6.2.4.5 Budget. The approximate budget for installataion and maintenance of each research site that includes the minimum nine core treatments is:

| Task                                  | Average cost                  | Responsibility          |
|---------------------------------------|-------------------------------|-------------------------|
| Installation and preliminary analysis | \$50,000-65,000 in first year | National Forest Systems |
| Research                              | 26,020 per year               | Research                |
| Maintenance                           | 4,350 per year                | National Forest Systems |

### 6.3. SUMMARY

Our ability to maintain a site's productive capacity faces increasing challenge through public review of Forest Land Management Plans and timber sales. In response to NFMA, Forest Service Regions are developing threshold soil quality monitoring standards for detecting signs of declining soil productivity. Such standards are based on best available information. But until standards are validated, we can expect challenges from many sectors. In response, this national network of study sites provides researchers with a means for comparing stand production with more fundamental measures of productivity, and will provide the scientific basis for validating soil quality standards established by National Forest Systems. Basic models of soil and growth processes can be integrated with site and climatic data to extrapolate findings to a broad array of sites. Installing some LTSP sites on ecotones will help us judge possible impacts of changing climate on future productivity because ecotones will offer the first indications of climatic change. The LTSP



effort is of such unusual scope that it creates landmark opportunities for developing a fundamental understanding of the functioning of managed forest ecosystems. Further, it is possibly the strongest vehicle yet for fostering close cooperation and collaboration between the scientific and administrative arms of the U.S. Forest Service, university and industry colleagues, and scientists in other nations.

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7. DEVELOPMENT AND APPLICATION OF SOIL QUALITY CRITERIA  
FOR ALBERTA'S RESOURCE EXTRACTION INDUSTRIES

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ABSTRACT

Soil quality criteria for Alberta's resource extraction industries were prepared by the Soil Quality Criteria Subcommittee of the Alberta Soils Advisory Committee. The document produced was intended to be a scientific and technical manual for use by professionals. The criteria developed were compiled from a review of the pertinent literature and ongoing research and tempered in some situations by making the "best" guess where data were incomplete. Criteria were established for each of the Plains, Eastern Slopes and Northern Forested Regions of Alberta. They included the topics of soil mapping and sampling procedures, analytical requirements and criteria for evaluating the suitability of soil materials for revegetation. Criteria tables were developed for evaluating the suitability of topsoil and subsoil in the Plains Region, surface material (upper lift) and subsurface material (lower lift) in the Northern Forest Region, and root zone material in the Eastern Slopes Region. The criteria are used by a wide range of practitioners to assist in evaluating reclamation success which is defined in terms of equivalent land capability in Alberta. Specifically, the criteria are used to evaluate the baseline situation relative to soils, develop materials handling plans, predict the resultant post-disturbance soil characteristics, and determine the actual post-disturbance soil characteristics. Significant advances in "environmental soil science" research and field practices currently used relative to resource extraction activities provides the opportunity and the basis for expanding and improving the existing soil quality criteria. The updating of the criteria could include further subdivision of the three defined regions, adding criteria for additional chemical and physical properties, ranking or weighting of the various soil parameters, and consideration of the timing for completing post-disturbance soil quality measurements. This revision should be completed in a manner that results in a manageable and "user friendly" system that will be readily used by various practitioners.



## 7.1 INTRODUCTION

Land disturbances arising from resource extraction and transport are intended to be only temporary disruptions to the normal use of land. Although no two sites are absolutely identical, disturbances cause similar types of problems and concerns but in varying degrees of intensity. Assurance that such disturbances are temporary is possible only if information concerning a specific site is well documented and an appropriate reclamation program is planned prior to disturbance. Furthermore, measurement of reclamation success requires the ability to compare the baseline and post-disturbance characteristics of a given location or parcel of land. Evaluation of the nature of the materials at hand prior to disturbance and subsequent to reclamation, however, requires criteria by which to assess the quality of those materials.

The development of criteria that were first officially published in 1981, resulted from a process that was initiated in 1978, and was precipitated by a number of related factors:

1. Increased level of resource development
  - a) during the late 1960's and into the 1970's, surface mining of coal was increasing significantly both in terms of expansion of existing operations, and the addition of new developments.
  - b) oil sands development in northeastern Alberta resulted in two major operations being in place by 1970, with several more predicted to come on stream.
2. New and enhanced legislation
  - a) the Land Conservation and Reclamation Act enacted by the province in 1973 (Alberta Government 1973) outlined a number of new requirements relative to rehabilitating lands impacted by resource development.
  - b) the Coal Development Policy for Alberta (Alberta Energy and Natural Resources 1976) stated that "the primary objective in land reclamation is to ensure that the mined or disturbed land will be returned to a state which will support plant and animal life, or be otherwise productive or useful to man, at least to the degree it was before it was disturbed. In many instances the land can be reclaimed to make it more productive, useful, or desirable than it was in its original state; every effort will be made towards this end." It went on to indicate that "land reclamation

will include the contouring of the mined or disturbed lands, the replacement of the topsoil, revegetation for soil stabilization, biological productivity and appearance, and suitable maintenance of the vegetation or where appropriate, the conversion of the land to agricultural or other desirable use”.

3. Concerns raised by industry and regulatory staff. In light of increased development and regulatory requirement, the regulators were not certain of what they should be requesting or requiring, and industry was not certain of what they should commit to in terms of achievable objectives and what the associated costs might be.

It seemed logical therefore, that the most effective approach to providing consistent guidance would be to prepare a document that could be used by all individuals concerned. As a result, the Alberta Soils Advisory Committee took the initiative and formed the Soil Quality Criteria Subcommittee.

## 7.2 OBJECTIVE

The objective of the Soil Quality Criteria Subcommittee was to develop a guide to assist people involved in a professional capacity in land reclamation (Alberta Soils Advisory Committee 1981). The group was to develop criteria relative to:

1. soil mapping and sampling for baseline and post-disturbance activity;
2. overburden sampling;
3. analytical requirements; and
4. physical, chemical, and biological criteria for evaluating the suitability of soil materials for revegetation.

The guidelines and criteria prepared were to provide a single or uniform target for both industry staff and government regulatory personnel. The document produced was intended to be a scientific and technical manual for use by professionals and did not contain any reference to policies or regulations of any government agency, nor was it to address economic, social or political issues. Economic and political decisions must make use of quality criteria, but the criteria themselves are independent of such considerations. It was inevitable, however, that the criteria would eventually wind up in the “policy” or “regulatory” arena.

### 7.3 MATERIALS AND METHODS

The soil quality criteria relative to disturbance and reclamation were compiled by a group of five soil scientists representing the private sector, regulatory agencies and research community with each individual having experience in land management, conservation and reclamation. The criteria developed were compiled from a review of the pertinent literature and ongoing research, and tempered in some situations by making the "best" or most "educated" guess where data were incomplete. In many instances the research to support the basis for specific criteria was almost complete and in some cases development of the criteria identified specific research needs or topics that were not being addressed.

More definitive guidelines and criteria could have been developed pending completion of additional research, however, the subcommittee felt it was critical to develop the best possible document and circulate it to stimulate thinking and discussion. The resulting documents entitled "Proposed Criteria Relative to Disturbance and Reclamation" (Alberta Soils Advisory Committee 1981) certainly stimulated a wealth of discussion and debate. It also stimulated the development of relevant and focused research efforts that might otherwise not have been undertaken.

#### 7.3.1 Division of Province into Regions

The first step in the process was to divide the province into three distinct regions to allow for the establishment of criteria that would apply to each region in general. There are differences within each of these regions but it was beyond the scope of the document (Alberta Soils Advisory Committee 1987a) produced to suggest criteria for subdivisions. Individual operations within each of the major zones would have conditions or characteristics unique to that specific location or operation. The three major regions (Figure 1) are the:

1. Plains Region which includes the Central Plains and Peace River Plains and has a predominantly agricultural land use;
2. Eastern Slopes Region which includes the Lower and Upper Foothills, and the Rocky Mountains to the British Columbia border; and
3. Northern Forested Region which includes the remainder of the province.

### 7.3.2 Soil Mapping and Sampling

The next step in the process was to provide guidelines relative to soil survey activities. A soil survey with relevant interpretations helps in understanding the soil relationships in an area prior to preparing a development plan to ensure adequate evaluation of the potential for reclamation. These were largely adopted from guidelines prepared over several decades by the National Soil Survey Committee and its successor the Expert Committee for Soil Survey. Guidelines relative to mapping and sampling reconstructed soils were developed.

The document entitled "Soil Quality Criteria Relative to Disturbance and Reclamation" (Alberta Soils Advisory Committee 1987a) provides guidelines relative to recommended inspection density, soil profile characteristics, landscape features to be recorded, and map presentation. Use of a photo mosaic base is recommended in part because it is particularly helpful in working with post disturbance landscapes. Guidelines pertinent to sampling for baseline or evaluation purposes including sampling intensity and sampling methodology are described. Similarly, guidelines pertinent to post-disturbance or reconstructed soil sampling are provided. Again, this includes guidelines regarding sampling intensity and sampling methodology. For example, the document states that "sampling of reconstructed soils should be done on the basis of layers or materials such as topsoil, subsoil and spoil and on depth intervals within each of these discrete layers". Table 1 provides an indication of the total depth and intervals that should be sampled in reconstructed soil areas.



Figure 1. The major land regions of Alberta.

Table 1. Sampling depth intervals for reconstructed soils in the three regions.<sup>1</sup>

| Region          | Depth Interval (cm)                                   | Notes  |
|-----------------|---|--|
| Plains          | 0 to 15   | or The topsoil layer should be taken in one sample, If topsoil depth is less than 15 cm then that depth of material should be segregated from material below. If topsoil is greater than 15 cm then first sample can exceed 15 cm in thickness. If topsoil layer is greater than 20 cm in thickness topsoil should be split into two sample intervals. |
|                 | 15 to 30  |  |
|                 | 30 to 45  |  |
|                 | 45 to 60  |  |
|                 | 60 to 90  |  |
|                 | 90 to 120   |  |
|                 | 120 to 150  |  |
|                 |   | Sample should be collected to and including one depth increment of spoil if depth to spoil is greater than 1.5 m.  |
| Northern Forest | 0 to 15   | If the upper lift is less than 30 cm in thickness it could be sampled in one or two intervals. For example, if 20 cm thick then one sample interval would be appropriate, if greater than 20 cm thick it should be split into two samples.   |
|                 | 15 to 30  |  |
|                 | 30 to 60  |  |
|                 | 60 to 90  |  |
|                 | 90 to 120   |  |
|                 |   | Samples should be collected to and including one depth increment of spoil if depth to spoil is greater than 1.2 m.   |
| Eastern Slopes  | 0 to 15   | If the thickness of replaced soil material is less than 30 cm then sampling could be done in one or two intervals. For example, if 20 cm thick then one sample interval would be appropriate, if greater than 20 cm thick the recommended intervals should be utilized.  |
|                 | 15 to 30  |  |
|                 | then 30 cm increments <u>where possible</u> to 120 cm |  |

<sup>1</sup> Sampling should be conducted on the basis of the layers replaced and depth intervals within these layers.

### 7.3.3 Analytical Requirements

Analytical requirements are defined for both baseline characterization and post-disturbance or reconstructed areas. The minimum analytical requirements listed aid in properly characterizing soils for classification and mapping purposes and making interpretations relative to the quality of the soils as they occur in the undisturbed and reconstructed states. They also assist in developing predictions about the degree of usefulness they may have in the post disturbance situation. Preferred methods of analysis are described in the document.

### 7.3.4 Criteria for Evaluating the Suitability of Undisturbed and Reconstructed Soils

In attempting to establish criteria for evaluating soils and overburden materials, a number of factors including the respective physical and chemical properties must be considered. It must be recognized however, that the establishment and maintenance of vegetation requires more than the properties of the soil namely water, light and carbon dioxide. To optimize plant production in a given environment the factors associated with the soil such as nutrients, water retention and availability must be in balance with all other factors.

Depth criteria were not spelled out - neither for undisturbed soils nor for reconstructed soils. However, occurrence and depth of master horizons (A, B, C) in the predisturbance state has a bearing or influence on how materials are salvaged, with respect to the different lifts involved, and subsequently the manner of replacement.

Replaced soil thickness should be no more limiting to plant growth than it was in the undisturbed state. It must be emphasized that thickness replaced depends not only upon soil quality but the quality of the overburden, and other factors such as mean annual precipitation, topography, slope angle, and water table position.

The materials handling procedures utilized in the three major regions identified would vary significantly since each region has unique climate features and soil types. General procedures for materials handling for each of the regions were defined in order that suitability criteria could be established.

To evaluate the suitability of soils and overburden materials in a given area one requires that a soil survey in sufficient detail is available and that the soils and overburden have been adequately sampled and characterized. The requirement for evaluating reconstructed soil areas would be similar.

Evaluations of soil suitability are made by considering the interaction of various soil properties and characteristics to give an overall rating of the degree of suitability. Three categories of suitability and one category to indicate unsuitable areas are used. The four categories are as follows:

1. Good (G) - None to slight soil limitations that affect use as a plant growth medium.
2. Fair (F) - Moderate soil limitations that affect use but which can be overcome by proper planning and good management.
3. Poor (P) - Severe soil limitations that make use questionable. This does not mean the soil cannot be used, but rather careful planning and very good management are required.
4. Unsuitable (U) - Chemical or physical properties of the soil are so severe reclamation would not be economically feasible or in some cases impossible.

7.3.4.1 Plains Region. In agricultural areas, the selective salvage of topsoil and subsoil and subsequent sequential replacement of these materials is currently required and practiced. It is also useful to characterize the material below the subsoil in the predisturbance setting because this usually becomes the "spoil" upon which the reconstructed soils are built. In some instances these parent materials can and do become part of the reconstructed subsoil. To facilitate the identification of suitable sources of soil materials for replacement relative to operations such as surface mines or quarries that result in deep disturbance, it is recommended that the upper five metres be characterized prior to disturbance. Topsoil is defined as the surface "A" (organo-mineral) horizons of the soil profile. Subsoil is defined as the "B" horizon(s) and the upper portion of the parent material.

The criteria for evaluating the suitability of the soils for their use as topsoil and subsoil are provided in Tables 2 and 3.



Table 2. Criteria for evaluating suitability of topsoil in the Plains Region (ASAC 1987a).

| Rating/Property                     | Good (G)                    | Fair (F)                   | Poor (P)  | Unsuitable (U)    |
|-------------------------------------|-----------------------------|----------------------------|---|-------------------|
| Reaction (pH)                       | 6.5 to 7.5                  | 5.5 to 6.4 &<br>7.6 to 8.4 | 4.5 to 5.4 &<br>8.5 to 9.0                      | <4.5 and >9.0     |
| Salinity (EC)<br>(dS/m)             | <2                          | 2 to 4                     | 4 to 8  | >8                |
| Sodicity (SAR)                      | <4                          | 4 to 8                     | 8 to 12   | >12 <sup>1</sup>  |
| Saturation (%)                      | 30 to 60                    | 20 to 30,<br>60 to 80      | 15 to 20,<br>80 to 120                          | <15 and >120      |
| Stoniness Class                     | SO, S1                      | S2                         | S3, S4  | S5                |
| Texture                             | FSL, VFSL,<br>L, SL, SiL    | CL, SCL,<br>SiCL           | LS, SiC,<br>C <sup>2</sup> , S, HC <sup>3</sup> |                   |
| Moist Consistency                   | very<br>friable,<br>friable | loose                      | firm,<br>very firm                              | extremely<br>firm |
| Organic Carbon (%)                  | >2                          | 1 to 2                     | <1  |                   |
| CaCO <sub>3</sub><br>Equivalent (%) | <2                          | 2 to 20                    | 20 to 70  | >70               |

<sup>1</sup> Materials characterized by an SAR of 12 to 20 may be rated as poor if texture is sandy loam or coarser and saturation % is less than 100.

<sup>2</sup>C May be upgraded to fair or good in some arid areas.

<sup>3</sup>HC (Heavy Clay) - May be upgraded to fair or good in some arid areas.

Table 3. Criteria for evaluating suitability of subsoil materials in the Plains Region (ASAC 1987a).

| Rating/Property                               | Good (G)   | Fair (F)                   | Poor (P)                                       | Unsuitable (U)   |
|---|--|----------------------------|--|------------------|
| Reaction (pH)                                 | 6.5 to 7.5   | 5.5 to 6.4 &<br>7.6 to 8.5 | 4.5 to 5.4 &<br>8.6 to 9.0                     | <4.5 and >9.0    |
| Salinity (EC)<br>(dS/m)                       | <3   | 3 to 5                     | 5 to 10  | >10              |
| Sodicity (SAR)                                | <4   | 4 to 8                     | 8 to 12  | >12 <sup>1</sup> |
| Saturation (%)                                | 30 to 60   | 20 to 30,<br>60 to 80      | 15 to 20,<br>80 to 120                         | <15 and >120     |
| Stone Content<br>(% Vol)                      | <3   | 3 to 25                    | 25 to 50                                       | >50              |
| Texture                                       | FSL, VFSL,<br>L, SiL, SL   | CL, SCL,<br>SiCL           | S, LS, SiC,<br>C <sup>2</sup> HCL <sup>2</sup> | Bedrock          |
| Moist Consistency                             | very friable,<br>friable   | loose firm                 | very firm                                      | extremely firm   |
| Gypsum<br>CaCO <sub>3</sub><br>Equivalent (%) | The suitability criteria for sodicity (SAR) may be altered by the presence of high levels of either lime (CaCO <sub>3</sub> ) or gypsum (CaSO <sub>4</sub> ) in excess of other soluble salts. |                            |  |                  |

<sup>1</sup> Materials characterized by an SAR of 12 to 20 may be rated as poor if texture is sandy loam or coarser and saturation % is less than 100.

<sup>2</sup>HCL - Heavy Clay Loam.

7.3.4.2 Northern Forest Region. In the Northern Forest Region it is appropriate to salvage soil materials in two lifts. The upper lift comprising a mixture of the organic and A horizons of the soil solum and perhaps a portion of the B horizon to a depth of about 30 cm depending upon site specific conditions. The second (lower lift) comprises the material below the upper lift to a depth deemed appropriate relative to specific site conditions. The second lift need not be salvaged in areas where the overburden material is rated as suitable for use as subsoil or lower lift material. Salvage of the top lift as a separate unit is important in that:

1. Organic matter levels as well as important soil macro- and micro-organisms are less diluted.
2. It generally has better growth support capability, and
3. It may serve as an excellent seed source for some native species.

The criteria for evaluating the soil properties are listed in Tables 4 and 5.

Organic soils should be considered for salvage and used as a soil conditioner.

Origin, degree of decomposition and reaction will determine the suitability of these materials.

#### 7.3.4.3 Eastern Slopes Region

In the Eastern Slopes Region salvage and replacement of one lift of material is commonly practiced. In this region, as for the Plains and Northern Forested Regions, the material handling procedures will reflect specific site conditions.

The criteria for evaluating the soil properties are listed in Table 6.

#### 7.3.5 Use of the Criteria to Develop Ratings

The ratings (good, fair, poor, unsuitable) are determined by assessing the site factors and analytical data in terms of the limits presented in the criteria tables. Each horizon or layer is rated relative to the individual parameters and an overall rating can be developed for each horizon or layer. The most limiting property (rating) determines the ultimate rating for each horizon or layer.

A number of the parameters assessed and used in developing ratings are interrelated. For example, sodicity, saturation percentage and texture are fairly closely related.

Table 4. Criteria for evaluating the suitability of surface material (upper lift) for revegetation in the Northern Forest Region (ASAC 1987a).

| Rating/Property                                  | Good (G)                    | Fair (F)                 | Poor (P)                 | Unsuitable (U)    |
|--|-----------------------------|--------------------------|--------------------------|-------------------|
| Reaction (pH) <sup>1</sup>                       | 5.0 to 6.5                  | 4.0 to 5.0<br>6.5 to 7.5 | 3.5 to 4.0<br>7.5 to 9.0 | <3.5 and >9.0     |
| Salinity (EC) <sup>2</sup><br>(dS/m)             | <2                          | 2 to 4                   | 4 to 8                   | >8                |
| Sodicity (SAR) <sup>2</sup>                      | <4                          | 4 to 8                   | 8 to 12                  | >12 <sup>3</sup>  |
| Saturation (%) <sup>2</sup>                      | 30 to 60                    | 20 to 30,<br>60 to 80    | 15 to 20,<br>80 to 120   | <15 and >120      |
| Stoniness/<br>Rockiness <sup>4</sup><br>(% Area) | <30/<20                     | 30-50/20-40              | 50-80/40-70              | >80/>70           |
| Texture  | FSL, VFSL,<br>L, SiL, SL    | CL, SCL,<br>SiCL         | LS, SiC,<br>C, HC, S     |                   |
| Moist Consistency                                | very<br>friable,<br>friable | loose,<br>firm           | very<br>firm             | extremely<br>firm |
| CaCO <sub>3</sub><br>Equivalent (%)              | <2                          | 2 to 20                  | 20 to 70                 | >70               |

<sup>1</sup> pH values presented are most appropriate for trees, primarily conifers. Where reclamation objective is for other end land uses, such as erosion control, and where other plant species may be more important, refer to Table 6.

<sup>2</sup> Limits may vary depending on plant species to be used.

<sup>3</sup> Materials characterized by an SAR of 12 to 20 may be rated as poor if texture is sandy loam or coarser and saturation % is less than 100.

<sup>4</sup> <25 cm diameter stones/rocks intercepting surface.

Table 5. Criteria for evaluating the suitability of the subsurface material (lower lift) for revegetation in the Northern Forest Region (ASAC 1987a).

| Rating/Property                      | Good (G)                             | Fair (F)                                       | Poor (P)                                       | Unsuitable (U)                       |
|--------------------------------------|--------------------------------------|--|--|--------------------------------------|
| Reaction (pH) <sup>1</sup>           | 5.0 to 7.0 <sup>2</sup>              | 4.0 to 5.0<br>7.0 to 8.0 <sup>2</sup>          | 3.5 to 4.5<br>8.0 to 9.0                       | 3.5 and >9.0                         |
| Salinity (EC) <sup>3</sup><br>(dS/m) | <3                                   | 3 to 5   | 5 to 8   | >8                                   |
| Sodicity (SAR)                       | <4                                   | 4 to 8   | 8 to 12  | >12 <sup>4</sup>                     |
| Saturation (%)                       | 30 to 60                             | 20 to 30,<br>60 to 80                          | 15 to 20,<br>80 to 100                         | <15 and >100                         |
| Coarse<br>Fragments<br>(%/Vol)       | <30 <sup>5</sup><br><15 <sup>6</sup> | 30 to 50 <sup>5</sup><br>15 to 30 <sup>6</sup> | 50 to 70 <sup>5</sup><br>30 to 50 <sup>6</sup> | >70 <sup>5</sup><br>>50 <sup>6</sup> |
| Texture                              | FS, VFSL,<br>L, SiL, SL              | CL, SiC,<br>SiCL                               | S, LS, S,<br>C, HC                             | bedrock                              |
| Moist Consistency                    | very<br>friable,<br>friable,<br>firm | loose,<br>very firm                            | extremely<br>firm                              | hard rock                            |
| CaCO <sub>3</sub><br>Equivalent (%)  | <5                                   | 5 to 20  | 20 to 70                                       | >70                                  |

<sup>1</sup> pH values presented are most appropriate for trees, primarily conifers. Where reclamation objective is for other end land uses, such as erosion control, and where other plant species may be more important, refer to Table 6.

<sup>2</sup> Higher value takes into consideration that in the lower lift the pH values of the soils are generally higher. Normally the pH rating should not be different from those shown in Tables 9 and 11.

<sup>3</sup> Limit may vary depending on plant species to be used.

<sup>4</sup> Materials characterized by an SAR of 12 to 20 may be rated as poor if texture is sandy loam or coarser and saturation % is less than 100.

<sup>5</sup> Matrix texture (modal) finer than sandy loam.

<sup>6</sup> Matrix texture (modal) sandy loam and coarser.

Table 6. Criteria for evaluating the suitability of root zone material in the Eastern Slopes Region (ASAC 1987a).

| Rating/Property                                 | Good (G)                             | Fair (F)                                       | Poor (P)                                       | Unsuitable (U)                       |
|---|--------------------------------------|--|--|--------------------------------------|
| Reaction (pH) <sup>1</sup>                      | 5.0 to 6.5                           | 4.0 to 5.0<br>6.5 to 7.5                       | 3.5 to 4.0<br>7.5 to 9.0                       | <3.5 and >9.0                        |
| Salinity (EC) <sup>2</sup><br>(dS/m)            | <2                                   | 2 to 4   | 4 to 8   | >8                                   |
| Sodicity (SAR) <sup>2</sup>                     | <4                                   | 4 to 8   | 8 to 12  | >12 <sup>3</sup>                     |
| Saturation (%) <sup>2</sup>                     | 30 to 60                             | 20 to 30,<br>60 to 80                          | 15 to 20,<br>80 to 100                         | <15 and >100                         |
| Coarse<br>Fragments <sup>4</sup><br>(%/Vol/Vol) | <30 <sup>5</sup><br><15 <sup>6</sup> | 30 to 50 <sup>5</sup><br>15 to 30 <sup>6</sup> | 50 to 70 <sup>5</sup><br>30 to 50 <sup>6</sup> | >70 <sup>5</sup><br>>50 <sup>6</sup> |
| Texture   | L, SiCL,<br>SCL, SL,<br>FSL          | CL, SiL,<br>VFSL, SC,<br>SiC                   | LS, S,<br>Si, C, HC                            | Consolidated<br>Bedrock              |
| Moist Consistency                               | very<br>friable,<br>friable          | loose,<br>firm                                 | very<br>firm                                   | extremely<br>firm                    |
| CaCO <sub>3</sub>                               | <2                                   | 2 to 20  | 20 to 70                                       | >70                                  |

- <sup>1</sup> pH values presented are most appropriate for trees, primarily conifers. Where reclamation objective is for other end land uses, such as erosion control, and where other plant species may be more important, refer to Table 6.
- <sup>2</sup> Limits may vary depending on plant species to be used.
- <sup>3</sup> Materials characterized by an SAR of 12 to 20 may be rated as poor if texture is sandy loam or coarser and saturation % is less than 100.
- <sup>4</sup> 0.2 to 25 cm diameter fragments in the soil material.
- <sup>5</sup> Matrix texture (modal) finer than sandy loam.
- <sup>6</sup> Matrix texture (modal) sandy loam and coarser.

It is important to note that some parameters are likely more important than others in terms of assessing quality and there are situations where management practices can overcome or compensate for some limitations. It was not the intent of the document to suggest the extent to which management practice could impact ratings that are developed. Some pertinent comments can, however, be made. For example, a soil could be rated fair, poor, or unsuitable on the basis of degree of stoniness while the remaining parameters considered are not limiting. In this instance it would be reasonable to qualify the rating with a statement to the effect that management practice (stone picking) could be utilized to improve soil quality.

#### 7.4. THE USE OF SOIL QUALITY CRITERIA

The soil quality criteria developed are used by a wide range of practitioners for the general purpose of assessing soil material quality prior to disturbance to determine soil suitability for reclamation, and subsequent to reclamation procedures to evaluate reclamation success. The overall goal relative to use of the criteria is to minimize environmental impact occurring as a result of land disturbance.

Personnel in the government regulatory process utilize the criteria to provide guidance to industry with respect to what is expected in terms of evaluating pre-disturbance and post-disturbance conditions, and to evaluate industrial plans for soil salvage and replacement. Industry personnel utilize the criteria to evaluate the baseline situation relative to soils, develop materials handling plans, and predict the resultant expected post-disturbance or reconstructed soil characteristics. Measurements after soil reconstruction are used to evaluate reclamation success at a given time.

Despite the fact that the criteria established (ASAC 1981, 1987a) were driven to a large extent initially by surface mining activities in Alberta, they are applicable to any land disturbance in the province including oil and gas development, pipeline construction, sand and gravel operations, and a variety of others. It should be noted that use of the criteria is not limited just to the activities and impacts associated with the disturbance of the soil resulting from extraction of the resource and development of transportation infrastructure, but also those associated with treatment and disposal of the respective by-products or wastes generated.

#### 7.4.1 Soil Quality and Measurement of Reclamation Success

The criteria are used primarily to assist in measuring reclamation success or comparing the undisturbed setting with the post-disturbance or reconstructed condition. The process of adopting and implementing a system for measuring reclamation success was and continues to be evolutionary, and is based on several strategic activities and research efforts.

Initially the productivity concept which considered measurements in terms of bushels per acre or bales per acre was used. In the early 1980's the capability concept was deemed more suitable because it considered the intrinsic characteristics of the soil and did not deal with specific crops and defined management practices.

A number of systems have been developed to measure land/soil capability in Alberta and Canada (Alberta Soils Advisory Committee 1987b, Brocke 1977; Canada Land Inventory 1965). Systems for measuring reconstructed soil capability have also been developed and are based largely on the original CLI Land Capability System (Macyk 1987, Leskiw and Lapointe 1992).

The current objective or goal of reclamation in Alberta is defined in terms of "equivalent land capability" under the draft Alberta Environmental Protection and Enhancement Act (Alberta Environment 1992). Equivalent land capability is defined as "the ability of the land to support various land uses after reclamation is similar to the ability that existed prior to an activity being conducted on the land, but that the ability support individual land uses will not necessarily be identical after reclamation". Land capability is defined as "the ability of the land to support a given land use on a sustained basis irrespective of future management inputs, activities or alterations". It refers to an evaluation or rating of the kind and degree of limitations on land use, in terms of physical, chemical and biological characteristics such as topography, drainage, hydrology, soils, and vegetation. It includes any existing abilities and conditions which are the result of previous alterations or management practices (Alberta Environment 1992). For the purposes of the definitions of land capability and equivalent land capability, land is defined as "terrestrial, semi-aquatic, and aquatic landscapes" (Alberta Environment 1992).



Put in economic terms, it is clearly the intent of reclamation legislation in Alberta that the cost of assuring equivalent land capability or any other measure of reclamation success in the post-disturbance landscape is to be borne as a capital investment in the land, rather than as an operating cost by the end land user.

Determining land capability and soil capability as done in the past includes the development of a rating based on climate and landscape factors as well as physical and chemical soil properties. Capability is determined on the basis of a class (1 to 7) which denotes relative level of capability and a subclass designation which denotes the limiting characteristic(s).

Comparing pre- and post-disturbance capability allows for a comparison in capability class but not necessarily a comparison of soil properties. For example, in some situations changes in topographic factors may have more impact on post-disturbance capability than change in soil parameters. Therefore comparing pre-and post-disturbance capability ratings may not explicitly or clearly indicate the relationships with respect to soil properties.

Measurement or comparison of soil quality allows for a better assessment of individual soil parameters and is a critical component in evaluating land capability. Soil quality embraces the quantification of specific soil parameters whereas soil capability is a holistic ranking of soil, landscape and climate factors.

7.4.1.1 Baseline Assessment. Prior to most land impacting activities the proponent must provide the appropriate regulatory agencies with a plan detailing what the baseline or undisturbed condition is, the nature of the activity or disturbance, and how the land will be reclaimed. Completion of a soil survey as referred to previously is one of the baseline assessments that provides an indication of the type and extent of the soils in the area to be affected. The various soil physical and chemical parameters outlined in the suitability tables can be measured directly in the field and by analyzing representative soil samples.

Based on the compilation of field and analytical data, soil suitability ratings can be prepared.

7.4.1.2      Decision Making. Once the soil suitability ratings have been prepared for a given development these ratings combined with all other considerations allow for decision-making relative to the feasibility of proceeding with a given development.

It is possible, however unlikely, that approval for a given development would be rejected solely because of soil quality issues.

7.4.1.3      Materials Handling. Soil quality and/or suitability ratings play an integral role in developing materials handling plans. Soil salvage/replacement requirements and practices are fairly well established in Alberta with the general requirement of salvaging topsoil, subsoil and parent materials where necessary. For example, in the Plains or agricultural regions of the province the general practice is to salvage and replace 15 cm of topsoil and 1 m of subsoil over spoil material. In the non-agricultural or "forested" portion of the province a "coversoil" is replaced based upon the depth and properties of the pre-disturbance soils.

Having knowledge regarding the characteristics of these different materials allows one to determine the relative suitability of the materials and their overall usefulness for reclamation purposes. Assessment of the suitability or quality of the various materials will allow for planning selective salvage and replacement of materials. In some situations suitable overburden material could be used as the surface layer for a reconstructed soil, especially if more suitable materials are not available. For example, in areas where sodic materials are present it is possible that the parent materials may be more suitable for use or provide better overall soil quality than the indigenous subsoil materials.

7.4.1.3.1      Surface Mining (Drastic Disturbance). Resource extraction operations result in different levels or degrees of disturbance. For example, surface mining of coal can result in the removal of soil and overburden to depths up to 100 m or more in some locations. Sand and gravel operations can also have impacts to significant depths.

An example of using the criteria to evaluate the impact of surface mining on soils in the subalpine region where parameters such as texture and pH are critical soil properties is provided (Table 7).

Table 7. Pre-Mining and Reconstructed Soil Characteristics (0 to 15 cm depth)

| Soil          | pH  | Texture | Coarse Fragments<br>(% Vol/Vol) |
|---------------|-----|---------|---------------------------------|
| Pre-mining    | 5.8 | SiL-L   | 2.5                             |
| Reconstructed | 6.6 | L       | 40                              |

According to the criteria presented in Table 6 the pre-mining soil would have an overall "good" rating in terms of soil suitability. The reconstructed soil would have an overall "fair" rating due mainly to coarse fragment content. In this situation management practices such as coarse fragment removal or adopting specific revegetation practices could be undertaken to mitigate the limitation.

7.4.1.3.2 Other Disturbances. Less drastic disturbances such as road, pipeline and wellsite construction would not involve the extent or volume of material movement per unit area that is often associated with mining and quarrying operations. These disturbances may be considered less drastic in the sense that the overall depth of disturbance is generally not as great as for mining and quarrying, however considerable surface disturbance does occur. As a result soil quality and soil capability are affected.

In the realm of pipeline construction the soil quality criteria are used to assess the need for three-lift vs two-lift handling of soil to maintain soil capability. Two major types of soils require separate handling of major soil horizons to maintain soil capability (Ferguson 1990). In areas where gravel occurs in the pipeline trench it should be replaced at pre-construction depths. Similarly, soil materials that are saline and/or sodic may require three-lift soil handling when they exist below a non-saline/non-sodic subsoil layer (Ferguson 1990).

7.4.1.3.3 Waste (By-product) Disposal. Land-based disposal of industrial wastes or by-products is becoming more widely practiced in Alberta. Landspreading and landfarming are commonly used land application techniques.

Soil quality is impacted by the addition of waste materials. In some situations or for some parameters, the quality is improved whereas in others it is reduced. Time is a major consideration when assessing soil quality. For instance quality might be reduced immediately following waste application/incorporation, however it may improve with time such as in one, two or however many years thereafter.

Soil quality criteria are useful in determining how much waste can be applied to a given soil. Loading rates for various wastes have been established and used such as those associated with the application of municipal wastewater sludges to agricultural lands (Alberta Environment 1982). Similarly guidelines are in place regarding loading rates for drilling waste disposal (ERCB 1975) which are currently under revision by the joint government/industry Drilling Waste Review Committee.

An example of how the criteria can be used in assessing the impact of drilling waste landspreading is provided. The example is taken from a study of the landspreading of a salt-based mud system on a replaced "surface" soil with emphasis on EC and SAR values in (Table 8).

Table 8. Mean Values for EC and SAR in the Various Plot Treatments (0 to 15 cm depth).

| Waste<br>Rate<br>(kg Cl/ha) | EC(dS/m) |      |        |        |        | SAR |      |        |        |        |
|-----------------------------|----------|------|--------|--------|--------|-----|------|--------|--------|--------|
|                             | Pre*     | Post | Year 1 | Year 2 | Year 3 | Pre | Post | Year 1 | Year 2 | Year 3 |
| 0                           | 0.5      | 0.6  | 0.5    | 0.4    | 0.4    | 0.2 | 0.3  | 0.2    | 0.2    | 0.2    |
| 350                         | 0.5      | 2.0  | 1.2    | 0.5    | 0.5    | 0.3 | 4.7  | 2.9    | 1.4    | 1.1    |
| 700                         | 0.5      | 2.4  | 1.8    | 0.6    | 0.5    | 0.3 | 5.2  | 4.5    | 1.7    | 1.4    |
| 1400                        | 0.6      | 3.0  | 1.8    | 0.7    | 0.6    | 0.3 | 8.5  | 5.3    | 3.4    | 2.4    |
| 2800                        | 0.5      | 7.3  | 5.4    | 2.4    | 1.3    | 0.5 | 23.5 | 15.2   | 11.4   | 8.3    |

\*Pre - Baseline (prior to waste application)  
 Post - 1 month following waste application.  
 Year 1 - 1 year following waste application.  
 Year 2 - 2 years following waste application.  
 Year 3 - 3 years following waste application.

The Alberta Soils Advisory Committee (1977, 1987a) presented the following limitation criteria and suitability ratings for EC and SAR levels in soil in the Northern Forested Region:

| <u>Limitation</u>   | <u>Suitability Rating</u> | <u>EC Value (dS/m)</u> | <u>SAR Value</u> |
|---------------------|---------------------------|------------------------|------------------|
| No limitation       | good                      | <2                     | <4               |
| Slight limitation   | fair                      | 2 to 4                 | 4 to 8           |
| Moderate limitation | poor                      | 4 to 8                 | 8 to 12          |
| Severe limitation   | unsuitable                | >8                     | >12              |

The data in Table 8 indicate that based on EC and SAR levels the receiving soil was rated good or would present no limitation to plant growth. Following waste application the limitation due to EC level ranged from none to moderate depending upon waste rate applied. In subsequent years the degree of limitation decreased or level of suitability increased. By year 3 only the highest waste rate had values exceeding baseline levels. A similar trend was also exhibited by the SAR levels reported in Table 8.

This approach could be utilized for all parameters for which limitation and suitability criteria have been defined to assess soil quality.

Soil quality criteria can also be utilized to evaluate the suitability of non-soil materials for use as a plant growth medium. For example, a waste or by-product of coal mining was characterized with a view to revegetation of areas where this material had been placed (Table 9).

Table 9. Physical and Chemical Properties of a Coal Waste Material.

| pH<br>(H <sub>2</sub> O) | Texture | CaCO <sub>3</sub> Eq.<br>(%) | Sat'n<br>(%) | EC<br>dS/m | SAR |
|--------------------------|---------|------------------------------|--------------|------------|-----|
| 8.2                      | Loam    | 3.69                         | 85           | 3.6        | 10  |

Utilizing the criteria for evaluating the suitability of root zone material in the Eastern Slopes Region provided in Table 6 one can assess the overall suitability of the material for revegetation purposes. The parameters of pH, SAR, and saturation % would be rated as poor,  $\text{CaCO}_3$  equivalent and EC as fair, and texture as good. The overall suitability rating would be poor or there would be a moderate limitation to using the material for revegetation purposes. At this stage one would look at options available in terms of management practice or amendments that might be used to improve the overall suitability of the material.

#### 7.5. EXPANDING THE SOIL QUALITY CRITERIA

The current soil quality criteria for agriculture were published in 1977 and the criteria relative to land disturbance and reclamation were initially released in 1981 followed by a revised version in 1987. The revised version was based on the existing research and the available literature to 1982. Great strides have been made in soils research and practical experience since then. Significant changes have occurred in many areas including:

1. increased public awareness regarding the environment and associated expectations;
2. improved analytical techniques;
3. improved equipment for both laboratory and field measurements;
4. improved field practices; and
5. longer record for research studies or more long-term data.

Increased public awareness has resulted in the move to more consciousness of soil conservation and better land management practices. Combining this increased awareness with enhanced regulatory requirements has resulted in the modification of practices used to extract natural resources in this province.

Improved analytical equipment and methodologies allow for more extensive and precise analytical work. For example, in the late 1970's knowledge about the trace element content of Alberta soils and wastes was minimal compared to the data currently available. Field practices associated with the preparation for resource development, the actual resource removal and reclamation/rehabilitation thereafter have improved.

As mentioned previously, the criteria currently utilized were based largely on relevant scientific data obtained prior to 1982. At that time "environmental soil science" research was really in its infancy in Alberta and in the rest of Canada and North America. A significant amount of reclamation research had been initiated by that date however very few of the projects had a record of more than two or three years. Reclamation research expanded in the early 1980's and some of it was specifically directed at evaluating the applicability, usefulness, and relevance of the criteria that had been established. Furthermore, in addition to the value of long-term research results came the transfer of research efforts to the operational scale. It is this combination of more long-term measurements at the research or plot scale and application of results to operational efforts that provides guidance to expanding the existing criteria. Results from the operational scale or the "real world" provide the most sound guidance with respect to what is feasible and practical to expect and to achieve.

As a result there is the opportunity to expand and improve the soil quality criteria currently being used. As mentioned previously criteria associated with specific practices that impact soil have been developed, others are currently in the process of being developed, and certainly others will be worked on in the future.

Suggestions regarding potential additions or modifications are described.

#### 7.5.1 Regions of the Province

The existing criteria are defined for three discrete regions in the province. There is the potential to subdivide at least the Plains and Northern Forested Regions using alternatives such as an eco-region approach. The Plains Region currently encompasses a broad range of soil zones or Orders and climatic regimes where subdivisions could be made.

The Northern Forested Region could be subdivided primarily on the basis of climate. The Eastern Slopes Region could also be potentially subdivided with the eastern portion of the existing unit being added to the Forested Region.

Further subdivision of the various regions could be undertaken resulting in the development of more specific criteria for more well defined regions. However it must be noted that with more subdivision comes the need to understand and handle the "transition zone" that occurs in the vicinity of each subdivision or delineation.

### 7.5.2 Additional Parameters

Several parameters could be added to the list of physical and chemical properties for which criteria are currently defined. Both analytical (laboratory) and field measurement techniques have advanced over the past decade. As a result of these advances there is a much broader base of information available relative to Alberta soils including both the undisturbed and reconstructed.

Soil chemical properties have been emphasized in reclamation research and monitoring to date. This can be largely attributed to the fact that many of the chemical parameters utilized are measured in the laboratory where standard procedures have been utilized for many decades and that threshold values could be adopted. A limited understanding of soil physical properties and how they are measured has impacted the use of these parameters in soil quality assessment. In contrast to the chemical properties, many of the physical parameters are measured in the field and often there are a number of techniques that can be used to measure a given physical property (Naeth et al. 1991). For example, bulk density can be measured by a variety of techniques each having advantages and disadvantages for specific applications.

With the addition of selected properties comes the need to add or define the most appropriate respective analytical technique(s) or field measurement(s). These techniques must be standardized so that relevant comparisons can be made.

7.5.2.1 Chemical Properties. The existing criteria (ASAC 1987a) already include most of the more critical chemical properties pertinent to soil quality. Properties that might be added for which there are recognized standard measurement techniques include soluble ions such as  $\text{Na}^+$  and  $\text{Cl}^-$  as well as trace element content. The latter is particularly relevant in terms of addressing soil suitability and quality issues associated with waste disposal. This is critical in evaluating the suitability of the potential receiving soil and the impact of the addition on the soil.

7.5.2.2 Physical Properties. The existing criteria include only three physical property measurements and two of these (stoniness/coarse fragments and consistency) are field measurements. Texture can be done in the field but is generally confirmed by analytical



work. As mentioned previously there is a more limited understanding of soil physical properties and their role in soil - plant relationships than is the case for soil chemical properties.

Additional parameters can and should be added to address at least the general areas of soil structure and soil water characteristics. The properties should be relatively easy to measure with standard procedures that all practitioners can utilize. Bulk density and penetration resistance are two parameters that should be added along with consideration for infiltration and hydraulic conductivity.

The critical aspect of adding parameters is the availability of adequate data and experience to define the criteria or threshold values for the rating classes.

### 7.5.3 Ranking of Parameters

The current system used for evaluating soil quality criteria does not allow for ranking or weighting of parameters. For example, the system does not imply that pH or sodicity or any other parameter is more important or weighted more heavily relative to the remaining parameters. The lowest suitability ranking for any given parameter determines the overall suitability class which makes the system simple, straightforward and therefore relatively easy to use.

Ranking or weighting of factors is difficult because of the interrelationships between the properties, the interrelationship with plants and the landscape overall. It seems reasonable to suggest that salinity could be weighted more heavily than moist consistency or stoniness class. The implication is that stoniness class could be modified by stone removal. However this approach brings "management" practices into the process. It must be recognized that development of a weighting system or approach will likely improve the overall assessment or evaluation process, however it will be more difficult to use. A certain amount of calculation would be required to determine specific ratings. It would be appropriate to consider development of a computer program to simplify the task.

#### 7.5.4 When to Measure Soil Quality

Another issue that needs to be addressed relative to soil quality assessment relates to when the measurement is undertaken. To establish the baseline or pre-disturbance situation the measurement is done at a reasonable time prior to development. In the post-disturbance or reconstructed setting it seems reasonable to complete the evaluation soon after the post-disturbance activities. The definition of "soon" in this context and in actual practice likely varies from a number of days to as much as one year.

Undertaking soil quality assessments one or two or more years following completion of work at a site can result in a change in ratings compared to one completed shortly after soil reconstruction. For example, bulk density values could be lower two to three years after site reconstruction compared to weeks thereafter. Similarly, oil and grease content or chloride content could be reduced due to degradation and leaching processes respectively. In summary, soil quality will change with time and these changes can be positive or negative.

These examples raise the question of the purpose of completing soil quality and ultimately land capability ratings following the site reconstruction. The investigations can be done to "certify" or demonstrate that reclamation requirements have been met and that designated end land use activities can be undertaken. They can also be undertaken to determine what specific management practices might be required.

The nature of the activity or type of resource development will have a bearing on when the post-disturbance measurements are undertaken.

#### 7.6. SUMMARY AND CONCLUSIONS

Soil quality criteria relative to resource extraction activities have been in place in Alberta since 1981. They have been used to evaluate the suitability of pre-disturbance soils for revegetation purposes and have also been used to determine soil quality and ultimately contributed to evaluating land capability in the post-disturbance setting. The criteria and guidelines developed relative to disturbance and reclamation were originally geared to surface mining activities however, they can be applied to all land disturbing activities.

Significant advances have been made in "environmental soil science" research since the criteria were developed thereby providing the basis for upgrading or improving the existing criteria and their application in the measurement of reclamation success.

A note of caution relates to the fact that any revision or upgrading should result in a manageable and reasonably "user friendly" system that can and will be readily used by the various practitioners.

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8. **DEVELOPMENT OF SOIL QUALITY CRITERIA FOR  
CONTAMINATED SITE REMEDIATION**

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8.1 **INTRODUCTION**

There can be little argument that contaminants are now a ubiquitous presence in our environment. Though large-scale efforts to deal with contaminant issues have traditionally focused on water and air media, it has become increasingly apparent that contaminated soil is also placing human and environmental health at risk, not only in Canada but world-wide ( Foote 1989; Gaudet *et al.* 1992). In response to the urgency of the problem, large-scale national programs such as the U.S. EPA Superfund and Canada's National Contaminated Site Remediation Program (NCSRP) have been created to promote the cleanup of high priority contaminated sites. Implementation of such programs presents unique regulatory and scientific challenges in the development of an effective and scientifically-defensible infrastructure to guide the assessment and remediation of contaminated soils. This challenge is accentuated not only by the short time-frame over which these programs have been developed (Sheppard et al. 1992) and the broad range of contaminants and sources that must be dealt with (**Table 1**), but by a still evolving understanding of the effects of contaminants in the complex soil environment and on the myriad of uses it sustains.

**Table 1: Profile of contaminated site problems in Canada**

|   | <b>Primary Concern</b>                                  |
|---|---|
| <b>Treatment/Disposal of Wastes</b>     |   |
| Municipal sanitary landfills (dumps)    | methane, toxic organics and inorganics                  |
| Industrial waste landfills (dumps)      | toxic organics and inorganics                           |
| Mine tailings                           | heavy metals, radionuclides, acids                      |
| <b>Industrial/Commercial Activities</b> |   |
| Chemical and petrochemical facilities   | toxic organics, inorganics, hydrocarbons                |
| Metallurgical Facilities                | heavy metals  |
| Foundries/steel mills                   | heavy metals, hydrocarbons                              |
| Wood preservation facilities            | chlorophenolics, metals                                 |
| Coal gasification facilities            | polyaromatic hydrocarbons (PAH)                         |
| Scrap yards/ shipyards/ rail yards      | metals, solvents, hydrocarbons, asbestos, PCBs          |
| Storage sites                           | pesticides, PCBs, PAH (tires), heavy metals (batteries) |

While technologies for the remediation of contaminated soils are undergoing a rapid evolution and now range from innovative bioremediation techniques to vitrification, solidification, thermal desorption and vapour extraction, (e.g., AWMA 1990), remediation will not have long-term effectiveness in restoring and sustaining functional soil systems and associated uses without the concomitant development of measurable endpoints of acceptable soil quality or health that can serve as remediation goals. Because it is rarely feasible to clean up to pristine levels, these endpoints (referred

to as soil remediation or soil quality guidelines/criteria) are usually based on a systematic consideration of the existing and potential risks of soil contaminants to the environment and human health. In this paper we outline the major issues, challenges and directions in the development of soil quality criteria for the remediation of contaminated sites in Canada.

## 8.2 THE NATIONAL CONTAMINATED SITES REMEDIATION PROGRAM

In recognition of the potential magnitude of the contaminated site problem in Canada, and the lack of a consistent national approach to deal with it, the Canadian Council of Ministers of the Environment (CCME) initiated the National Contaminated Sites Remediation Program in October 1989. The Program was established to:

1. promote a coordinated, nationally consistent approach to the identification, assessment and remediation (cleanup) of contaminated sites in Canada which have the potential to impact on human health or the environment;
2. provide the necessary government funds to remediate high risk "orphan" sites for which the responsible party cannot be identified or is unable to carry out the work; and
3. stimulate the development and demonstration of new and innovative remediation technologies.

To ensure national consistency and effective implementation, the NCSRP is based on the following general principles:

1. jurisdictions will have the necessary laws, regulations and programs in place



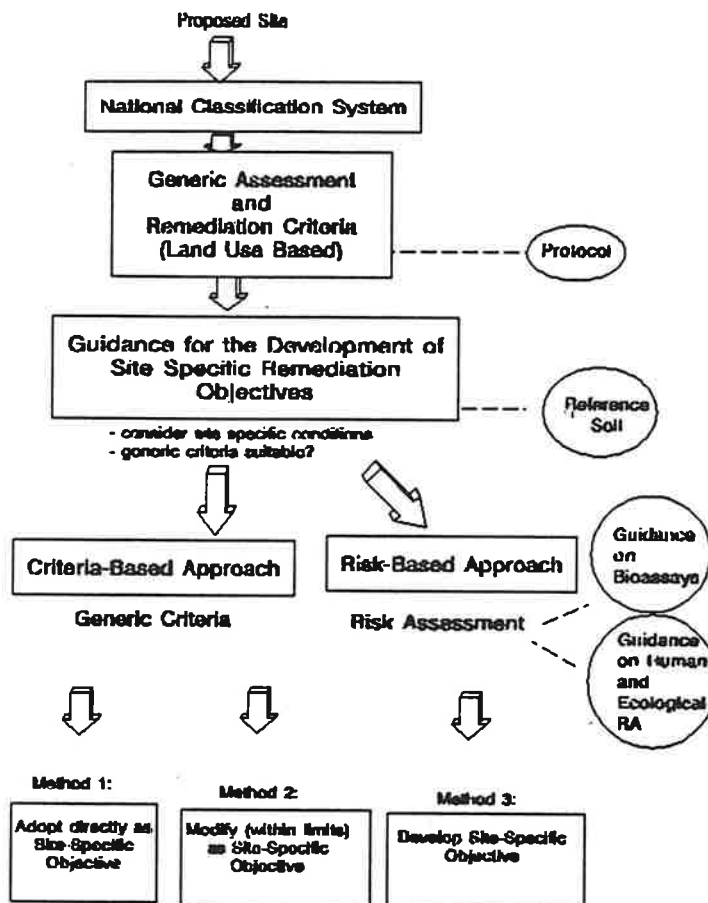
to ensure remediation of high-risk contaminated sites where the responsible party can be held accountable, consistent with the *polluter pays principle*; and

2. common assessment and remediation criteria/guidelines will be used in the management of contaminated sites.

Over the first five years of the Program, \$250 million has been committed to the remediation of high risk orphan sites based on a federal/provincial cost-sharing formula. An additional \$50 million has been committed to promote the development and demonstration of innovative remedial technologies in Canada.

#### 8.2.1 A National Framework for Contaminated Site Assessment and Remediation

In order that site assessment and remediation could be initiated as soon as possible, the development of common assessment and remediation tools was identified as an urgent priority in the NCSRP. Based on the results of two multi-stakeholder workshops held in the first year of the Program (Environment Canada 1990 a,b), a framework for contaminated site assessment and remediation was developed (**Figure 1**). This framework encompasses: (1) a National Classification System (CCME 1992) for screening contaminated sites in terms of the existing or potential risk to human and environmental health; (2) Canadian Environmental Quality Criteria for Contaminated Sites - assessment and remediation criteria that serve as benchmarks in evaluating the nature and extent of contamination at a site and in setting remediation goals that are protective of human health and the environment (CCME 1991a); and, (3) nationally consistent approaches to the development of site-specific remediation objectives.



**Figure 1: National Framework for Contaminated Site Assessment and Remediation in Canada**

Accordingly, the CCME Subcommittee on Classification of Contaminated Sites and the CCME Subcommittee on Environmental Quality Criteria for Contaminated Sites, representing Provincial Ministries of the Environment, Environment Canada and Health and Welfare Canada, were formed to guide the development of these common assessment and remediation tools.

### 8.3 ENVIRONMENTAL QUALITY CRITERIA FOR CONTAMINATED SITES

#### 8.3.1 Generic or Site-Specific: Resolving the Conflict

Though there is currently a myriad of approaches to the development of remediation goals for soil quality (Sheppard *et al.* 1992), most approaches fall generally into two categories: absolute (generic) and relative (site-specific). Absolute approaches are based on the development and application of soil quality criteria that recommend levels of contaminants in soil considered to be generally protective of human health and/or the environment across a broad range of potential sites and conditions. Absolute approaches provide simple, consistent and objective benchmarks for evaluating and remediating contaminated soil which can be easily understood, communicated, and incorporated into legislative or other regulatory processes. However, this approach has been criticized because it does not consider site-specific circumstances, potentially leading to situations where clean-up levels (and therefore ensuing costs) are established beyond that required to protect human health and the environment. Currently there is no consistent approach to the derivation of generic criteria and they are variously based on weight-of-evidence, defined exposure scenarios for different land uses or professional judgement. Not only internationally but even within Canada, existing soil quality criteria vary widely both in terms of their underlying scientific rationale and their application to contaminated site remediation (Table 2).

A relative approach considers a diverse group of methods for determining a site-specific clean-up level by weighing the many factors relevant to a particular site (Sheppard *et al.* 1992). The establishment of site-specific clean-up levels can be based on human health or ecological risk assessment, as well as other factors including cost-benefit and social issues. Typically this approach requires a detailed, and often

**Table 2: Historical overview of the development and application of generic soil quality criteria.**

| <b>Jurisdiction<br/>Program<br/>Initiation</b>                         | <b>Criteria/Guidelines</b>  | <b>Application</b>   | <b>Scientific Basis and Factors<br/>Considered</b>  | <b>Reference</b>           |
|--|---|--|---|----------------------------|
| US EPA<br>1977   | Multimedia Exposure Goals (MEGs) for soil, water and air  | assessing environmental conditions   | <ul style="list-style-type: none"> <li>- based on limited information</li> <li>- simple equations convert existing federal guidelines or toxicity information into MEGs</li> </ul>  | Cleland and Kingsbury 1977 |
| United Kingdom<br>late 1970s   | U.K. Trigger Concentrations for Contaminants in Soil<br><br>1) threshold trigger<br>2) action trigger | <ul style="list-style-type: none"> <li>- below <b>threshold</b> trigger: soil is "uncontaminated" / no restrictions;</li> <li>- greater than <b>threshold</b> trigger: investigation/ professional judgement required to decide action needed</li> <li>- greater than or equal to <b>action</b> trigger: remedial action required</li> </ul> | <ul style="list-style-type: none"> <li>- professional judgement</li> <li>- factors include human health, phytotoxic effects, hazards such as explosion, background levels</li> </ul>  | United Kingdom, 1990       |
| Netherlands<br>Ministry of Housing<br>Planning and Environment<br>1983 | "ABC" Soil Quality Guidelines   | A - the boundary between contaminated and uncontaminated land;<br>B - potential for harmful effects and need for investigation;<br>C - contamination at a level that presents an intolerable risk to man and the environment and remedial action/investigation required.   | <ul style="list-style-type: none"> <li>- professional judgement</li> <li>- factors include background levels, analytical detection limits, toxicity, solubility, accumulation</li> <li>- standard approach has been developed and values currently being revised based on soil characteristics (clay fraction and organic content), ecotoxicological and human health effects data</li> </ul> | Moen 1988                  |

| Jurisdiction<br><br>Program<br>Initiation   | Criteria/Guidelines  | Application  | Scientific Basis and Factors<br>Considered  | Reference  |
|---|--|--|---|--|
| Ontario Ministry<br>of the<br>Environment<br><br>1984                             | MOE Soil Clean-Up<br>Guidelines<br><br>- based on two<br>categories of land<br>use (agricultural/<br>residential and<br>parkland;<br>commercial/<br>industrial) and two<br>categories of soil<br>texture (medium/fine<br>and coarse) | - threshold values<br>for remedial<br>action.<br>- proponent may<br>elect to develop<br>site-specific<br>guidelines  | - based primarily on<br>considerations of<br>phytotoxicity, human health<br>and health of grazing animals   | Ontario MOE<br>1989  |
| Ministere de<br>l'Environnement<br>du Quebec<br>(MENVIQ)<br><br>1988              | "ABC" Soil<br>Guidelines   | - between A and<br>B, soil is<br>considered<br>"slightly<br>contaminated" and<br>action may be<br>required for<br>sensitive land uses<br>- between B and<br>C soil is<br>"contaminated"<br>and investigation/<br>remedial action or<br>certain land use<br>restrictions may<br>be required<br>- above C it may<br>be necessary to<br>take prompt<br>remedial action/<br>restrict all land<br>uses. | - professional judgment in<br>adoption and modification of<br>existing criteria from other<br>agencies<br>- factors include background<br>levels in Quebec soils,<br>toxicity, carcinogenicity  | MENVIQ 1988  |
| New Jersey<br>Department of<br>Environmental<br>Protection (DEP)<br><br>mid-1980s | Interim Soil Action<br>Levels (ISALS)  | - identify the<br>presence of<br>contamination and<br>need for<br>investigation.<br>- site-specific<br>clean-up<br>objectives are<br>developed on a<br>case-by-case basis  | - professional judgement<br>- factors include background<br>levels, potential human health<br>effects and protection of<br>groundwater quality.<br>- methods for including direct<br>exposure to soil (e.g.,<br>ingestion) are under<br>development | New Jersey<br>Dept. of<br>Environmental<br>Protection 1990 |

| Jurisdiction<br>Program<br>Initiation   | Criteria/Guidelines   | Application  | Scientific Basis and Factors<br>Considered  | Reference                      |
|---|---|--|---|--------------------------------|
| Alberta<br>Environment<br>1990  | Alberta Tier 1<br>Criteria for<br>Contaminated Soil<br>Assessment and<br>Remediation  | <ul style="list-style-type: none"> <li>- represent upper limits of a "healthy soil system".</li> <li>- option for Tier 2 (site-specific) criteria development</li> </ul>   | <ul style="list-style-type: none"> <li>- professional judgement</li> <li>- factors include consistency with other guidelines, animal health, plant health, background conditions</li> </ul>   | Alberta<br>Environment<br>1990 |
| British Columbia<br>Ministry of the<br>Environment<br>1989                            | Criteria for<br>Managing<br>Contaminated Sites<br><br>(ABC)   | <ul style="list-style-type: none"> <li>- dependent on the land use, the criteria will serve as investigation criteria (above which site investigation is needed) and remediation criteria (above which remedial action is required)</li> </ul>   | <ul style="list-style-type: none"> <li>- values adopted from other agencies based on consideration of potential human exposure associated with levels of acceptable lifetime cancer risk, background levels, existing standards</li> </ul>  | B.C. MOE<br>1989               |
| Canada<br><br>National<br>Contaminated<br>Sites<br>Remediation<br>Program<br><br>1989 | Environmental<br>Quality Criteria for<br>Contaminated Sites <ul style="list-style-type: none"> <li>● assessment criteria</li> <li>● remediation criteria for agricultural; residential/parkland; and commercial/industrial land uses</li> </ul> | <ul style="list-style-type: none"> <li>- assessment criteria represent contaminant levels at which no action is required</li> <li>- remediation criteria are considered to be generally protective of specified uses of soil and serve as benchmarks for evaluating the need for remedial action/ investigation, and as the basis for setting site-specific remediation (clean-up) objectives</li> </ul> | <ul style="list-style-type: none"> <li>- interim criteria based on a critical evaluation of existing values from other agencies</li> <li>- values will be updated based on standard protocols incorporating human health effects /exposure pathways for specified land uses, ecotoxicological effects (plant, invertebrate, microbial), bioaccumulation (livestock , wildlife), background levels, analytical detection limits, soil condition (organic content, pH, clay)</li> </ul> | CCME 1991a                     |

expensive characterization of the site and use of computer models to estimate the fate of contaminants (Sheppard et al. 1992). However, the relative approach is criticized because it does not provide a consistent basis for decision making, especially during early stages of site assessment and investigation. This may lead to a great differences in the level of protection afforded to the environment (including human health).

Given the fundamental difference between these two approaches, it is hardly surprising that there has been a great deal of controversy over whether the absolute or relative approach is best suited to setting clean-up levels for contaminated sites. Though generic and relative approaches are often viewed as competing, each with inherent strength and weaknesses (Table 3), the potential for application of both site-specific and generic approaches in assessing and managing contaminated soils is now emerging as an important marriage of options (Gaudet et al. 1992). In the NCSRP, a combination of both approaches is used in order to target clean-up efforts as efficiently and effectively as possible.

### 8.3.2 NCSRP's Tiered Framework

In recognition of the need for both generic and site-specific approaches in a comprehensive framework for contaminated site assessment and remediation, the NCSRP has adopted a tiered framework that combines the strengths of each. Generic national criteria (Canadian Environmental Quality Criteria for Contaminated Sites) are intended to provide a consistent scientific basis for evaluating contamination with respect to potential effects on human health and the environment, and in the development of remediation strategies. However, it is recognized that generic criteria cannot be applied directly to setting remediation endpoints for contaminated sites without due consideration of site-specific factors (CCME 1991a).

**Table 3: Advantages of the Absolute versus Relative Approach to Establishing Clean-up Levels**

|                      | GENERIC   | SITE-SPECIFIC  |
|----------------------|---|--|
| <b>ADVANTAGES</b>    | <ul style="list-style-type: none"><li>- simple and objective</li><li>- facilitates broad-based soil protection programs</li><li>- inexpensive</li><li>- consistent</li></ul>                        | <ul style="list-style-type: none"><li>- uses site information</li><li>- can give estimate of risk level</li><li>- allows the management of risk to only the 'necessary level'</li></ul>                          |
| <b>DISADVANTAGES</b> | <ul style="list-style-type: none"><li>- site-specific circumstances not considered</li><li>- criteria lacking for many substances</li><li>- implies level of knowledge that may not exist</li></ul> | <ul style="list-style-type: none"><li>- may lead to inconsistent decision making</li><li>- change in site or receptors may invalidate analysis</li><li>- many assumptions required</li><li>- expensive</li></ul> |

For this reason, emphasis has also been placed on the development of a consistent national approach to setting site-specific remediation objectives for contaminated sites. Dependent on circumstances, such a site-specific approach may include direct adoption or adaptation of existing generic criteria incorporating site-specific factors such as background levels of contaminants and potential land use. Alternatively, ecological/human-health risk assessment may be conducted to provide a detailed evaluation of existing and potential risk to the human and ecological receptors in consideration of factors such as contaminant transport and fate in the various media, and land use patterns at a particular site.

Currently, site-specific guidance is in the early developmental stages. The focus of the current paper is on the development of generic (absolute) soil quality criteria for Canada.



### 8.3.3 Interim Environmental Quality Criteria

The CCME Subcommittee has released a set of "Interim Canadian Environmental Quality Criteria for Contaminated Sites", which are numerical limits for contaminants intended to protect, maintain or improve current and future uses(s) of soil and water at contaminated sites. The interim criteria include both assessment criteria (approximate background concentrations or analytical detection limits for contaminants that when exceeded indicate that investigative actions should be considered), and remediation criteria for soil that are considered generally protective of specified land uses (agricultural, residential/parkland and commercial /industrial). The interim remediation criteria also include the Canadian Water Quality Guidelines (CCREM 1987) and the Guidelines for Canadian Drinking Water Quality (HWC 1989) for uses of water likely of concern at contaminated sites.

To meet the urgent needs of the NCSRP, these criteria were adopted directly from values currently in use in Canada based on a critical evaluation of their underlying rationale (CCME 1991a; Gaudet et al. 1992). Several characteristics considered desirable in a set of national criteria were used as the basis for this evaluation (Table 4). Based on an initial review of twenty-one jurisdictions from across Canada, the U.S., The Netherlands, United Kingdom, Australia, West Germany and France, ten agencies were selected as potential candidates for NCSRP criteria. Table 5 summarizes the extent to which these ten agencies met the desired characteristics. Because the interim soil quality criteria generally lack adequate supporting rationale, and did not fulfil all of the characteristics expected in a set of national criteria, it was decided that the interim values would be updated on an ongoing basis to reflect emerging information on the effects of contaminants to environmental and human health. Though the CCME advocates the protection of all media of concern at contaminated sites, the initial emphasis of the Program is on the soil media due to the critical need to build a consistent scientific basis for the development of soil quality criteria not only in Canada, but world-wide (Sheppard et al. 1992). Accordingly, the CCME Subcommittee on Environmental

**Table 4. Desired Characteristics of NCSRP Environmental Quality Criteria for Contaminated Sites**

- 
- be applicable to a wide range of sites, site conditions, and contaminants
  - consider all environmental media or compartments
  - consider various exposure pathways and associated risks
  - adapt to missing data
  - consider present and future land use(s)
  - place equal emphasis on the environment and human health
  - consider aesthetics and phytotoxicity
  - consider background or ambient concentrations of contaminants
  - consider analytical detection limits
- 

Quality Criteria for Contaminated Sites was formed to guide a research and development program to produce scientifically defensible effects-based soil quality criteria for use in contaminated site assessment and remediation that place equal emphasis on protection of human health and the environment. Over the first five years of the program, emphasis will be placed on evaluation and recommendation of generic effects-based soil remediation criteria for protection of human health and the environment in Canada.

**Table 5: Evaluation of Criteria from Primary Agencies for Use in the NCSRP According to NCSRP Desirable Characteristics**

| Character-<br>istic                 | AGENCY |      |       |               |               |       |      |      |      |      |
|-------------------------------------|--------|------|-------|---------------|---------------|-------|------|------|------|------|
|                                     | Alta.  | B.C. | Calf. | CCME<br>(PAH) | CCME<br>(PCB) | Neth. | N.J. | Ont. | Que. | U.K. |
| Widely Applied                      | L      | Y    | Y     | N             | N             | Y     | L    | L    | Y    | L    |
| All Media                           | N      | L    | L     | L             | Y             | L     | N    | N    | L    | N    |
| All Routes of Exposure              | N      | L    | Y     | N             | Y             | N     | N    | N    | N    | L    |
| Various Receptors                   | N      | L    | Y     | N             | Y             | N     | L    | N    | L    | L    |
| Missing Data                        | L      | L    | L     | N             | N             | N     | N    | N    | L    | N    |
| Various Land Uses                   | L      | Y    | Y     | L             | Y             | Y     | L    | Y    | Y    | Y    |
| Neighbours                          | N      | N    | N     | N             | N             | N     | N    | N    | N    | N    |
| Environmental Health = Human Health | L      | L    | Y     | N             | N             | ?     | ?    | L    | ?    | L    |
| Aesthetics                          | ?      | ?    | N     | N             | N             | ?     | N    | L    | ?    | L    |
| Phyto-toxicity                      | N      | ?    | N     | N             | N             | N     | N    | Y    | N    | Y    |
| Back-ground                         | Y      | Y    | N     | L             | L             | Y     | Y    | Y    | Y    | Y    |
| Detection Limits                    | Y      | Y    | N     | N             | N             | Y     | N    | N    | Y    | N    |

Notes: Y = Yes N = No L = Limited ? = Uncertain

## 8.4 DEVELOPMENT OF EFFECTS-BASED SOIL QUALITY CRITERIA

### 8.4.1 Soil: A Multifunctional Resource

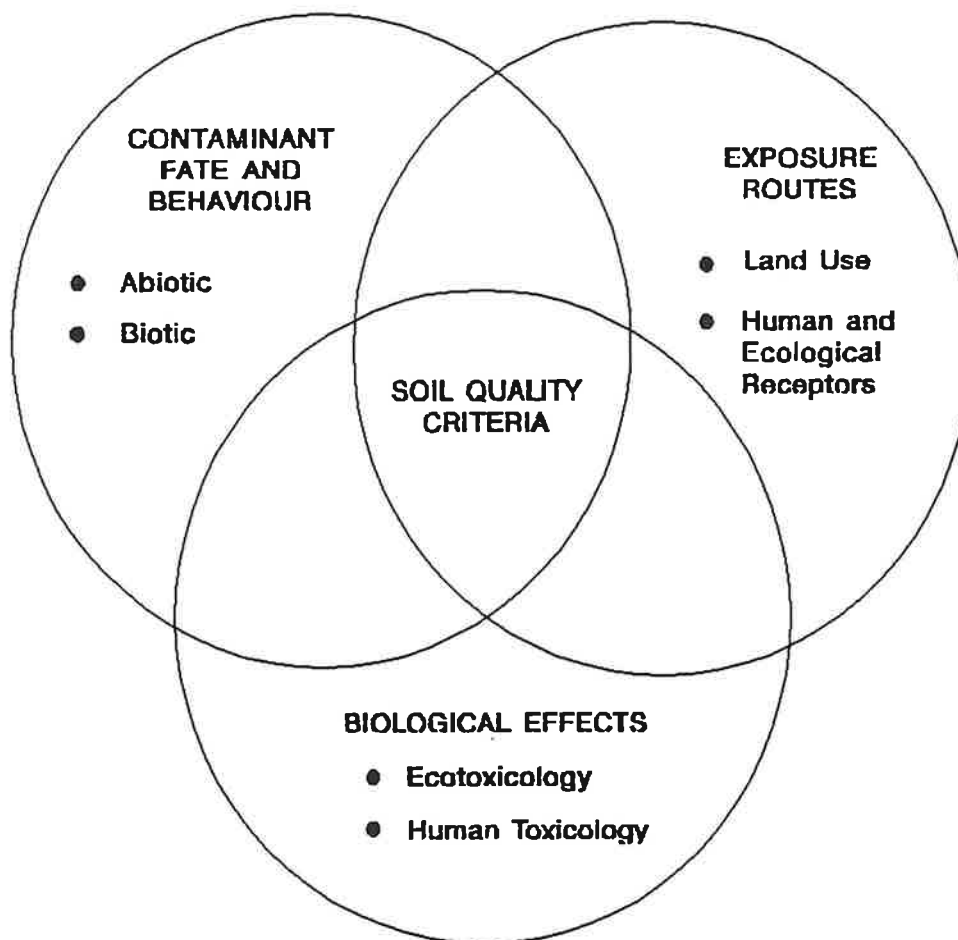
The development of effects-based soil quality criteria for the assessment and remediation of contaminated sites is a complex task that must begin from the fundamental re-evaluation of what is meant by soil quality. A unique challenge in the development of generic criteria is in determining the combination of factors that should be considered in the development of a generic soil quality criterion for a specified land use that will not lead to adverse human-health or ecological effects. Protection and restoration of "soil quality", and the development of soil quality criteria, requires a fundamental shift in the way we view soil - from an inert physical medium that can be measured in terms of stoniness or organic content, to a dynamic and multifunctional ecological system critical to sustaining the terrestrial environment and associated uses. Moen (1988) provides a definition of a soil of good quality as one which "must pose no harm to any normal use by humans, plants or animals; not adversely affect natural cycles or functions, and not contaminate other components of the ecosystem". Though this definition does not provide any positive quantitative estimate or measures for soil of "good" quality, it does set the stage for considering soil as a multifunctional resource.

There are significant challenges in the development of soil quality criteria. Soil is a complex heterogeneous medium that consists of variable amounts of mineral material, organic matter, water and air, and is capable of supporting organisms, including plants, bacteria, fungi, protozoans, invertebrates and other animal life. The derivation of effects-based soil quality criteria must provide a sufficient level of protection such that soil returned (remediated) to the criteria level will be a healthy functioning ecosystem capable of sustaining the current and likely future uses of the site by ecological receptors and humans, including the protection of groundwater. Not only must the physical and biotic integrity of the soil medium be protected, but consideration must be given to all

supporting and associated uses. In addition, criteria must not be protective only of immediate concerns, but ensure long-term sustainability of soil quality in its broader context.

#### 8.4.2 Wheels Within Wheels

Development of soil quality criteria that are protective of human and environmental health must be based not only on direct estimates of the toxicity of a contaminant, but on a comprehensive understanding of the fate and effects of contaminants in the soil environment and the various routes of exposure to human and ecological receptors. Though the scientific information required is diverse and transcends a number of disciplines, the scope and nature of the problem is greatly clarified when viewed in the context of three key areas: (1) contaminant fate and behaviour; (2) exposure assessment; and, (3) biological effects (toxicity) assessment (**Figure 2**). Essentially, it is the interaction between these three areas that serves as the basis for estimating the "risk" of soil contaminants to the environment and human health and as the basis for soil quality criteria development. It is, however, an extreme oversimplification to suggest that the task is not a complicated one. Within these broadly overlapping areas, there exists an infinite number of possible receptors, exposure pathways and toxicity endpoints to be considered, all of which may be modified by existing soil conditions. For example, soil supports a number of different uses, which in turn will affect the potential receptors and exposure pathways that are of concern. These exposure pathways can vary from direct contact or ingestion of soil to uptake through the food chains. Soil characteristics such as pH, clay and percent organic content will further affect not only the availability of contaminants to receptors, but this effect may vary widely depending on the particular contaminant under consideration.



**Figure 2: Information Required for the Development of Ecological Effects-Based and Human Health-Based Soil Quality Criteria**

Though many of these questions may be answered at the site-specific level through a detailed analysis and evaluation of contaminant effects relevant to the particular conditions, receptors and exposure pathways at a site, the derived criterion is relevant only to that site and cannot be generalized to other sites or conditions. Generic criteria, on the other hand, are intended to provide conservative estimates of potential ecological and human-health effects that are applicable to a broad range of sites and conditions. Accordingly, they are usually based on standardized toxicological endpoints for

representative or sensitive receptors (e.g., Denneman and van Gestel 1990) and/or generic exposure scenarios (e.g., Linders et al. 1992). The incorporation of underlying conservative assumptions (such as protection of the most sensitive species) ensure that recommended levels are generally protective. At the same time, it is recognized that not only soil characteristics such as clay content, but also existing or expected land use at a site can greatly affect the receptors, exposure pathways and ultimate effects that may be of concern in setting remediation goals for contaminated sites. Although generic criteria, by definition, do not consider site-specific conditions, a degree of specificity can be gained through consideration of receptors and exposure pathways, including uptake through the food chain, that are relevant to major land uses and/or soil types (e.g., B.C. MOE 1989; CCME 1991a; Ontario MOE 1990). Given the broad range of soil conditions in Canada and the influence of master variables (pH, % clay, % organic matter) the concept of a reference soil is emerging as an important component in the development of generic criteria (e.g., Lexmond et al. 1986). By specifying a reference soil condition for Canada, guidance can be provided to users of the generic criteria on the range of soil conditions (as specified by the master variables) within which the generic criteria apply. If soil conditions at a particular site fall outside of the reference soil condition, then the generic criteria may not be directly applicable to the site. The development of a site-specific remediation objectives will therefore be required. Currently, research is being initiated to define a range of reference soils for Canada to aid in the development and application of the generic criteria.

**Table 6** shows some of the potential receptors, exposure pathways and toxicological endpoints that may be of concern with regard to key land uses in Canada. Despite broad overlap, significant differences exist in the approach and scientific data required for development of generic criteria for human and ecological receptors. These differences reflect not only differences in sensitivity and exposure to soil contaminants between human and non-human receptors, but also differences in concepts of "acceptable

risk", and the availability of toxicological and exposure data.

The current challenge is to define realistic, scientifically defensible approaches to the development of national generic criteria that not only take into account critical differences in receptors, sensitivity, and direct and indirect exposure to soil contaminants with respect to land uses, but that, at the same time, address a level of generality that will afford environmental protection across a broad range of sites and conditions. The following sections address the key considerations in the development of human health-based and ecological effects-based soil quality criteria.

Despite comparability in basic principles, soil quality criteria for human and ecological receptors are derived using substantially different methodologies and are addressed separately in this chapter. This difference in approach is due not only to differences in the state of knowledge and the availability of toxicity and exposure data for each of these groups, but also to the fact that only one receptor (and sensitive life stages) is considered when dealing with the relationship between soil quality and human health while "ecological-effects-based" criteria must consider the relationship between soil quality and virtually all other system attributes. At this time, an evaluation of the effects of soil contaminants on sensitive and/or key receptors provides a reliable and consistent basis for derivation of such ecological effects-based soil quality criteria.

However, in the evolution of this field, increasing emphasis must be placed on developing integrated indicators and measures of soil quality which consider important interrelationships and processes critical to the sustainability of the soil "ecosystem".



**Table 6: Examples of land uses, receptors, toxicological endpoints and exposure routes that should be considered in the derivation of generic soil quality criteria.**

| EXISTING OR POTENTIAL LAND USE | POTENTIAL RECEPTORS OF CONCERN | CONTAMINANT CHARACTERISTICS | TOXICOLOGICAL ENDPOINTS | POTENTIAL EXPOSURE PATHWAYS             | INFLUENCING SOIL CHARACTERISTICS |
|--------------------------------|--------------------------------|-----------------------------|-------------------------|---|----------------------------------|
| AGRICULTURE                    | soil invertebrates             | bioaccumulation potential   | survival                | direct soil contact/dermal absorption   | organic matter                   |
|                                | plants/crops                   | volatility                  | reproduction            |   | pH                               |
| RESIDENTIAL/<br>PARKLAND       | microbial activity             | solubility                  | growth                  | direct ingestion of soil                | clay content                     |
|                                | livestock                      | persistence                 | behaviour               | ingestion of food/produce grown on soil | redox potential                  |
| COMMERCIAL/<br>INDUSTRIAL      | wildlife                       |                             | carcinogenicity         | ingestion of food/produce grown on soil | moisture content                 |
|                                | human (child/adult)            |                             |                         | inhalation of soil/dust particles       |                                  |
|                                |                                |                             |                         | inhalation of vapour (volatiles)        |                                  |
|                                |                                |                             |                         | drinking water                          |                                  |

## 8.5 DEVELOPMENT OF HUMAN HEALTH-BASED SOIL QUALITY CRITERIA

This section of the this chapter will describe the important aspects of developing soil criteria for the protection of human health. Of prime concern in developing soil remediation criteria is considering the possibility of adverse human health effects from exposure to a particular contaminant. The process of setting site-specific standards is usually done by performing a baseline risk assessment and comparing the

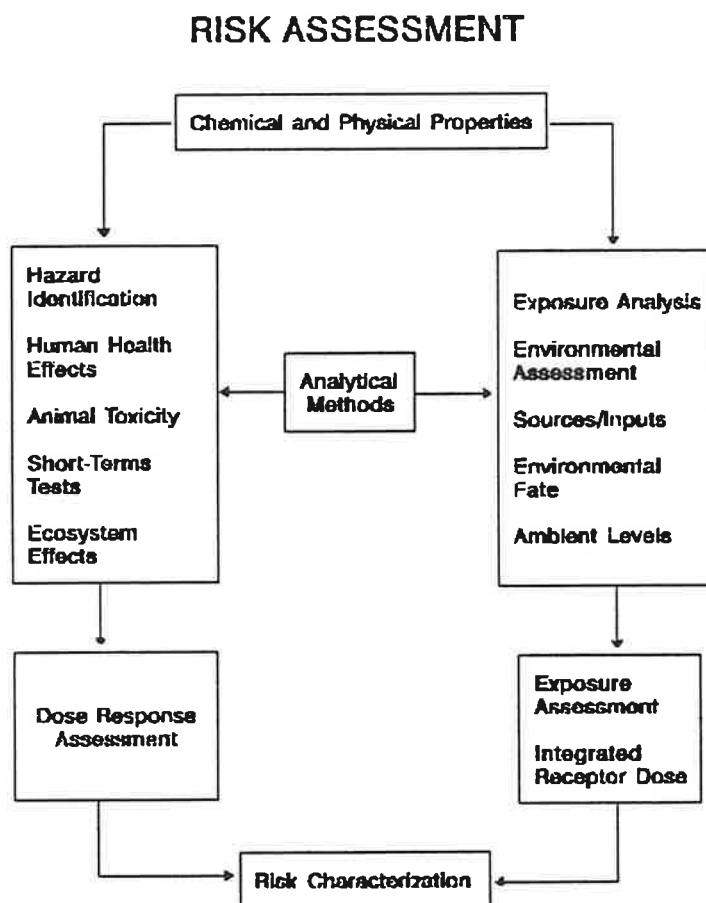
results with a risk assessment at a contaminated site. Setting generic criteria uses risk assessment to quantify the exposure and the toxicology for defined reference conditions for an "average Canadian".

#### 8.5.1 Human Health Risk Assessment

A risk assessment consists of four main areas: hazard identification, toxicological assessment, exposure assessment, and risk characterization (**Figure 3**). Each of these areas provides an important part of the risk associated with a specific contaminant.

8.5.1.1 *Hazard Identification.* Under hazard identification, general information about a contaminant, such as physical and chemical properties, persistence, bioaccumulation potential, and toxicity, is gathered. This step helps identify candidate chemical parameters which require additional information provided by subsequent steps in the risk assessment. It provides general qualitative information on the toxicology and persistence of a contaminant.

8.5.1.2 *Toxicological Assessment.* The toxicological assessment provides the "acceptable" level of exposure, either as an allowable daily intake (ADI) for a non-carcinogen or the virtually safe dose (VSD) at a specific risk level for carcinogens. This information is derived from the dose-response information about a specific chemical. It is the quantitative investigation of the response by an organism to a specific amount (or dose) of a contaminant.



**Figure 3: Generalized framework for human health risk assessment**

The best measurement of the dose would be the amount of a chemical reaching the target organ. However most often this information is not available. The risk assessor relies on contaminant concentrations in air, soil or water, and makes some assumptions about their uptake or absorption into the body and their distribution within the body to the target organ. In addition, for many contaminants there can be metabolic activation or deactivation of a specific chemical leading to either enhanced or reduced toxicity, respectively. Target organs for a contaminant can vary according to the specific uptake route. For example, inhalation of a particular contaminant could lead to lung

cancer, whereas its ingestion could lead to different effects or even no effect.

The risk assessor prefers to use long term or chronic studies to assess the risk from a contaminant. Often such studies are not available and data from acute toxicological studies are used. In the latter studies, animals are exposed to very high doses of a contaminant or toxic substance so as to produce a particular adverse effect, such as death or development of tumours in a short period of time. Use of acute studies results in another difficulty, extrapolating the effects of a concentrated time to the effects of a lifetime exposure to a very low contaminant exposure.

There is a fundamental difference in the dose-response curves for carcinogens and non-carcinogens. With non-carcinogens, it is expected that there is some threshold concentration or amount of exposure below which an organism will show no adverse effects (no-observable adverse effect level, NOAEL). For a carcinogen, theoretically, there is no threshold below which there is no risk of developing cancer.

For non-carcinogens, which have a threshold effects level, toxicologists often apply a safety factor of ten to the results of acute toxicological studies. Other safety factors attempt to account for extrapolation of results between species (e.g., from rat toxicity to human toxicity) and for protection of sensitive individuals within a population. Therefore, the allowable daily intake (ADI) is the product of toxicological data and the application of safety factors.

For carcinogens, a number of extrapolation models, such as the linear multi-stage and the "model-free" or one-point model have been developed to estimate the incremental cancer risk at low contaminant concentrations. Each model has its own strengths and weaknesses. As different models can result in different estimates, this area of high to low dose extrapolation continues to be an important research area.

For carcinogens, the slope factor is derived from the extrapolated dose-response curve. This slope provides the potency factor or the risk-specific dose. The intake of a contaminant over a lifetime is estimated to provide the excess incidence or the

incremental risk of developing cancer over a lifetime resulting from exposure to a particular concentration of a carcinogen (i.e., risk per unit dose). Depending on the specific extrapolation model used, this slope factor may represent an upper bound estimate of the risk.

8.5.1.3 *Exposure Assessment.* The third area of a risk assessment is the exposure assessment. This investigation provides information on whether an organism will come in contact with a contaminant, and if so, it will quantify the duration and the concentration into an "exposure estimate". No matter how toxic a chemical is, there is no risk if there is no exposure to an organism.

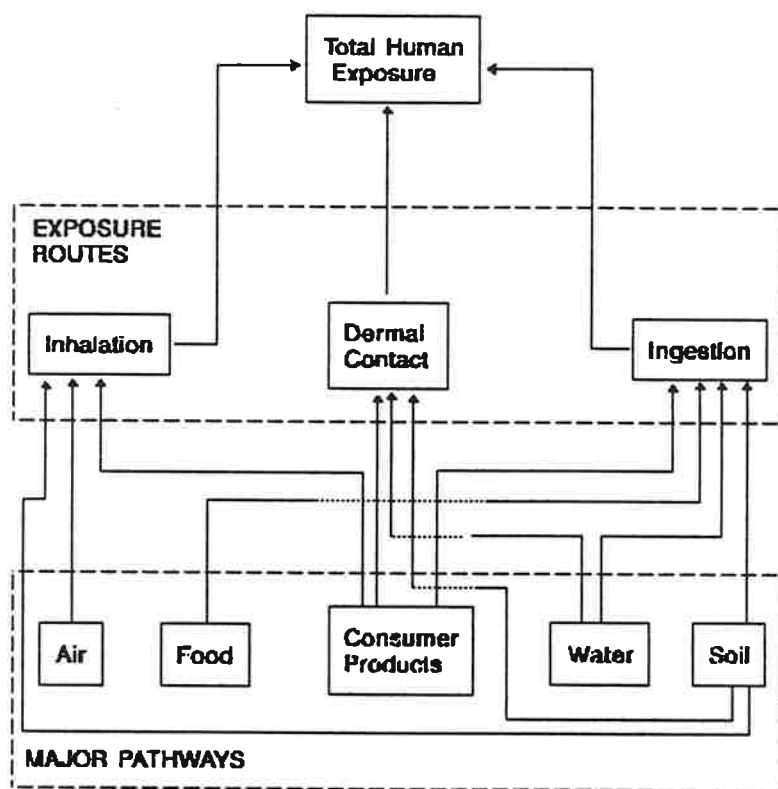
**Figure 4** schematically diagrams a multi-media exposure pattern. It starts at the bottom of the diagram with the main exposure media, soil, air, water, and food (consumer goods have not been included). The arrows represent different exposure pathways that contribute to the overall total exposure. It becomes readily apparent how complicated an exposure assessment is. In addition, there are other factors to be considered in any exposure assessment. **Table 7** lists some of these. The contaminant concentration in different media must be measured, as well as the exposure frequency and duration. The latter factors often vary with age, and can be difficult to measure. While criteria are generic in nature, it is important in an exposure assessment to identify subpopulations whose exposure to a contaminant is not well represented by the general case.

Factors such as amount of soil ingested by children, the amount of soil in contact with the skin, and the rate of dermal absorption from soil in contact with the skin are important areas which require research to provide more accurate estimates of exposure.

It is also important to identify the specific toxic endpoints associated with particular routes of exposure. For example, exposure to a contaminant through inhalation

could lead to lung cancer, while exposure to the same contaminant through ingestion of food or water could be associated with a very different toxic endpoint, such as liver or kidney toxicity. For other contaminants, the toxic endpoint is the same, whatever the exposure pathway.

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**Figure 4: Significant Pathways of Human Exposure to Contaminated Soil.**

**8.5.1.4 Risk Characterization.** This step in the risk assessment process integrates the information gathered in the exposure and toxicological assessments. It characterizes or describes the probability of occurrence of adverse health effects. By comparing the

risks of adverse effects for baseline conditions to those at a contaminated site, one is able to quantify the added or incremental risk at contaminated sites. An important piece of information necessary for completing the risk characterization step is called the apportionment of the ADI. This step divides the allowable daily intake of a contaminant among the exposure media (air, soil, water, and food).

**Table 7: Factors to Consider in Human Health Exposure Assessment**

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**Exposure Pathways**

air: inhalation (indoors and outdoors), during showering/bathing

soil: ingestion of soil/dust, contaminated food, dermal uptake

water: ingestion, dermal uptake during showering/bathing

**Other Factors to Consider**

|                                       |                              |
|---------------------------------------|------------------------------|
| Exposure Frequency                    | Exposure Duration            |
| Exposure Concentration (contact rate) | Estimates of Chemical Uptake |
| Subpopulations                        | (bioavailability)            |

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This multi-media approach is important so that no one medium is allocated 100% of the allowable exposure to a contaminant, resulting in a population that is overexposed to a contaminant from that medium. This is a management decision which involves other considerations, such as scientific (exposure and toxicology), socio-economic factors, and technological factors. The ease and cost of pollution controls must be also examined. It may be that it is impossible or very expensive to reduce the exposure through one route. A management decision could be to apportion a larger amount of the ADI to one medium, with a resulting smaller proportion to another medium, which is more feasible and less expensive to control. In deciding the

apportionment, it is important to study the pattern of exposure which is found in the multi-media exposure assessment. Using this as starting point, the other socio-economic and technological factors can modify the apportionment factors. This is an area which has been a stumbling block in guideline development. In most cases, criteria are developed for a single medium and there is no appropriate regulatory body to make this decision.

## 8.5.2 Soil Guideline Development

8.5.2.1 *Multi-Media Approach.* Many contaminants have become so ubiquitous that people are exposed to a specific chemical from many different sources and through different pathways. The multi-media approach to setting health-based guidelines was developed to deal with this situation. People are exposed to chemicals through different media - air, water, soil, food and consumer products. Since this occurs, the regulator must take into account exposures from other media when setting a standard for a single medium.

The multi-media approach requires a comprehensive review and evaluation of all scientific data, but has a number of benefits. First, by considering human exposure from all media, the regulator can ensure that the total exposure of a person to a contaminant does not exceed the maximum allowable intake. Second, this is an integrated approach which promotes consistency in the handling of a particular contaminant. Thus, risk estimates based decisions concerning different exposure pathway are consistent and provide the framework for more consistent management. Third, criteria for that contaminant in other media can be readily developed. Thus there needs to be no duplication of effort, resulting in considerable savings in time and resources for standard setting jurisdictions.



8.5.2.2 *Identification of Significant Exposure Pathways.* In developing soil remediation criteria to protect human health, one must ensure that exposure to a remediated soil concentration will not result in adverse human health effects. The process of setting soil criteria is one of working backward from an allowable daily intake (ADI) of contaminant through the soil exposure pathways to a soil concentration. There are a number of important steps in this process.

**Figure 4** provides a schematic diagram of soil exposure pathways. These pathways can be the result of a direct exposure to soil or an indirect exposure to soil, i.e., a cross-media transfer from soil to another medium, such as water, air, or food. Direct exposure pathways include ingestion of soil/dust, dermal uptake of contaminants in contact with the skin, and inhalation of soil particles into the lungs. Indirect exposure pathways include ingestion of food contaminated soil and inhalation of contaminated vapours resulting from the volatilization of contaminants from soil into air. An extremely important indirect exposure is the ingestion of groundwater contaminated by the leaching of contaminants from soil into groundwater.

The physical and chemical properties of a contaminant will determine its environmental fate. These properties will also focus the possible important exposure pathways to humans. For example, the dermal exposure pathway will be primarily important for contaminants which are lipophilic and can readily cross the epidermal layer of the skin. Also, only contaminants with a high vapour pressure are likely to volatilize from soil to inhaled air.

### 8.5.3 Calculation of Soil Criterion

Using the identified direct pathways from the first step above, the following general equation can be used to generate an approximation of the soil criterion.

soil quality criterion =

$$\frac{\text{allowable exposure or intake of contaminant from soil pathway}}{\text{estimated exposure from direct soil pathways}}$$

One can now see that the soil guideline is backcalculated from the "safe" or allowable intake from soil exposure divided by the estimated exposure from soil pathways.

#### 8.5.4 Modification of Criteria for Indirect Exposure Pathways

As mentioned previously, cross media transfer of a chemical from contaminated soil to another medium, such as water, air, or food, can result in indirect exposure to contaminants from soil. Each of these cross-media transfers can be modelled using a number of assumptions about the exposure scenario. For example, the uptake of soil contaminants by plants and the subsequent ingestion of backyard garden produce by people can be estimated from a given soil contaminant concentration. Similar estimates can be made of the migration of vapours from soil into the basement of a house and the exposure via inhalation of contaminated gases. The information from these models can then be compared to allowable daily intakes for these media to ensure that safe levels are not exceeded. If levels resulting from cross-media transfer are too high, then soil criteria can be modified. Another iteration of comparison with the modelled values can then be performed.

### 8.6 DEVELOPMENT OF ECOLOGICAL EFFECTS-BASED CRITERIA

To date, little work has been done on the development of approaches that incorporate ecotoxicological information in the derivation of soil quality criteria. Currently, only The Netherlands has proposed a defined mathematical approach to

developing soil quality guidelines (criteria) based on ecotoxicological evidence (Dennemen and van Gestel 1990; van Strallen and Dennemen 1989). However, one common element that is apparent in current or proposed procedures for deriving environmental quality guidelines or criteria for three media (i.e., soil, sediment and water), is the use of a reference toxicological endpoint (e.g. NOEC/NOEL,  $EC_{50}/LC_{50}$ ) with an applied safety (uncertainty) factor (e.g., CCME, 1991a,b; Stephan et al. 1985; U.S. EPA/OTS 1984; van Straalen and Dennemen 1989). This approach is generally paralleled in the development of ecological effects-based soil quality criteria for contaminated site remediation as discussed in the following sections.

#### 8.6.1 Ecological Basis for Developing Soil Quality Criteria

An important distinction between soil and underlying regolith material is the presence of an active biota. Most soil biological activity is heterotrophic and depends on energy from organic matter added by plants. The combined activities of the soil biota serve to decompose plant residues and recycle organically-bound nutrients back to growing plants. As such, the vitality of soils is critically linked to an unencumbered plant-decomposer system. A principal property of soil quality criteria for contaminants must be that they ensure the proper functioning of the soil-plant system within the expectations of a given land use. Specifically, our expectations are to sustain biotic values, including the ability to extract commodities, such as crops. In addition, sustainability of the soil-plant system relies on the functioning of the complete suite of soil biota, as well as, other important physical and chemical properties of the soil. Ultimately, protection of desired plant species can only be accomplished through protection of soil organisms. However, controversy exists over how to best accomplish protection of the soil ecosystem.

Ecosystems have been described as hierarchical entities with populations

nested in communities, and organisms nested in populations etc. Stressors such as a contaminant may affect an ecosystem at one or more levels of organization. Because of the complexity of biotic interactions in soil, linking these levels has proven difficult - even in the absence of contaminants. Pastorak and Sampson (1992) proposed that, for examining effects due to contaminants, an ideal scale of descriptive resolution is the functional web. Progress has been made in functional web analysis of soils, but knowledge is still well short of what is needed for development of generic soil quality criteria.

Classical toxicological approaches to criteria or guideline development have generally relied on data from single species exposed to individual contaminants (e.g., Greene et al. 1989; ISO 1991; OECD 1984). To engender confidence that a single species can provide protection to whole ecosystems, considerable effort has gone into identification of sensitive species. Cairns (1992) argues that the "most sensitive species approach" is hampered by: (1) our ability to culture specific organisms for testing; (2) variable sensitivity to a range of contaminants within a species; and, (3) poor predictive power in scaling contaminant effects from the species level to the community or ecosystem.

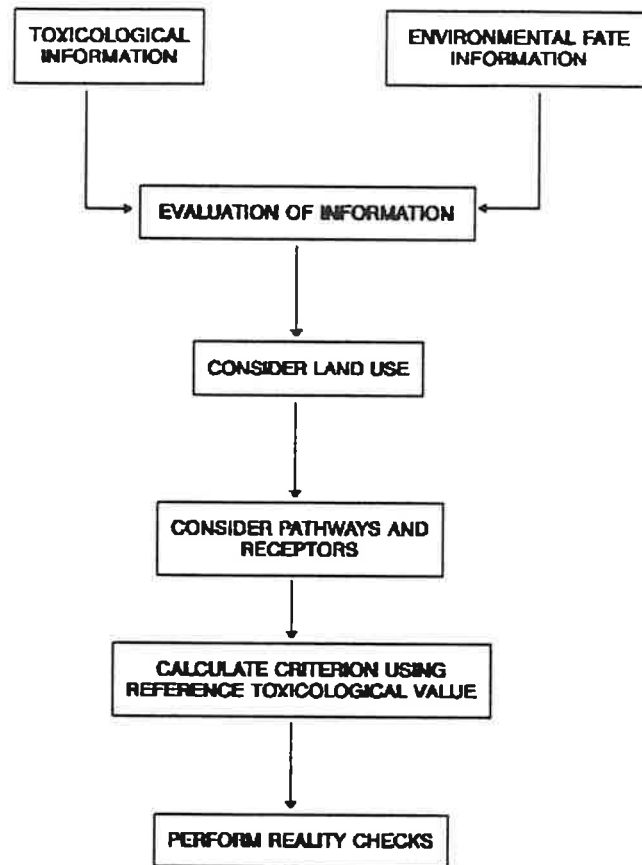
Notwithstanding these criticisms, no clear alternative has emerged to displace the most sensitive species approach. Developmental work is underway on binary or ternary species bioassay but reliable systems for soil species are not yet available (Keddy et al. 1992). Community-level measures of biological activity in soils are commonly performed (e.g. decomposition, respiration, nutrient cycling) and these can be applied in evaluating contaminant effects. However, difficulties exist with appropriate controls and representative assay conditions.

### 8.6.2 General Approach to Effects-Based Criteria Derivation

Effects-based criteria have been developed mainly for aquatic environments (CCME 1991b,c; Stephan et al. 1985; van Straalen and Denneman 1989), but soils have recently been addressed (Denneman and van Gestel 1990; van Leeuwen 1990; van Strallen and Dennemen, 1989). In the development of ecological effects-based criteria a soil contaminant concentration is estimated which represents a level at which no adverse effects are observed in key ecological receptors for a given land use (i.e. agricultural, residential/parkland, commercial/industrial). This can be achieved through the protection of the "most sensitive species" that can be identified in relation to the land use under consideration. Whether or not this is practically achieved (i.e., wide range of sensitivities, limited data) is a site-specific environmental management decision and does affect the process for developing effects-based criteria.

The generalized framework for developing ecological effects-based criteria is given in **Figure 5**. The process begins by drawing together all relevant scientific information on toxicology and environmental fate. Toxicological data are generally regarded as acceptable if a recognized and accepted biological testing protocol has been used in the study. Toxicological and environmental databases are assembled and evaluated. Any implications for criteria derivation related to land use are then considered. The relevant exposure pathways and receptors of contaminated soil for these land uses are identified and used in the process for deriving effects-based soil quality criteria.

In agricultural land use scenarios there must be no contaminant-imposed constraints on the ability of the soil to sustain microbial and invertebrate populations, grow crops and raise livestock of acceptable quality for human consumption. In residential/parkland land uses there must be no contaminant-imposed constraints on the ability of the soil to sustain microbial and invertebrate populations as well as native flora



**Figure 5: Generalized Framework for Developing Ecological Effects-Based Soil Quality Criteria**

(and ornamental) and pose no-adverse effects to the health of wildlife. In commercial/industrial land use scenarios there must be no serious impairment by contaminants on the ability of the soil to sustain microbial and invertebrate populations and grow ornamental plants.

### 8.6.3 Criteria for Direct Contact with Contaminated Soil

Given the paucity of soil toxicity data and reliable models for evaluation of soil contamination at the population level, at present it appears possible only to meld "effects" information from single species assays with measures of community-level function (as a check mechanism) such as metabolic quotient and N mineralization. To be useful, such information must be based on a reference toxicological endpoint (e.g. NOEC, LC50). For soil organisms and plants these endpoints are usually obtained from dose-response studies that involve direct contact with contaminated soil (or elutriate) for the exposure (e.g. ISO 1991). Effects-based soil quality criteria developed using this information can only therefore be considered protective of soil organisms and plants from direct contact with contaminated soil and/or pore water.

#### 8.6.3.1 General Calculation of Soil Criterion

A soil quality criterion can be calculated using the general formula outlined below. Reference toxicological endpoints are usually determined from single chemical exposures applied to one species at a time. As applied to pure substances in soil, the usual chronic endpoints are the no observed effect concentration (NOEC) or lowest observed effect concentration (LOEC) whereas the common acute endpoint is the median lethal concentration ( $LC_{50}$ ). Preferably, a reference toxicological endpoint at which no observable (adverse) effects are observed (NOEC) from a long-term study is used, but short-term endpoints (e.g., EC50) are alternatively used with an application factor to approximate NOEC conditions. NOEC values from toxicity tests are usually a function of the concentrations selected for the test and will vary from test to test. The "true" level at which no effects are observed could lie between the highest test concentration that results in no effect and the lowest test concentration that produces an effect. A

standardized or scalable uncertainty factor is used to accommodate uncertainty in the estimate of the "true" level at which no effects are observed.

$$\text{Soil Quality Criterion} = \frac{\text{Reference Toxicological Endpoint}}{\text{Uncertainty Factor}}$$

#### 8.6.4 Criteria for Direct Ingestion of Contaminated Soil or Food

Given the land uses previously identified, livestock and wildlife are considered to be the receptors of concern from exposures to contaminated soil from the ingestion of soil and food. Criteria that are developed to consider contaminant exposures to livestock or wildlife from direct ingestion of contaminated soil or food make use of reference toxicological values from single chemical exposures to single species, but must also take into account the rate of soil ingestion, body weight and bioaccumulation information of the organism in question. For agricultural land use scenarios this may involve contaminant exposures to livestock from the soil directly and from accumulated contaminants in plants tissues used as food. For residential/parkland land uses this may involve contaminant exposures to wildlife from the soil directly and from accumulated contaminant in invertebrates ingested as food. For commercial industrial land uses this route of exposure to livestock or wildlife is not expected to be significant given the nature of activities performed on these sites.

Information is generally available on the uptake and accumulation of chemicals from soil by plants. The consumption of contaminated plant material and soil particles by livestock is also generally known and has been identified as a significant exposure pathway (Fries, 1987; Paustenbach, 1989). Information is however, lacking on the these pathways of exposure to wildlife living in close association with soil or wildlife consumers of soil-dwelling invertebrates or plants. Currently it is feasible to develop



criteria based on ingestion of contaminants from soil or food by livestock that will be suitable for an agricultural land use scenario. Further information is needed on the rate of ingestion of food and soil particles by wildlife before attempts can be made to develop criteria that can account for effects to wildlife incurred from this pathway of exposure. General calculating formulas for deriving soil quality criteria for livestock and wildlife ingestion are in the developmental stages and will be finalized at a later date.

#### 8.6.5 Reality Checks

Soil quality criteria that are developed using the general framework outlined in Figure 5 should undergo a battery of reality checks as a final step. Other factors that must be considered in a generalized approach to environmentally protective soil quality criteria include potential for groundwater contamination, detection limits, plant nutrition requirements and geochemical background.

Because traditionally effects-based criteria or guidelines developed for various media have been established using single species exposures, it is difficult to experimentally measure individual dose-effect relationships in complex soil microbial populations, which contain multiple species. Therefore a "microbial check" can be performed using community level toxicological information (e.g., CO<sub>2</sub> production, N mineralization) by comparing it to any nominated soil quality criteria to ensure that adverse effects are not expected.

If the contaminant is a naturally occurring inorganic substance (e.g. As) geochemical background databases can be consulted to determine whether any criteria nominated are above the normal range found in the Canadian environment. Normally a soil quality criterion would not be set below the upper limit of normal unless there was strong evidence that such a concentration was limiting to biota.

Plant nutrition requirements present another possible check for some

inorganic substances (e.g., B, Cu, Zn). These elements are required in small amounts by plants but are toxic in high concentrations. A soil quality criterion nominee should meet plant nutrition requirements for common crops that can be grown sustainably in Canada. Finally, a soil criterion nominee must not be expected to lead to contamination of groundwater beyond some benchmark (e.g., drinking water guideline).

During execution of the above checks it may be necessary to adjust a soil criterion nominee to generate a final soil quality criterion. Such an adjustment, however, would require full scientific documentation.

## 8.7 A CANADIAN REFERENCE SOIL ?

The term "generic criteria" implies applicability across a broad, but not all-inclusive, range of site and receptor conditions. When dealing with human health protection, this broad applicability is ensured by the multi-media approach and conservative assumptions built into receptor characteristics, exposure scenarios and toxicological derivations. Conservative assumptions acknowledge the existence of variation in important parameters that are influential upon biological effects, and respond by choosing upper or lower quantile values for these parameters as necessary to achieve the desired protection.

On the environmental health side, both mobility and bioavailability of contaminants are strongly influenced by key soil parameters such as pH, and organic matter and clay contents. Mobility and bioavailability mediate, respectively, transfer of contaminants to groundwater and toxicity to soil fauna. These considerations have lead the Dutch to define a "standard" soil in terms of clay and organic matter content (Moen et al. 1986), upon which they base their generic criteria. Rather than seek a conservative boundary condition for their standard soil, the Dutch have identified a central-to-liberal condition (25% clay, 10% organic matter), attached generic criteria to that condition, and

provided tools for estimating appropriate criteria for non-standard conditions (Denneman and van Gestel 1990).

Could the Dutch approach be applied in Canada? The present answer appears to be: yes, in principle and no, in practice. To effectively deal with variation in bioavailability of metals as affected by organic matter and clay contents requires extensive data collection for the range of soil types to be managed. In the Netherlands this work is well underway, likely due in part to the relatively small area and strong need for sound soil management. Variation of contaminant distribution and behaviour in Canadian soils is poorly characterized by comparison with the Netherlands situation. Because Canadian soils differ substantially from those in the Netherlands it is expected that relationships developed there may be unreliable here -- necessitating a costly and time consuming replication of the Dutch effort or an alternative approach.

The urgent need for improved remediation criteria and the expense of commissioning the necessary studies indicate an alternative is needed. It is proposed that a Canadian reference soil condition be identified by coupling a boundary condition analysis to an overview of the distribution of Canadian soil types within the NCSRP land use framework. Such an analysis would seek an optimum balance in meeting four objectives:

1. The soil condition chosen should allow a high degree of contaminant bioavailability
2. Ecotoxicological effects criteria developed for the reference soil should be protective of a large proportion of Canadian soils classified under the NCSRP land use framework
3. Areas of prevalent soil contamination should not be excluded by the

reference condition

4. At the reference condition, small changes in master variables should not result in large fluctuations in toxicity and transport for most contaminants.

Advantages of incorporating a reference soil condition in the CCME criterion development process include:

1. Judging the applicability of generic criteria to a particular site will be more straightforward. Because the master variables defining the reference condition are normally measured in routine site contaminant investigations, it will be immediately apparent whether it is appropriate to apply criteria as site-specific objectives.
2. Evaluation of existing ecotoxicological data is simplified. Studies carried out in systems approximating the reference condition could be targeted for inclusion whereas studies of insensitive soil systems might be rejected or de-emphasized.
3. Development of new bioassay systems or acquisition of new data from old systems may be improved.
4. Information gaps will be better delineated. Clear identification of soil conditions incompatible with generic criteria may better inform industrial land management strategies and spur research.

## 8.8 SUMMARY

In Canada it has been identified that there is a need to deal with the growing concern over the potential impacts of contaminated sites on human and environmental health. Under the National Contaminated Sites Remediation Program a consistent approach to the assessment and remediation of sites is being developed so that cleanup can begin. The development of environmental quality criteria play an integral part in the assessment phase as well as the defining remediation targets for cleanup.

The Canadian Interim Environmental Quality Criteria for Contaminated Sites provide a conservative set of values for the assessment and remediation of soil and water as part of an overall framework for contaminated site cleanup in Canada. The interim criteria have been adopted directly from existing agencies based on desirable characteristics for a national set of criteria. Because many of these criteria lack supporting rationale, it was determined that these values would be revised on an ongoing basis to reflect evolving information on contaminant effects to human and ecological receptors.

The development of human health-based and ecological effects-based soil quality criteria reflect a process by which current environmental behaviour and toxicological information is evaluated and used in a process to produce soil quality criteria protective of both human and environmental health. Proposals for the development of human health-based criteria involve the use of risk assessment to define hazard and exposure based on a multi-media exposure assessment. Development of ecological effects-based criteria relies on the use of a reference toxicological endpoint for key receptors for given land uses. These criteria together are intended to represent levels of contaminants in soil which present no appreciable additional risk to humans and represent no observable effects to ecological receptors.

Some of the research still needed as part of the criteria development process

involves the identification of a suitable reference soil for Canadian conditions, soil ingestion and bioaccumulation rates for wildlife exposed to contaminated soil and food.

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